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VOLUME 11

CHEMICAL THERMODYNAMICS OF THORIUM

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CHEMICAL THERMODYNAMICS OF THORIUM

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In these and related tasks, the NEA works in close collaboration with the International Atomic Energy Agency in Vienna, with which it has a Co-operation Agreement, as well as with other international organisations in the nuclear field.

CHEMICAL THERMODYNAMICS

Vol. 1. Chemical Thermodynamics of Uranium, Wanner, H., Forest, I., OECD Nuclear Energy Agency Data Bank, Eds., North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1992).

Vol. 2. Chemical Thermodynamics of Americium, OECD Nuclear Energy Agency Data Bank, Ed., North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1995).

Vol. 3. Chemical Thermodynamics of Technetium, Sandino, M. C. A., Östhols, E., OECD Nuclear Energy Agency Data Bank, Eds., North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1999).

Vol. 4. Chemical Thermodynamics of Neptunium and Plutonium, OECD Nuclear Energy Agency Data Bank, Ed., North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2001).

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Vol. 6. Chemical Thermodynamics of Nickel, OECD Nuclear Energy Agency Data Bank, Ed., North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2005).

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Vol. 8. Chemical Thermodynamics of Zirconium, OECD Nuclear Energy Agency Data Bank, Ed., North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2005).

Vol. 9. Chemical Thermodynamics of complexes and compounds of U, Np, Pu, Am, Tc, Zr, Ni and Se with selected organic ligands, OECD Nuclear Energy Agency Data Bank, Ed., North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2005).

Vol. 10. Chemical Thermodynamics of Solid Solutions of Interest in Nuclear Waste Management. A State-of-the-Art Report, OECD Nuclear Energy Agency Data Bank, Eds., OECD Publications, Paris, France, (2007).

Preface

This volume is the eleventh in the series "Chemical Thermodynamics" edited by the OECD Nuclear Energy Agency (NEA). It is a critical review of the thermodynamic properties of thorium, its compounds and aqueous complexes, initiated by the Management Board of the NEA Thermochemical Database Project Phase III (NEA-TDB III). The first meeting of the review team was held in May 2004 at the OECD Headquarters, Paris at which the scope of the review and the distribution of the responsibilities for the assessments and text were determined. Three further meetings were held, and several of the review team met at various scientific conferences during the review period, particularly those in the “Migration” series. All the members contributed fully to the main text and the discussions, but the workload was distributed according to the expertise of each member. Malcolm Rand and Jean Fuger reviewed gas and solid-state thermodynamics, while the other members were involved in solution thermodynamics. Cindy Atkins-Duffin participated in the meetings of the review team as the designated member of the Executive Group.

At the NEA Data Bank the responsibility for the overall co-ordination of the Project was with Federico Mompean who until his departure in September 2007, was in charge of the preparation of the successive drafts to the semifinal version, and updating the NEA thermodynamic database. Myriam Illemassène (until December 2006) and Jane Perrone, (who also oversaw the production of the final version) were responsible, most capably, for the editing of the numerous drafts. The present volume owes a great deal to the invaluable efforts of these NEA staff.

One aspect of the final assessment that should be noted is that we have increased the standard entropy of Th(cr) slightly from that given in the seminal CODATA Key Values volume [1989COX/WAG]. Naturally, such a change in an important selected value was very carefully considered, and a full justification for the change is presented. It is clear that new measurements of the low temperature specific heat of Th(cr) are required to define the standard entropy more precisely.

Most of the recent experimental work on the detailed thermodynamic properties of thorium compounds has been on solubilities and aqueous solutions. The large number of hydroxide complexes of Th(IV) and the propensity to form colloidal solutions, makes the interpretation of these studies a challenging task. As noted in previous reviews, the development of laser-based spectroscopic techniques has been a useful tool in our increased understanding of these phenomena, and it is gratifying that data obtained by these new techniques in general agrees very well with data obtained by more traditional methods. Quantum chemical methods are also emerging as tools to understand the coordination chemistry of *f*-elements, thereby providing further valuable information when discussing speciation. Such calculations are also providing more reliable estimates for the vibrational properties of gases (for example, for the thorium tetrahalide gases)

This volume provides the first detailed, well-documented and comprehensive review of the thermodynamic properties of thorium, its compounds and aqueous species, supplementing the earlier, less-detailed reviews noted in the Introduction (Chapter I).

Dry Sandford, Oxford, England, October, 2008 Malcolm Rand, Chairman

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Malcolm Rand and Jean Fuger would like to acknowledge valuable contributions from John Arblaster and Mike Mortimer in the U.K. and Georgii Bergman at the Glushko Thermocenter in Moscow concerning the low temperature specific heat of Th(cr). John Arblaster first drew the reviewers' attention to the need for additional precise data in this area and provided us with full details of his assessment, which has been adopted by the review. Georgii Bergman kindly provided us with full details of the CODATA assessment of the heat capacity of Th(cr) and made helpful comments on the discrepancy, and Mike Mortimer gave us helpful advice about low-temperature heat capacity measurements and the general behaviour of Debye temperatures as a function of temperature. We are also grateful to Paul Potter (Oxford) for help with some Russian translations and Rudy Konings (ITU, Karlsruhe, Germany), who kindly provided a preprint of a paper on the *ab initio* calculations of the structures of ThC_2(g) and ThC_4(g), and made many other helpful comments.

Dhan Rai would like to thank Dr. Andrew Felmy of the Pacific Northwest National Laboratory for making the NONLINT-SIT program available to the review and for providing help in its correct application.

The entire manuscript of this book has undergone a peer review by four independent 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 OECD Nuclear Energy Agency. The peer reviewers were:

Pr. Robert Guillaumont, French Academy of Sciences, former Professor at Université de Paris, XI, Orsay, France

Dr. Rudy Konings, Institute for Transuranium Elements (Joint Research Centre, European Commission), Karlsruhe, Germany.

Dr. Leslie Pettit, University of Leeds, England,

Dr. Tom Wolery, Lawrence Livermore National Laboratory, Livermore, CA, USA

Their valuable contributions to the quality of this review are gratefully acknowledged.

Editor's note

This is the eleventh 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 thorium. 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, on-line access to selected data and computer programs, as well as many documents in electronic format are available at

www.nea.fr.

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@nea.fr. If this is not possible, write to:

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FRANCE

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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], 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: that reported in the present volume dealing with inorganic compounds and complexes of thorium and two further volumes dealing with tin and 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, eleventh in the Series, is therefore the second deliverable from this phase of the NEA-TDB Project.

The earlier ten 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/KON2], the series edited by Freeman *et al.* [1984FRE/LAN], [1985FRE/LAN], [1985FRE/KEL], [1986FRE/KEL], [1987FRE/LAN], [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, which has been used in the present review, 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 thorium 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 thorium in aqueous solution at ambient temperatures and makes independent analyses of the available literature in this area. As discussed in Chapter VII, the hydrolysis of the Th(IV) ion in aqueous solutions is particularly complex; at least nine Th-OH complexes (including polymeric species of high ionic charge) are fairly firmly established, and a number of additional species have been proposed in the literature.

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 thorium compounds.

This book contains a summary and critical reviews of the thermodynamic data on compounds and complexes containing thorium, as reported in the available chemical literature up to the end of 2006, but a few more recent references are also included. A large number of primary references are discussed separately in Appendix A. In addition to being relevant on their own account, the relatively abundant thermodynamic data for thorium species are of value because of the position of thorium as the first member of the actinide series to show quadrivalency. The data for Th(IV) species are therefore of considerable value in correlations of actinide properties. For example, in solid phases the Th(IV) compound is normally diamagnetic, and is thus very useful in establishing the diamagnetic contributions (*e.g.* to the heat capacity or entropy) to the values for the corresponding higher An(IV) compounds.

Although the focus of this review is on thorium, 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 thorium 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 thorium 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 carbonate and hydroxide solubilities might need to be re-interpreted to take into account the crystal structure and particle size of the phases actually investigated).

Re-evaluation of literature values might be also necessary to correct for known systematic errors (for example, if the junction potentials are 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], [2000GRE/WAN], [2000OST/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.

One aspect of the present review that is different from earlier volumes is that a fitting code incorporating the SIT model, NONLINT-SIT, has been used in some systems to optimise the values of $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ} / \mathrm{R}T$ of the relevant solid and aqueous species and the SIT ion-interaction parameters, using all the experimental solubility, ion-exchange, and solvent extraction data. From these, the optimised values of the different quantities can be compared with the other reported values. Appendix D describes the *modus operandi* of the NONLINT-SIT program, with an illustrative example.

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, emf 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 XII), and this information may be used as a basis for the assignment of future research priorities.

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
emf	Electromotive force, not specified

(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
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	Emf 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
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]. 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
density (mass divided by volume)	ρ
molar surface area	$\mathcal{A}$
time	t
frequency	ν
wavelength	λ
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: $A / c_B l$	ε
relaxation time	τ
Avogadro constant	$\mathrm{N_A}$
relative molecular mass of a substance$^{(a)}$	M_r
thermodynamic temperature, absolute temperature	T
Celsius temperature	t
(molar) gas constant	R
Boltzmann constant	k
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	μ_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$^{(b)}$	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)$^{(c)}$	c_B, [B]
molality of a solute substance B (amount of B divided by the mass of the solvent)$^{(d)}$	m_B
factor for the conversion of molarity to molality of a solution: m_B/c_B	ξ
mean ionic molality$^{(e)}$, $m_{\pm}^{(\nu_+ + \nu_-)} = m_+^{\nu_+} m_-^{\nu_-}$	$m_{\pm}$
activity of substance B	a_B
activity coefficient, molality basis: a_B / m_B	γ_B
activity coefficient, concentration basis: a_B / c_B	y_B
mean ionic activity$^{(e)}$, $a_{\pm}^{(\nu_+ + \nu_-)} = a_B = a_+^{\nu_+} a_-^{\nu_-}$	$a_{\pm}$
mean ionic activity coefficient$^{(e)}$, $\gamma_{\pm}^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$	$y_{\pm}$
osmotic coefficient, molality basis	ϕ
ionic strength: $I_m = \frac{1}{2}\sum_i m_i z_i^2$ or $I_c = \frac{1}{2}\sum_i c_i z_i^2$	I
SIT ion interaction coefficient between substance B_1 and substance B_2)	$\varepsilon(B_1, B_2)$
stoichiometric coefficient of substance B (negative for reactants, positive for products	ν_B
general equation for a chemical reaction	$0 = \sum_B \nu_B B$
equilibrium constant$^{(f)}$	K
charge number of an ion B (positive for cations, negative for anions)	z_B
charge number of a cell reaction	n
electromotive force	E
$\text{pH} = -\log_{10}[a_{H^+}/(\text{mol}\cdot\text{kg}^{-1})]$	pH
electrolytic conductivity	κ
superscript for standard state$^{(g)}$	$^\circ$

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}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 $\text{mol}\cdot\text{kg}^{-1}$ 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.

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 $UF_2O(cr)$.

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, $(UO_2)_2CO_3(OH)_3^-$ is standard, $(UO_2)_2(OH)_3CO_3^-$ is not recommended.

It is convenient to have a shorthand method of referring to an a 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 $(Na)ClO_4$" could be a mixture of 0.01 M $Th(ClO_4)_4$ and 2.96 M $NaClO_4$ 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: H_3edta^-, 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, 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_2O(l).
- The designator (aq) is used for undissociated, uncharged aqueous species, *e.g.*, $U(OH)_4$(aq), CO_2(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_2O (*e.g.*, D_2O, 90% ethanol/10% H_2O), then (aq) is replaced by a more explicit designator, *e.g.*, "(in D_2O)" 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_2O in Eqs.(II.2) and (II.3). H_2O(l) in Reaction (II.2) indicates that H_2O 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_2O(sln) may not be the same as those of the pure liquid H_2O(l). In dilute solutions, however, this difference in the thermodynamic properties of H_2O can be neglected, and H_2O(sln) may be regarded as pure H_2O(l).

  Example:

  $$UO_2Cl_2(cr) + 2\ HBr(sln) \rightleftharpoons UO_2Br_2(cr) + 2HCl(sln) \qquad (II.1)$$

  $$UO_2Cl_2\cdot 3H_2O(cr) \rightleftharpoons UO_2Cl_2\cdot H_2O(cr) + 2\ H_2O(l) \qquad (II.2)$$

  $$UO_3(\gamma) + 2\ HCl(sln) \rightleftharpoons UO_2Cl_2(cr) + H_2O(sln) \qquad (II.3)$$

- 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_2(quar) for quartz and SiO_2(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_5, β-UF_5.

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:

$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{Na}^{+}, 298.15\ \mathrm{K})$	standard molar Gibbs energy of formation of aqueous Na^{+} at 298.15 K
$S^{\circ}_{\mathrm{m}}(\mathrm{UO_2(SO_4)\cdot 2.5H_2O}, \mathrm{cr}, 298.15\ \mathrm{K})$	standard molar entropy of $\mathrm{UO_2(SO_4)\cdot 2.5H_2O(cr)}$ at 298.15 K
$C^{\circ}_{p,\mathrm{m}}(\mathrm{UO_3}, \alpha, 298.15\ \mathrm{K})$	standard molar heat capacity of $\alpha-\mathrm{UO_3}$ at 298.15 K
$\Delta_{\mathrm{f}}H_{\mathrm{m}}(\mathrm{HF}, \mathrm{sln}, \mathrm{HF\cdot 7.8H_2O})$	enthalpy of formation of HF diluted 1:7.8 with water.

II.1.5 Processes

Chemical processes are denoted by the operator Δ, 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 Δ, *e.g.*, the Gibbs energy of formation, $\Delta_{\mathrm{f}}G_{\mathrm{m}}$, the enthalpy of sublimation, $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$, *etc*. The abbreviations of chemical processes are summarised in Table II-3.

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

Subscript of Δ	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 $\Delta_{\mathrm{f}}G$ and $\Delta_{\mathrm{f}}H$, 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 Spectroscopic constants and statistical mechanics calculations for gaseous species

In most cases, the thermal functions for gaseous species have been calculated by well-known statistical-mechanical relations (see for example Chapter 27 of [1961LEW/RAN]). The required molecular parameters are given in Appendix E.

The parameters defining the vibrational and rotational energy levels of the molecule in terms of the rotational (J) and vibrational (v) quantum numbers, and thus many of its thermodynamic properties, are:

- for diatomic molecules (non–rigid rotator, anharmonic oscillator approximation): ω (vibrational frequency in wavenumber units), x (anharmonicity constant), B (rotational constant for equilibrium position), D (centrifugal distortion constant), α (rotational constant correction for excited vibrational states), and σ (symmetry number), where the energy levels with quantum numbers v and J are given by:

$$\begin{aligned} \mathrm{E}_{(v,J)}/\mathrm{h\,c} &= \omega\,(v+1/2)-\omega\,x(v+1/2)^2+B\,J(J+1) \\ &\quad -D\,J^2\,(J+1)^2-\alpha\,(v+1/2)\,J\,(J+1) \end{aligned} \qquad \text{(II.4)}$$

- for linear polyatomic molecules, the parameters are the same as those for diatomic molecules, except that the contributions for anharmonicity are usually neglected.
- for non-linear polyatomic molecules (rigid rotator, harmonic oscillator approximation): $I_x\, I_y\, I_z$, the product of the principal moments of inertia (readily calculated from the geometrical structure of the molecule), v(i), the vibration frequencies and σ, the symmetry number. While the vibrational energy levels for polyatomic molecules are given approximately by the first term of equation (II.4) for each of the normal vibrations, the rotational energy levels cannot be expressed as a simple general formula. However, the required rotational partition function can be expressed with sufficient accuracy simply in terms of the product of the principal moments of inertia. As for linear polyatomic molecules, anharmonic contributions are usually neglected.

In each case, the symmetry number σ, the number of indistinguishable positions into which the molecule can be turned by simple rotations, is required to calculate the correct entropy.

The relations for calculating the thermal functions from the partition function defined by the energy levels are well-known – again, see Chapter 27 of [1961LEW/RAN], for a simple description. In each case, the relevant translational and electronic contributions (calculated from the molar mass and the electronic energy levels and degeneracies) must be added. Except where accurate spectroscopic data exist, the geometry and parameters of the excited states are assumed to be the same as those for the ground state.

II.1.7 Nomenclature in log terms

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

II.1.8 Equilibrium constants

The IUPAC has not explicitly defined the symbols and terminology for equilibrium constants of reactions in aqueous solution. The NEA 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:

$$m\,\mathrm{M} + q\,\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q \qquad \text{(II.5)}$$

both $\beta_{q,m}$ and β (II.5) would be appropriate, and $\beta_{q,m}$ (II.5) is accepted, too. Note that, in general, K is used for the consecutive or stepwise formation constant, and β 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).

II.1.8.1 Protonation of a ligand

$$\mathrm{H}^+ + \mathrm{H}_{r-1}\mathrm{L} \rightleftharpoons \mathrm{H}_r\mathrm{L} \qquad K_{1,r} = \frac{[\mathrm{H}_r\mathrm{L}]}{[\mathrm{H}^+][\mathrm{H}_{r-1}\mathrm{L}]} \qquad \text{(II.6)}$$

$$r\,\mathrm{H}^+ + \mathrm{L} \rightleftharpoons \mathrm{H}_r\mathrm{L} \qquad \beta_{1,r} = \frac{[\mathrm{H}_r\mathrm{L}]}{[\mathrm{H}^+]^r[\mathrm{L}]} \qquad \text{(II.7)}$$

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.8) is used.

$$\mathrm{HL}_{q-1} + \mathrm{L} \rightleftharpoons \mathrm{HL}_q \qquad K_q = \frac{[\mathrm{HL}_q]}{[\mathrm{HL}_{q-1}][\mathrm{L}]} \qquad \text{(II.8).}$$

Eq.(II.9) refers to the overall formation constant of the species $\mathrm{H}_r\mathrm{L}_q$.

$$r\,\mathrm{H}^+ + q\,\mathrm{L} \rightleftharpoons \mathrm{H}_r\mathrm{L}_q \qquad \beta_{q,r} = \frac{[\mathrm{H}_r\mathrm{L}_q]}{[\mathrm{H}^+]^r[\mathrm{L}]^q} \qquad \text{(II.9).}$$

In Eqs.(II.6), (II.7) and (II.9), the second subscript r can be omitted if $r = 1$, as shown in Eq.(II.8).

Example:

$$\mathrm{H}^+ + \mathrm{PO}_4^{3-} \rightleftharpoons \mathrm{HPO}_4^{2-} \qquad \beta_{1,1} = \beta_1 = \frac{[\mathrm{HPO}_4^{2-}]}{[\mathrm{H}^+][\mathrm{PO}_4^{3-}]}$$

$$2\,\mathrm{H}^+ + \mathrm{PO}_4^{3-} \rightleftharpoons \mathrm{H}_2\mathrm{PO}_4^{-} \qquad \beta_{1,2} = \frac{[\mathrm{H}_2\mathrm{PO}_4^{-}]}{[\mathrm{H}^+]^2[\mathrm{PO}_4^{3-}]}$$

II.1.8.2 Formation of metal complexes

$$\mathrm{ML}_{q-1} + \mathrm{L} \rightleftharpoons \mathrm{ML}_q \qquad K_q = \frac{[\mathrm{ML}_q]}{[\mathrm{ML}_{q-1}][\mathrm{L}]} \qquad \text{(II.10)}$$

$$\mathrm{M} + q\,\mathrm{L} \rightleftharpoons \mathrm{ML}_q \qquad \beta_q = \frac{[\mathrm{ML}_q]}{[\mathrm{M}][\mathrm{L}]^q} \qquad \text{(II.11)}$$

For the addition of a metal ion, *i.e.*, the formation of polynuclear complexes, the following notation is used, analogous to Eq.(II.6):

$$\mathrm{M} + \mathrm{M}_{m-1}\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L} \qquad K_{1,m} = \frac{[\mathrm{M}_m\mathrm{L}]}{[\mathrm{M}][\mathrm{M}_{m-1}\mathrm{L}]} \qquad \text{(II.12)}$$

Eq.(II.13) refers to the overall formation constant of a complex $\mathrm{M}_m\mathrm{L}_q$.

$$m\,\mathrm{M} + q\,\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q \qquad \beta_{q,m} = \frac{[\mathrm{M}_m\mathrm{L}_q]}{[\mathrm{M}]^m[\mathrm{L}]^q} \qquad \text{(II.13)}$$

The second index can be omitted if it is equal to 1, *i.e.*, $\beta_{q,m}$ becomes β_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, OH^-. This practice is not adopted in this review. If 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 $\mathrm{H}_2\mathrm{O}$ occurs as a reactant to form hydroxide complexes, $\mathrm{H}_2\mathrm{O}$ is considered as a protonated ligand, HL, so that the reaction is treated as described below in Eqs.(II.14) to (II.16) using n as the index variable. For convenience, no general form is used for the stepwise constants for the formation of the complex $\mathrm{M}_m\mathrm{L}_q\mathrm{H}_r$. 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.14) and (II.15) for mononuclear and in Eq.(II.16) for polynuclear complexes.

$$\mathrm{ML}_{q-1} + \mathrm{HL} \rightleftharpoons \mathrm{ML}_q + \mathrm{H}^+ \qquad {}^*K_q = \frac{[\mathrm{ML}_q][\mathrm{H}^+]}{[\mathrm{ML}_{q-1}][\mathrm{HL}]} \tag{II.14}$$

$$\mathrm{M} + q\,\mathrm{HL} \rightleftharpoons \mathrm{ML}_q + q\mathrm{H}^+ \qquad {}^*\beta_q = \frac{[\mathrm{ML}_q][\mathrm{H}^+]^q}{[\mathrm{M}][\mathrm{HL}]^q} \tag{II.15}$$

$$m\,\mathrm{M} + q\,\mathrm{HL} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q + q\mathrm{H}^+ \qquad {}^*\beta_{q,m} = \frac{[\mathrm{M}_m\mathrm{L}_q][\mathrm{H}^+]^q}{[\mathrm{M}]^m[\mathrm{HL}]^q} \tag{II.16}$$

Example:

$$\mathrm{UO}_2^{2+} + \mathrm{HF(aq)} \rightleftharpoons \mathrm{UO}_2\,\mathrm{F}^+ + \mathrm{H}^+ \qquad {}^*K_1 = {}^*\beta_1 = \frac{[\mathrm{UO}_2\mathrm{F}^+][\mathrm{H}^+]}{[\mathrm{UO}_2^{2+}][\mathrm{HF(aq)}]}$$

$$3\,\mathrm{UO}_2^{2+} + 5\,\mathrm{H}_2\mathrm{O(l)} \rightleftharpoons (\mathrm{UO}_2)_3(\mathrm{OH})_5^+ + 5\,\mathrm{H}^+ \quad {}^*\beta_{5,3} = \frac{[(\mathrm{UO}_2)_3(\mathrm{OH})_5^+][\mathrm{H}^+]^5}{[\mathrm{UO}_2^{2+}]^3}$$

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.17).

$$\mathrm{M} + q\,\mathrm{H}_r\mathrm{L} \rightleftharpoons \mathrm{M(H}_r\mathrm{L)}_q \qquad \beta_q = \frac{[\mathrm{M(H}_r\mathrm{L)}_q]}{[\mathrm{M}][\mathrm{H}_r\mathrm{L}]^q} \tag{II.17}$$

Example:

$$\mathrm{UO}_2^{2+} + 3\,\mathrm{H}_2\mathrm{PO}_4^- \rightleftharpoons \mathrm{UO}_2(\mathrm{H}_2\mathrm{PO}_4)_3^- \qquad \beta_3 = \frac{[\mathrm{UO}_2(\mathrm{H}_2\mathrm{PO}_4)_3^-]}{[\mathrm{UO}_2^{2+}][\mathrm{H}_2\mathrm{PO}_4^-]^3}$$

II.1.8.3 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.18) to (II.20).

$$\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) \rightleftharpoons a\,\mathrm{M} + b\,\mathrm{L} \qquad K_{s,0} = [\mathrm{M}]^a\,[\mathrm{L}]^b \qquad \text{(II.18).}$$

$K_{s,0}$ 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.13) is used:

$$\frac{m}{a}\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) \rightleftharpoons \mathrm{M}_m\mathrm{L}_q + \left(\frac{mb}{a}-q\right)\mathrm{L} \qquad K_{s,q,m} = \left[\mathrm{M}_m\mathrm{L}_q\right]\left[\mathrm{L}\right]^{(\frac{mb}{a}-q)} \qquad \text{(II.19).}$$

Example:

$$\mathrm{UO_2F_2(cr)} \rightleftharpoons \mathrm{UO_2F^+} + \mathrm{F^-} \qquad K_{s,1,1} = K_{s,1} = \left[\mathrm{UO_2F^+}\right]\left[\mathrm{F^-}\right] \ .$$

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

$$\frac{m}{a}\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) + \left(\frac{mb}{a}-q\right)\mathrm{H^+} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q + \left(\frac{mb}{a}-q\right)\mathrm{HL}$$

$$^*K_{s,q,m} = \frac{\left[\mathrm{M}_m\mathrm{L}_q\right]\left[\mathrm{HL}\right]^{(\frac{mb}{a}-q)}}{\left[\mathrm{H^+}\right]^{(\frac{mb}{a}-q)}} \qquad \text{(II.20)}$$

Example:

$$\mathrm{U(HPO_4)_2\cdot 4H_2O(cr) + H^+} \rightleftharpoons \mathrm{UHPO_4^{2+} + H_2PO_4^- + 4\ H_2O(l)}$$

$$^*K_{s,1,1} = {}^*K_{s,1} = \frac{\left[\mathrm{UHPO_4^{2+}}\right]\left[\mathrm{H_2PO_4^-}\right]}{\left[\mathrm{H^+}\right]}\ .$$

II.1.8.4 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.21).

$$\mathrm{ML}_{q-1} + \mathrm{L(g)} \rightleftharpoons \mathrm{ML}_q \qquad K_{\mathrm{p},q} = \frac{\left[\mathrm{ML_q}\right]}{\left[\mathrm{ML}_{q-1}\right]p_{\mathrm{L}}} \qquad \text{(II.21)}$$

The subscript "p" can be combined with any other notations given above.

Example:

$$\mathrm{CO_2(g)} \rightleftharpoons \mathrm{CO_2(aq)} \qquad K_{\mathrm{p}} = \frac{\left[\mathrm{CO_2(aq)}\right]}{p_{\mathrm{CO_2}}}$$

$$3\ \mathrm{UO_2^{2+}} + 6\ \mathrm{CO_2(g)} + 6\ \mathrm{H_2O(l)} \rightleftharpoons \mathrm{(UO_2)_3(CO_3)_6^{6-}} + 12\ \mathrm{H^+}$$

$$^*\beta_{\mathrm{p},6,3} = \frac{\left[\mathrm{(UO_2)_3(CO_3)_6^{6-}}\right]\left[\mathrm{H^+}\right]^{12}}{\left[\mathrm{UO_2^{2+}}\right]^3\ p_{\mathrm{CO_2}}^6}$$

$$\mathrm{UO_2CO_3(cr) + CO_2(g) + H_2O(l) \rightleftharpoons UO_2(CO_3)_2^{2-} + 2\,H^+}$$

$$^{*}K_{\mathrm{p,s,2}} = \frac{\left[\mathrm{UO_2(CO_3)_2^{2-}}\right]\left[\mathrm{H^+}\right]^2}{p_{\mathrm{CO_2}}}$$

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.1.8.5 Redox equilibria

Redox reactions are usually quantified in terms of their electrode (half cell) potential, E, which is identical to the electromotive force (emf) of a galvanic cell in which the electrode on the left is the standard hydrogen electrode, SHE[1], 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, $\mathrm{H_2(g)}$ is at unit fugacity (an ideal gas at unit pressure, 0.1 MPa), and $\mathrm{H^+}$ 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°, *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 $\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\circ}$ and the standard (or thermodynamic) equilibrium constant K° as outlined in Eq.(II.22):

$$E^{\circ} = -\frac{1}{n\mathrm{F}}\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\circ} = \frac{\mathrm{R}T}{n\mathrm{F}}\ln K^{\circ} \qquad \text{(II.22)}$$

and the potential, E, is related to E° by:

$$E = E^{\circ} - (\mathrm{R}\,T/n\,\mathrm{F})\sum \nu_i \ln a_i. \qquad \text{(II.23)}$$

For example, for the hypothetical galvanic cell:

$$\mathrm{Pt}\ \Big|\ \mathrm{H_2(g},\ p = 1\ \mathrm{bar)}\ \Big|\ \begin{array}{l}\mathrm{HCl(aq},\ a_{\mathrm{H^+}} = 1,\ f_{\mathrm{H_2}} = \\ 1)\end{array}\ \vdots\ \begin{array}{l}\mathrm{Fe(ClO_4)_2\,(aq},\ a_{\mathrm{Fe^{2+}}} = 1) \\ \mathrm{Fe(ClO_4)_3\,(aq},\ a_{\mathrm{Fe^{3+}}} = 1)\end{array}\ \Big|\ \mathrm{Pt} \qquad \text{(II.24)}$$

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

$$\mathrm{Fe^{3+}} + \frac{1}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{H^+} \qquad \text{(II.25)}$$

Formally Reaction (II.25) can be represented by two half cell reactions, each involving an equal number of electrons, (designated "$\mathrm{e^-}$"), as shown in the following equations:

---

[1] The definitions of SHE and NHE are given in Section II.1.1.

$$\mathrm{Fe^{3+}} + \mathrm{e^-} \rightleftharpoons \mathrm{Fe^{2+}} \qquad \text{(II.26)}$$

$$\frac{1}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{H^+} + \mathrm{e^-}\,. \qquad \text{(II.27)}$$

The terminology is useful, although it must be emphasised "$\mathrm{e^-}$" here does not represent the hydrated electron.

Equilibrium (II.27) and Nernst law can be used to introduce $a_{\mathrm{e^-}}$:

$$E = E^{\circ}\,\text{(II.27)} + \frac{\mathrm{R}T}{\mathrm{F}}\ln\left(\sqrt{f_{\mathrm{H_2}}}\,/(a_{\mathrm{H^+}}a_{e^-})\right) \qquad \text{(II.28)}$$

According to the SHE convention E° (II.27) = 0, $f_{\mathrm{H_2}} = 1$, $a_{\mathrm{H^+}} = 1$, hence

$$E = -\frac{\mathrm{R}T}{\mathrm{F}}\ln a_{e^-} \qquad \text{(II.29)}$$

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

$$K^{\circ}\,\text{(II.26)} = \frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}\cdot a_{\mathrm{e^-}}} \qquad \text{(II.30)}$$

$$K^{\circ}\,\text{(II.27)} = \frac{a_{\mathrm{H^+}}\cdot a_{\mathrm{e^-}}}{\sqrt{f_{\mathrm{H_2}}}} = 1 \quad \text{(by definition)} \qquad \text{(II.31)}$$

In addition, $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}$ (II.27) = 0, $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ (II.27) = 0, $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}$ (II.27) = 0 by definition, at all temperatures, and therefore $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}$ (II.26) = $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}$ (II.25). From $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}$ (II.27) and the values given at 298.15 K in selected auxiliary data for $\mathrm{H_2(g)}$ and $\mathrm{H^+}$, the corresponding values for $\mathrm{e^-}$ 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.25), if $p_{\mathrm{H_2}}$ and $a_{\mathrm{H^+}}$ are equal to unity *(cf.* Eq.(II.23)):

$$E\text{(II.25)} = E^{\circ}\,\text{(II.25)} - \mathrm{R}T\ln\left(\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}\right) \qquad \text{(II.32)}$$

For the standard hydrogen electrode $a_{\mathrm{e^-}}$ = 1 (by the convention expressed in Eq.(II.31)), while rearrangement of Eq.(II.30) for the half cell containing the iron perchlorates in cell (II.24) gives:

$$-\log_{10} a_{\mathrm{e^-}} = \log_{10} K^{\circ}\,\text{(II.26)} - \log_{10}\left(\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}\right)$$

and from Eq.(II.28):

$$-\log_{10} a_{\mathrm{e^-}} = \log_{10} K^{\circ}\,\text{(II.25)} - \log_{10}\left(\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}\right) \qquad \text{(II.33)}$$

and $$-\log_{10} a_{e^-} = \frac{F}{RT\ln(10)} E \text{ (II.25)} \qquad \text{(II.34)}$$

which is a specific case of the general equation (II.29).

The splitting of redox reactions into two half cell reactions by introducing the symbol"e^-", which according to Eq.(II.28) 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 "pε"($= -\log_{10} a_{e^-}$) 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'^{o} 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'^{o} parallels that of "concentration quotients" for equilibria). Therefore, from

$$E = E'^{o} - \frac{RT}{nF}\sum \nu_i \ln c_i \qquad \text{(II.35)}$$

E'^{o} 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

$$E'^{o} = E^{o} - \frac{RT}{nF}\sum \nu_i \ln \xi\, \gamma_i = -\frac{\Delta_r G_m}{nF} \qquad \text{(II.36)}$$

where the γ_i are the molality activity coefficients and ξ is $\left({}^{m_i}\!/_{c_i}\right)$, the ratio of molality to molarity (*cf.* Section II.2). The medium must be specified.

II.1.9 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.

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 emf measurements of galvanic cells involving liquid junctions [1969ROS], [1973BAT]. A common 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):

$$\text{Pt(s)} \;\Big|\; \text{Ag(s)} \;\Big|\; \text{AgCl(s)} \;\Big|\; \text{KCl(aq)} \;\underset{a}{\vdots}\; \begin{matrix}\text{salt}\\ \text{bridge}\end{matrix} \;\underset{b}{\vdots}\; \begin{matrix}\text{test}\\ \text{solution}\end{matrix} \;\wr\; \text{KCl(aq)} \;\Big|\; \text{AgCl(s)} \;\Big|\; \text{Ag(s)} \;\Big|\; \text{Pt(s)} \qquad \text{(II.37)}$$

where $\wr$ stands for a glass membrane (permeable to hydrogen ions).

The emf of such a cell is given by:

$$E = E^* - \frac{\text{R}T}{n\text{F}} \ln a_{\text{H}^+} + E_{\text{j}}$$

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[1] 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 $NaClO_4$). 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 $[\text{ClO}_4^-] = 0.1$ M as background electrolyte, the dependence of the liquid junction at "*b*" on acidity is $E_{\text{j}} \approx -440 \times [\text{H}^+]$ mV·dm^3·mol^{-1} at 25°C [1969ROS] (p.110), which corresponds to an error at pH = 2 of ≥ 0.07 pH units.

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[1] $KClO_4$(cr) has a solubility of ≈ 0.15 M in pure water at 25°C

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 γ_{H^+} and E_j cancel each other when emf values are substracted).

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

$$\log_{10} a_{\mathrm{HCl}} = 1/2\,(\log_{10} m_{\mathrm{H}^+} + \log_{10} m_{\mathrm{Cl}^-} + \log_{10} \gamma_{\mathrm{H}^+} + \log_{10} \gamma_{\mathrm{Cl}^-}) \qquad \text{(II.38)}$$

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

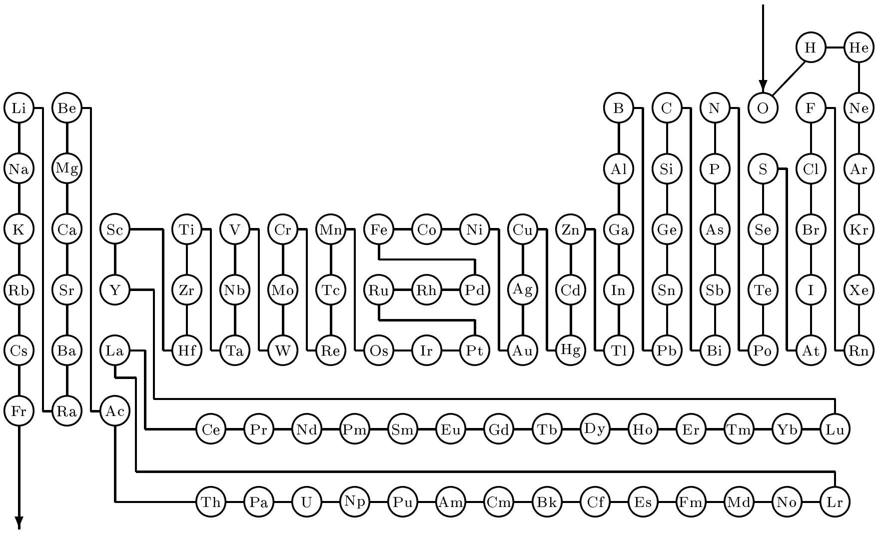
The measurement and use of pH in equilibrium analytical investigations creates many problems that have not always been taken into account by the investigators, as discussed in many reviews in Appendix A. In order to deduce the stoichiometry and equilibrium constants of complex formation reactions and 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 $-\log_{10}[\mathrm{H}^+]$ (also often referred to as pcH) rather than on the activity scale as pH, and the value of $-\log_{10}[\mathrm{H}^+]$ and pH will differ by a constant term, *i.e.*, $\log_{10}\gamma_{\mathrm{H}^+}$. 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 – $\log_{10}[H^+]$ and pH is virtually the same, in very good experiments, ± 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 – $\log_{10}[H^+]$ calibration standards can be prepared far more accurately than the commercial pH standards.

II.1.10 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.

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



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 $UOF_2(cr)$, $UOF_4(cr)$, $UOF_4(g)$, $UO_2F(aq)$, UO_2F^+, $UO_2F_2(aq)$, $UO_2F_2(cr)$, $UO_2F_2(g)$, $UO_2F_3^-$, $UO_2F_4^{2-}$, $U_2O_3F_6(cr)$, *etc.* [1992GRE/FUG]. Formulae with identical stoichiometry are in alphabetical order of their designators.

II.1.11 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)	1×10^{-10} (exactly)
standard atmosphere (atm)	pascal (Pa)	1.01325×10^{5} (exactly)
bar (bar)	pascal (Pa)	1×10^{5} (exactly)
thermochemical calorie (cal)	joule (J)	4.184 (exactly)
entropy unit e.u. $\triangleq \text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	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 “$\text{mol}\cdot\text{dm}^{-3}$” for molarity, *c*, and, in Appendices B and C, “m” as an abbreviation of “$\text{mol}\cdot\text{kg}^{-1}$” for molality, *m*. It is often necessary to convert concentration 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 theory, which works in molality units (*cf.* Appendix B). This conversion is made in the following way. Molality is defined as m_B moles of substance B dissolved in 1 kilogram of pure water. Molarity is defined as c_B moles of substance B dissolved in $(\rho - c_\mathrm{B}M)$ kilogram of pure water, where ρ is the density of the solution in $\mathrm{kg \cdot dm^{-3}}$ and M the molar weight of the solute in $\mathrm{kg \cdot mol^{-1}}$. From this it follows that:

$$m_\mathrm{B} = \frac{c_\mathrm{B}}{\rho - c_\mathrm{B}M} .$$

Baes and Mesmer [1976BAE/MES], (*p*.439) give a table with conversion factors (from molarity to molality) for nine electrolytes and 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:

$1.00\ \mathrm{M\ NaClO_4} \triangleq 1.05\ \mathrm{m\ NaClO_4}$

$1.00\ \mathrm{M\ NaCl} \triangleq 1.02\ \mathrm{m\ NaCl}$

$4.00\ \mathrm{M\ NaClO_4} \triangleq 4.95\ \mathrm{m\ NaClO_4}$

$6.00\ \mathrm{M\ NaNO_3} \triangleq 7.55\ \mathrm{m\ NaNO_3}$

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, $0 = \sum_\mathrm{B} \nu_\mathrm{B}\mathrm{B}$, the equilibrium constants can be expressed either in molarity or molality units, K_c or K_m , respectively:

$$\log_{10} K_c = \sum_\mathrm{B} \nu_\mathrm{B} \log_{10} c_\mathrm{B}$$

$$\log_{10} K_m = \sum_\mathrm{B} \nu_\mathrm{B} \log_{10} m_\mathrm{B}$$

With $(m_\mathrm{B} / c_\mathrm{B}) = \xi$, or $(\log_{10} m_\mathrm{B} - \log_{10} c_\mathrm{B}) = \log_{10} \xi$, the relationship between K_c and K_m becomes very simple, as shown in Eq.(II.39).

$$\log_{10} K_m = \log_{10} K_c + \sum_\mathrm{B} \nu_\mathrm{B} \log_{10} \xi \qquad \text{(II.39)}$$

$\sum_\mathrm{B} \nu_\mathrm{B}$ is the sum of the stoichiometric coefficients of the solutes, *cf.* Eq. (II.55) and the values of ξ 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 $\pm 0.003\ \mathrm{dm^3 \cdot kg^{-1}}$, reflecting the accuracy expected in this type of conversion. The uncertainty introduced by the use of Eq.(II.39) in the values of $\log_{10} K_m$ will be no larger than $\pm 0.001 \sum_\mathrm{B} \nu_\mathrm{B}$.

Table II-5: Factors ξ 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]).

	$\xi = m_B / c_B$ (dm^3 of solution per kg of H_2O)							
c (M)	$HClO_4$	$NaClO_4$	$LiClO_4$	NH_4ClO_4	$Ba(ClO_4)_2$	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_4Cl	$MgCl_2$	$CaCl_2$	NaBr	HNO_3	$NaNO_3$	$LiNO_3$
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_4NO_3	H_2SO_4	Na_2SO_4	$(NH_4)_2SO_4$	H_3PO_4	Na_2CO_3	K_2CO_3	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, $p^\circ = 0.1$ 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 a hypothetical liquid 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 γ_B is unity.

It should be emphasised that the use of superscript, $^\circ$, *e.g.*, in $\Delta_\text{f}H_\text{m}^\circ$, 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_2	gaseous	Zn	crystalline, hexagonal
H_2	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_2	gaseous	Tc	crystalline, hexagonal
Cl_2	gaseous	V	crystalline, cubic
Br_2	liquid	Ti	crystalline, hexagonal
I_2	crystalline, orthorhombic	Am	crystalline, dhcp
S	crystalline, orthorhombic	Pu	crystalline, monoclinic
Se	crystalline, trigonal	Np	crystalline, orthorhombic
Te	crystalline, hexagonal	U	crystalline, orthorhombic
N_2	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 the International Union of Pure and Applied Chemistry IUPAC [1982LAF].

However, the majority of the thermodynamic data published in the scientific literature and used for the evaluations in this review, refer 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 propagation 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:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = V(1-\alpha T) \qquad \text{(II.40)}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \qquad \text{(II.41)}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\alpha = -\left(\frac{\partial V}{\partial T}\right)_p \qquad \text{(II.42)}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \text{(II.43)}$$

$$\text{where} \quad \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \qquad \text{(II.44)}$$

For ideal gases, $V = \mathrm{R}T / p$ and $\alpha = \mathrm{R} / pV = 1/T$. The conversion equations listed below (Eqs. (II.45) to (II.52)) 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 $^{(atm)}$, and those that refer to the new standard state pressure of 1 bar are assigned the superscript $^{(bar)}$.

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.

$$\Delta_\mathrm{f} H^{(\mathrm{bar})}(T) - \Delta_\mathrm{f} H^{(\mathrm{atm})}(T) = 0 \qquad \text{(II.45)}$$

$$C_p^{(\mathrm{bar})}(T) - C_p^{(\mathrm{atm})}(T) = 0 \qquad \text{(II.46)}$$

For gaseous substances, the entropy difference is:

$$S^{(\mathrm{bar})}(T) - S^{(\mathrm{atm})}(T) = \mathrm{R}\ \ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right) = \mathrm{R}\ \ln\ 1.01325$$
$$= 0.1094\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} \qquad \text{(II.47)}$$

This is exactly true for ideal gases, as follows from Eq.(II.42) with $\alpha = \mathrm{R} / pV$. The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

$$\Delta_\mathrm{r} S^{(\mathrm{bar})} - \Delta_\mathrm{r} S^{(\mathrm{atm})} = \delta \cdot \mathrm{R} \ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right)$$

$$= \delta \times 0.1094 \text{ J·K}^{-1}\text{·mol}^{-1} \qquad \text{(II.48)}$$

where δ 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:

$$\Delta_\mathrm{r} G^{(\mathrm{bar})} - \Delta_\mathrm{r} G^{(\mathrm{atm})} = -\delta \cdot \mathrm{R}T \ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right)$$

$$= -\delta \times 0.03263 \text{ kJ·mol}^{-1} \text{ at } 298.15\text{ K}. \qquad \text{(II.49)}$$

Eq.(II.49) applies also to $\Delta_\mathrm{f} G^{(\mathrm{bar})} - \Delta_\mathrm{f} G^{(\mathrm{atm})}$, since the Gibbs energy of formation describes the formation process of a compound or complex from the reference states of the elements involved:

$$\Delta_\mathrm{f} G^{(\mathrm{bar})} - \Delta_\mathrm{f} G^{(\mathrm{atm})} = -\delta \times 0.03263 \text{ kJ·mol}^{-1} \text{ at } 298.15\text{ K}. \qquad \text{(II.50).}$$

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.49),

$$\log_{10} K^{(\mathrm{bar})} - \log_{10} K^{(\mathrm{atm})} = -\frac{\Delta_\mathrm{r} G^{(\mathrm{bar})} - \Delta_\mathrm{r} G^{(\mathrm{atm})}}{\mathrm{R}T \ln 10}$$

$$= \delta \cdot \frac{\ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right)}{\ln 10} = \delta \cdot \log_{10}\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right)$$

$$= \delta \times 0.005717 \qquad \text{(II.51)}$$

$$E^{(\mathrm{bar})} - E^{(\mathrm{atm})} = -\frac{\Delta_\mathrm{r} G^{(\mathrm{bar})} - \Delta_\mathrm{r} G^{(\mathrm{atm})}}{n\mathrm{F}}$$

$$= \delta \cdot \frac{\mathrm{R}T \ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right)}{n\mathrm{F}}$$

$$= \delta \cdot \frac{0.0003382}{n} \mathrm{V} \quad \text{at } 298.15\text{ K} \qquad \text{(II.52)}$$

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

$$\mathrm{H}^+ + e^- \rightleftharpoons \frac{1}{2}\mathrm{H}_2(\mathrm{g}) \qquad E^\circ \overset{\mathrm{def}}{=} 0.00\mathrm{V} \qquad \text{(II.53).}$$

This definition will not be changed, although a gaseous substance, $H_2(g)$, is involved in the process. The change in the potential with pressure for an electrode potential conventionally written as:

$$Ag^+ + e^- \rightleftharpoons Ag\,(cr)$$

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

$$Ag^+ + \frac{1}{2}H_2\,(g) \rightleftharpoons Ag\,(cr) + H^+$$

Here $\delta = -0.5$. Hence, the contribution to δ 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 δ as the combination with the hydrogen half cell.

Example:

$Fe(cr) + 2\,H^+ \rightleftharpoons Fe^{2+} + H_2(g)$	$\delta = 1$	$E^{(bar)} - E^{(atm)} = 0.00017\ V$
$CO_2(g) \rightleftharpoons CO_2(aq)$	$\delta = -1$	$\log_{10} K^{(bar)} - \log_{10} K^{(atm)} = -0.0057$
$NH_3(g) + \frac{5}{4}O_2 \rightleftharpoons NO(g) + \frac{3}{2}H_2O(g)$	$\delta = 0.25$	$\Delta_r G^{(bar)} - \Delta_r G^{(atm)} = -0.008\ kJ \cdot mol^{-1}$
$\frac{1}{2}Cl_2(g) + 2\,O_2(g) + e^- \rightleftharpoons ClO_4^-$	$\delta = -3$	$\Delta_f G^{(bar)} - \Delta_f G^{(atm)} = 0.098\ kJ \cdot mol^{-1}$

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 $T = 298.15$ K or $t = 25.00$°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 (°C) is defined by $t = (T - T_o)$ where $T_o = 273.15$ K.

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. Note that 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	299 792 458	$\mathrm{m \cdot s^{-1}}$
permeability of vacuum	μ_0	$4\pi\times10^{-7} = 12.566\ 370\ 614\ldots$	$10^{-7}\ \mathrm{N \cdot A^{-2}}$
permittivity of vacuum	ϵ_0	$1/\mu_0\, c^2 = 8.854\ 187\ 817\ldots$	$10^{-12}\ \mathrm{C^2 \cdot J^{-1} \cdot m^{-1}}$
Planck constant	h	6.626 0755(40)	$10^{-34}\ \mathrm{J \cdot s}$
elementary charge	e	1.602 177 33(49)	$10^{-19}\mathrm{C}$
Avogadro constant	N_A	6.022 1367(36)	$10^{23}\ \mathrm{mol^{-1}}$
Faraday constant	F	96 485.309(29)	$\mathrm{C \cdot mol^{-1}}$
molar gas constant	R	8.314 510(70)	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
Boltzmann constant, R/N_A	k	1.380 658(12)	$10^{-23}\ \mathrm{J \cdot K^{-1}}$
Non–SI units used with SI:			
electron volt, (e/C) J	eV	1.602 177 33(49)	$10^{-19}\ \mathrm{J}$
atomic mass unit,	u	1.660 5402(10)	$10^{-27}\ \mathrm{kg}$
$1\mathrm{u} = m_{\mathrm{u}} = \frac{1}{12} m\,(^{12}C)$			

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:

$\Delta_\mathrm{f} G^\circ_\mathrm{m}$	the standard molar Gibbs energy of formation from the elements in their reference state ($\mathrm{kJ \cdot mol^{-1}}$)
$\Delta_\mathrm{f} H^\circ_\mathrm{m}$	the standard molar enthalpy of formation from the elements in their reference state ($\mathrm{kJ \cdot mol^{-1}}$)
S°_m	the standard molar entropy ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)
$C^\circ_{p,\mathrm{m}}$	the standard molar heat capacity ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$).

For aqueous neutral species and ions, the values of $\Delta_\mathrm{f} G^\circ_\mathrm{m}$, $\Delta_\mathrm{f} H^\circ_\mathrm{m}$, S°_m and $C^\circ_{p,\mathrm{m}}$ 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 $\Delta_\mathrm{f} H^\circ_\mathrm{m}(\mathrm{H}^+, T) = 0$ and that $S^\circ_\mathrm{m}(\mathrm{H}^+, T) = 0$. Furthermore, for an *ionised solute* B containing any number of different cations and anions:

$$\Delta_\mathrm{f} H^\circ_\mathrm{m}(\mathrm{B}_\pm, \mathrm{aq}) = \sum_+ \nu_+ \, \Delta_\mathrm{f} H^\circ_\mathrm{m}(\text{cation, aq}) + \sum_- \nu_- \, \Delta_\mathrm{f} H^\circ_\mathrm{m}(\text{anion, aq})$$

$$S^\circ_\mathrm{m}(\mathrm{B}_\pm, \mathrm{aq}) = \sum_+ \nu_+ \, S^\circ_\mathrm{m}(\text{cation, aq}) + \sum_- \nu_- \, S^\circ_\mathrm{m}(\text{anion, aq})$$

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:

$$\begin{aligned} X(T) &= a_X + b_X \cdot T + c_X \cdot T^2 + d_X \cdot T^{-1} + e_X \cdot T^{-2} + f_X \cdot \ln T + g_X \cdot T \ln T \\ &\quad + h_X \cdot \sqrt{T} + \frac{i_X}{\sqrt{T}} + j_X \cdot T^3 + k_X \cdot T^{-3}. \end{aligned} \qquad \text{(II.54)}$$

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

$$C_{p,\mathrm{m}}(T) = a + b \cdot T + c \cdot T^2 + d \cdot T^{-1} + e \cdot T^{-2}$$

(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:

$$0 = \sum_{\mathrm{B}} \nu_{\mathrm{B}}^{r}\ \mathrm{B} \qquad \text{(II.55)}$$

where the stoichiometric coefficients $\upsilon_{\mathrm{B}}^{r}$ 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
$\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\circ}$	the molar Gibbs energy of reaction ($\mathrm{kJ \cdot mol^{-1}}$)
$\Delta_{\mathrm{r}} H_{\mathrm{m}}^{\circ}$	the molar enthalpy of reaction ($\mathrm{kJ \cdot mol^{-1}}$)
$\Delta_{\mathrm{r}} S_{\mathrm{m}}^{\circ}$	the molar entropy of reaction ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)
$\Delta_{\mathrm{r}} C_{p,\mathrm{m}}^{\circ}$	the molar heat capacity of reaction ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$).

The temperature functions of these data, if available, are stored according to Eq.(II.54).

The equilibrium constant, K_r°, is related to $\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\circ}$ according to the following relation:

$$\log_{10} K_r^{\circ} = -\frac{\Delta_{\mathrm{r}} G_{\mathrm{m}}^{\circ}}{\mathrm{R}T \ln(10)}$$

and can be calculated from the individual values of $\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{B})$ (for example, those given in selected values tables), according to:

$$\log_{10} K_r^{\circ} = -\frac{1}{\mathrm{R}T \ln(10)} \sum_{\mathrm{B}} \nu_{\mathrm{B}}^{r}\ \Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{B}) \qquad \text{(II.56)}$$

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 298.15K (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 thorium (Table III-1), a table of selected reaction data (Table III-2) for reactions concerning thorium species and a table containing the heat capacities of individual species of thorium (Table III-3) that have been used in the evaluations. The selection of all these data is discussed in Chapters V to XII. For the gaseous species, in particular, only the more important of the heat capacity equations have been given explicitly in the relevant sections of these chapters.

Chapter IV contains, for auxiliary compounds and complexes that do not contain thorium, a table of the thermodynamic data for individual species (Table IV-1) and a table of reaction data (Table IV-2). 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] and [2005OLI/NOL].

All the selected data presented in Table III-1, Table III-2, Table III-3 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 data base system, *cf.* Section II.6. Therefore, when using the selected data for organic species, 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 there from 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 that 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 later 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:

$$\Delta_r G^\circ_m(T) \;=\; \Delta_r H^\circ_m(T_0) + \int_{T_0}^{T} \Delta_r C^\circ_{p,m}(\mathrm{T})\,\mathrm{d}T - T\left(\Delta_r S^\circ_m(T_0) + \int_{T_0}^{T} \frac{\Delta_r C^\circ_{p,m}(\mathrm{T})}{T}\mathrm{d}T\right),$$

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

$$\begin{aligned}\log_{10} K^\circ(T) \;&=\; \log_{10} K^\circ(T_0) \;-\; \frac{\Delta_r H^\circ_m(T_0)}{\mathrm{R}\ln(10)}\left(\frac{1}{T} - \frac{1}{T_0}\right)\\ &\quad -\; \frac{1}{\mathrm{R}T\ln(10)}\int_{T_0}^{T} \Delta_r C^\circ_{p,m}(T)\,\mathrm{d}T \;+\; \frac{1}{\mathrm{R}\ln(10)}\int_{T_0}^{T} \frac{\Delta_r C^\circ_{p,m}(T)}{T}\mathrm{d}T,\end{aligned}$$

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 1 to 2 logarithmic units, due to neglecting 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 25°C 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° at $I = 0$ using activity coefficients γ, is explained in Appendix B. The corresponding Gibbs energy of dilution is:

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

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

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

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

depends only on the variation of γ with T, which is neglected in this review, when no data on the temperature dependence of γ'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 $\Delta_{\text{r}}G^{\circ}_{\text{m}} = \Delta_{\text{r}}H^{\circ}_{\text{m}} - T\Delta_{\text{r}}S^{\circ}_{\text{m}}$, the above assumption $\Delta_{\text{dil}}H_{\text{m}} = 0$, and $\Delta_{\text{dil}}G_{\text{m}}$.

Part 2

Tables of selected data

Chapter III

Selected thorium data

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

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 Chapter V of this review. These selected reaction data are used, together with data for key thorium 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 thorium 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 $\Delta_{\mathrm{r}}G_{\mathrm{m}}^{\circ}$ for many reactions are known more accurately than would be calculated directly from the uncertainties of the $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ 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

$$C_{p,\mathrm{m}}^{\circ}(T) = a + b \times T + c \times T^{2} + d \times T^{-1} + i \times T^{-1/2}$$

A detailed discussion of the selection procedure is presented in Chapter V. 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 thorium 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 XII. 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	$\Delta_f G^o_m$ (kJ·mol^{-1})	$\Delta_f H^o_m$ (kJ·mol^{-1})	S^o_m (J·K^{-1}·mol^{-1})	$C^o_{p,m}$ (J·K^{-1}·mol^{-1})
Th(cr, α) (fcc)	0.000	0.000	52.640 ±0.500	26.230 ±0.500
Th(g)	560.995 (a) ±6.002	602.000 ±6.000	190.170 ±0.010	20.790 ±0.005
Th^{4+}	– 704.783 (a) ±5.298	– 768.700 ±2.300	– 423.100 ±16.000	– 224.000 ±15.000
ThO(g)	– 51.299 (a) ±6.002	– 26.000 ±6.000	240.070 ±0.050	31.270 ±0.100
ThO$_2$(cr)	– 1168.988 (a) ±3.504	– 1226.400 ±3.500	65.230 ±0.200	61.740 ±0.150
ThO$_2$(g)	– 462.128 (a) ±15.430	– 455.000 (b) ±15.403	281.700 ±3.000	46.840 ±0.500
ThH(g)			233.500 ±5.000	29.600 ±4.000
ThH$_2$(cr)	– 105.468 (a) ±2.006	– 145.000 ±2.000	50.730 ±0.100	36.710 ±0.070
ThD$_2$(cr)			55.720 ±0.560	47.670 ±0.470
ThT$_2$(cr)			60.460 ±0.600	54.300 ±0.540
ThH$_{3.75}$(cr)	– 142.877 (a) ±8.001	– 215.400 ±8.000	54.420 ±0.110	51.320 ±0.100
ThD$_{3.75}$(cr)			63.970 ±0.640	69.710 ±0.700
ThT$_{3.75}$(cr)			72.650 ±0.730	81.490 ±0.810

(Continued on next page)

Table III-1 (Continued)

Compound	$\Delta_f G^o_m$ (kJ·mol^{-1})	$\Delta_f H^o_m$ (kJ·mol^{-1})	S^o_m (J·K^{-1}·mol^{-1})	$C^o_{p,m}$ (J·K^{-1}·mol^{-1})
$Th(OH)^{3+}$	– 927.653 (b) ±6.018	– 1010.330 (b) ±6.707	– 252.765 (b) ±28.180	
$Th(OH)_2^{2+}$	– 1143.673 (b) ±6.018	– 1254.660 (b) ±41.464	– 114.459 (b) ±140.102	
$Th(OH)_4(aq)$	– 1554.024 (b) ±6.638			
$Th_2(OH)_2^{6+}$	– 1850.168 (b) ±10.974	– 2050.760 (b) ±7.325	– 623.716 (b) ±38.485	
$Th_2(OH)_3^{5+}$	– 2082.171 (b) ±10.658			
$Th_4(OH)_8^{8+}$	– 4599.809 (b) ±21.317	– 5118.440 (b) ±23.204	– 708.329 (b) ±96.221	
$Th_4(OH)_{12}^{4+}$	– 5512.980 (b) ±21.228			
$Th_6(OH)_{14}^{10+}$	– 7338.604 (b) ±32.523			
$Th_6(OH)_{15}^{9+}$	– 7575.744 (b) ±32.927	– 8426.850 (b) ±25.977	– 608.102 (b) ±124.441	
ThF(g)	– 0.788 (a) ±15.422	30.000 ±15.000	257.300 ±12.000	34.700 ±6.000
ThF^{3+}	– 1036.936 (b) ±5.411	– 1104.450 (b) ±3.116	– 268.427 (b) ±17.604	
$ThF_2(g)$	– 601.857 (a) ±20.222	– 590.000 ±20.000	295.200 ±10.000	52.400 ±5.000
ThF_2^{2+}	– 1357.046 (b) ±5.631	– 1442.700 (b) ±2.672	– 162.534 (b) ±16.726	
$ThF_3(g)$	– 1159.774 (a) ±15.294	– 1165.000 ±15.000	339.300 ±10.000	73.300 ±5.000
ThF_3^{+}	– 1667.337 (b) ±5.763			
$ThF_4(cr)$	– 2005.736 (a) ±10.001	– 2100.000 ±10.000	142.060 ±0.170	110.710 ±0.130
$ThF_4(g)$	– 1719.328 (a) ±10.217	– 1750.700 (b) ±10.198	353.000 ±2.000	93.400 ±2.000
$ThF_4(aq)$	– 1976.887 (b) ±6.066			

(Continued on next page)

Table III-1 (Continued)

Compound	$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ ($\mathrm{kJ\cdot mol^{-1}}$)	$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{kJ\cdot mol^{-1}}$)	S°_{m} ($\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$)	$C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$)
ThOF(g)	– 566.186 (a) ±12.366	– 550.000 ±12.000	310.900 ±10.000	49.500 ±5.000
$ThOF_2$(cr)	– 1589.171 (a) ±7.948	– 1663.800 ±7.800	107.700 ±5.100	
ThCl(g)	215.688 (a) ±20.318	247.000 ±20.000	269.200 ±12.000	36.400 ±6.000
$ThCl^{3+}$	– 845.704 (b) ±5.330			
$ThCl_2$(g)	– 191.337 (a) ±22.202	– 179.000 ±22.000	317.100 ±10.000	55.300 ±5.000
$ThCl_3$(g)	– 563.764 (a) ±25.178	– 569.000 ±25.000	369.700 ±10.000	78.000 ±5.000
β-$ThCl_4$	– 1092.293 (a) ±1.984	– 1186.300 ±1.300	183.500 ±5.000	120.300 ±6.000
$ThCl_4\cdot 2H_2O$(cr)		– 1822.400 ±12.000		
$ThCl_4\cdot 4H_2O$(cr)		– 2456.200 ±12.000		
$ThCl_4\cdot 7H_2O$(cr)		– 3361.900 ±12.000		
$ThCl_4\cdot 8H_2O$(cr)		– 3661.300 ±12.000		
$ThCl_4$(g)	– 922.956 (a) ±5.304	– 951.400 (b) ±5.166	403.400 ±4.000	101.400 ±3.000
$ThOCl_2$(cr)	– 1153.564 (a) ±2.276	– 1231.500 ±2.100	116.900 ±2.900	
$ThClO_3^{3+}$	– 721.534 (b) ±5.515			
ThBr(g)	319.575 (a) ±20.318	365.000 ±20.000	281.100 ±12.000	37.400 ±6.000
$ThBr^{3+}$	– 816.510 (b) ±5.352			
$ThBr_2$(g)	– 0.027 (a) ±20.222	40.000 ±20.000	339.100 ±10.000	56.700 ±5.000
$ThBr_3$(g)	– 371.073 (a) ±15.295	– 334.000 ±15.000	405.300 ±10.000	80.800 ±5.000

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Table III-1 (Continued)

Compound	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
β-$ThBr_4$	– 925.023 [(a)] ±2.505	– 963.800 ±2.000	227.000 ±5.000	125.200 ±6.000
$ThBr_4 \cdot 7 H_2O(cr)$		– 3163.900 ±12.000		
$ThBr_4 \cdot 10 H_2O(cr)$		– 4074.600 ±12.000		
$ThBr_4 \cdot 12 H_2O(cr)$		– 4677.800 ±12.000		
$ThBr_4(g)$	– 769.026 [(a)] ±5.593	– 742.300 [(b)] ±5.385	446.700 ±5.000	104.900 ±3.000
$ThOBr_2(cr)$		– 1129.800 ±5.400		
$ThBrO_3^{3+}$	– 696.558 [(b)] ±5.366			
$ThI(g)$			288.600 ±12.000	37.500 ±6.000
$ThI_2(g)$			355.600 ±10.000	57.400 ±5.000
$ThI_3(g)$			430.000 ±10.000	81.800 ±5.000
$ThI_4(cr)$	– 659.487 [(a)] ±2.668	– 669.600 ±2.200	251.000 ±5.000	137.100 ±10.000
$ThI_4(g)$	– 518.316 [(a)] ±5.753	– 460.600 [(b)] ±5.463	478.500 ±6.000	106.200 ±4.000
$ThOI_2(cr)$		– 996.600 ±2.300		
$ThIO_3^{3+}$	– 854.752 [(b)] ±5.385			
$Th(IO_3)_2^{2+}$	– 997.243 [(b)] ±5.565			
$Th(IO_3)_3^{+}$	– 1140.134 [(b)] ±5.825			
$ThS(cr)$	– 391.862 [(a)] ±6.205	– 396.300 ±6.200	69.810 ±0.700	47.720 ±0.500
$ThS_2(cr)$			96.230 ±1.700	70.290 ±0.500

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Table III-1 (Continued)

Compound	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
$Th_2S_3(cr)$		– 1079.000 ±5.500		
$ThOS(cr)$			76.300 ±1.500	67.250 ±1.350
$ThSO_4^{2+}$	– 1484.006 (b) ±5.620	– 1657.120 (b) ±2.449	– 216.308 (b) ±17.316	
$Th(SO_4)_2(cr)$				173.500 ±5.000
$Th(SO_4)_2\cdot 9\ H_2O(cr)$	– 4391.269 (b) ±5.404			
$Th(SO_4)_2(aq)$	– 2248.102 (b) ±5.580	– 2547.000 (b) ±2.664	– 65.151 (b) ±17.219	
$Th(SO_4)_3^{2-}$	– 2998.147 (b) ±5.461			
$ThOSe(cr)$			93.500 ±1.900	72.650 ±1.500
$ThN(cr)$	– 353.638 (a) ±10.011	– 381.200 (b) ±10.000	56.000 ±1.500	45.000 ±1.100
ThN_3^{3+}	– 381.926 (b) ±6.739			
$Th(N_3)_2^{2+}$	– 57.415 (b) ±7.577			
$Th_3N_4(cr)$	– 1200.051 (a) ±15.659	– 1306.800 ±15.000	183.100 ±15.000	147.700 ±8.000
$Th(NO_3)_4\cdot 4\ H_2O(cr)$		– 2702.400 ±3.800		
$Th(NO_3)_4\cdot 5\ H_2O(cr)$	– 2322.651 (a) ±2.814	– 3005.400 ±2.800	543.100 ±0.800	480.700 ±0.800
$ThNO_3^{3+}$	– 822.997 (b) ±5.436			
$Th(NO_3)_2^{2+}$	– 939.499 (b) ±5.829			
$Th_4(PO_4)_4P_2O_7(cr)$				569.000 ±15.000
$ThH_2PO_4^{3+}$	– 1873.843 (b) ±5.822			

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Table III-1 (Continued)

Compound	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
$ThH_3PO_4^{4+}$	– 1864.938 (b) ±5.804			
$Th(H_2PO_4)_2^{2+}$	– 3038.907 (b) ±6.430			
$Th(H_3PO_4)(H_2PO_4)^{3+}$	– 3034.455 (b) ±6.430			
ThAs(cr)			79.800 ±0.500	50.500 ±0.500
Th_3As_4(cr)			274.600 ±1.500	183.300 ±1.500
ThBi(cr)		– 162.300 ±4.200		
$ThBi_2$(cr)		– 207.100 ±6.300		
Th_3Bi_4(cr)		– 597.500 ±14.600		
Th_5Bi_3(cr)		– 532.200 ±16.700		
Th_5Sn_3(cr)		– 510.400 ±32.000		
$ThC_{0.97}$(cr)	– 124.466 (a) ±6.308	– 124.200 ±6.300	59.100 ±0.900	45.200 ±0.400
$ThC_{1.94}$(s)	– 126.705 (a) ±7.503	– 124.700 ±7.500	70.500 ±0.400	56.800 ±0.200
$Th(CO_3)_5^{6-}$	– 3521.231 (b) ±6.917			
$Th(OH)_2(CO_3)_2^{2-}$	– 2285.078 (b) ±6.070			
$ThOH(CO_3)_4^{5-}$	– 3176.808 (b) ±6.217			
$Th(OH)_4(CO_3)^{2-}$	– 2092.167 (b) ±6.327			
$ThSCN^{3+}$	– 623.499 (b) ±7.226			
$Th(SCN)_2^{2+}$	– 538.790 (b) ±10.626			

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Table III-1 (Continued)

Compound	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
$ThSi_2$(cr)		– 169.500 ±9.600		
$ThSiO_4$(huttonite)		– 2110.800 ±4.700		
$ThSiO_4$(Thorite)		– 2117.500 ±4.200		
$Na_6Th(CO_3)_5\cdot 12\ H_2O$(cr)	– 8002.562 (b) ±7.301			
$ThTi_2O_6$(cr)		– 3095.000 ±4.300		

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

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

Table III-2: Selected thermodynamic data for reactions involving thorium 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 XII. 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				
		$\log_{10} K^{\circ}$	$\Delta_r G^{\circ}_m$ (kJ·mol^{-1})	$\Delta_r H^{\circ}_m$ (kJ·mol^{-1})	$\Delta_r S^{\circ}_m$ (J·K^{-1}·mol^{-1})
Th(g)	$Th(cr) \rightleftharpoons Th(g)$				
				602.000 ±6.000	
$ThO_2(g)$	$ThO_2(cr) \rightleftharpoons ThO_2(g)$				
				771.400 ±15.000	
ThO_2(am, hyd, fresh)	$4OH^- + Th^{4+} \rightleftharpoons 2H_2O(l) + ThO_2$(am, hyd, fresh)				
		46.700 ±0.900	−266.566 ±5.137		
ThO_2(am, hyd, aged)	$4OH^- + Th^{4+} \rightleftharpoons 2H_2O(l) + ThO_2$(am, hyd, aged)				
		47.500 ±0.900	−271.132 ±5.137		
$Th(OH)^{3+}$	$H_2O(l) + Th^{4+} \rightleftharpoons H^+ + Th(OH)^{3+}$				
		−2.500 ±0.500	14.270 ±2.854	44.200 ±6.300	100.385 (a) ±23.197
$Th(OH)_2^{2+}$	$2H_2O(l) + Th^{4+} \rightleftharpoons 2H^+ + Th(OH)_2^{2+}$				
		−6.200 ±0.500	35.390 ±2.854	85.700 ±41.400	168.741 (a) ±139.186
$Th(OH)_4(aq)$	$4H_2O(l) + Th^{4+} \rightleftharpoons 4H^+ + Th(OH)_4(aq)$				
		−17.400 ±0.700	99.320 ±3.996		
$Th_2(OH)_2^{6+}$	$2H_2O(l) + 2Th^{4+} \rightleftharpoons 2H^+ + Th_2(OH)_2^{6+}$				
		−5.900 ±0.500	33.677 ±2.854	58.300 ±5.700	82.584 (a) ±21.380

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Table III-2 (Continued)

Species	Reaction			
	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$	$\Delta_r H^\circ_m$	$\Delta_r S^\circ_m$
		(kJ·mol^{-1})	(kJ·mol^{-1})	(J·K^{-1}·mol^{-1})
$Th_2(OH)_3^{5+}$	$3H_2O(l) + 2Th^{4+} \rightleftharpoons 3H^+ + Th_2(OH)_3^{5+}$			
	–6.800	38.815		
	±0.200	±1.142		
$Th_4(OH)_8^{8+}$	$8H_2O(l) + 4Th^{4+} \rightleftharpoons 8H^+ + Th_4(OH)_8^{8+}$			
	–20.400	116.444	243.000	424.471 (a)
	±0.400	±2.283	±21.300	±71.850
$Th_4(OH)_{12}^{4+}$	$12H_2O(l) + 4Th^{4+} \rightleftharpoons 12H^+ + Th_4(OH)_{12}^{4+}$			
	–26.600	151.834		
	±0.200	±1.142		
$Th_6(OH)_{14}^{10+}$	$14H_2O(l) + 6Th^{4+} \rightleftharpoons 14H^+ + Th_6(OH)_{14}^{10+}$			
	–36.800	210.056		
	±1.200	±6.850		
$Th_6(OH)_{15}^{9+}$	$15H_2O(l) + 6Th^{4+} \rightleftharpoons 15H^+ + Th_6(OH)_{15}^{9+}$			
	–36.800	210.056	472.800	881.248 (a)
	±1.500	±8.562	±22.000	±79.180
ThF^{3+}	$F^- + Th^{4+} \rightleftharpoons ThF^{3+}$			
	8.870	–50.630	–0.400	168.473 (a)
	±0.150	±0.856	±2.000	±7.297
ThF_2^{2+}	$2F^- + Th^{4+} \rightleftharpoons ThF_2^{2+}$			
	15.630	–89.217	–3.300	288.166 (a)
	±0.230	±1.313	±0.400	±4.603
ThF_3^+	$3F^- + Th^{4+} \rightleftharpoons ThF_3^+$			
	20.670	–117.985		
	±0.160	±0.913		
ThF_4(cr, hyd)	$4HF(aq) + Th^{4+} \rightleftharpoons 4H^+ + ThF_4(cr, hyd)$			
	19.110	–109.081		
	±0.400	±2.283		
ThF_4(g)	$ThF_4(cr) \rightleftharpoons ThF_4(g)$			
			349.300	
			±2.000	
ThF_4(aq)	$4F^- + Th^{4+} \rightleftharpoons ThF_4(aq)$			
	25.580	–146.012		
	±0.180	±1.027		

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Table III-2 (Continued)

Species	Reaction			
	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$	$\Delta_r H^\circ_m$	$\Delta_r S^\circ_m$
		(kJ·mol^{-1})	(kJ·mol^{-1})	(J·K^{-1}·mol^{-1})
$ThCl^{3+}$	$Cl^- + Th^{4+} \rightleftharpoons ThCl^{3+}$			
	1.700	–9.704		
	±0.100	±0.571		
$ThCl_4(g)$	β-$ThCl_4 \rightleftharpoons ThCl_4(g)$			
			234.900	
			±5.000	
$ThClO_3^{3+}$	$ClO_3^- + Th^{4+} \rightleftharpoons ThClO_3^{3+}$			
	1.550	–8.847		
	±0.130	±0.742		
$ThBr^{3+}$	$Br^- + Th^{4+} \rightleftharpoons ThBr^{3+}$			
	1.380	–7.877		
	±0.130	±0.742		
$ThBr_4(g)$	β-$ThBr_4 \rightleftharpoons ThBr_4(g)$			
			221.500	
			±5.000	
$ThBrO_3^{3+}$	$BrO_3^- + Th^{4+} \rightleftharpoons ThBrO_3^{3+}$			
	1.900	–10.845		
	±0.100	±0.571		
$ThI_4(g)$	$ThI_4(cr) \rightleftharpoons ThI_4(g)$			
			209.000	
			±5.000	
$ThIO_3^{3+}$	$IO_3^- + Th^{4+} \rightleftharpoons ThIO_3^{3+}$			
	4.140	–23.631		
	±0.100	±0.571		
$Th(IO_3)_2^{2+}$	$2IO_3^- + Th^{4+} \rightleftharpoons Th(IO_3)_2^{2+}$			
	6.970	–39.785		
	±0.120	±0.685		
$Th(IO_3)_3^{+}$	$3IO_3^- + Th^{4+} \rightleftharpoons Th(IO_3)_3^{+}$			
	9.870	–56.338		
	±0.110	±0.628		
$ThSO_4^{2+}$	$SO_4^{2-} + Th^{4+} \rightleftharpoons ThSO_4^{2+}$			
	6.170	–35.219	20.920	188.292 (a)
	±0.320	±1.827	±0.740	±6.610

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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^{-1})	(kJ·mol^{-1})	(J·K^{-1}·mol^{-1})
$Th(SO_4)_2 \cdot 9H_2O(cr)$	$9H_2O(l) + 2SO_4^{2-} + Th^{4+} \rightleftharpoons Th(SO_4)_2 \cdot 9H_2O(cr)$			
	11.250	–64.215		
	±0.096	±0.548		
$Th(SO_4)_2(aq)$	$2SO_4^{2-} + Th^{4+} \rightleftharpoons Th(SO_4)_2(aq)$			
	9.690	–55.311	40.380	320.949 (a)
	±0.270	±1.541	±1.080	±6.312
$Th(SO_4)_3^{2-}$	$3SO_4^{2-} + Th^{4+} \rightleftharpoons Th(SO_4)_3^{2-}$			
	10.748	–61.352		
	±0.076	±0.434		
$Th(SeO_3)_2(cr)$	$Th(SeO_3)_2 \cdot H_2O(cr) \rightleftharpoons H_2O(g) + Th(SeO_3)_2(cr)$			
	–6.499	37.094	94.100	191.200
	±0.560	±3.195	±2.900	±4.500
ThN_3^{3+}	$N_3^- + Th^{4+} \rightleftharpoons ThN_3^{3+}$			
	4.440	–25.344		
	±0.640	±3.653		
$Th(N_3)_2^{2+}$	$2N_3^- + Th^{4+} \rightleftharpoons Th(N_3)_2^{2+}$			
	8.590	–49.032		
	±0.640	±3.653		
$ThNO_3^{3+}$	$NO_3^- + Th^{4+} \rightleftharpoons ThNO_3^{3+}$			
	1.300	–7.420		
	±0.200	±1.142		
$Th(NO_3)_2^{2+}$	$2NO_3^- + Th^{4+} \rightleftharpoons Th(NO_3)_2^{2+}$			
	2.300	–13.128		
	±0.400	±2.283		
$ThH_2PO_4^{3+}$	$H_3PO_4(aq) + Th^{4+} \rightleftharpoons H^+ + ThH_2PO_4^{3+}$			
	3.450	–19.693		
	±0.320	±1.827		
$ThH_3PO_4^{4+}$	$H_3PO_4(aq) + Th^{4+} \rightleftharpoons ThH_3PO_4^{4+}$			
	1.890	–10.788		
	±0.310	±1.769		
$Th(H_2PO_4)_2^{2+}$	$2H_3PO_4(aq) + Th^{4+} \rightleftharpoons 2H^+ + Th(H_2PO_4)_2^{2+}$			
	6.200	–35.390		
	±0.320	±1.827		

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Table III-2 (Continued)

Species	Reaction			
	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$ $(kJ \cdot mol^{-1})$	$\Delta_r H_m^\circ$ $(kJ \cdot mol^{-1})$	$\Delta_r S_m^\circ$ $(J \cdot K^{-1} \cdot mol^{-1})$
$Th(H_3PO_4)(H_2PO_4)^{3+}$	$2H_3PO_4(aq) + Th^{4+} \rightleftharpoons H^+ + Th(H_3PO_4)(H_2PO_4)^{3+}$			
	5.420	–30.938		
	±0.320	±1.827		
$Th(CO_3)_5^{6-}$	$5CO_3^{2-} + Th^{4+} \rightleftharpoons Th(CO_3)_5^{6-}$			
	31.000	–176.949		
	±0.700	±3.996		
$ThOH(CO_3)_4^{5-}$	$4CO_3^{2-} + OH^- + Th^{4+} \rightleftharpoons ThOH(CO_3)_4^{5-}$			
	35.600	–203.206		
	±0.500	±2.854		
$Th(OH)_2(CO_3)_2^{2-}$	$2CO_3^{2-} + 2OH^- + Th^{4+} \rightleftharpoons Th(OH)_2(CO_3)_2^{2-}$			
	36.800	–210.056		
	±0.500	±2.854		
$Th(OH)_4(CO_3)^{2-}$	$CO_3^{2-} + 4OH^- + Th^{4+} \rightleftharpoons Th(OH)_4(CO_3)^{2-}$			
	40.400	–230.605		
	±0.600	±3.425		
$ThSCN^{3+}$	$SCN^- + Th^{4+} \rightleftharpoons ThSCN^{3+}$			
	2.000	–11.416		
	±0.500	±2.854		
$Th(SCN)_2^{2+}$	$2SCN^- + Th^{4+} \rightleftharpoons Th(SCN)_2^{2+}$			
	3.400	–19.407		
	±0.800	±4.566		
$Na_6Th(CO_3)_5 \cdot 12H_2O(cr)$	$5CO_3^{2-} + 12H_2O(l) + 6Na^+ + Th^{4+} \rightleftharpoons Na_6Th(CO_3)_5 \cdot 12H_2O(cr)$			
	42.200	–240.879		
	±0.800	±4.566		

(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 $C^{\circ}_{p,\mathrm{m}}(T) = a + bT + cT^2 + eT^{-2}$. The functions are valid between the temperatures T_{min} and T_{max} (in K). Units for $C^{\circ}_{p,\mathrm{m}}$ are $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

Compound	*a*	*b*	*c*	*e*	*T*(min)	*T*(max)
Th(cr, α) (fcc)	2.34350×10^{1}	8.94500×10^{-3}	0	1.14000×10^{4}	298.15	1633
Th(g)	2.41480×10^{1}	-1.45623×10^{-2}	1.77473×10^{-5}	-5.27700×10^{4}	298.15	700
ThO(g)	2.95010×10^{1}	1.33228×10^{-2}	-6.01025×10^{-6}	-1.48640×10^{5}	298.15	700
ThO_2(cr)	7.15780×10^{1}	6.33610×10^{-3}	7.44770×10^{-7}	-1.04834×10^{6}	298.15	2300
ThO_2(g)	4.69010×10^{1}	2.01352×10^{-2}	-1.02652×10^{-5}	-4.57730×10^{5}	298.15	800
ThH_2(cr)	8.29500	1.25602×10^{-1}	-5.05319×10^{-5}	-4.04100×10^{5}	298.15	1000
$ThH_{3.75}$(cr)	-7.42600	2.37538×10^{-1}	-9.33488×10^{-5}	-3.35550×10^{5}	298.15	1000
ThF(g)*	3.57170×10^{1}	4.00180×10^{-3}	-1.83420×10^{-6}	-1.85670×10^{5}	298.15	700
ThF_2(g)*	5.46630×10^{1}	7.46700×10^{-3}	-4.51541×10^{-6}	-3.62070×10^{5}	298.15	600
ThF_3(g)*	7.71500×10^{1}	1.26203×10^{-2}	-7.61875×10^{-6}	-6.16320×10^{5}	298.15	600
ThF_4(cr)	1.21734×10^{2}	9.06400×10^{-3}	-2.85740×10^{-7}	-1.21821×10^{6}	298.15	1383
ThF_4(g)	1.02950×10^{2}	7.43050×10^{-3}	-2.91682×10^{-6}	-1.02068×10^{6}	298.15	1300
ThOF(g)	4.89090×10^{1}	1.90003×10^{-2}	-1.12413×10^{-5}	-3.59500×10^{5}	298.15	600
$ThOF_2$(cr)	9.66560×10^{1}	7.70000×10^{-3}	-2.29500×10^{-7}	-1.13330×10^{6}	298.15	1500
ThCl(g)*	3.73210×10^{1}	1.02980×10^{-3}	-3.18700×10^{-8}	-1.04870×10^{5}	298.15	1900
$ThCl_2$(g)*	5.77010×10^{1}	8.49700×10^{-4}	-3.99960×10^{-7}	-2.34380×10^{5}	298.15	1000
$ThCl_3$(g)*	8.22270×10^{1}	1.55540×10^{-3}	-7.31790×10^{-7}	-4.10980×10^{5}	298.15	1000
$ThCl_4$(β)	1.20290×10^{2}	2.32672×10^{-2}	0	-6.15050×10^{5}	298.15	1043
$ThCl_4$(g)*	1.07721×10^{2}	2.99300×10^{-4}	-6.02300×10^{-8}	-5.73880×10^{5}	298.15	3000
$ThOCl_2$(cr)	9.59360×10^{1}	1.48040×10^{-2}	3.73900×10^{-7}	-8.31700×10^{5}	298.15	1500
ThBr(g)*	3.74030×10^{1}	1.82430×10^{-3}	-2.05000×10^{-9}	-5.05800×10^{4}	298.15	3000
$ThBr_2$(g)*	5.81670×10^{1}	2.85000×10^{-5}	-5.82000×10^{-9}	-1.28280×10^{5}	298.15	3000
$ThBr_3$(g)*	8.30940×10^{1}	4.13000×10^{-5}	-8.28000×10^{-9}	-2.05080×10^{5}	298.15	3000
$ThBr_4$(β)	1.27600×10^{2}	1.50624×10^{-2}	0	-6.15050×10^{5}	298.15	970
$ThBr_4$(g)*	1.08009×10^{2}	6.53000×10^{-5}	-1.31700×10^{-8}	-2.80920×10^{5}	298.15	3000
ThI(g)*	3.74110×10^{1}	1.54660×10^{-3}	-5.00000×10^{-10}	-3.15000×10^{4}	298.15	3000
ThI_2(g)*	5.81910×10^{1}	8.80000×10^{-6}	-1.79000×10^{-9}	-7.24600×10^{4}	298.15	3000
ThI_3(g)*	8.31280×10^{1}	1.42000×10^{-5}	-2.92000×10^{-9}	-1.18660×10^{5}	298.15	3000
ThI_4(cr)	1.40000×10^{2}	1.35000×10^{-2}	0	-6.15000×10^{5}	298.15	839
ThI_4(g)*	1.08061×10^{2}	2.27000×10^{-5}	-4.55000×10^{-9}	-1.69610×10^{5}	298.15	3000
$ThOI_2$(cr)	1.05789×10^{2}	9.91800×10^{-3}	3.72400×10^{-7}	-8.31700×10^{5}	298.15	1500
ThS(cr)	5.01240×10^{1}	5.46000×10^{-3}	0	-3.58600×10^{5}	298.15	2000
$Th(SO_4)_2$(cr)	1.04600×10^{2}	2.3096×10^{-1}	0		298.15	900
ThN(cr)	4.78360×10^{1}	1.37750×10^{-2}	0	-6.17200×10^{5}	298.15	2000
Th_3N_4(cr)	1.81517×10^{2}	2.61810×10^{-2}	0	-3.70000×10^{6}	298.15	2000
$Th_4(PO_4)_4P_2O_7$(cr)	6.96700×10^{2}	1.04550×10^{-1}	-1.86250×10^{-7}	-1.41590×10^{7}	298.15	1273

* Fitted from heat capacity values calculated from the molecular parameters given in Table E-1.

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 thorium 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 thorium. 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-2the 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}, $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ and $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$, 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 ± 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 ± terms attached to the recommended values”.

- for values from [1992GRE/FUG], [1999RAR/RAN], [2003GUI/FAN], [2005GAM/BUG] and [2005OLI/NOL], the ± terms are derived from total uncertainties in the corresponding equilibrium constant of reaction (*cf.* Table IV-2), and from the ± terms listed for the necessary CODATA key values.

CODATA [1989COX/WAG] values are available for $CO_2(g)$, HCO_3^-, CO_3^{2-}, $H_2PO_4^-$ and HPO_4^{2-}. From the values given for $\Delta_f H_m^\circ$ and S_m° 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 $CO_2(g)$, HCO_3^-, CO_3^{2-}, which were absent form 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	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
$O(g)$ [1992GRE/FUG]	**231.743** (a) **±0.100**	**249.180** **±0.100**	**161.059** **±0.003**	**21.912** **±0.001**
$O_2(g)$ [1992GRE/FUG]	**0.000**	**0.000**	**205.152** **±0.005**	**29.378** **±0.003**
$H(g)$ [1992GRE/FUG]	**203.276** (a) **±0.006**	**217.998** **±0.006**	**114.717** **±0.002**	**20.786** **±0.001**
H^+ [1992GRE/FUG]	**0.000**	**0.000**	**0.000**	**0.000**
$H_2(g)$ [1992GRE/FUG]	**0.000**	**0.000**	**130.680** **±0.003**	**28.836** **±0.002**
$D_2(g)$ [2008RAN/FUG]	0.000 ±0.000	0.000 ±0.000	144.958 ±0.005	29.195 ±0.005
$T_2(g)$ [2008RAN/FUG]	0.000 ±0.000	0.000 ±0.000	153.327 ±0.005	29.199 ±0.005
OH^- [1992GRE/FUG]	**– 157.220** (a) **±0.072**	**– 230.015** **±0.040**	**– 10.900** **±0.200**	
$H_2O(g)$ [1992GRE/FUG]	**– 228.582** (a) **±0.040**	**– 241.826** **±0.040**	**188.835** **±0.010**	**33.609** **±0.030**
$H_2O(l)$ [1992GRE/FUG]	**– 237.140** (a) **±0.041**	**– 285.830** **±0.040**	**69.950** **±0.030**	**75.351** **±0.080**

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G^\circ_m$ (kJ·mol^{-1})	$\Delta_f H^\circ_m$ (kJ·mol^{-1})	S°_m (J·K^{-1}·mol^{-1})	$C^\circ_{p,m}$ (J·K^{-1}·mol^{-1})
H_2O_2(aq) [1992GRE/FUG]		– 191.170 ±0.100		
He(g) [1992GRE/FUG]	**0.000**	**0.000**	**126.153** **±0.002**	**20.786** **±0.001**
Ne(g) [1992GRE/FUG]	**0.000**	**0.000**	**146.328** **±0.003**	**20.786** **±0.001**
Ar(g) [1992GRE/FUG]	**0.000**	**0.000**	**154.846** **±0.003**	**20.786** **±0.001**
Kr(g) [1992GRE/FUG]	**0.000**	**0.000**	**164.085** **±0.003**	**20.786** **±0.001**
Xe(g) [1992GRE/FUG]	**0.000**	**0.000**	**169.685** **±0.003**	**20.786** **±0.001**
F(g) [1992GRE/FUG]	**62.280** (a) **±0.300**	**79.380** **±0.300**	**158.751** **±0.004**	**22.746** **±0.002**
F^- [1992GRE/FUG]	**– 281.523** (a) **±0.692**	**– 335.350** **±0.650**	**– 13.800** **±0.800**	
F_2(g) [1992GRE/FUG]	**0.000**	**0.000**	**202.791** **±0.005**	**31.304** **±0.002**
HF(aq) [1992GRE/FUG]	– 299.675 ±0.702	– 323.150 ±0.716	88.000 (a) ±3.362	
HF(g) [1992GRE/FUG]	**– 275.400** (a) **±0.700**	**– 273.300** **±0.700**	**173.779** **±0.003**	**29.137** **±0.002**
HF_2^- [1992GRE/FUG]	– 583.709 ±1.200	– 655.500 ±2.221	92.683 (a) ±8.469	
Cl(g) [1992GRE/FUG]	**105.305** (a) **±0.008**	**121.301** **±0.008**	**165.190** **±0.004**	**21.838** **±0.001**
Cl^- [1992GRE/FUG]	**– 131.217** (a) **±0.117**	**– 167.080** **±0.100**	**56.600** **±0.200**	
Cl_2(g) [1992GRE/FUG]	**0.000**	**0.000**	**223.081** **±0.010**	**33.949** **±0.002**
ClO^- [2005OLI/NOL]	– 37.669 (b) ±0.962	– 108.300 (b) ±1.500	42.560 (b) ±9.238	
ClO_2^- [1992GRE/FUG]	10.250 ±4.044			
ClO_3^- [1992GRE/FUG]	– 7.903 (a) ±1.342	– 104.000 ±1.000	162.300 ±3.000	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\mathrm{o}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$ (kJ·mol^{-1})	$S_{\mathrm{m}}^{\mathrm{o}}$ (J·K^{-1}·mol^{-1})	$C_{p,\mathrm{m}}^{\mathrm{o}}$ (J·K^{-1}·mol^{-1})
ClO_4^- [1992GRE/FUG]	**– 7.890** (a) **±0.600**	**– 128.100** **±0.400**	**184.000** **±1.500**	
HCl(g) [1992GRE/FUG]	**– 95.298** (a) **±0.100**	**– 92.310** **±0.100**	**186.902** **±0.005**	**29.136** **±0.002**
HClO(aq) [2005OLI/NOL]	– 80.023 (a) ±0.613	– 125.700 ±1.500	– 126.255 ±5.434	
$HClO_2$(aq) [1992GRE/FUG]	– 0.938 ±4.043			
Br(g) [1992GRE/FUG]	**82.379** (a) **±0.128**	**111.870** **±0.120**	**175.018** **±0.004**	**20.786** **±0.001**
Br^- [1992GRE/FUG]	**– 103.850** (a) **±0.167**	**– 121.410** **±0.150**	**82.550** **±0.200**	
Br_2(aq) [1992GRE/FUG]	4.900 ±1.000			
Br_2(g) [1992GRE/FUG]	**3.105** (a) **±0.142**	**30.910** **±0.110**	**245.468** **±0.005**	**36.057** **±0.002**
Br_2(l) [1992GRE/FUG]	**0.000**	**0.000**	**152.210** **±0.300**	
BrO^- [1992GRE/FUG]	– 32.095 ±1.537			
BrO_3^- [1992GRE/FUG]	19.070 (a) ±0.634	– 66.700 ±0.500	161.500 ±1.300	
HBr(g) [1992GRE/FUG]	**– 53.361** (a) **±0.166**	**– 36.290** **±0.160**	**198.700** **±0.004**	**29.141** **±0.003**
HBrO(aq) [1992GRE/FUG]	– 81.356 (b) ±1.527			
I(g) [1992GRE/FUG]	**70.172** (a) **±0.060**	**106.760** **±0.040**	**180.787** **±0.004**	**20.786** **±0.001**
I^- [1992GRE/FUG]	**– 51.724** (a) **±0.112**	**– 56.780** **±0.050**	**106.450** **±0.300**	
I_2(cr) [1992GRE/FUG]	**0.000**	**0.000**	**116.140** **±0.300**	
I_2(g) [1992GRE/FUG]	**19.323** (a) **±0.120**	**62.420** **±0.080**	**260.687** **±0.005**	**36.888** **±0.002**
IO_3^- [1992GRE/FUG]	– 126.338 (a) ±0.779	– 219.700 ±0.500	118.000 ±2.000	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$S^{\mathrm{o}}_{\mathrm{m}}$ (J·K^{-1}·mol^{-1})	$C^{\mathrm{o}}_{p,\mathrm{m}}$ (J·K^{-1}·mol^{-1})
HI(g)	**1.700** (a)	**26.500**	**206.590**	**29.157**
[1992GRE/FUG]	**±0.110**	**±0.100**	**±0.004**	**±0.003**
HIO_3(aq)	– 130.836			
[1992GRE/FUG]	±0.797			
S(cr)(orthorhombic)	**0.000**	**0.000**	**32.054**	**22.750**
[1992GRE/FUG]			**±0.050**	**±0.050**
S(g)	**236.689** (a)	**277.170**	**167.829**	**23.674**
[1992GRE/FUG]	**±0.151**	**±0.150**	**±0.006**	**±0.001**
S^{2-}	120.695			
[1992GRE/FUG]	±11.610			
S_2(g)	**79.686** (a)	**128.600**	**228.167**	**32.505**
[1992GRE/FUG]	**±0.301**	**±0.300**	**±0.010**	**±0.010**
SO_2(g)	**– 300.095** (a)	**– 296.810**	**248.223**	**39.842**
[1992GRE/FUG]	**±0.201**	**±0.200**	**±0.050**	**±0.020**
SO_3^{2-}	– 487.472			
[1992GRE/FUG]	±4.020			
$S_2O_3^{2-}$	– 519.291			
[1992GRE/FUG]	±11.345			
SO_4^{2-}	**– 744.004** (a)	**– 909.340**	**18.500**	
[1992GRE/FUG]	**±0.418**	**±0.400**	**±0.400**	
HS^-	**12.243** (a)	**– 16.300**	**67.000**	
[1992GRE/FUG]	**±2.115**	**±1.500**	**±5.000**	
H_2S(aq)	**– 27.648** (a)	**– 38.600**	**126.000**	
[1992GRE/FUG]	**±2.115**	**±1.500**	**±5.000**	
H_2S(g)	**– 33.443** (a)	**– 20.600**	**205.810**	**34.248**
[1992GRE/FUG]	**±0.500**	**±0.500**	**±0.050**	**±0.010**
HSO_3^-	– 528.684			
[1992GRE/FUG]	±4.046			
$HS_2O_3^-$	– 528.366			
[1992GRE/FUG]	±11.377			
H_2SO_3(aq)	– 539.187			
[1992GRE/FUG]	±4.072			
HSO_4^-	**– 755.315** (a)	**– 886.900**	**131.700**	
[1992GRE/FUG]	**±1.342**	**±1.000**	**±3.000**	
Se(cr) (trigonal)	0.000	0.000	42.090	25.090 (c)
[2005OLI/NOL]			±0.330	±0.300

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$S^{\mathrm{o}}_{\mathrm{m}}$ (J·K^{-1}·mol^{-1})	$C^{\mathrm{o}}_{p,\mathrm{m}}$ (J·K^{-1}·mol^{-1})
Se(monoclinic) [2005OLI/NOL]	1.281 (a) ±0.184	2.140 ±0.100	44.970 ±0.400	25.090 (c) ±0.800
Se(l) [2005OLI/NOL]				(c)
Se(g) [2005OLI/NOL]	195.927 (a) ±1.524	236.070 (b) ±1.521	176.729 ±0.006	20.819 (c) ±0.001
Se^{2-} [2005OLI/NOL]	128.600 (b) ±3.000			
Se$_2$(g) [2005OLI/NOL]	92.442 (a) ±3.009	141.100 ±3.000	247.380 ±0.400	41.710 (c) ±0.200
Se$_2^{2-}$ [2005OLI/NOL]	112.670 (b) ±6.294			
Se$_3$(g) [2005OLI/NOL]	123.549 (a) ±10.439	178.000 ±10.000	308.900 ±10.000	
Se$_3^{2-}$ [2005OLI/NOL]	100.590 (b) ±9.198			
Se$_4$(g) [2005OLI/NOL]	111.647 (a) ±13.406	163.000 ±12.000	340.000 ±20.000	
Se$_4^{2-}$ [2005OLI/NOL]	97.580 (b) ±12.149			
Se$_5$(g) [2005OLI/NOL]	88.393 (a) ±5.256	144.400 ±4.300	398.300 ±10.000	
Se$_6$(g) [2005OLI/NOL]	83.638(a) ±4.866	136.100 ±3.800	428.500 ±10.000	
Se$_7$(g) [2005OLI/NOL]	92.845(a) ±4.891	150.200 ±4.500	487.000 ±6.000	
Se$_8$(g) [2005OLI/NOL]	100.307(a) ±3.580	156.800 ±3.000	526.200 ±6.000	
SeO(g) [2005OLI/NOL]	30.855 (a) ±6.218	57.400 ±6.210	233.700 ±1.000	32.520 (c) ±0.250
SeO$_2$(cr) [2005OLI/NOL]	–171.797 (a) ±0.620	–225.390 ±0.600	67.490 ±0.400	58.230 (c) ±0.180
SeO$_2$(g) [2005OLI/NOL]	–115.166 (a) ±2.600	–110.590 (b) ±2.571	262.590 ±1.250	43.360 (c) ±0.150
SeO$_3$(cr) [2005OLI/NOL]	–86.154 (a) ±2.222	–163.100 ±2.200	91.740 ±1.000	77.240 (c) ±0.790

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
SeO_3^{2-} [2005OLI/NOL]	–362.392 (b) ±1.756	–507.160 ±1.130	–5.055 (a) ±7.011	
SeO_4^{2-} [2005OLI/NOL]	–439.485 (b) ±1.431	–603.500 (b) ±3.500	32.965 (b) ±12.687	
Se_2O_5(cr) [2005OLI/NOL]		–414.590 (b) ±2.577		
HSe^- [2005OLI/NOL]	43.471 (b) ±2.024			
H_2Se(g) [2005OLI/NOL]	15.217 (a) ±2.003	29.000 ±2.000	219.000 ±0.100	34.700 (c) ±0.100
H_2Se(aq) [2005OLI/NOL]	21.495 (b) ±2.003	14.300 (b) ±2.022	148.637 (b) ±1.029	
$HSeO_3^-$ [2005OLI/NOL]	–410.112 (b) ±1.166	–512.330 ±1.010	137.656 (a) ±5.184	
$HSeO_4^-$ [2005OLI/NOL]	–449.474 (b) ±1.312	–582.700 (d) ±4.700	136.232 (a) ±16.370	
H_2SeO_3(cr) [2005OLI/NOL]		–524.720 (b) ±0.650		
H_2SeO_3(aq) [2005OLI/NOL]	–425.181 (b) ±0.849	–505.320 ±0.650	211.710 (a) ±3.601	
H_2SeO_4(cr) [2005OLI/NOL]		–530.500 ±1.880		
Te(cr) [1992GRE/FUG]	0.000	0.000	49.221 ±0.050	25.550 ±0.100
TeO_2(cr) [2003GUI/FAN]	– 265.996 (a) ±2.500	– 321.000 ±2.500	69.890 ±0.150	60.670 ±0.150
N(g) [1992GRE/FUG]	**455.537 (a)** **±0.400**	**472.680** **±0.400**	**153.301** **±0.003**	**20.786** **±0.001**
N_2(g) [1992GRE/FUG]	**0.000**	**0.000**	**191.609** **±0.004**	**29.124** **±0.001**
N_3^- [1992GRE/FUG]	348.200 ±2.000	275.140 ±1.000	107.710 (a) ±7.500	
NO_3^- [1992GRE/FUG]	**– 110.794 (a)** **±0.417**	**– 206.850** **±0.400**	**146.700** **±0.400**	
HN_3(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	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
$NH_3(aq)$ [1992GRE/FUG]	– 26.673 ±0.305	– 81.170 ±0.326	109.040 ±0.913	
$NH_3(g)$ [1992GRE/FUG]	**– 16.407** (a) **±0.350**	**– 45.940** **±0.350**	**192.770** **±0.050**	**35.630** **±0.005**
NH_4^+ [1992GRE/FUG]	**– 79.398** (a) **±0.278**	**– 133.260** **±0.250**	**111.170** **±0.400**	
P(am)(red) [1992GRE/FUG]		– 7.500 ±2.000		
P(cr)(white, cubic) [1992GRE/FUG]	**0.000**	**0.000**	**41.090** **±0.250**	**23.824** **±0.200**
P(g) [1992GRE/FUG]	**280.093** (a) **±1.003**	**316.500** **±1.000**	**163.199** **±0.003**	**20.786** **±0.001**
$P_2(g)$ [1992GRE/FUG]	**103.469** (a) **±2.006**	**144.000** **±2.000**	**218.123** **±0.004**	**32.032** **±0.002**
$P_4(g)$ [1992GRE/FUG]	**24.419** (a) **±0.448**	**58.900** **±0.300**	**280.010** **±0.500**	**67.081** **±1.500**
PO_4^{3-} [1992GRE/FUG]	– 1025.491 ±1.576	– 1284.400 ±4.085	– 220.970 ±12.846	
$P_2O_7^{4-}$ [1992GRE/FUG]	– 1935.503 ±4.563			
HPO_4^{2-} [1992GRE/FUG]	**– 1095.985** (a) **±1.567**	**– 1299.000** **±1.500**	**– 33.500** **±1.500**	
$H_2PO_4^-$ [1992GRE/FUG]	**– 1137.152** (a) **±1.567**	**– 1302.600** **±1.500**	**92.500** **±1.500**	
$H_3PO_4(aq)$ [1992GRE/FUG]	– 1149.367 ±1.576	– 1294.120 ±1.616	161.912 ±2.575	
$HP_2O_7^{3-}$ [1992GRE/FUG]	– 1989.158 ±4.482			
$H_2P_2O_7^{2-}$ [1992GRE/FUG]	– 2027.117 ±4.445			
$H_3P_2O_7^-$ [1992GRE/FUG]	– 2039.960 ±4.362			
$H_4P_2O_7(aq)$ [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	$\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$S^{\mathrm{o}}_{\mathrm{m}}$ (J·K^{-1}·mol^{-1})	$C^{\mathrm{o}}_{p,\mathrm{m}}$ (J·K^{-1}·mol^{-1})
AsO_2^- [1992GRE/FUG]	– 350.022 (a) ±4.008	– 429.030 ±4.000	40.600 ±0.600	
AsO_4^{3-} [1992GRE/FUG]	– 648.360 (a) ±4.008	– 888.140 ±4.000	– 162.800 ±0.600	
As_2O_5(cr) [1992GRE/FUG]	– 782.449 (a) ±8.016	– 924.870 ±8.000	105.400 ±1.200	116.520 ±0.800
As_4O_6(cubic) [1992GRE/FUG]	– 1152.445 (a) ±16.032	– 1313.940 ±16.000	214.200 ±2.400	191.290 ±0.800
As_4O_6(monoclinic) [1992GRE/FUG]	– 1154.009 (a) ±16.041	– 1309.600 ±16.000	234.000 ±3.000	
As_4O_6(g) [2005GAM/BUG]	– 1092.716 (a) ±16.116	– 1196.250 ±16.000	408.600 ±6.000	
$HAsO_2$(aq) [1992GRE/FUG]	– 402.925 (a) ±4.008	– 456.500 ±4.000	125.900 ±0.600	
$H_2AsO_3^-$ [1992GRE/FUG]	– 587.078 (a) ±4.008	– 714.790 ±4.000	110.500 ±0.600	
H_3AsO_3(aq) [1992GRE/FUG]	– 639.681 (a) ±4.015	– 742.200 ±4.000	195.000 ±1.000	
$HAsO_4^{2-}$ [1992GRE/FUG]	– 714.592 (a) ±4.008	– 906.340 ±4.000	– 1.700 ±0.600	
$H_2AsO_4^-$ [1992GRE/FUG]	– 753.203 (a) ±4.015	– 909.560 ±4.000	117.000 ±1.000	
H_3AsO_4(aq) [1992GRE/FUG]	– 766.119 (a) ±4.015	– 902.500 ±4.000	184.000 ±1.000	
$(As_2O_5)_3\cdot$ 5 H_2O(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]	**0.000**	**0.000**	**5.740** **±0.100**	**8.517** **±0.080**
C(g) [1992GRE/FUG]	**671.254** (a) **±0.451**	**716.680** **±0.450**	**158.100** **±0.003**	**20.839** **±0.001**
CO(g) [1992GRE/FUG]	**– 137.168** (a) **±0.173**	**– 110.530** **±0.170**	**197.660** **±0.004**	**29.141** **±0.002**

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}$ (kJ·mol^{-1})	$S^{\mathrm{o}}_{\mathrm{m}}$ (J·K^{-1}·mol^{-1})	$C^{\mathrm{o}}_{p,\mathrm{m}}$ (J·K^{-1}·mol^{-1})
CO_2(aq) [1992GRE/FUG]	**– 385.970** (a) **±0.270**	**– 413.260** **±0.200**	**119.360** **±0.600**	
CO_2(g) [1992GRE/FUG]	**– 394.373** (a) **±0.133**	**– 393.510** **±0.130**	**213.785** **±0.010**	**37.135** **±0.002**
CO_3^{2-} [1992GRE/FUG]	**– 527.900** (a) **±0.390**	**– 675.230** **±0.250**	**– 50.000** **±1.000**	
HCO_3^- [1992GRE/FUG]	**– 586.845** (a) **±0.251**	**– 689.930** **±0.200**	**98.400** **±0.500**	
CN^- [2005OLI/NOL]	166.939 (b) ±2.519	147.350 (b) ±3.541	101.182 (b) ±8.475	
HCN(aq) [2005OLI/NOL]	114.368 (b) ±2.517	103.750 (b) ±3.536	131.271 (b) ±8.440	
HCN(g) [2005OLI/NOL]	119.517 (a) ±2.500	129.900 ±2.500	201.710 ±0.100	
SCN^- [1992GRE/FUG]	92.700 ±4.000	76.400 ±4.000	144.268 (a) ±18.974	
Si(cr) [1992GRE/FUG]	**0.000**	**0.000**	**18.810** **±0.080**	**19.789** **±0.030**
Si(g) [1992GRE/FUG]	**405.525** (a) **±8.000**	**450.000** **±8.000**	**167.981** **±0.004**	**22.251** **±0.001**
SiO_2(α– quartz) [1992GRE/FUG]	**– 856.287** (a) **±1.002**	**– 910.700** **±1.000**	**41.460** **±0.200**	**44.602** **±0.300**
$SiO_2(OH)_2^{2-}$ [1992GRE/FUG]	– 1175.651 ±1.265	– 1381.960 ±15.330	– 1.488 ±51.592	
$SiO(OH)_3^-$ [1992GRE/FUG]	– 1251.740 ±1.162	– 1431.360 ±3.743	88.024 ±13.144	
$Si(OH)_4$(aq) [1992GRE/FUG]	– 1307.735 (b) ±1.156	– 1456.960 (b) ±3.163	189.973 (b) ±11.296	
$Si_2O_3(OH)_4^{2-}$ [1992GRE/FUG]	– 2269.878 ±2.878			
$Si_2O_2(OH)_5^-$ [1992GRE/FUG]	– 2332.096 ±2.878			
$Si_3O_6(OH)_3^{3-}$ [1992GRE/FUG]	– 3048.536 ±3.870			
$Si_3O_5(OH)_5^{3-}$ [1992GRE/FUG]	– 3291.955 ±3.869			

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\mathrm{o}}$ $(\mathrm{kJ\cdot mol^{-1}})$	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$ $(\mathrm{kJ\cdot mol^{-1}})$	$S_{\mathrm{m}}^{\mathrm{o}}$ $(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$	$C_{p,\mathrm{m}}^{\mathrm{o}}$ $(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$
$Si_4O_8(OH)_4^{4-}$ [1992GRE/FUG]	– 4075.179 ±5.437			
$Si_4O_7(OH)_5^{3-}$ [1992GRE/FUG]	– 4136.826 ±4.934			
$SiF_4(g)$ [1992GRE/FUG]	**– 1572.773** [(a)] **±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** [(a)] **±3.000**	**372.000** **±3.000**	**167.904** **±0.005**	**30.733** **±0.001**
GeO_2(tetragonal) [1992GRE/FUG]	**– 521.404** [(a)] **±1.002**	**– 580.000** **±1.000**	**39.710** **±0.150**	**50.166** **±0.300**
$GeF_4(g)$ [1992GRE/FUG]	**– 1150.018** [(a)] **±0.584**	**– 1190.200** **±0.500**	**301.900** **±1.000**	**81.602** **±1.000**
Sn(cr) [1992GRE/FUG]	**0.000**	**0.000**	**51.180** **±0.080**	**27.112** **±0.030**
Sn(g) [1992GRE/FUG]	**266.223** [(a)] **±1.500**	**301.200** **±1.500**	**168.492** **±0.004**	**21.259** **±0.001**
Sn^{2+} [1992GRE/FUG]	**– 27.624** [(a)] **±1.557**	**– 8.900** **±1.000**	**– 16.700** **±4.000**	
SnO(tetragonal) [1992GRE/FUG]	**– 251.913** [(a)] **±0.220**	**– 280.710** **±0.200**	**57.170** **±0.300**	**47.783** **±0.300**
SnO_2(cassiterite, tetragonal) [1992GRE/FUG]	**– 515.826** [(a)] **±0.204**	**– 577.630** **±0.200**	**49.040** **±0.100**	**53.219** **±0.200**
Pb(cr) [1992GRE/FUG]	**0.000**	**0.000**	**64.800** **±0.300**	**26.650** **±0.100**
Pb(g) [1992GRE/FUG]	**162.232** [(a)] **±0.805**	**195.200** **±0.800**	**175.375** **±0.005**	**20.786** **±0.001**
Pb^{2+} [1992GRE/FUG]	**– 24.238** [(a)] **±0.399**	**0.920** **±0.250**	**18.500** **±1.000**	
$PbSO_4$(cr) [1992GRE/FUG]	**– 813.036** [(a)] **±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** [(a)] **±5.000**	**565.000** **±5.000**	**153.436** **±0.015**	**20.796** **±0.005**

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\mathrm{o}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$ (kJ·mol^{-1})	$S_{\mathrm{m}}^{\mathrm{o}}$ (J·K^{-1}·mol^{-1})	$C_{p,\mathrm{m}}^{\mathrm{o}}$ (J·K^{-1}·mol^{-1})
B_2O_3(cr) [1992GRE/FUG]	**– 1194.324** (a) **±1.404**	**– 1273.500** **±1.400**	**53.970** **±0.300**	**62.761** **±0.300**
$B(OH)_3$(aq) [1992GRE/FUG]	**– 969.268** (a) **±0.820**	**– 1072.800** **±0.800**	**162.400** **±0.600**	
$B(OH)_3$(cr) [1992GRE/FUG]	**– 969.667** (a) **±0.820**	**– 1094.800** **±0.800**	**89.950** **±0.600**	**86.060** **±0.400**
BF_3(g) [1992GRE/FUG]	**– 1119.403** (a) **±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**
Al(g) [1992GRE/FUG]	**289.376** (a) **±4.000**	**330.000** **±4.000**	**164.554** **±0.004**	**21.391** **±0.001**
Al^{3+} [1992GRE/FUG]	**– 491.507** (a) **±3.338**	**– 538.400** **±1.500**	**– 325.000** **±10.000**	
Al_2O_3(corundum) [1992GRE/FUG]	**– 1582.257** (a) **±1.302**	**– 1675.700** **±1.300**	**50.920** **±0.100**	**79.033** **±0.200**
AlF_3(cr) [1992GRE/FUG]	**– 1431.096** (a) **±1.309**	**– 1510.400** **±1.300**	**66.500** **±0.500**	**75.122** **±0.400**
Tl^{+} [1999RAR/RAN]	– 32.400 ±0.300			
Zn(cr) [1992GRE/FUG]	**0.000**	**0.000**	**41.630** **±0.150**	**25.390** **±0.040**
Zn(g) [1992GRE/FUG]	**94.813** (a) **±0.402**	**130.400** **±0.400**	**160.990** **±0.004**	**20.786** **±0.001**
Zn^{2+} [1992GRE/FUG]	**– 147.203** (a) **±0.254**	**– 153.390** **±0.200**	**– 109.800** **±0.500**	
ZnO(cr) [1992GRE/FUG]	**– 320.479** (a) **±0.299**	**– 350.460** **±0.270**	**43.650** **±0.400**	
Cd(cr) [1992GRE/FUG]	**0.000**	**0.000**	**51.800** **±0.150**	**26.020** **±0.040**
Cd(g) [1992GRE/FUG]	**77.230** (a) **±0.205**	**111.800** **±0.200**	**167.749** **±0.004**	**20.786** **±0.001**
Cd^{2+} [1992GRE/FUG]	**– 77.733** (a) **±0.750**	**– 75.920** **±0.600**	**– 72.800** **±1.500**	
CdO(cr) [1992GRE/FUG]	**– 228.661** (a) **±0.602**	**– 258.350** **±0.400**	**54.800** **±1.500**	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\mathrm{o}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}$ (kJ·mol^{-1})	$S_{\mathrm{m}}^{\mathrm{o}}$ (J·K^{-1}·mol^{-1})	$C_{p,\mathrm{m}}^{\mathrm{o}}$ (J·K^{-1}·mol^{-1})
$CdSO_4 \cdot 2.667\ H_2O$(cr) [1992GRE/FUG]	**– 1464.959** (a) **±0.810**	**– 1729.300** **±0.800**	**229.650** **±0.400**	
Hg(g) [1992GRE/FUG]	**31.842** (a) **±0.054**	**61.380** **±0.040**	**174.971** **±0.005**	**20.786** **±0.001**
Hg(l) [1992GRE/FUG]	**0.000**	**0.000**	**75.900** **±0.120**	
Hg^{2+} [1992GRE/FUG]	**164.667** (a) **±0.313**	**170.210** **±0.200**	**– 36.190** **±0.800**	
Hg_2^{2+} [1992GRE/FUG]	**153.567** (a) **±0.559**	**166.870** **±0.500**	**65.740** **±0.800**	
HgO(montroydite, red) [1992GRE/FUG]	**– 58.523** (a) **±0.154**	**– 90.790** **±0.120**	**70.250** **±0.300**	
Hg_2Cl_2(cr) [1992GRE/FUG]	**– 210.725** (a) **±0.471**	**– 265.370** **±0.400**	**191.600** **±0.800**	
Hg_2SO_4(cr) [1992GRE/FUG]	**– 625.780** (a) **±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** (a) **±1.200**	**337.400** **±1.200**	**166.398** **±0.004**	**20.786** **±0.001**
Cu^{2+} [1992GRE/FUG]	**65.040** (a) **±1.557**	**64.900** **±1.000**	**– 98.000** **±4.000**	
CuCl(g) [2003GUI/FAN]		76.800 ±10.000		
$CuSO_4$(cr) [1992GRE/FUG]	**– 662.185** (a) **±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** (a) **±0.802**	**284.900** **±0.800**	**172.997** **±0.004**	**20.786** **±0.001**
Ag^+ [1992GRE/FUG]	**77.096** (a) **±0.156**	**105.790** **±0.080**	**73.450** **±0.400**	
AgCl(cr) [1992GRE/FUG]	**– 109.765** (a) **±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

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
Ni^{2+} [2005GAM/BUG]	– 45.773 ±0.771	– 55.012 (a) ±0.878	– 131.800 ±1.400	– 46.100 ±7.500
NiF_2(cr) [2005GAM/BUG]	–609.852 (a) ±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** (a) **±3.000**	**473.000** **±3.000**	**180.298** **±0.010**	**24.430** **±0.030**
TiO_2(rutile) [1992GRE/FUG]	**– 888.767** (a) **±0.806**	**– 944.000** **±0.800**	**50.620** **±0.300**	**55.080** **±0.300**
$TiCl_4$(g) [1992GRE/FUG]	**– 726.324** (a) **±3.229**	**– 763.200** **±3.000**	**353.200** **±4.000**	**95.408** **±1.000**
Am^{3+} [1995SIL/BID]	–598.698 (a) ±4.755	–616.700 ±1.500	–201.000 ±15.000	
Pu^{3+} [2001LEM/FUG]	–578.984 ±2.688	–591.790 ±1.964	–184.510 (b) ±6.154	
Np^{4+} [2001LEM/FUG]	–491.774 (a) ±5.586	–556.022 ±4.185	–426.390 (b) ±12.386	
NpO_2^+ [2001LEM/FUG]	–907.765 (a) ±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^{4+} [2003GUI/FAN]	–529.860 (b) ±1.765	–591.200 ±3.300	–416.895 (a) ±12.553	–220.000 ±50.000
UO_2^{2+} [1992GRE/FUG]	**–952.551** (a) **±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** (a) **±5.000**	**324.000** **±5.000**	**136.275** **±0.003**	**20.786** **±0.001**
BeO(bromellite) [1992GRE/FUG]	**– 580.090** (a) **±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** (a) **±0.801**	**147.100** **±0.800**	**148.648** **±0.003**	**20.786** **±0.001**

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
Mg^{2+} [1992GRE/FUG]	**– 455.375** (a) **±1.335**	**– 467.000** **±0.600**	**– 137.000** **±4.000**	
MgO(cr) [1992GRE/FUG]	**– 569.312** (a) **±0.305**	**– 601.600** **±0.300**	**26.950** **±0.150**	**37.237** **±0.200**
MgF_2(cr) [1992GRE/FUG]	**– 1071.051** (a) **±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** (a) **±0.809**	**177.800** **±0.800**	**154.887** **±0.004**	**20.786** **±0.001**
Ca^{2+} [1992GRE/FUG]	**– 552.806** (a) **±1.050**	**– 543.000** **±1.000**	**– 56.200** **±1.000**	
CaO(cr) [1992GRE/FUG]	**– 603.296** (a) **±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^{2+} [1992GRE/FUG]	– 563.864 (a) ±0.781	– 550.900 ±0.500	– 31.500 ±2.000	
SrO(cr) [1992GRE/FUG]	– 559.939 (a) ±0.914	– 590.600 ±0.900	55.440 ±0.500	
$SrCl_2$(cr) [1992GRE/FUG]	– 784.974 (a) ±0.714	– 833.850 ±0.700	114.850 ±0.420	
$Sr(NO_3)_2$(cr) [1992GRE/FUG]	– 783.146 (a) ±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^{2+} [1992GRE/FUG]	– 557.656 (a) ±2.582	– 534.800 ±2.500	8.400 ±2.000	
BaO(cr) [1992GRE/FUG]	– 520.394 (a) ±2.515	– 548.100 ±2.500	72.070 ±0.380	

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
BaF(g) [2003GUI/FAN]	– 349.569 ±6.705	– 324.992 ±6.700	246.219 ±0.210	34.747 ±0.300
$BaCl_2$(cr) [1992GRE/FUG]	– 806.953 (a) ±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** (a) **±1.002**	**159.300** **±1.000**	**138.782** **±0.010**	**20.786** **±0.001**
Li^+ [1992GRE/FUG]	**– 292.918** (a) **±0.109**	**– 278.470** **±0.080**	**12.240** **±0.150**	
Na(cr) [1992GRE/FUG]	**0.000**	**0.000**	**51.300** **±0.200**	**28.230** **±0.200**
Na(g) [1992GRE/FUG]	**76.964** (a) **±0.703**	**107.500** **±0.700**	**153.718** **±0.003**	**20.786** **±0.001**
Na^+ [1992GRE/FUG]	**– 261.953** (a) **±0.096**	**– 240.340** **±0.060**	**58.450** **±0.150**	
NaF(cr) [2001LEM/FUG]	– 546.327 (a) ±0.704	– 576.600 ±0.700	51.160 ±0.150	
NaCl(cr) [2001LEM/FUG]	– 384.221 ±0.147	– 411.260 ±0.120	72.150 ±0.200	50.500
$NaNO_3$(cr) [2003GUI/FAN]		– 467.580 ±0.410		
K(cr) [1992GRE/FUG]	**0.000**	**0.000**	**64.680** **±0.200**	**29.600** **±0.100**
K(g) [1992GRE/FUG]	**60.479** (a) **±0.802**	**89.000** **±0.800**	**160.341** **±0.003**	**20.786** **±0.001**
K^+ [1992GRE/FUG]	**– 282.510** (a) **±0.116**	**– 252.140** **±0.080**	**101.200** **±0.200**	
KCl(cr) [2005GAM/BUG]		– 436.461 ±0.129		
KBr(cr) [2005GAM/BUG]		– 393.330 ±0.188		
KI(cr) [2005GAM/BUG]		– 329.150 ±0.137		
Rb(cr) [1992GRE/FUG]	**0.000**	**0.000**	**76.780** **±0.300**	**31.060** **±0.100**

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Table IV-1 (continued)

Compound and review where adopted	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})	$C_{p,m}^o$ (J·K^{-1}·mol^{-1})
Rb(g) [1992GRE/FUG]	**53.078** (a) **±0.805**	**80.900** **±0.800**	**170.094** **±0.003**	**20.786** **±0.001**
Rb^+ [1992GRE/FUG]	**– 284.009** (a) **±0.153**	**– 251.120** **±0.100**	**121.750** **±0.250**	
Cs(cr) [1992GRE/FUG]	**0.000**	**0.000**	**85.230** **±0.400**	**32.210** **±0.200**
Cs(g) [1992GRE/FUG]	**49.556** (a) **±1.007**	**76.500** **±1.000**	**175.601** **±0.003**	**20.786** **±0.001**
Cs^+ [1992GRE/FUG]	**– 291.456** (a) **±0.535**	**– 258.000** **±0.500**	**132.100** **±0.500**	
CsCl(cr) [2001LEM/FUG]	– 413.807 (a) ±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 $\Delta_f G_m^o = \Delta_f H_m^o - T\sum_i S_{m,i}^o$.

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

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_{r}G_{m}^{\circ}$ $(\mathrm{kJ\cdot mol^{-1}})$	$\Delta_{r}H_{m}^{\circ}$ $(\mathrm{kJ\cdot mol^{-1}})$	$\Delta_{r}S_{m}^{\circ}$ $(\mathrm{J\cdot K^{-1}\cdot mol^{-1}})$
$HIO_3(aq)$	$H^+ + IO_3^- \rightleftharpoons HIO_3(aq)$			
[1992GRE/FUG]	0.788	– 4.498		
	±0.029	±0.166		
S^{2-}	$HS^- \rightleftharpoons H^+ + S^{2-}$			
[1992GRE/FUG]	– 19.000	108.450		
	±2.000	±11.416		
SO_3^{2-}	$H_2O(l) + SO_4^{2-} + 2\,e^- \rightleftharpoons 2OH^- + SO_3^{2-}$			
[1992GRE/FUG]	– 31.400 (b)	179.230		
	±0.700	±3.996		
$S_2O_3^{2-}$	$3H_2O(l) + 2SO_3^{2-} + 4\,e^- \rightleftharpoons 6OH^- + S_2O_3^{2-}$			
[1992GRE/FUG]	– 39.200 (b)	223.760		
	±1.400	±7.991		
$H_2S(aq)$	$H_2S(aq) \rightleftharpoons H^+ + HS^-$			
[1992GRE/FUG]	– 6.990	39.899		
	±0.170	±0.970		
HSO_3^-	$H^+ + SO_3^{2-} \rightleftharpoons HSO_3^-$			
[1992GRE/FUG]	7.220	– 41.212	66.000	359.590 (a)
	±0.080	±0.457	±30.000	±100.630
$HS_2O_3^-$	$H^+ + S_2O_3^{2-} \rightleftharpoons HS_2O_3^-$			
[1992GRE/FUG]	1.590	– 9.076		
	±0.150	±0.856		
$H_2SO_3(aq)$	$H^+ + HSO_3^- \rightleftharpoons H_2SO_3(aq)$			
[1992GRE/FUG]	1.840	– 10.503	16.000	88.891 (a)
	±0.080	±0.457	±5.000	±16.840
HSO_4^-	$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$			
[1992GRE/FUG]	1.980	– 11.302		
	±0.050	±0.285		
$Se(g)$	$0.5Se_2(g) \rightleftharpoons Se(g)$			
[2005OLI/NOL]			–165.520	
			±0.250	
Se^{2-}	$Se(cr) + 2\,e^- \rightleftharpoons Se^{2-}$			
[2005OLI/NOL]	–22.530	128.600		
	±0.526	±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^{-1})	$\Delta_r H_m^{\circ}$ (kJ·mol^{-1})	$\Delta_r S_m^{\circ}$ (J·K^{-1}·mol^{-1})
Se_2^{2-}	$2Se^{2-} \rightleftharpoons Se_2^{2-} + 2\,e^-$			
[2005OLI/NOL]	25.320 ±0.333	–144.530 ±1.900		
Se_3^{2-}	$3Se^{2-} \rightleftharpoons Se_3^{2-} + 4\,e^-$			
[2005OLI/NOL]	49.966 ±0.333	–285.210 ±1.900		
Se_4^{2-}	$4Se^{2-} \rightleftharpoons Se_4^{2-} + 6\,e^-$			
[2005OLI/NOL]	73.023 ±0.333	–416.820 ±1.900		
$SeO_2(g)$	$SeO_2(cr) \rightleftharpoons SeO_2(g)$			
[2005OLI/NOL]			114.800 ±2.500	
SeO_3^{2-}	$HSeO_3^- \rightleftharpoons H^+ + SeO_3^{2-}$			
[2005OLI/NOL]	–8.360 ±0.230	47.719 ±1.313		
SeO_4^{2-}	$HSeO_4^- \rightleftharpoons H^+ + SeO_4^{2-}$			
[2005OLI/NOL]	–1.750 ±0.100	–9.989 ±0.571	–20.800 ±3.200	–103.267 (a) ±10.902
$Se_2O_5(cr)$	$SeO_2(cr) + SeO_3(cr) \rightleftharpoons Se_2O_5(cr)$			
[2005OLI/NOL]			–26.100 ±1.200	
HSe^-	$H_2Se(aq) \rightleftharpoons H^+ + HSe^-$			
[2005OLI/NOL]	–3.850 ±0.050	21.976 ±0.285		
$H_2Se(aq)$	$H_2Se(g) \rightleftharpoons H_2Se(aq)$			
[2005OLI/NOL]	–1.100 ±0.010	6.279 ±0.057	–14.700 ±0.300	–70.363 (a) ±1.024
$HSeO_3^-$	$H_2SeO_3(aq) \rightleftharpoons H^+ + HSeO_3^-$			
[2005OLI/NOL]	–2.640 ±0.140	15.069 ±0.799		
$HSeO_4^-$	$H_2O(l) + H_2SeO_3(aq) \rightleftharpoons 3H^+ + HSeO_4^- + 2\,e^-$			
[2005OLI/NOL]	–37.289 (c) ±0.175	212.847 ±1.000		

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$ ($kJ \cdot mol^{-1}$)	$\Delta_r H_m^{\circ}$ ($kJ \cdot mol^{-1}$)	$\Delta_r S_m^{\circ}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
$H_2SeO_3(cr)$	$H_2O(l) + SeO_2(cr) \rightleftharpoons H_2SeO_3(cr)$			
[2005OLI/NOL]			−13.500 ±0.180	
$H_2SeO_3(aq)$	$3H_2O(l) + Se(cr) \rightleftharpoons 2H_2(g) + H_2SeO_3(aq)$			
[2005OLI/NOL]	−50.147 ±0.147	286.240 ±0.840		
$HN_3(aq)$	$H^+ + N_3^- \rightleftharpoons HN_3(aq)$			
[1992GRE/FUG]	4.700 ±0.080	− 26.828 ±0.457	− 15.000 ±10.000	39.671 (a) ±33.575
$NH_3(aq)$	$NH_4^+ \rightleftharpoons H^+ + NH_3(aq)$			
[1992GRE/FUG]	− 9.237 ±0.022	52.725 ±0.126	52.090 ±0.210	− 2.130 (a) ±0.821
$HNO_2(aq)$	$H^+ + NO_2^- \rightleftharpoons HNO_2(aq)$			
[1992GRE/FUG]	3.210 ±0.160	− 18.323 ±0.913	− 11.400 ±3.000	23.219 (a) ±10.518
PO_4^{3-}	$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$			
[1992GRE/FUG]	− 12.350 ±0.030	70.494 ±0.171	14.600 ±3.800	− 187.470 (a) ±12.758
$P_2O_7^{4-}$	$HP_2O_7^{3-} \rightleftharpoons H^+ + P_2O_7^{4-}$			
[1992GRE/FUG]	− 9.400 ±0.150	53.656 ±0.856		
$H_2PO_4^-$	$H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^-$			
[1992GRE/FUG]	7.212 ±0.013	− 41.166 ±0.074	− 3.600 ±1.000	126.000 (a) ±3.363
$H_3PO_4(aq)$	$H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4(aq)$			
[1992GRE/FUG]	2.140 ±0.030	− 12.215 ±0.171	8.480 ±0.600	69.412 (a) ±2.093
$HP_2O_7^{3-}$	$H_2P_2O_7^{2-} \rightleftharpoons H^+ + HP_2O_7^{3-}$			
[1992GRE/FUG]	− 6.650 ±0.100	37.958 ±0.571		
$H_2P_2O_7^{2-}$	$H_3P_2O_7^- \rightleftharpoons H^+ + H_2P_2O_7^{2-}$			
[1992GRE/FUG]	− 2.250 ±0.150	12.843 ±0.856		
$H_3P_2O_7^-$	$H_4P_2O_7(aq) \rightleftharpoons H^+ + H_3P_2O_7^-$			
[1992GRE/FUG]	− 1.000 ±0.500	5.708 ±2.854		

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_r G^{\circ}_m$ ($kJ\cdot mol^{-1}$)	$\Delta_r H^{\circ}_m$ ($kJ\cdot mol^{-1}$)	$\Delta_r S^{\circ}_m$ ($J\cdot K^{-1}\cdot mol^{-1}$)
$H_4P_2O_7(aq)$	$2H_3PO_4(aq) \rightleftharpoons H_2O(l) + H_4P_2O_7(aq)$			
[1992GRE/FUG]	– 2.790	15.925	22.200	21.045 $^{(a)}$
	±0.170	±0.970	±1.000	±4.673
$CO_2(aq)$	$H^+ + HCO_3^- \rightleftharpoons CO_2(aq) + H_2O(l)$			
[1992GRE/FUG]	6.354	– 36.269		
	±0.020	±0.114		
$CO_2(g)$	$CO_2(aq) \rightleftharpoons CO_2(g)$			
[1992GRE/FUG]	1.472	– 8.402		
	±0.020	±0.114		
HCO_3^-	$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$			
[1992GRE/FUG]	10.329	– 58.958		
	±0.020	±0.114		
CN^-	$HCN(aq) \rightleftharpoons CN^- + H^+$			
[2005OLI/NOL]	– 9.210	52.571	43.600	– 30.089 $^{(a)}$
	±0.020	±0.114	±0.200	±0.772
$HCN(aq)$	$HCN(g) \rightleftharpoons HCN(aq)$			
[2005OLI/NOL]	0.902	– 5.149	– 26.150	– 70.439 $^{(a)}$
	±0.050	±0.285	±2.500	±8.440
$SiO_2(OH)_2^{2-}$	$Si(OH)_4(aq) \rightleftharpoons 2H^+ + SiO_2(OH)_2^{2-}$			
[1992GRE/FUG]	– 23.140	132.080	75.000	– 191.460 $^{(a)}$
	±0.090	±0.514	±15.000	±50.340
$SiO(OH)_3^-$	$Si(OH)_4(aq) \rightleftharpoons H^+ + SiO(OH)_3^-$			
[1992GRE/FUG]	– 9.810	55.996	25.600	– 101.950 $^{(a)}$
	±0.020	±0.114	±2.000	±6.719
$Si(OH)_4(aq)$	$2H_2O(l) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons Si(OH)_4(aq)$			
[1992GRE/FUG]	– 4.000	22.832	25.400	8.613 $^{(a)}$
	±0.100	±0.571	±3.000	±10.243
$Si_2O_3(OH)_4^{2-}$	$2Si(OH)_4(aq) \rightleftharpoons 2H^+ + H_2O(l) + Si_2O_3(OH)_4^{2-}$			
[1992GRE/FUG]	– 19.000	108.450		
	±0.300	±1.712		
$Si_2O_2(OH)_5^-$	$2Si(OH)_4(aq) \rightleftharpoons H^+ + H_2O(l) + Si_2O_2(OH)_5^-$			
[1992GRE/FUG]	– 8.100	46.235		
	±0.300	±1.712		
$Si_3O_6(OH)_3^{3-}$	$3Si(OH)_4(aq) \rightleftharpoons 3H^+ + 3H_2O(l) + Si_3O_6(OH)_3^{3-}$			
[1992GRE/FUG]	– 28.600	163.250		
	±0.300	±1.712		

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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^{-1})	$\Delta_r H_m^{\circ}$ (kJ·mol^{-1})	$\Delta_r S_m^{\circ}$ (J·K^{-1}·mol^{-1})
$Si_3O_5(OH)_5^{3-}$	$3Si(OH)_4(aq) \rightleftharpoons 3H^+ + 2H_2O(l) + Si_3O_5(OH)_5^{3-}$			
[1992GRE/FUG]	– 27.500 ±0.300	156.970 ±1.712		
$Si_4O_8(OH)_4^{4-}$	$4Si(OH)_4(aq) \rightleftharpoons 4H^+ + 4H_2O(l) + Si_4O_8(OH)_4^{4-}$			
[1992GRE/FUG]	– 36.300 ±0.500	207.200 ±2.854		
$Si_4O_7(OH)_5^{3-}$	$4Si(OH)_4(aq) \rightleftharpoons 3H^+ + 4H_2O(l) + Si_4O_7(OH)_5^{3-}$			
[1992GRE/FUG]	– 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

V Thorium elemental

V.1 Thorium crystal and liquid

V.1.1 Crystal structure and phase transitions

Thorium metal has a face centred cubic structure, (space group $Fm\overline{3}m$, Cu type) at 298.15 K and undergoes a structural change to a bcc-phase (space group $Im\overline{3}m$, W type) at *ca*. 1630 K. The lattice parameters are 5.0842 Å at 298.15 K [1956JAM/STR] and 4.11 Å at 1723 K [1954CHI]. Rand [1975RAN] critically examined the data of 15 studies of this transformation with the reported transition temperatures ranging from 1605 to 1698 K, with most values lying between 1623 and 1653 K. The probable reason for this seemingly wide range of values is the effect of impurities in the thorium used. It is clear that small amounts of carbon, nitrogen and oxygen, which are difficult to remove from thorium, raise the transformation temperature, whereas additions of niobium, tantalum and zirconium tend to lower the temperature of the phase change. We have therefore given considerable weight to the work of Chiotti and Dooley [1967CHI/DOO] ((1623 ± 10) K) and Takeuchi *et al.* [1966TAK/HON] ((1633 ± 10) K) who both extrapolated the transition temperature to zero carbon content and select for the transformation temperature:

$$T_{\text{trs}}(\text{Th, cr}) = (1633 \pm 20)\text{ K.}$$

Glushko *et al.* [1982GLU/GUR] selected the slightly higher, but not inconsistent, value of (1650 ± 20) K, possibly giving more weight to the fact that Levinson [1966LEV] reported two measurements (at 1639 and 1650 K) which apparently referred to the low temperature phase.

The enthalpy of transformation has been taken from the work of Levinson [1966LEV], who investigated the enthalpy of thorium metal to just beyond the melting point and found $\Delta_{\text{trs}}H_{\text{m}}(\text{Th, cr}) = (3.6 \pm 0.1)\text{ kJ·mol}^{-1}$. This value has been confirmed by the more recent study [1996BOI/COL] of some physicochemical properties of thorium (0.5 mass% impurities) up to 5000 K by the very rapid heating technique. No temperatures were measured, but the discontinuity on the electrical resistivity curve at the transition gave a transformation enthalpy of 3.5 kJ·mol^{-1} with an uncertainty estimated by the review to be 0.2 kJ·mol^{-1}.

Rand [1975RAN] and Glushko *et al.* [1982GLU/GUR] also assessed the melting point and enthalpy of fusion of thorium, selecting $T_{\text{fus}}(\text{Th}, \beta) = (2023 \pm 10)$ K from eight studies and $\Delta_{\text{fus}}H_{\text{m}}(\text{Th}, \beta, 2023\text{ K}) = (13.8 \pm 0.1)\text{ kJ·mol}^{-1}$ from Levinson [1966LEV]. As for the enthalpy of transformation, this has been confirmed by the recent work of Boivineau *et al.* [1996BOI/COL]. No other recent studies of the melting point of thorium have been found.

V.1.2 Heat capacity and entropy

The heat capacity data for Th(cr) are rather unsatisfactory, especially those from 4 to 30 K and a more definitive study with high purity thorium of the values below 300 K is clearly required.

V.1.2.1 Heat capacity below 298.15 K

The experimental studies in this temperature range are summarised in Table V-1, and shown in Figure V-1 (0 to 300 K) and in more detail for the very low temperature data in Figure V-2 (0 to 35 K).

Table V-1: Experimental studies on $C_{p,\mathrm{m}}$ (Th, cr) below 300 K.

Reference	Temperature range (K)	Comments
[1953GRI/SKO]	18 – 300	No individual points, rounded values from 20 K only. Accuracy estimated by the authors to be 0.1% at 20 K, 0.3% at 30 K and above 35 K, 0.1%
[1955SMI/WOL]	1.2 – 19	Individual points 1.4 – 4 K given on a $C_{p,\mathrm{m}}/T$ *vs.* T^2 plot. Above 4 K, the only data given are a (small) plot of θ_D *vs.* T (up to 19 K).
[1966GOR/MON]	1.374 – 4	Data from 1 – 2.2 K plotted on a $C_{p,\mathrm{m}}/T$ *vs.* T^2 line; further data to 4 K (no details) correspond to a constant $\theta_D = (163.3 \pm 0.7)$ K.
[1972LUE/COT]	1.5 – 5	Deals mainly with the effect of small additions of U to Th, but measurements were made on pure Th. No $C_{p,\mathrm{m}}$ values reported, only the values of constant γ and $\theta_D = (160.4 \pm 0.5)$ K.
[1973SAT/KUM]	Not given, probably 1 to 4 K	Deals mainly with Th-Y and Th-La alloys, but measurements were made on pure Th. No $C_{p,\mathrm{m}}$ values are reported, only plots of $C_{p,\mathrm{m}}/T$ *vs.* T^2, together with the derived constants γ (4.24 $\mathrm{mJ\cdot K^{-2}\cdot mol^{-1}}$) and θ_D (166 K). The temperature range of the measurements for pure Th(cr) is not clear. The plotted data for pure Th and Th-Y and Th-rich Th-La alloys extend only to 3.8 K, but to 7.5 K for La-rich Th-La alloys.
[1975SCH/WOL]	Not given, possibly up to 11 K	Data for Th(cr) and Th_4H_{15}(cr) were measured. The only values given for Th are γ and θ_D (167 K); the temperature range from which these were derived is not stated. There is a plot of $C_{p,\mathrm{m}}/T$ up to 11 K for Th_4H_{15}(cr), so it is possible that Th(cr) was studied over the same temperature range.
[1980NAK/TAK]	84 – 991	Values of 213 measurements from 84.15 to 991.32 K are tabulated in detail.

Figure V-1: Heat capacity of Th(cr) from 0 to 300 K.

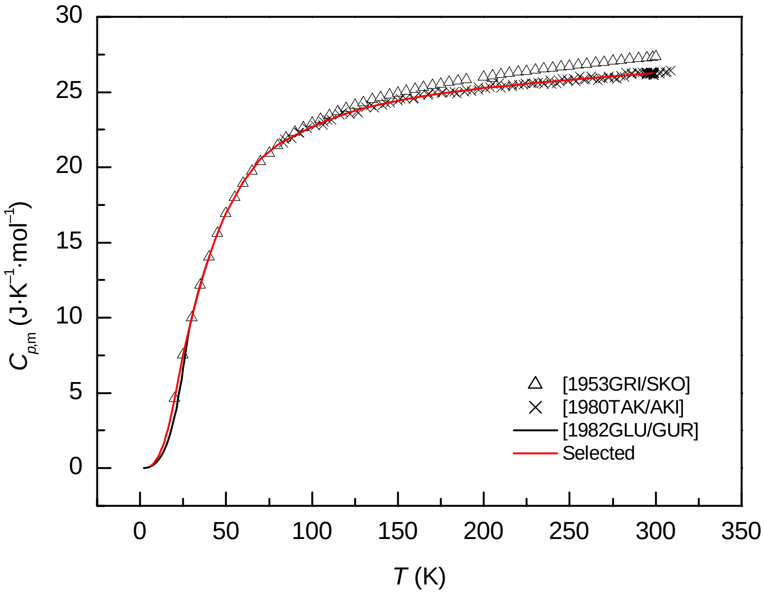
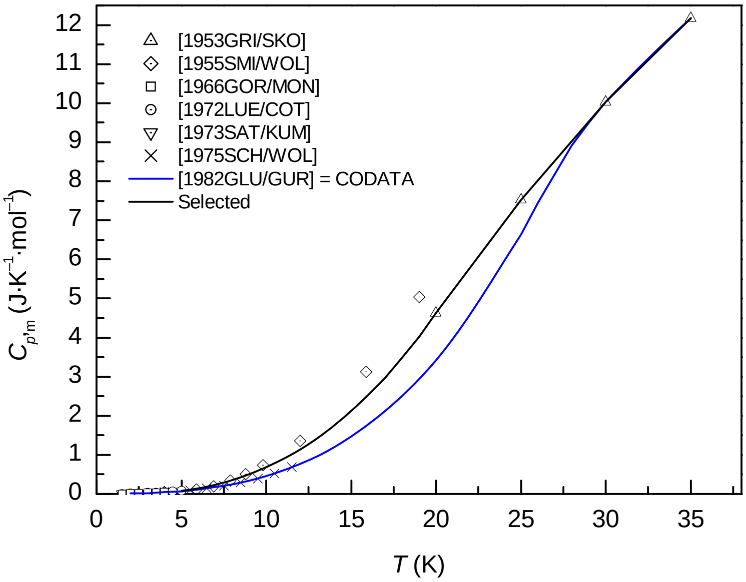


Figure V-2: Heat capacity of Th(cr) from 0 to 35 K.



None of the papers describing the studies below 20 K gives the measured values of $C_{p,\mathrm{m}}$; they report only the values of γ and θ_D derived from the relation

$$C_{v,\mathrm{m}} = \gamma T + (12\,\mathrm{R}/5)\,\pi^4\,(T/\theta_\mathrm{D})^3. \qquad \text{(V.1)}$$

The difference between $C_{p,\mathrm{m}}$ and $C_{v,\mathrm{m}}$ is quite small (< 5 mJ·K^{-1}·mol^{-1} up to 35 K), according to the calculations presented in [1953GRI/SKO].

Since the heat capacity values from 4 to at least 20 K are very poorly defined, we shall discuss the relevant publications in some detail. The values of γ, relating to the electronic contribution and θ_D, relating to the contribution from lattice vibrations, from these studies are summarised in Table V-2.

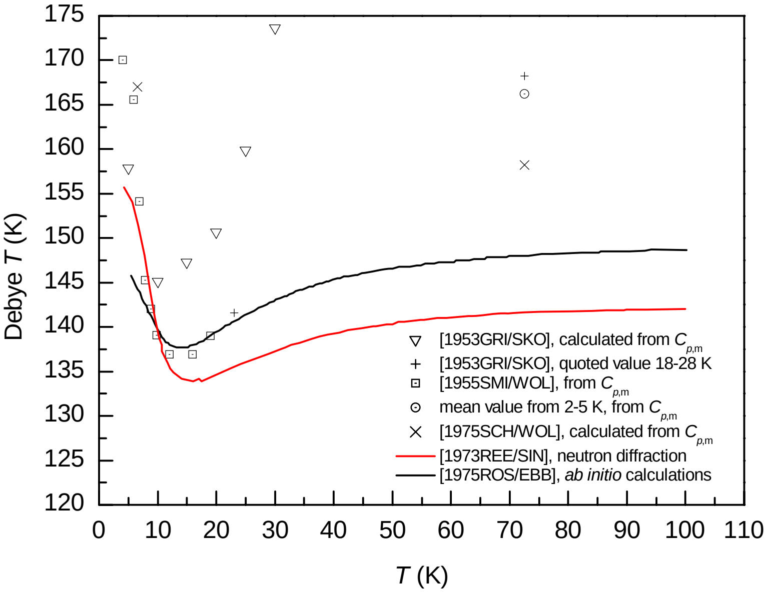
Table V-2: Summary of experimental γ and θ_D values for Th(cr).

Rerefence	γ (mJ·K^{-2}·mol^{-1})	θ_D (K)	Temperature range (K)
[1955SMI/WOL]	4.69	Varies with T 0 – 4 K = 170 10 K = 139 16 K = 137 19 K =139 (Values above 4 K digitised from a small plot)	1.4 – 19
[1966GOR/MON]	4.31 ± 0.05	163.3 ± 0.7	1.4 – 4
[1972LUE/COT]	4.08 ± 0.03	160.4 ± 0.5	1.5 – 5
[1973SAT/KUM]	4.24	166	1.4 – 3.8, possibly to 7.5
[1975SCH/WOL]	4.23	167	Not stated, possibly 2 – 11

However, the temperature range of the measurements from which these values of γ and θ_D are derived is also rarely stated explicitly, or even at all. This is important, since although the value of θ_D below 4 K is *ca.* 165 K (see Table V-2), the measurements of Smith and Wolcott [1955SMI/WOL], although made on a material containing 200 ppm iron and 50 ppm silicon, indicate clearly that θ_D decreases to a minimum of *ca.* 137 K at *ca.* 16 K. This minimum in θ_D is the normal behaviour of most metals, including alpha-uranium, as shown in the detailed study of Flotow and Osborne [1966FLO/OSB]. Note that on Figure V-2, values of [1975SCH/WOL] are plotted to 11 K, though these authors do not state the temperature range of their measurements (see Table V-1) (and according to [1955SMI/WOL], θ_D is not constant in the range 4 – 11 K).

There are also two papers which report values of θ_D from other sources. Reese *et al.* [1973REE/SIN] describe a neutron diffraction study (at room temperature) to give the phonon distribution (distribution of vibration frequencies), from which the variation of θ_D as a function of temperature is derived, and Rosengren *et al.* [1975ROS/EBB] report a theoretical *ab initio* calculation of $\theta_D(T)$. As shown in Figure V-3, from 10 to 20 K, they agree reasonably with each other and rather well with the experimental values from the $C_{p,\mathrm{m}}$ measurements of [1955SMI/WOL]. Above 20 K, they both give θ_D values which are much smaller than those derived from the $C_{p,\mathrm{m}}$ measurements of [1953GRI/SKO], and would thus correspond to much bigger heat capacities than the experimental values of [1953GRI/SKO], which seems very unlikely.

Figure V-3: Debye temperature of Th(cr).



Thus, although the best values of θ_D above 4 K are not clear, it does seem certain that the Debye temperature has a minimum just below 20 K, and that the use of a constant Debye temperature, particularly that derived from $C_{p,\mathrm{m}}$ measurements in the range 2 − 10 K is not appropriate.

For temperatures from 20 to 300 K, there are two sets of heat capacity measurements. Griffel and Skochdopole [1953GRI/SKO] reported measurements from 18 to 300 K obtaining a value of $C^{\circ}_{p,\mathrm{m}}(298.15\ \mathrm{K}) = (27.32 \pm 0.29)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. No anomalies in the low-temperature heat capacity were found, although there was a slight irregularity observed in the measurements from 135 to 155 K. Nakamura *et al.* [1980NAK/TAK] measured the heat capacity of thorium containing 0.05 mass% impurities from 84 to 991 K, using a laser-flash technique. Their measurements agree with those of [1953GRI/SKO] from 80 to 100 K, but become increasingly lower from 100 to 300 K, with $C^{\circ}_{p,\mathrm{m}}$ (298.15 K) = (26.24 ± 0.13) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

From these rather unsatisfactory experimental data, Glushko *et al.* [1982GLU/GUR] and Ward *et al.* [1986WAR/KLE] have made assessments of the thermal functions. The CODATA assessment [1989COX/WAG] is the same as that by [1982GLU/GUR]. Arblaster [2004ARB] has also provided the reviewers with full details of a thorough assessment (so far unpublished), which gives values very similar to those of [1986WAR/KLE], though made quite independently of it. These reviewers have adopted the same philosophy in selecting the values from 30 to 298.15 K:

- From 30 to 80 K, to accept the values of [1953GRI/SKO] (which are the only data available in this temperature range).
- Above 80 K, to rely heavily on the extensive and well-documented data of Nakamura *et al.* [1980NAK/TAK] from 84 to 991 K, since these merge extremely well with both with the measurements of [1953GRI/SKO] at 80 K and with the high temperature enthalpy data of Levinson [1966LEV] (discussed in Section V.1.2.2) at 1000 to 1200 K.

However, [1982GLU/GUR] and [1986WAR/KLE] extrapolated the heat capacity from 35 K down to 4 K differently, which results in the noticeably different values for S(Th, cr, 298.15 K) of (51.83 ± 0.50) and (52.64 ± 0.50) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ respectively.

Dr. Bergman at the Glushko Thermocenter, Moscow has kindly provided us with the detailed heat capacity data from 1.374 to 298.15 K selected in [1982GLU/GUR], together with following summary of these selections:

- From 1.37 to 11 K: data from [1975SCH/WOL].
- From 11 to 20 K: extrapolation of data from [1975SCH/WOL], using θ_D = 167 K.
- From 20 to 30 K: smoothed data to reflect the sharp growth of $C_{p,\mathrm{m}}$ from the value extrapolated from the data of [1975SCH/WOL] at 20 K to the experimental value of $C_{p,\mathrm{m}}$ (30 K) from [1953GRI/SKO].
- From 30 to 80 K: data from [1953GRI/SKO].
- From 80 to 298.15 K: data from [1980NAK/TAK].

However, the values of γ = 4.23 $\mathrm{mJ{\cdot}K^{-2}{\cdot}mol^{-1}}$ and a constant θ_D of 167 K, used by [1982GLU/GUR] to calculate the $C^{\circ}_{p,\mathrm{m}}$ data from 11 to 20 K, are those obtained by [1975SCH/WOL] from measurements over an unspecified temperature range from 2 K upwards. For reasons stated above, we suggest that this underestimates the heat capacity in this range, (and thus up to 25 K), since θ_D is almost certainly smaller than 167 K in this temperature range.

[1986WAR/KLE] accepted the data of [1953GRI/SKO] from 80 down to 20 K; they do not state how they extrapolated the heat capacity to 0 K, but since their value of S(Th, cr) at 50 K is identical with that given by [1953GRI/SKO], we assume they adopted the values calculated by the latter authors, which as already noted, were derived from the extrapolation to 0 K using a constant θ_D of 141.6 K from 0 to 20 K This is confirmed by the value at 10 K tabulated by [1986WAR/KLE].

In view of the uncertainties in the Debye temperature of Th(cr) discussed in detail above, we have preferred to estimate the $C_{p,\mathrm{m}}$ data from 4 to 20 K without recourse to these uncertain values and have adopted the values suggested to us by Arblaster [2004ARB], who kindly provided us with his recent (so far unpublished) assessment of the thermodynamic properties of Th(cr). For this the selected values are the following:

- From 0 to 4 K: data from [1966GOR/MON], as being representative of the consistent data in this region, including the superconducting transition at 1.374 K.
- From 4 to 20 K: data fitted to a cubic equation in T, so that $C_{p,\mathrm{m}}$ and $dC_{p,\mathrm{m}} / dT$ are continuous with the values from [1966GOR/MON] at 4 K and from [1953GRI/SKO] at 20 K.
- From 20 to 80 K: data of [1953GRI/SKO].
- From 80 to 300 K: data of [1980NAK/TAK].

These data give S_m (Th, cr, 298.15 K) = (52.64 ± 0.50) J·K^{-1}·mol^{-1}, where the estimated uncertainty is due principally to the uncertain values of $C_{p,\mathrm{m}}$ from 4 to 20 K (including the effect of the non metallic impurities in the thorium used by [1953GRI/SKO]). Although this value of S_m (Th, cr, 298.15 K) is identical to that given by [1986WAR/KLE], it is calculated entirely independently, with a different procedure for the extrapolation from 20 K down to 0 K (although the data selection from 20 to 300 K is essentially the same).

As a matter of interest, the θ_D values calculated from the selected data from 4 to 20 K pass through a minimum of 145.1 K at 10 K and are close to those derived from the $C_{p,\mathrm{m}}$ measurements of [1955SMI/WOL], which perhaps gives added confidence to the selection.

The selected values at 298.15 K are

$$S^\circ_\mathrm{m}\text{ (Th, }\alpha\text{, 298.15 K)} = (52.64 \pm 0.50)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$C^\circ_{p,\mathrm{m}}\text{ (Th, }\alpha\text{, 298.15 K)} = (26.23 \pm 0.50)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

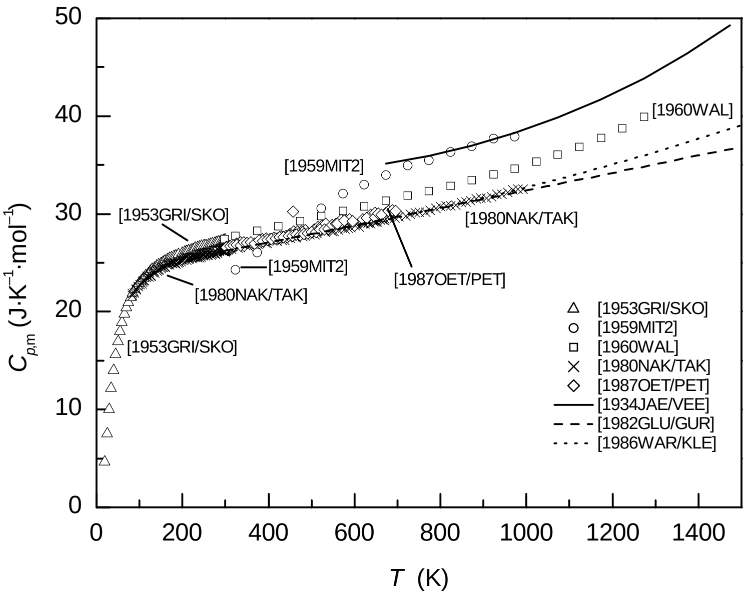
V.1.2.2 Heat capacity above 298.15 K

There are also inconsistencies in the four measurements of the heat capacity of Th(cr) above 298.15 K (see Table V-3 and Figure V-4).

Table V-3: Experimental studies on $C_{p,\mathrm{m}}$ (Th, cr) above 300 K.

Reference	Temperature range (K)	Comments
[1959MIT2]	323 – 973	Precise details of experimental method not clear, and the data have an unusually high temperature coefficient. These data were not utilised
[1960WAL]	300 – 1273	Data probably too high, and not utilised – see Appendix A
[1980NAK/TAK]	84 – 991	$C_{p,\mathrm{m}}$ values of 213 measurements from 84.15 to 991.32 K are tabulated in detail.
[1987OET/PET]	303 – 695	Data agree reasonably well with those of [1980NAK/TAK]

Figure V-4: Heat capacity of Th(cr).



The heat capacity measurements of Wallace [1960WAL] from 298.15 to 1273 K merge smoothly with the low temperature data of [1953GRI/SKO]. However, Nakamura *et al.* [1980NAK/TAK] measured the heat capacity of thorium containing 0.05 mass% impurities using a laser-flash technique. This a valuable study, as not only are the results given in detail, but the 206 measurements extend from 84 to 991 K using the same equipment, thus obviating the awkward join normally required between low temperature adiabatic calorimetry and other techniques used at higher temperatures. Their measurements agree with those of [1953GRI/SKO] from 80 to 100 K, but become increasingly lower from 100 to 300 K, with $C^{\circ}_{p,\mathrm{m}}$(298.15 K) = 26.24 J·K^{-1}·mol^{-1}. Later adiabatic measurements by [1987OET/PET] from 303 to 695 K are slightly higher than those of [1980NAK/TAK], but appreciably below those of Wallace [1960WAL]. There are also $C_{p,\mathrm{m}}$ measurements by Mit'kina [1959MIT2] which are even higher than those of Wallace above 500 K, with an unusually high temperature coefficient.

The only reliable enthalpy increment measurements are those of Levinson [1966LEV] from 1269 to 2100 K, although Jaeger and Veenstra [1934JAE/VEE] reported measurements on thorium containing 6 mass% ThO_2, which are clearly too high.

As noted earlier, the assessments of the reviews of [1982GLU/GUR] and [1986WAR/KLE] (and the unpublished assessment of Arblaster) have relied heavily on the extensive and well-documented data of Nakamura *et al.* [1980NAK/TAK] from 80 to 1000 K, since these merge extremely well with the high temperature enthalpy data of Levinson [1966LEV] and we have adopted the same philosophy.

The selected values above 298.15 K are those of [1982GLU/GUR], but with a transformation temperature of (1633 ± 20) K rather than (1650 ± 20) K, as discussed earlier. These values are essentially identical to the assessment of [1986WAR/KLE] up to 1000 K, but above this temperature, the $C_{p,\mathrm{m}}$ equation of [1982GLU/GUR] reproduces the enthalpy data of [1966LEV] better than that of [1986WAR/KLE] and has been preferred.

$$[C^{\circ}_{p,\mathrm{m}}]^{1633\,\mathrm{K}}_{298.15\,\mathrm{K}}(\mathrm{Th}, \alpha, T) = 23.435 + 8.945\times10^{-3}\,T + 1.14\times10^{6}\,T^{-2}\quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$\Delta_{\mathrm{trs}}H_{\mathrm{m}}(\mathrm{Th, cr, 1633\ K}) = (3.6 \pm 0.1)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$[C^{\circ}_{p,\mathrm{m}}]^{2023\,\mathrm{K}}_{1633\,\mathrm{K}}(\mathrm{Th}, \beta, T) = 15.702 + 1.1950\times10^{-2}\,T\quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$\Delta_{\mathrm{fus}}H_{\mathrm{m}}(\mathrm{Th, cr, 2023\ K}) = (13.8 \pm 0.1)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$[C^{\circ}_{p,\mathrm{m}}]^{3000\,\mathrm{K}}_{2023\,\mathrm{K}}(\mathrm{Th, l}) = 46.0\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

V.2 Thorium ideal monatomic gas

V.2.1 Heat capacity and entropy

The early calculations of the thermal functions of Th(g) (*e.g.* [1965FEB/HER]) used the 200 or so energy levels published by Zalubas [1959ZAL]. In subsequent calculations, Rand [1975RAN] and Oetting *et al.* [1976OET/RAN] used the 523 levels up to 40000 cm^{-1} given in a later paper by Zalubas [1968ZAL]. It is not clear how many levels Glushko *et al.* [1982GLU/GUR] and Ward *et al.* [1986WAR/KLE] used in their calculations, but their calculated values are very similar to those of [1976OET/RAN].

Blaise and Wyart [1992BLA/WYA] have more recently published a comprehensive listing of the known energy levels of all the actinide gases, which contains 693 levels for Th(g), and we have used these in our calculations. The lowest levels of the seven configurations below the ionisation level so far unidentified, estimated by Brewer [1971BRE], have also been added in the current calculation. The Gibbs energy functions differ from those given by [1982GLU/GUR] and [1986WAR/KLE] by less than 0.01 $\text{J·K}^{-1}\text{·mol}^{-1}$ at all temperatures up to 3000 K after allowing for the different standard-state pressure. The values at 298.15 K are:

$$C^{\circ}_{p,\mathrm{m}}\,(\mathrm{Th, g, 298.15\ K}) = (20.790 \pm 0.005)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}\,(\mathrm{Th, g, 298.15\ K}) = (190.170 \pm 0.010)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

The derived heat capacity equation at low temperatures is:

$$[C^{\circ}_{p,\mathrm{m}}]^{700\mathrm{K}}_{298.15\mathrm{K}}\,(\mathrm{Th, g}, T) = 24.1480 - 1.45623 \times 10^{-2}\,T + 1.77473 \times 10^{-5}\,T^{2} - 5.27700 \times 10^{4}\,T^{-2} \quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

V.2.2 Enthalpy of formation

The early measurements of the vapour pressure of thorium are all vitiated by the problem of oxygen contamination, as discussed by Rand [1975RAN] and Glushko et al. [1982GLU/GUR]. Therefore we consider below only the two more recent measurements in which this problem was explicitly considered. The vapour pressure of solid thorium was determined by the Langmuir evaporation method in the temperature range of 1757 to 1956 K by Darnell et al. [1960DAR/MCC]. Their sublimation pressure corresponds to $\log_{10}(p/\mathrm{bar}) = -(28780 \pm 620)/T + (5.997 \pm 0.333)$. From this equation and the selected thermal functions, the derived enthalpy of sublimation for thorium metal at 298.15 K is $(581.6 \pm 5.0)\ \mathrm{kJ{\cdot}mol^{-1}}$ by a third-law analysis and $(561.5 \pm 23.7)\ \mathrm{kJ{\cdot}mol^{-1}}$ by a second-law analysis. The study by Ackermann and Rauh [1972ACK/RAU], discussed below, suggests that the measurements of [1960DAR/MCC] were probably significantly too high due to oxygen contamination, and the consequent formation of ThO(g). Although Darnell *et al.* attempted to reduce the oxygen contamination (initially ~1000 ppm) of their sample by volatilisation of ThO(g) for 200 h at 1883 K, their sample still contained 30 ppm oxygen. Moreover, their resulting steady-state vapour pressures are greater by a factor of about three than those reported by Ackermann and Rauh [1972ACK/RAU] who measured the vapour pressure of crystal-bar thorium, which normally contains 50 − 100 ppm oxygen, by the target-effusion method, only after the intensity of $\mathrm{ThO^{+}(g)}$ had decreased to less than 0.5% of that of $\mathrm{Th^{+}(g)}$ as observed mass-spectrometrically; initially the $\mathrm{ThO^{+}(g)}$ intensity was approximately five times that of $\mathrm{Th^{+}(g)}$. It is, therefore, quite likely that the vapour in pseudo steady-state conditions observed by Darnell *et al.* still contained appreciable amounts of ThO(g). Indeed the calculated pressure of ThO(g) in oxygen-saturated Th is about a factor of 100 greater that of Th(g) from 2000 to 3000 K.

In their investigation, Ackermann and Rauh [1972ACK/RAU] measured the vapour pressure of liquid thorium containing less than 3 at.% dissolved tungsten from 2010 to 2460 K by combined mass-effusion and mass-spectrometric techniques and derived the vapour pressure equation equivalent to:

$$\log_{10}(p/\text{bar}) = -(29770 \pm 440)/T + (6.030 \pm 0.196)$$

from 2010 to 2460 K.

The third-law $\Delta_{\text{vap}}H_{\text{m}}$ (298.15 K) from these data is (601.8 ± 4.2) $\text{kJ}\cdot\text{mol}^{-1}$, with only a small trend with temperature and a second-law value (597.0 ± 8.4) $\text{kJ}\cdot\text{mol}^{-1}$. The results of Ackermann and Rauh are selected because of the more complete description of the role of oxygen contamination and the good agreement of the second- and third-law values of $\Delta_{\text{vap}}H_{\text{m}}$ (298.15 K):

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{Th, g, 298.15 K}) = (602 \pm 6)\ \text{kJ}\cdot\text{mol}^{-1}.$$

This is identical to the value selected by the CODATA Key Values group [1989COX/WAG].

Gingerich [1969GIN2] detected very small amounts of $Th_2(g)$ molecules in a mass-spectrometric study of the Th-B-P system and, using the estimated molecular parameters of $Th_2(g)$ (ω_e = 92.2 cm^{-1}; r_e = 3.30 Å; doublet ground state), suggested that $D°(Th_2$, g, 0 K) ≤ (285 ± 33) $\text{kJ}\cdot\text{mol}^{-1}$ giving $\Delta_{\text{f}}H^{\circ}_{\text{m}}(Th_2$, g, 298.15 K) > (914 ± 34) $\text{kJ}\cdot\text{mol}^{-1}$, and $S^{\circ}_{\text{m}}(Th_2$, g, 298.15 K) = 289 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 298.15 K (values recalculated by the reviewers). This is an unusually high value for the dissociation energy and these values for $Th_2(g)$ are given for information only, and are not selected. The calculated fraction of dimer in the saturated vapour is less than 0.1% even at the (extrapolated) boiling point, around 5000 K.

The above selections yield:

$$\Delta_{\text{f}}G^{\circ}_{\text{m}}(\text{Th, g, 298.15 K}) = (561.0 \pm 6.0)\ \text{kJ}\cdot\text{mol}^{-1}.$$

VI The aqueous Th^{4+} ion

There is no firm evidence for the stability of any valency state other than Th(IV) in aqueous media. Recently, Klapköte and Schulz [1997KLA/SCH] claimed to have identified Th^{3+} in the reaction of Th^{4+} with HN_3 in slightly acidic solutions (pH = *ca.* 3.5), by absorption and ESR spectra. However, as noted in Appendix A, Ionova *et al.* [1998ION/MAD] have seriously questioned both the value of E° (Th^{3+}/Th^{4+}) chosen by [1997KLA/SCH] in their thermodynamic analysis and the validity of their conclusions, pointing out that the absorption bands observed by these authors could equally well be due to azide complexes of Th(IV), with or without Cl^- ligands. Moreover, the stability of HN_3 in dilute aqueous solutions suggests that the proposed reduction of Th^{4+} is unlikely to be thermodynamically controlled as suggested in [1997KLA/SCH]. Thus there seems no incontrovertible evidence for the existence of any stable ions in aqueous solutions other than Th(IV) and its derivatives.

VI.1 Thermodynamic data for the Th^{4+} ion

The enthalpy of formation of Th^{4+} is derived from measurements of the enthalpy of solution in HCl solutions. Unless some fluorosilicate ion is present, this reaction leaves variable amounts of a black residue, probably an oxide hydride containing chloride and hydroxide ions, ThO(Cl,OH)H [1962KAT/KAP], [1973ACK/RAU3] (see Appendix A).

The standard enthalpy of formation of Th^{4+}, $\Delta_f H^{\circ}_m(Th^{4+}, 298.15\ K)$, is obtained from $\Delta_f H^{\circ}_m(ThCl_4, \beta, 298.15\ K)$, and the extrapolation of the enthalpy of solution of $ThCl_4$ in HCl solutions to infinite dilution, according to reaction:

$$\beta\text{-}ThCl_4 \rightleftharpoons Th^{4+} + 4Cl^- \qquad (VI.1)$$

The enthalpy of formation of thorium tetrachloride itself (see Section VIII.2) involves the enthalpy of dissolution of thorium metal and of thorium tetrachloride in HCl solutions at various concentrations, the data for which are summarised in Table VI-1.

With the exception of the result from [1981BUR/KIJ2], which is cited for information only (see Appendix A), Figure VI-1 shows a plot of all the existing values for the enthalpy of solution of β-$ThCl_4$ as a function of the molality (m) of the HCl solutions, after correction ($-1.25\ kJ\cdot mol^{-1}$) for the presence of Na_2SiF_6 in some experiments. A linear extrapolation:

$$\Delta_{sol} H^{\circ}_m(ThCl_4, \beta) = -250.658 + 9.4002\, m \quad kJ\cdot mol^{-1} \qquad (VI.2)$$

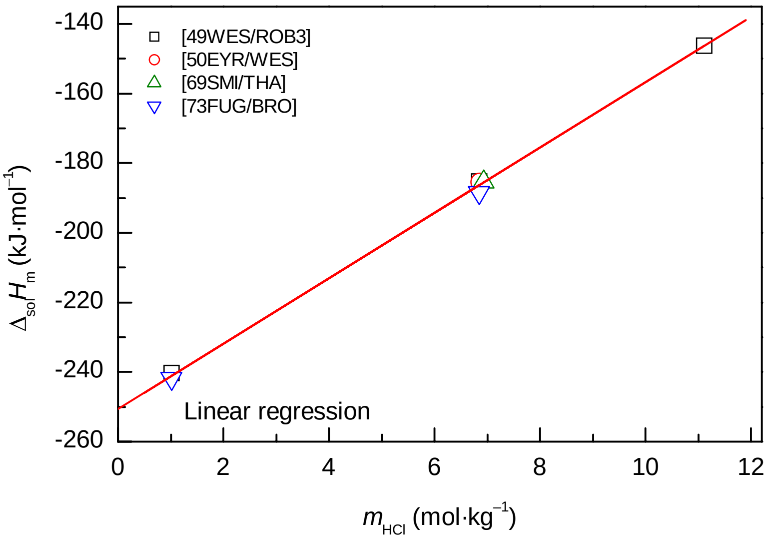
yields at zero ionic strength the selected value $\Delta_{sol} H^{\circ}_m(ThCl_4, \beta, 298.15\ K) = -(250.7 \pm 1.8)\ kJ\cdot mol^{-1}$, the uncertainty being the 2σ value from the linear regression; hence, using $\Delta_f H^{\circ}_m(Cl^-, 298.15\ K) = -(167.080 \pm 0.100)\ kJ\cdot mol^{-1}$ from [1989COX/WAG] and $\Delta_f H^{\circ}_m(ThCl_4, \beta, 298.15\ K) = -(1186.3 \pm 1.3)\ kJ\cdot mol^{-1}$ (see Section VIII.2), $\Delta_f H^{\circ}_m(Th^{4+}, 298.15\ K) = -(768.7 \pm 2.3)\ kJ\cdot mol^{-1}$. This is very similar to the value obtained by [1975RAN] and [1976FUG/OET], using slightly different auxiliary data.

Table VI-1: Enthalpy of solution of β-$ThCl_4$ in hydrochloric acid at various concentrations.

Medium		$\Delta_{sol}H_m$ (kJ·mol^{-1})	Reference
HCl Molarity	HCl Molality		
1.000	1.0222	– 240.25 ± 0.42	[1949WES/ROB3]
1.00	1.0222	– 241.8 ± 0.7	[1973FUG/BRO]
1.00	1.0222	– 242.4 ± 1.9	[1981BUR/KIJ2]
6.000	6.8510	– 185.23 ± 0.42	[1949WES/ROB3]
6.00	6.8510	– 188.3 ± 0.4	[1973FUG/BRO]
6.004	6.8563	– 185.27 ± 0.25	[1950EYR/WES]
6.004 *	6.8563	– 186.52 ± 0.33	[1950EYR/WES]
6.06 *	6.9297	– 186.8 ± 0.8	[1969SMI/THA]
9.000	11.1107	– 146.15 ± 0.42	[1949WES/ROB3]

*: containing 0.005M Na_2SiF_6. The influence of the fluorosilicate ion on the enthalpy of solution of β-$ThCl_4$ in hydrochloric acid is discussed in Section VIII.2.1.3.1.

Figure VI-1: Enthalpy of solution of β-$ThCl_4$ as a function of HCl molality.



In spite of its theoretical limitations, this linear extrapolation of the thorium data was adopted by [1975RAN] and [1976FUG/OET]. As pointed out by Wagman [1976WAG], a Debye-Hückel correction of the solution data, followed by an extrapolation against the ionic strength, yields an extrapolated value of $\Delta_{\text{sol}}H^{\circ}_{\text{m}}$ (ThCl$_4$, β) = −(260.7 ± 4.2) kJ·mol^{-1} while a correction using Vasil'ev's method [1967VAS] as modified by Khodakovsky [1975KHO] yielded $\Delta_{\text{sol}}H^{\circ}_{\text{m}}$ (ThCl$_4$, β) = −262.3 kJ·mol^{-1}. The extrapolation of thermal data to infinite dilution is discussed in some detail in [1997GRE/PLY2].

It was indeed noted by Wagman [1976WAG] that, although the more elaborate extrapolation was proper, the same situation occurs with the values for the dissolution of UCl$_4$(cr) in HCl solutions. In that case also, substitution of a linear extrapolation by a more elaborate Debye-Hückel treatment would shift the enthalpy of formation of U^{4+} and several other values. Wagman noted that such a shift would result in a slightly poorer agreement in the various paths in the uranium ion network.

It is interesting to note that in both of the subsequent NBS assessments, [1977WAG/SCH] and the latest NBS Tables [1982WAG/EVA], the linear extrapolation was used to obtain the reported $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (Th^{4+}) = −769.0 kJ·mol^{-1}, using the then current auxiliary data.

In view of this situation, and also for consistency with other actinides, we will maintain in this review, as in [1976FUG/OET], the use of a linear extrapolation for the enthalpy of solution of β-ThCl$_4$ to infinite dilution.

With $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (ThCl$_4$, β, 298.15 K) = −(1186.3 ± 1.3) kJ·mol^{-1} (see Section VIII.2), we thus obtain, from Reaction (VI.1):

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{Th}^{4+}, 298.15\ \text{K}) = -(768.7 \pm 2.3)\ \text{kJ}\cdot\text{mol}^{-1}$$

which is the selected value.

So-called "absolute" standard molar enthalpies of hydration of a number of individual ions, including Th^{4+}, have been obtained by using a combination of experimental data and estimates based on the extra-thermodynamic assumptions that $\Delta_{\text{hyd}}H^{\circ}_{\text{m}}$ ((C$_6$H$_5$)$_4$As$^+$) = $\Delta_{\text{hyd}}H^{\circ}_{\text{m}}$ ((C$_6$H$_5$)$_4$P$^+$) = $\Delta_{\text{hyd}}H^{\circ}_{\text{m}}$ (B(C$_6$H$_5$)$_4^-$). There is an extensive survey of the literature on the hydration of ions in the paper of Marcus [1987MAR2] and a claim that the "absolute" enthalpy of hydration of H$^+$ is known with an accuracy of 5 kJ·mol^{-1}. This value is then used to calculate the individual ion enthalpies of hydration listed therein; the value for $\Delta_{\text{hyd}}H^{\circ}_{\text{m}}$ (Th^{4+}) is −6057 kJ·mol^{-1}. As this value is based on extra-thermodynamic assumptions it is not accepted by this review.

Use of $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (ThCl$_4$, β, 298.15 K) = −(1186.3 ± 1.3) kJ·mol^{-1} and Equation (VI.2) leads to the values $\Delta_{\text{f}}H_{\text{m}}$ (Th^{4+}, 1.00 M HCl) = −(769.877 ± 1.600) kJ·mol^{-1} and $\Delta_{\text{f}}H_{\text{m}}$ (Th^{4+}, 6.00 M HCl) = −(758.957 ± 1.600) kJ·mol^{-1}; these values are used in later assessments. They include the contributions from all the complex species present in 1.00 and 6.00 M HCl media.

The entropy of Th^{4+} was calculated by Morss and McCue [1976MOR/MCC], based on the measurement of the solubility and the enthalpy of solution of thorium nitrate pentahydrate, at infinite dilution, according to reaction:

$$Th(NO_3)_4{\cdot}5H_2O(cr) \rightleftharpoons Th^{4+} + 4NO_3^- + 5H_2O(l) \qquad (VI.3)$$

which yielded $\Delta_r H_m^\circ$((VI.3), 298.15 K) = −(19.807 ± 0.250) kJ·mol^{-1}. The uncertainty limits of the latter value are estimated by this review taking into account the uncertainties in the individual experimental results and the correction for hydrolysis. The measured entropy S_m°($Th(NO_3)_4{\cdot}5H_2O$, cr, 298.15 K) = (543.1 ± 0.8) J·K^{-1}·mol^{-1} is from [1976CHE/WES]. This review has used these values, together with the solubility and activity coefficient data, to derive the standard entropy of Th^{4+}. The solubility of the salt at 298.15 K was taken by [1976MOR/MCC] as (3.7 ± 0.1) mol·kg^{-1} based on the values of 3.74 mol·kg^{-1} reported by Appelblat *et al.* [1973APE/AZO] and 3.66 mol·kg^{-1} obtained by [1976MOR/MCC]. The value of (3.7 ± 0.1) mol·kg^{-1} is also used in this review.

The activity coefficient data of thorium nitrate in saturated solution have been calculated by [1975WAG] (personal communication to the authors of [1976MOR/MCC]) based on the vapour pressure measurements of [1947ROB/LEV]. This calculation incorporated a Debye-Hückel treatment and yielded a mean activity coefficient, $\gamma_\pm$, of 0.377. The results of vapour pressure measurements of [1947ROB/LEV] are preferred to those of [1973APE/AZO2] because they are more consistent. For the calculation of the water activity, the molal osmotic coefficient, ϕ, was taken as 1.673 from [1973APE/AZO2].

Use of selected auxiliary data for the entropies of the nitrate ion and of water leads to the value S_m°(Th^{4+}, 298.15 K) = −(423.1 ± 2.3) J·K^{-1}·mol^{-1}. Noting that the use of the vapour pressure data of [1973APE/AZO2] would have led to an entropy value *ca.* 16 J·K^{-1}·mol^{-1} more negative, we will take more conservative uncertainty limits and adopt the value:

$$S_m^\circ(Th^{4+}, 298.15\ K) = -(423.1 \pm 16.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

Morss and McCue [1976MOR/MCC] reported a value of $C_{p,m}^\circ$(Th^{4+}, 298.15 K) = −(1 ± 11) J·K^{-1}·mol^{-1} based on their integral heats of dilution of $Th(NO_3)_4$ at 288.15, 298.15 and 308.15 K. Apelblat and Sahar [1975APE/SAH] reported bulk heat capacity and heat of dilution of thorium nitrate solutions at 303.15 K.

More recently, Hovey [1997HOV] obtained the value $C_{p,m}^\circ$(Th^{4+}, 298.15 K) = −(224 ± 5) J·K^{-1}·mol^{-1}. This author also reviewed earlier attempts to estimate the partial molar heat capacity of the Th^{4+} ion. Using a more recent value for the heat capacity of the nitrate ion $C_{p,m}^\circ$(NO_3^-, 298.15 K) = −72 J·K^{-1}·mol^{-1}, [1988HOV/HEP3], he recalculated the results of [1976MOR/MCC], obtaining $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}, 298.15\ \mathrm{K}) = -(60 \pm 11)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. He also obtained $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}, 303.15\ \mathrm{K}) = 111\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ from the data of [1975APE/SAH], using $C^{\circ}_{p,\mathrm{m}}(\mathrm{NO}_3^-, 303.15\ \mathrm{K}) = -63.7\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, from [1989HOV/HEP]. Reasons for the large discrepancy of the value deduced from the results of [1975APE/SAH] are briefly discussed in the comments on [1997HOV] in Appendix A. As the results of [1997HOV] arise from differential measurements, as compared to the integral enthalpy measurements by [1976MOR/MCC], and also because this author selected experimental conditions which minimised hydrolysis and complexation, his results are preferred. Nevertheless we feel that the differences from the earlier values noted above are so large that his estimated uncertainty of $\pm 5\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$ (assumed to be $1\,\sigma$) is probably too small. In view of this, and the lack of comparative determinations for other tetravalent ions, the uncertainty has been increased to $\pm 15\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$, and the selected value is

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}, 298.15\ \mathrm{K}) = -(224 \pm 15)\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}.$$

The analysis of the results of [1997HOV] in Appendix A is essentially that from [2003GUI/FAN], as these results served as basis for the adoption of new values for the heat capacity of the U^{4+} and U^{3+} aqueous ions.

Combining the selected molar standard enthalpy of formation and entropy yields the selected molar standard Gibbs energy of formation:

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{Th}^{4+}, 298.15\ \mathrm{K}) = -(704.783 \pm 5.298)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

This unusually large uncertainty arises mainly from the large uncertainty in the entropy, in turn arising from the uncertainty in the vapour pressure of saturated $Th(NO_3)_4$ solution.

VI.2 Hydration of the Th^{4+} ion

As a result of its high charge and large ionic radius one expects a high coordination number for the Th^{4+} ion. This has been confirmed by direct structure determinations using large angle X-ray scattering (LAXS) [1968JOH2], [1991JOH/MAG] and EXAFS data [1999MOL/DEN] and [2002ROT/DEN]. The first of these studies was made at a very high total concentration of Th(IV), 1.94 M. Johansson [1968JOH] reports a Th–O distance in the first shell equal to (2.51 ± 0.03) Å, relating to coordinated water and additional features assigned to the coordination of four bidentate nitrate ligands, resulting in a coordination number of 12 for Th(IV). This assignment seems reasonable, as the data have been collected in solutions with a very high concentration of nitrate; however, the structural model proposed is not unique. In [1991JOH/MAG], the authors have collected three different sets of LAXS data from concentrated (1 – 2.5 m) Th(IV) solutions containing high concentrations (4 – 11 m) of perchlorate, chloride and nitrate, respectively. The perchlorate data indicate a coordination number of (8.5 ± 0.5) with a

Th−OH_2 distance of 2.48 Å; the perchlorate ions are located in the second coordination sphere. The data from chloride solutions indicate a coordination number of 10.5, mainly coordinated water but with indications of some coordination of chloride (the model used is not unique). The large difference in coordination number is certainly an artefact due to experimental uncertainties and the difficulty in obtaining a unique structural model. The data from nitrate solution indicate very clearly bonding of nitrate, probably bidentate, in the first coordination sphere. The LAXS data suggests that the bonding of nitrate to Th(IV) is much stronger than that of perchlorate and chloride, in agreement with solution chemical data discussed in Sections VIII.2.2.1 and X.1.3.3. The EXAFS data were collected in perchlorate solutions with a much lower total concentration of thorium. In [1999MOL/DEN] the concentration of Th(IV) was 0.03 and 0.05 M in 1.5 M $HClO_4$ and these data are accordingly better suited to obtain information of the aquo ion. The reported bond distance Th–OH_2 is equal to (2.45 ± 0.01) Å and the coordination number (10 ± 1). The second EXAFS study [2002ROT/DEN] was made using 0.055 M Th(IV) in 1.5 M $HClO_4$, and gives a Th−OH_2 distance of 2.45 Å and a coordination number of 12.7. The uncertainty in the coordination number as determined from EXAFS data is in general large, while the bond distances are much more accurate as indicated above. The data above demonstrate that it is not possible to obtain an accurate value of the coordination number for the Th^{4+} ion from EXAFS data alone; it is also not possible to deduce a three-dimensional structure. Information of this type may be obtained by using quantum chemical methods as shown in [2001YAN/TSU], [2002YAN/TSU] and [2003OKA/MOC]. The authors suggest that the most stable geometry is obtained for the complex $[Th(OH_2)_9]^{4+}$ with C_{4v} geometry. The calculated Th−OH_2 distance for this complex is 2.54 Å in fair agreement with the experimental EXAFS data. The calculations also indicate that the energy difference between complexes of different geometry is small (a few $kJ{\cdot}mol^{-1}$), as is the energy difference between aquo ions with nine and ten coordinated water molecules.

The dynamics of water exchange between the water solvent and the Th^{4+} ion has been investigated using ^{17}O NMR [2000FAR/GRE] and these data indicate a rate constant at 25°C, $k_{ex} > 5 \times 10^{7}\ s^{-1}$, significantly larger than that for the corresponding U^{4+} ion, $k_{ex} = 5.4 \times 10^{6}\ s^{-1}$. Farkas *et al.* [2000FAR/GRE] discuss the mechanism of the exchange reaction and suggest that this is dissociative if the coordination number of the aqua ion is ten and associative if it is nine. This conclusion is supported by the quantum chemical studies of Yang *et al.* [2003TSU/YAN], [2003YAN/TSU].

Marcus [1991MAR2] has estimated the average hydration number of Th^{4+}, $n_{hyd} = 14.4$, and the Gibbs energy of hydration, $-5395\ kJ{\cdot}mol^{-1}$, by using a an empirical electrostatic model. The hydration number has also been estimated in [1972SAT], using compressibility data. For reasons given in Appendix A the data in these two studies have not been accepted by this review.

Based on the available experimental and quantum chemical data this review suggests that the coordination number in the Th^{4+} ion is either nine or ten and that the energy difference between them is small, less than 10 kJ·mol^{-1}.

VI.3 Ion interaction coefficients of the Th^{4+} ion

Experimental studies on the hydrolysis of the Th^{4+} ion, its complexes with strong inorganic ligands, and the solubility of thorium oxides or hydroxides are usually performed with low concentrations of thorium in perchlorate, chloride, and nitrate media. There is no evidence for complex formation between Th^{4+} and ClO_4^-; however, chloride and nitrate form weak Th(IV) complexes as discussed in Sections VIII.2.2.1 and X.1.3.3, respectively. For the evaluation of equilibrium constants at zero ionic strength from data in chloride and nitrate media we have therefore the general problem to decide if the activity of Th^{4+}, $a_{Th^{4+}} = m_{Th^{4+}} \cdot \gamma_{Th^{4+}}$, should be calculated using a complex formation or a strict ion interaction model.

- **Complex formation model**

The formation of complexes between Th^{4+} and $X^- = Cl^-$ or NO_3^- is described with the equilibrium constants β_n for the reactions:

$$Th^{4+} + nX^- \rightleftharpoons ThX_n^{4-n} \qquad (VI.4)$$

The concentration of free Th^{4+} is calculated from the total thorium concentration m_{Th} according to:

$$m_{Th^{4+}} = m_{Th} - \sum m_{ThX_n^{4-n}} = \frac{m_{Th}}{1+\sum \beta_n (m_{X^-})^n} \qquad (VI.5)$$

The activity coefficients of Th^{4+} and the complexes ThX_n^{4-n} are calculated with the specific ion interaction theory, SIT, assuming that $\log_{10}\gamma_{Th^{4+}}$ and $\log_{10}\gamma_{ThX_n^{4-n}}$ in chloride or nitrate solution or in $(H^+/Na^+)(X^-/ClO_4^-)$ mixtures are the same as in pure perchlorate solution of the same ionic strength, *i.e.*, with the simplifications $\varepsilon(Th^{4+},X^-) = \varepsilon(Th^{4+},ClO_4^-)$ and $\varepsilon(ThX_n^{4-n},X^-) = \varepsilon(ThX_n^{4-n},ClO_4^-)$. Since no negatively charged $ThCl_n^{4-n}$ complexes are formed, the Th^{4+} activity in chloride or nitrate solutions and in mixtures with perchlorate is given by:

$$\log_{10}a_{Th^{4+}} = \log_{10}m_{Th} - \log_{10}\{1+\sum \beta_n (m_{X^-})^n\} - 16\,D + \varepsilon(Th^{4+},ClO_4^-)\cdot(m_{X^-} + m_{ClO_4^-})\,. \qquad (VI.6)$$

- **Ion interaction model**

The weak Th(IV) chloride or nitrate complexes are not explicitly taken into account, *i.e.*, the simplification is made that $m_{Th^{4+}} = m_{Th}$. The decrease of the Th^{4+} activity due to complex formation with X^- is described by the specific ion interaction coefficient $\varepsilon(Th^{4+},X^-)$ which is therefore lower than $\varepsilon(Th^{4+},ClO_4^-)$. The Th^{4+} activity in chloride or nitrate solutions and in mixtures with perchlorate is thus given by:

$$\log_{10} a_{\text{Th}^{4+}} = \log_{10} m_{\text{Th}} - 16\,D + \varepsilon(\text{Th}^{4+},\text{X}^-)\cdot m_{\text{X}^-} + \varepsilon(\text{Th}^{4+},\text{ClO}_4^-)\cdot m_{\text{ClO}_4^-} \quad \text{(VI.7)}$$

SIT coefficients referring to this approach, mostly derived from osmotic coefficients in binary metal chloride or nitrate solutions [1980CIA], are reported in the previous NEA-TDB reviews. However, only the more recent reviews [2001LEM/FUG], [2003GUI/FAN] used the corresponding values of $\varepsilon(\text{AnO}_2^+,\text{Cl}^-)$, $\varepsilon(\text{An}^{3+},\text{Cl}^-)$, and $\varepsilon(\text{An}^{4+},\text{Cl}^-)$ to calculate equilibrium constants for the solubility, hydroxide and carbonate complexes of actinides from experimental data in chloride media.

In the following, the two models are illustrated using U(IV) as an analogue for Th(IV). Figure VI-2 shows a comparison between the complexation and ion interaction models for U(IV) as a trace component in nitrate and nitrate-perchlorate solution. The system U(IV)-NO_3^- is chosen as an example because it is well studied by different authors using different methods at widely varying ionic strength, including spectroscopy (*cf.* [1992GRE/FUG]). In the NEA-TDB review on uranium [1992GRE/FUG], the available experimental data were well described with the nitrate complexation model. Figure VI-2 shows that the activity of the U^{4+} ion and hence the equilibria in acidic nitrate solution and nitrate-perchlorate mixtures can be described with about same accuracy using the ion interaction approach.

The parameters used for the nitrate complexation model (all data from [1992GRE/FUG]) are:

$\log_{10} \beta_1^\circ = (1.47 \pm 0.13)$,
$\Delta\varepsilon(\text{(VI.4)}, \text{X}^- = \text{NO}_3^-, n = 1) = -(0.21 \pm 0.05)\ \text{kg}\cdot\text{mol}^{-1}$ in HClO_4-HNO_3 solution,

$\log_{10} \beta_2^\circ = (2.30 \pm 0.35)$,
$\Delta\varepsilon(\text{(VI.4)}, \text{X}^- = \text{NO}_3^-, n = 2) = -(0.41 \pm 0.13)\ \text{kg}\cdot\text{mol}^{-1}$ in HClO_4-HNO_3 solution,

$\varepsilon(\text{U}^{4+}, \text{NO}_3^-) = \varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.76 \pm 0.06)\ \text{kg}\cdot\text{mol}^{-1}$.

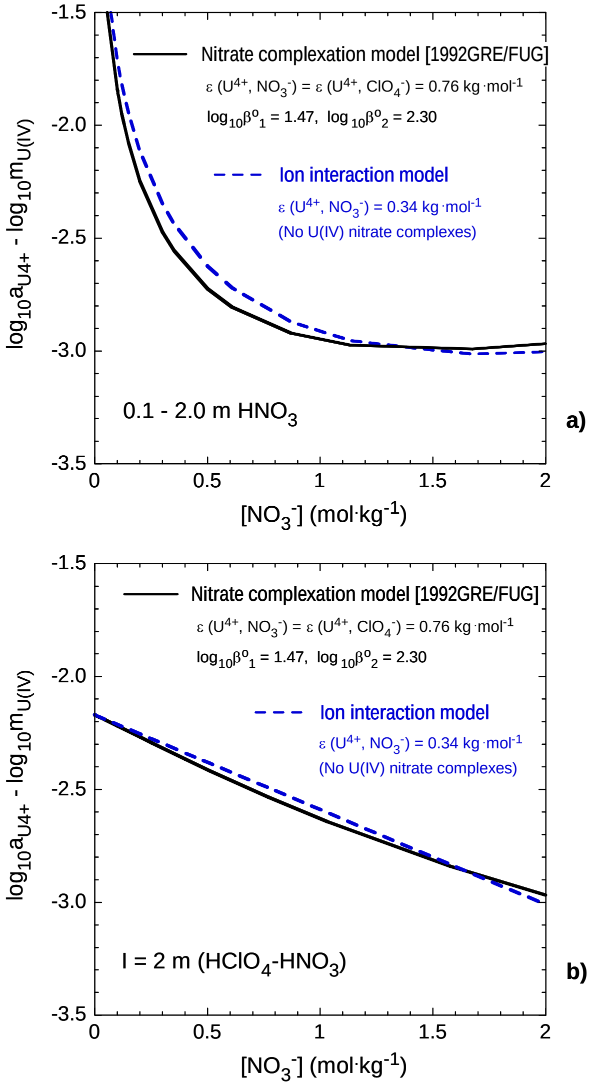
and the parameters used for the ion interaction model (fitted by this review) are:

$$\varepsilon(\text{U}^{4+}, \text{NO}_3^-) = (0.34 \pm 0.06)\ \text{kg}\cdot\text{mol}^{-1} < \varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.76 \pm 0.06)\ \text{kg}\cdot\text{mol}^{-1}.$$

Similarly to the activity of U(IV) in nitrate solution, shown in Figure VI-2, that of Th^{4+} in chloride and nitrate solution can be described equally well with either the complexation model or the ion interaction approach (*cf.* Appendix A reviews of [1952WAG/STO] and [2006NEC/ALT]). The application of the two models to thorium chloride and nitrate complexes is discussed in Sections VIII.2.2.1 and X.1.3.3, respectively.

The SIT coefficients used by this review for the determination of standard state solubility constants and equilibrium constants for hydroxide, fluoride, and carbonate complexes from experimental data in chloride and nitrate media refer to the strict ion interaction approach. They implicitly include the formation of weak Th(IV) complexes or ion pairs with nitrate and chloride ions. However, they must not be combined with the formation constants of chloride and nitrate complexes discussed in Sections VIII.2.2.1 and X.1.3.3, where further comments are given.

Figure VI-2: Activity of U^{4+} relative to the total U(IV) concentration ($\log_{10} a_{U^{4+}} - \log_{10} m_{U(IV)}$) at 25°C calculated with the complex formation model (solid lines) and the ion interaction model (dashed lines) for trace concentrations of U(IV) in (a) $0.1 - 2.0$ m HNO_3 and (b) 2.0 m $HClO_4$-HNO_3.



The Pitzer coefficients used in the literature for actinide and other metal ions (*e.g.* in [1973PIT/MAY], [1991PIT], [1991FEL/RAI], [1997RAI/FEL], [1999FEL/RAI], [2000RAI/MOO], [1995NEC/FAN], [1998NEC/FAN], [1998FAN/KIM]) usually also refer to an ion interaction approach where the formation of weak complexes is included in the interaction coefficients.

VI.3.1 SIT coefficients

The interaction coefficients $\varepsilon(Th^{4+}, NO_3^-)$ = (0.11 ± 0.02) kg·mol^{-1} and $\varepsilon(Th^{4+}, Cl^-)$ = (0.25 ± 0.03) kg·mol^{-1}, listed in the previous NEA-TDB reviews [1992GRE/FUG] to [2005HUM/AND], were calculated by Ciavatta [1980CIA]. They are based on isopiestic measurements and osmotic coefficients for $Th(NO_3)_4$ and $ThCl_4$ solutions up to rather high concentrations from [1947ROB/LEV], [1955ROB], [1965ROB/STO]. However, these data are not well established [1955ROB]. Activity coefficients calculated for the Th^{4+} ion as trace component in chloride solution with the ion interaction Pitzer parameters reported in [1992ROY/VOG] (based on emf data in $ThCl_4$-HCl mixtures, also at rather high Th concentrations) and [1997RAI/FEL] deviate considerably from those calculated with the SIT, *cf.* discussion in Section VI.3.2.

There are no experimental studies available from which $\varepsilon(Th^{4+}, ClO_4^-)$ can be deduced. A value of $\varepsilon(Th^{4+}, ClO_4^-)$ = (0.67 ± 0.10) kg·mol^{-1} has been estimated in [2001NEC/KIM] assuming a linear correlation between the values of $\varepsilon(U^{4+}, ClO_4^-)$ = (0.76 ± 0.06) kg·mol^{-1} [1992GRE/FUG], $\varepsilon(Np^{4+}, ClO_4^-)$ = (0.82 ± 0.05) kg·mol^{-1} [1992GRE/FUG] and $\varepsilon(Pu^{4+}, ClO_4^-)$ = (0.83 ± 0.10) kg·mol^{-1} [1998CAP/VIT] and the ionic radii of the tetravalent actinide ions, *cf.* Figure VI-3. In the later NEA-TDB reviews slightly different SIT coefficients were selected for Np^{4+} and Pu^{4+}, ($\varepsilon(Np^{4+}, ClO_4^-)$ = (0.84 ± 0.06) kg·mol^{-1}, $\varepsilon(Pu^{4+}, ClO_4^-)$ = (0.82 ± 0.06) kg·mol^{-1} [2001LEM/FUG], [2003GUI/FAN]). With these values, the correlation *vs.* the ionic radius of the An^{4+} ions (for coordination number CN = 8, [1994CHO/RIZ]) *cf.* Figure VI-3, leads to a slightly different value of:

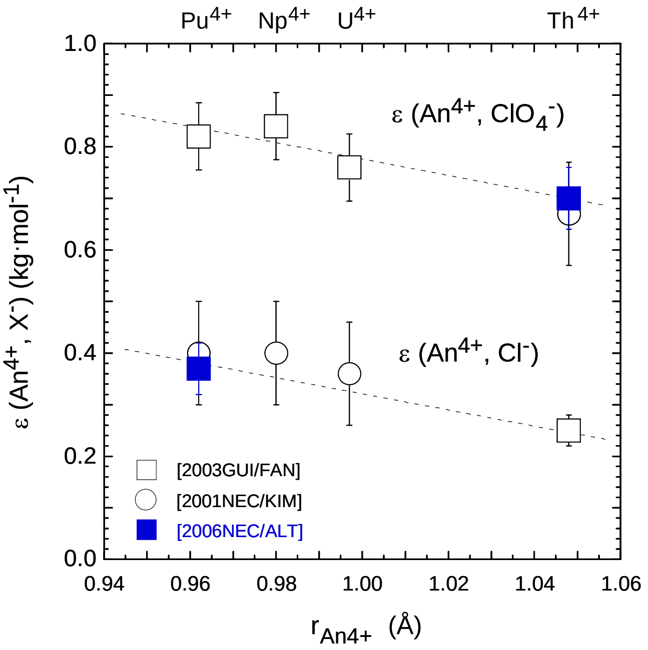
$$\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ \text{kg·mol}^{-1},$$

which is selected in the present review.

The SIT coefficient $\varepsilon(Pu^{4+}, Cl^-)$ = (0.37 ± 0.05) kg·mol^{-1} included in Figure VI-3 is calculated from the redox potentials $E°'(Pu^{4+}/Pu^{3+})$ at I = 0 and in 1.0 M HCl at 25°C, *i.e.* from the equilibrium constants $\log_{10} K_{IV/III}$ ($Pu^{4+} + e^- \rightleftharpoons Pu^{3+}$). The values of $E°(Pu^{4+}/Pu^{3+})$ = (1.047 ± 0.003) V and $\log_{10} K^{\circ}_{IV/III}$ = (17.69 ± 0.04) at I = 0 selected by [2001LEM/FUG] are based on the redox potential $E°'(Pu^{4+}/Pu^{3+})$ = (0.9821 ± 0.0005) V ($\log_{10} K_{IV/III}$ = (16.603 ± 0.01)) determined by Rabideau and Lemons [1951RAB/LEM] in 1.0 M $HClO_4$ at 25°C. Using the same experimental equipment, [1951RAB/LEM] also determined the redox potential in 1.0 M HCl at 25°C: $E°'(Pu^{4+}/Pu^{3+})$ = (0.9703 ± 0.0005) V, ($\log_{10} K_{IV/III}$ = (16.404 ± 0.01)). Lemire *et al.* [2001LEM/FUG] used the SIT coefficients $\varepsilon(Pu^{4+}, ClO_4^-)$ = (0.82 ± 0.07) kg·mol^{-1} and $\varepsilon(Pu^{3+}, ClO_4^-)$ =

(0.49 ± 0.05) kg·mol^{-1} [2001LEM/FUG], [2003GUI/FAN] for the extrapolation of $\log_{10} K_{IV/III}$ from 1.05 m $HClO_4$ to I = 0. The equilibrium constants at I = 0 and in 1.02 m HCl yield $\Delta\varepsilon(\log_{10} K_{IV/III}$ in HCl solution) = −(0.14 ± 0.04) kg·mol^{-1}, and with $\varepsilon(Pu^{3+},Cl^-) = \varepsilon(Am^{3+},Cl^-)$ = (0.23 ± 0.02) kg·mol^{-1} [2003GUI/FAN], we obtain $\varepsilon(Pu^{4+},Cl^-)$ = (0.37 ± 0.05) kg·mol^{-1}. A very similar value, $\varepsilon(Pu^{4+},Cl^-)$ = (0.4 ± 0.1) kg·mol^{-1}, was estimated by [2001NEC/KIM] from analogies and correlations between the tetravalent actinide ions (Figure VI-3) which confirms the possibility of estimating interaction coefficients in the series of the tetravalent actinide ions from the systematic dependence on the ionic radius.

Figure VI-3: SIT coefficients $\varepsilon(An^{4+},ClO_4^-)$ and $\varepsilon(An^{4+},Cl^-)$ of tetravalent actinide aquo ions as a function of the ionic radius ($r_{An^{4+}}$ for coordination number 8, taken from [1994CHO/RIZ]).



As the ion interaction coefficients for the Th^{4+} ion are important parameters for the evaluation of standard state equilibrium constants from experimental data in perchlorate, nitrate and chloride media, an additional experimental study was undertaken [2006NEC/ALT] where trace activity coefficients of the Th^{4+} ion in dilute to concentrated $NaClO_4$, $NaNO_3$ and NaCl solutions ([H^+] = 0.01 − 0.02 M) were determined at 22°C from liquid-liquid distribution equilibria between aqueous

$(1-8)\times 10^{-3}$ M Th^{4+} solutions and organic phases consisting of 10−50 vol% tri-*n*-butyl phosphate (TBP) in *n*-dodecane.

In the liquid-liquid extraction study with Th^{4+} by Neck *et al.* [2006NEC/ALT], the distribution coefficients D_{Th} at $m_{NaCl} < 3$ mol·kg^{-1} were too low to evaluate SIT coefficients by linear regression, but the equilibrium constants in 2.5−5.0 m NaCl were found to be compatible with the SIT coefficients selected in the NEA-TDB review [2003GUI/FAN], ($\varepsilon(Th^{4+},Cl^-) + 4\varepsilon(Na^+,Cl^-) = (0.37 \pm 0.04)$ kg·mol^{-1}). The results obtained in 0.05−1.5 m $NaClO_4$ and 0.05−3 m $NaNO_3$, combined with $\varepsilon(Na^+, NO_3^-) = -(0.04 \pm 0.03)$ kg·mol^{-1} and $\varepsilon(Na^+, ClO_4^-) = (0.01 \pm 0.01)$ kg·mol^{-1}, yield the following interaction coefficients for the Th^{4+} ion [2006NEC/ALT]: $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)$ kg·mol^{-1} and $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.06)$ kg·mol^{-1}.

The interaction coefficient $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.06)$ kg·mol^{-1} [2006NEC/ALT] confirms the value estimated from the correlation between $\varepsilon(An^{4+}, ClO_4^-)$ and the ionic radii of the An^{4+} ions (Figure VI-3). The interaction coefficient $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)$ kg·mol^{-1} [2006NEC/ALT] is close to the value of $\varepsilon(U^{4+}, NO_3^-) = (0.34 \pm 0.06)$ kg·mol^{-1} calculated in the present review if the ion interaction model is applied to the U(IV)-nitrate system. However, it differs considerably from $\varepsilon(Th^{4+}, NO_3^-) = (0.11 \pm 0.02)$ kg·mol^{-1} [1980CIA] adopted in the previous NEA-TDB reviews. Figure VI-4 strongly supports the ion interaction coefficient determined in [2006NEC/ALT]. It shows a linear correlation between known values of $\varepsilon(M^{Z+}, NO_3^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$ or $\varepsilon(M^{Z+}, Cl^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$ for numerous cations M^{Z+} with Z = 1−4. All values, including $\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)$ kg·mol^{-1}, $\varepsilon(U^{4+}, NO_3^-) = (0.34 \pm 0.06)$ kg·mol^{-1} and those determined in [2006NEC/ALT], $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)$ kg·mol^{-1} and $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.06)$ kg·mol^{-1} (filled points in Figure VI-4), fall on, or close to the correlation line, whereas the value of $\varepsilon(Th^{4+}, NO_3^-) = (0.11 \pm 0.02)$ kg·mol^{-1} is far out indicating that it is considerably in error.

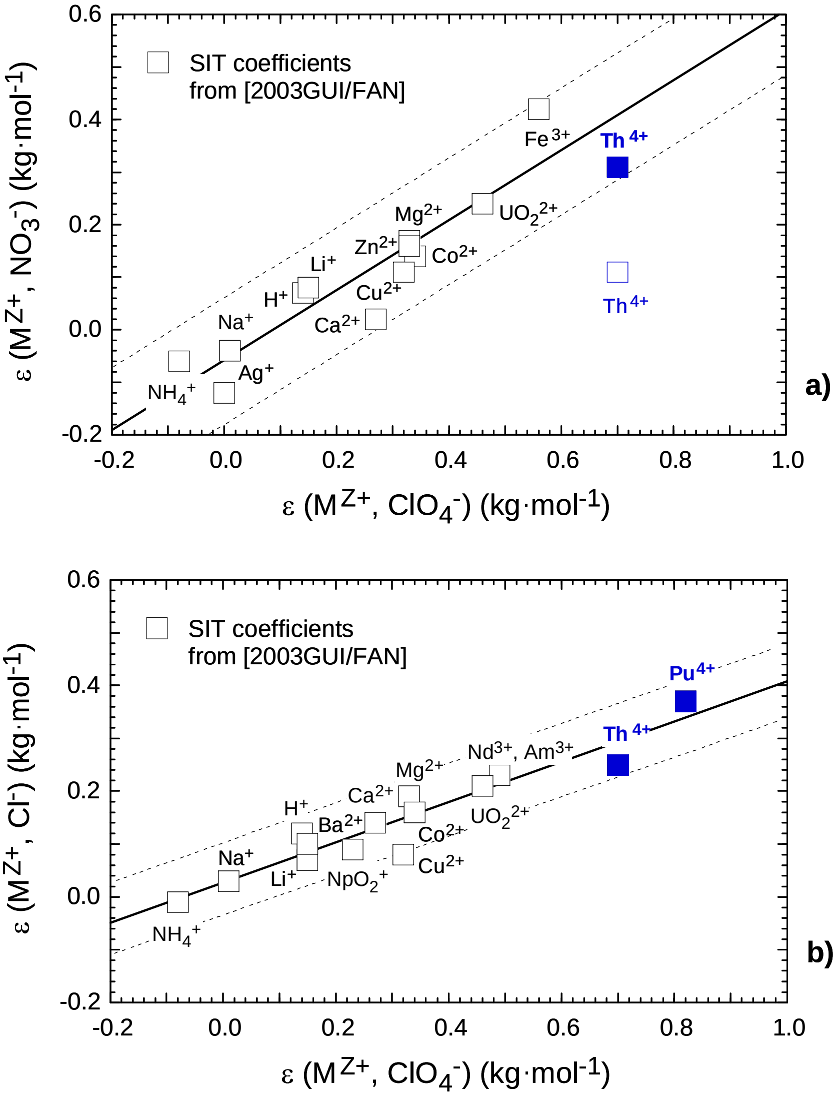
In summary this review selects the following interaction coefficients:

$$\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)\ \text{kg·mol}^{-1}$$

$$\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ \text{kg·mol}^{-1}$$

$$\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)\ \text{kg·mol}^{-1}.$$

Figure VI-4: Correlations between SIT coefficients of non-complexed cations M^{Z+}. (a) $\varepsilon(M^{Z+}, NO_3^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$, (b) $\varepsilon(M^{Z+}, Cl^-)$ and $\varepsilon(M^{Z+}, ClO_4^-)$. Open points are taken from the NEA-TDB [2003GUI/FAN], filled points from [2006NEC/ALT].



VI.3.2 Pitzer coefficients

Throughout the present review the SIT is used for ionic strength corrections. However, numerous computer codes for geochemical model calculations, in particular for calculations in concentrated chloride solutions, are based on the ion interaction equations of Pitzer [1991PIT]. Pitzer parameters reported in the literature to calculate activity coefficients for the Th^{4+} ion in chloride solutions are briefly discussed and summarised in Table VI-2.

Table VI-2: Ion interaction Pitzer parameters for the Th^{4+} ion at 25°C.

Binary interaction parameters Th^{4+}-Cl^-					
$\beta^{(0)}$ / (kg·mol^{-1})	$\beta^{(1)}$ / (kg·mol^{-1})	$\beta^{(2)}$ / (kg·mol^{-1})	C^{ϕ} / (kg^2·mol^{-2})	data source	Reference
1.014	13.33		– 0.1034	a	[1973PIT/MAY]
1.092	13.7 (α_1 = 2 kg^{½}·mol$^{-½}$)	– 160 (α_2 = 12 kg^{½}·mol$^{-½}$)	– 0.112	b	[1992ROY/VOG], [1997RAI/FEL]
Ternary interaction parameters					
θ_{Th^{4+}/H^+} = 0.60 kg·mol^{-1}		$\psi_{Th^{4+}/H^+/Cl^-}$ = 0.37 kg^2·mol^{-2}		b	[1992ROY/VOG]
θ_{Th^{4+}/Na^+} = 0.42 kg·mol^{-1}		$\psi_{Th^{4+}/Na^+/Cl^-}$ = 0.21 kg^2·mol^{-2}		c	[1997RAI/FEL]
$\theta_{Th^{4+}/Mg^{2+}}$ = 0.60 kg·mol^{-1}		$\psi_{Th^{4+}/Mg^{2+}/Cl^-}$ = 0.21 kg^2·mol^{-2}		c	[1997RAI/FEL]

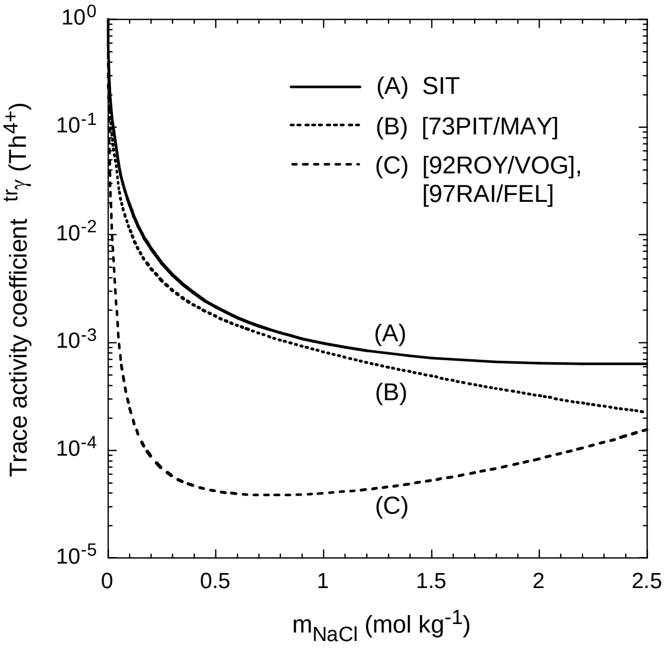
a: Isopiestic data for $ThCl_4$ [1955ROB].

b: HCl activities in aqueous HCl-$ThCl_4$ mixtures [1992ROY/VOG].

c: Solubility of ThO_2(am, hyd) at pH 3.5 − 5.5 in NaCl and $MgCl_2$ solutions [1997RAI/FEL], in combination with the binary parameters of Roy *et al.* [1992ROY/VOG].

Pitzer and Mayorga [1973PIT/MAY] calculated binary parameters from Robinson's isopiestic data for $ThCl_4$ solutions [1955ROB] which were also used by Ciavatta [1980CIA] to calculate the SIT coefficient $\varepsilon(Th^{4+},Cl^-) = (0.25 \pm 0.03)$ kg·mol^{-1} adopted in the NEA-TDB review [1992GRE/FUG]. Roy *et al.* [1992ROY/VOG] performed emf (a_{HCl}) measurements in aqueous HCl-$ThCl_4$ mixtures of various compositions at 25°C, including data at low H^+ concentrations (pH ≥ 3), where hydrolysis of the Th^{4+} ion was considered as negligible. Roy *et al.* [1992ROY/VOG] introduced a binary parameter $\beta^{(2)}$ to account for strong interactions between Th^{4+} and Cl^-. If this $\beta^{(2)}$ parameter is used in the expression for the trace activity coefficient of Th^{4+} in NaCl solution, this leads to activity coefficients $\gamma_{Th^{4+}}$ which deviate considerably from the Debye-Hückel law (at low ionic strength) and also from the SIT and [1973PIT/MAY] models (at higher ionic strength) (Figure VI-5).

Figure VI-5: Trace activity coefficients of Th^{4+} in NaCl solution at 25°C, calculated with the SIT coefficient $\varepsilon(Th^{4+}, Cl^-)$ = (0.25 ± 0.03) kg·mol^{-1} [1980CIA], [1992GRE/FUG] (A) and with the different sets of the Pitzer parameters reported by Pitzer and Mayorga [1973PIT/MAY] (B) and by Roy *et al.* [1992ROY/VOG] and Rai *et al.* [1997RAI/FEL] (C).



Felmy *et al.* [1991FEL/RAI] proposed a Pitzer model for the solubility of ThO_2(am, hyd) in 0.6−3.2 m NaCl solution. This model was refined in [1997RAI/FEL] where the solubility studies were extended up to 6 m NaCl and 3 m $MgCl_2$ solutions. Based on the binary parameters of [1992ROY/VOG], Rai *et al.* [1997RAI/FEL] fitted ternary parameters for the systems Na^+-Th^{4+}-Cl^- and Mg^{2+}-Th^{4+}-Cl^- to the solubility data for ThO_2(am, hyd) at pH 3.5−5.5 in NaCl and $MgCl_2$ solutions. Th(IV) hydroxide complexes are not included in this model. The Pitzer model used by Rai *et al.* [1997RAI/FEL] is appropriate to fit solubility data of ThO_2(am, hyd) in dilute to concentrated NaCl and $MgCl_2$ media. However it is not compatible with the selections in the present review because the underlying chemical model (without hydrolysis species) is completely different. The solubility and hydrolysis constants selected by this review must not be combined with the Pitzer parameters used by Rai *et al.* [1997RAI/FEL] for the Th^{4+} ion and *vice versa*, the solubility constants given in [1997RAI/FEL], [2000RAI/MOO] must not be combined with the SIT coefficients and hydrolysis constants evaluated in the present review.

As illustrated in Figure VI-5, the different approaches and ion interaction coefficients can lead to appreciably discrepant activity coefficients for the Th^{4+} ion. For instance the values of $\gamma_{\mathrm{Th}^{4+}}$ in 0.1 or 0.5 m NaCl and hence the solubility constants calculated in [2000RAI/MOO] and [2003NEC/ALT] with the Pitzer model and SIT respectively for microcrystalline ThO_2(cr) at low pH, where hydrolysis is actually negligible, differ by about two orders of magnitude.

VII Thorium oxygen and hydrogen compounds and complexes

VII.1 Solid and gaseous oxides

The only stable solid oxide of thorium is ThO_2, although the metastable monoxide, probably containing impurities, can be obtained from the black residue formed when thorium metal is dissolved in aqueous HCl. Ackermann and Rauh [1973ACK/RAU3] found that when this material, which has the approximate composition ThO(Cl,OH)H, Katzin [1958KAT], is heated, a phase with a face centred cubic cell with a = (5.302 ± 0.003) Å is first formed. On further heating, this disproportionates to, essentially, Th and ThO_2, see Appendix A.

VII.1.1 Thorium monoxide gas ThO(g)

Thorium monoxide gas is of some importance: it is in fact the major species in the vapour over normal thorium metal, since with even small amounts of oxygen impurity it is formed by the reaction:

$$\mathrm{Th(cr, l) + ThO_2(cr) \rightleftharpoons 2ThO(g)}.$$

VII.1.1.1 Standard entropy and heat capacity

Edvinsson has studied the energy levels for ThO(g) in considerable detail in a series of papers published from 1965 to 1991. At the last count, 28 levels had been identified experimentally, with only two inter-connected levels ‘floating’. These are summarised in Table VII-1 where the parameters in italics have been estimated.

We have estimated the lower of the two ‘floating’ states to be at 8000 cm^{-1}.

We have calculated the thermal functions from these spectroscopic data, which give the selected values:

$$S^{\circ}_{\mathrm{m}}\mathrm{(ThO, g, 298.15\ K)} = (240.07 \pm 0.05)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}\mathrm{(ThO, g, 298.15\ K)} = (31.27 \pm 0.10)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

These values are almost identical to those given by [1982GLU/GUR] calculated by energy-level summation of the 14 levels from Edvinsson’s work known at that time (sometimes with slightly different parameters from those in Table VII-1 because of improved analyses of the band structures by Edvinsson after 1982), and an estimated further 16 levels extending from 6800 cm^{-1} to 36000 cm^{-1}.

The heat capacity data have been fitted to the following equation:

$$[C^{\circ}_{p,\mathrm{m}}]^{700\mathrm{K}}_{298.15\mathrm{K}}\mathrm{(ThO, g, }T) = 29.501 + 1.33228 \times 10^{-2}\,T - 6.01025 \times 10^{-6}\,T^{2} - 1.48640 \times 10^{5}\,T^{-2}\quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

Table VII-1: Energy levels in ThO(g).

Level	Term (cm^{-1})	ω (cm^{-1})	$\omega\,x$ (cm^{-1})	B (cm^{-1})	$10^7\,D$ (cm^{-1})	$10^3\,\alpha$ (cm^{-1})	Degenerac	Reference
X	0	895.77	2.39	0.332644	1.833	1.302	1	[1985EDV/LAG2]
H	5316.6	857.2	2.4	0.326380	1.870	1.280	2	[1985EDV/LAG2]
Q	6127.92	858.4	2.29	0.327030	1.920	1.330	2	[1985EDV/LAG2]
W	*8000.00*	*858.4*	*2.29*	*0.327030*	*1.920*	*1.330*	*2*	estimated
A	10600.82	846.4	2.40	0.323044	1.866	1.294	1	[1985EDV/LAG2]
B	11129.14	842.8	2.18	0.324970	1.940	1.230	2	[1985EDV/LAG2]
C	14490.02	825.1	2.40	0.322460	1.930	1.280	2	[1985EDV/LAG2]
D	15946.22	839.2	2.50	0.321500	1.850	1.300	2	[1985EDV/LAG2]
E	16320.37	829.26	2.30	0.323090	1.990	1.303	1	[1985EDV/LAG2]
G	18009.93	809.1	2.30	0.318140	1.940	1.280	2	[1985EDV/LAG2]
F	18337.56	757.36	2.30	0.321400	2.042	1.280	1	[1985EDV/LAG2]
R	19050.75	862.0	2.80	0.332320	2.001	1.480	1	[1985EDV/LAG]
I	19539.06	800.85	1.47	0.330430	2.390	1.830	2	[1985EDV/LAG2]
S	20061.66	861.4	2.5	0.315050	2.000	1.900	2	[1985EDV/LAG]
M	21734.32	850.87	5.27	0.325860	2.060	1.394	2	[1985EDV/LAG2]
K	22635.65	795.50	2.27	0.318640	2.010	1.240	2	[1985EDV/LAG2]
O	23113.39	810.30	2.40	0.318770	1.970	1.300	2	[1985EDV/LAG2]
P	23155.74	810.30	2.40	0.318820	1.960	1.300	2	[1984EDV/LAG]
T	24035.58	810.30	2.40	0.316785	1.994	1.300	2	[1985EDV/LAG]
L	24856.59	836.18	5.77	0.324460	2.810	1.300	2	[1985EDV/LAG2]
U	25136.90	836.18	5.77	0.318680	0.540	1.300	2	[1987EDV/LAG]
N	27718.50	819.50	1.74	0.320700	1.960	1.000	2	[1985EDV/LAG2]
Z	25803.05	864	2.4	0.319230	1.864	1.260	2	[1987EDV/LAG]
A’	28028.83	864	2.4	0.317980	1.864	1.260	1	[1988EDV/LAG]
D’	28327.08	829.50	2.2	0.325930	2.610	1.260	1	[1990EDV/LAG]
C’	28578.30	830	2.4	0.327500	6.000	1.260	2	[1990EDV/LAG]
B’	30312.99	830	4.28	0.327650	1.820	1.940	2	[1988EDV/LAG]
Y	31416	830	2.4	0.324950	2.190	1.260	2	[1987EDV/LAG]

VII.1.1.2 Enthalpy of formation

The reliable studies from which the Gibbs energy of formation of ThO(g) can be derived are listed in Table VII-2; further details are given in the relevant Appendix A entries. The most reliable of these are the studies which involve, in part, mass-loss effusion to calculate the absolute pressures of ThO(g) in the diphasic {Th(l) + ThO_2(cr)} phase field, whereas the remaining mass-spectrometric studies relied on estimated ion cross-sections. Table VII-2 includes the calculated enthalpy of formation of ThO(g) from each of the studies, based on a third-law analysis. The study by

Shchukarev and Semenov [1965SHC/SEM], who give equations for the ThO_2(g) and ThO(g) partial pressures, measured mass-spectrometrically, over stoichiometric ThO_2(cr), have been processed by assuming they correspond to the reaction $ThO_2(cr) \rightleftharpoons ThO(g) + O(g)$, with $p_O = 0.254\,p_{ThO}$, corresponding to congruent effusion. However, this study gives an appreciably more negative value for $\Delta_f H_m^\circ$ (ThO, g, 298.15 K), and has been discounted.

Table VII-2: Enthalpy of formation of ThO(g).

Reference	Reaction and method	Temperature range (K)	$\Delta_f H_m^\circ$ (298.15 K) (kJ·mol^{-1}) Third-law
[1961DAR/MCC]	$Th(l) + ThO_2(cr) \rightleftharpoons 2ThO(g)$ Mass-loss effusion and mass-spectrometry	1984 – 2564	−28.6 ± 23.5
[1963ACK/RAU]	$Th(l) + ThO_2(cr) \rightleftharpoons 2ThO(g)$ Mass-loss effusion and mass-spectrometry	2337 – 2371	−28.0 ± 6.0
[1965SHC/SEM]	$ThO_2(cr) \rightleftharpoons ThO(g) + O(g)$ Mass-spectrometric effusion	2573 – 2973	−52.2 ± 20.0
[1973ACK/RAU2]	Mass-loss effusion $Th(l) + ThO_2(cr) \rightleftharpoons 2ThO(g)$	2080 – 2214	−26.5 ± 6.0
	Mass-spectrometry $Th(l) + ThO_2(cr) \rightleftharpoons 2ThO(g)$	1780 – 2420	−26.8 ± 8.0
	Mass spectrometry $YO(g) + Th(g) \rightleftharpoons Y(g) + ThO(g)$	1930 – 2280	−28.9 ± 10.5
[1974HIL/MUR]	$Th(cr) + ThO_2(cr) \rightleftharpoons 2ThO(g)$ Mass-loss effusion and mass-spectrometry	1782 – 1940	−20.3 ± 10.0
	$SiO(g) + Th(g) \rightleftharpoons Si(g) + ThO(g)$ mass-spectrometry	2064 – 2212	−27.2 ± 15.0
[1974NEU/ZMB]	$LaO(g) + Th(g) \rightleftharpoons La(g) + ThO(g)$ mass-spectrometry	1759 – 1961	−13.0 ± 15.0

In addition to the studies listed, two more investigations may be mentioned, by Hoch and Johnston [1954HOC/JOH] and Ackermann and Rauh [1974ACK/RAU]. Hoch and Johnston attempted to measure the vapour pressure of ThO_2(cr), but using a tantalum effusion cell. However, as shown by Caers *et al.* [1980CAE/CAS], tantalum reacts with ThO_2(cr) at high temperatures to give TaO(g) and ThO(g), and the principal gas in the system is ThO(g) rather than the dioxide (compare also the study of the vaporisation of hypostoichiometric thoria (thorium dioxide) by Ackermann and Tetenbaum [1980ACK/TET]). However, since the activity of thorium is undefined, these data cannot be used to calculate the properties of either ThO(g) or ThO_2(g). Ackermann and Rauh [1974ACK/RAU] studied mass-spectrometrically the equilibrium

Th(g) +ZrO(g) $\rightleftharpoons$ ThO(g) + Zr(g) from 2200 to 2550 K. However, as noted in Appendix F, the thermodynamic data for ZrO(g) are not well-defined, and we have not been able to utilise these data in this review.

The selected value is the weighted mean of the acceptable results, but with an increased uncertainty because of the rather uncertain solubility of oxygen in Th(l) at the higher temperatures:

$$\Delta_f H_m^o(\text{ThO, g, 298.15 K}) = -(26.0 \pm 6.0)\ \text{kJ·mol}^{-1},$$

which yields:

$$\Delta_f G_m^o(\text{ThO, g, 298.15 K}) = -(51.3 \pm 6.0)\ \text{kJ·mol}^{-1}.$$

VII.1.2 ThO_2(cr)

ThO_2(cr) has a face centred cubic fluorite structure, space group $Fm\bar{3}m$. Lattice parameters varying from 5.59525 to 5.5997 Å have been reported for ThO_2(cr), the variation perhaps being due to small differences in stoichiometry and/or the presence of impurities. The value of Skinner [1959SKI], a = (5.59525 ± 0.00010) Å, obtained using spectrographically analysed material (0.1 − 0.5% Si, Mg; 0.01 − 0.05% Fe, B, Al; 0.001 − 0.05% Sc, Cu; 0.0001 − 0.0005% Be) and under well defined conditions (1 atm air, 298.15 K) is preferred. Like many other phases with this structure, it undergoes a second-order transition at *ca.* $0.85T_{\text{fus}}$ due to anion disordering. The first evidence for this was found by Fischer *et al.* [1981FIS/FIN], who observed an increase in the enthalpy just below 3000 K. The transition was investigated in detail by Ronchi and Hiernaut, [1996RON/HIE] (see Appendix A) who measured the heat capacity of ThO_2(cr) from *ca.* 2400 to 3450 K by rapid laser pulse heating. The heat capacity shows a typical λ peak at (3090 ± 10) K, as discussed in detail in Section VII.1.2.2.

Thoria has a range of hypostoichiometry at high temperatures when equilibrated with Th(l). The detailed study of the vaporisation and oxygen potentials in the Th-ThO_2 system by Ackermann and Tetenbaum [1980ACK/TET], who found a lower phase boundary of $ThO_{1.96}$ at 2655 K, may suggest that lower compositions suggested by Benz [1969BEN] may be somewhat in error.

VII.1.2.1 Enthalpy of formation

The selected enthalpy of formation is taken from the only modern determination, by Huber *et al.* [1952HUB/HOL], who combusted well-characterised Th(cr) whose main impurity was 0.12 wt% oxygen. Their reported value −(1226.9 ± 1.5) kJ·mol^{-1} becomes −(1226.4 ± 1.5) kJ·mol^{-1} through the use of contemporary atomic masses. This value was adopted by CODATA [1989COX/WAG] with uncertainty limits increased to ± 3.5 kJ·mol^{-1} and these are selected by this review:

$$\Delta_f H_m^o(\text{ThO}_2\text{, cr, 298.15 K}) = -(1226.4 \pm 3.5)\ \text{kJ·mol}^{-1}.$$

The selected value overlaps with that measured at 293 K by Roth and Becker [1932ROT/BEC] $-(1224.2 \pm 5.8)$ kJ·mol^{-1}. Earlier values, using less pure thorium, are discussed in [1975RAN].

VII.1.2.2 Heat capacity and entropy

The only study of the low temperature heat capacity is that by Osborne and Westrum [1953OSB/WES] who made measurements from 10.2 to 305.4 K. As expected, no anomaly was observed in the heat capacity. The heat capacity and derived entropy, corrected for modern atomic masses:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThO_2, cr, 298.15K}) = (61.74 \pm 0.15)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThO_2, cr, 298.15\ K}) = (65.23 \pm 0.20)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

are the selected values, with increased uncertainties, following [1989COX/WAG].

The above selections yield:

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{ThO_2, cr, 298.15\ K}) = -(1169.0 \pm 3.5)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

There are many more studies of the enthalpy increments of thoria which are summarised with other relevant references in Table VII-3. Three earlier, less precise studies are noted in [1975RAN], but have not been considered. Fischer *et al.* [1981FIS/FIN] first showed that thoria undergoes a transition at a temperature around 3000 K. Although this was presumed to be a disordering transition, their data were represented sufficiently accurately as a first-order transition at 2950 K, with a small transition enthalpy. More recently, Ronchi and Hiernaut [1996RON/HIE] have studied this transition in detail, and showed that it is indeed second-order. Their results are discussed more in detail below, and in Appendix A.

Table VII-3: Experimental studies on the heat capacity and enthalpy of ThO_2(cr).

Experimental technique	Temperature range (K)	Reference
Drop calorimetry	671 − 1664	[1934JAE/VEE]
Drop calorimetry	522 − 786	[1941SOU]
Isothermal calorimetry	10 − 305	[1953OSB/WES]
Drop calorimetry	1456 − 2753	[1961HOC/JOH]
Drop calorimetry	323 − 1173	[1961VIC/DOU2]
Drop calorimetry	2415 − 3400	[1981FIS/FIN]
Laser heating	2400 − 3450	[1996RON/HIE]
Drop calorimetry	376 − 940	[2003AGA/PRA]

The drop calorimetric data are remarkably consistent, presumably due to the relative ease of purification of thoria, and its stability with respect to container materials, even at very high temperatures. All these data, except the two most recent studies, were assessed by [1982FIN], who used a four parameter fit of the enthalpy up to the transition at 2950 K, based on lattice (Einstein) and thermal expansion (plus anharmonic) contributions:

$$H_{\mathrm{m}}(T) - H_{\mathrm{m}}(298.15\,\mathrm{K}) = \mathrm{C}_1\theta/(\mathrm{e}^{\theta/T} - 1) + \mathrm{C}_2\,T^2 + \mathrm{C}_3$$

where the constant C_3 is determined from $H_{\mathrm{m}}(T) - H_{\mathrm{m}}(298.15\,\mathrm{K}) = 0$ at $T = 298.15$ K. The values for the constants for thoria are $\mathrm{C}_1 = 68.654$ J·K^{-1}·mol^{-1}, $\theta = 408.14$ K, $\mathrm{C}_2 = 4.8174 \times 10^{-3}$ J·K^{-2}·mol^{-1} and $\mathrm{C}_3 = -9988$ J·mol^{-1}. Peng and Grimvall [1994PEN/GRI] have suggested that a slightly better fit to the entropy as given by Fink's assessment is obtained by representing the lattice contribution by a Debye expression, and adding a quadratic anharmonic contribution. However, since Fink's expressions reproduce all the experimental heat capacity and enthalpy data up to *ca.* 2500 K quite accurately, we have not adopted this approach. Above 2950 K, the data of [1981FIS/FIN] suggest an essentially constant heat capacity of $C_{p,\mathrm{m}} = 142.3$ J·K^{-1}·mol^{-1}.

Bakker *et al.* [1997BAK/COR] have represented all the data by including a term in T^3 in the heat capacity, which is satisfactory up to 3000 K.

The assessment by [1982GLU/GUR] did not include the very high temperature study by [1981FIS/FIN], but gives values for the thermal functions very little different from those of [1982FIN] up to 2950 K. The heat capacities in both assessments were constrained to reproduce the value of $C_{p,\mathrm{m}}$ (298.15 K) from the low-temperature study by Osborne and Westrum [1953OSB/WES]. The most recent data of [2003AGA/PRA] from 376 to 940 K (see Appendix A) are in full agreement with these assessments.

Both these assessments give excellent representations of the experimental data, and either can be used up to *ca.* 2500 K. As will be seen below, for fitting the heat capacity in the region of the lambda transition, it is convenient to have data for the 'ordered' form up to the melting point, so we have selected the fit given by [1982GLU/GUR] up to *ca.* 2300 K. Above this temperature, additional terms representing the additional heat capacity from the transition are necessary, as described below.

The selected heat capacity is:

$$[C^{\circ}_{p,\mathrm{m}}]^{2300\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThO_2, cr}, T) = 71.578 + 6.3361 \times 10^{-3}\,T + 7.4477 \times 10^{-7}\,T^2 - 1.04834 \times 10^{6}\,T^{-2} \quad \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

For the high-temperature transition, the enthalpy [1981FIS/FIN] and heat capacity data [1996RON/HIE] are less consistent, especially above 3000 K. In the latter study the heat capacities were derived from discontinuities in the cooling curves, and thus are quite scattered, but they suggest that the heat capacity shows a typical λ peak, rising from *ca.* 110 J·K^{-1}·mol^{-1} at 2400 K to a peak of over 200 J·K^{-1}·mol^{-1} at (3090 ± 10) K, falling again to *ca.* 115 J·K^{-1}·mol^{-1} at 3450 K, where the transition temperature has been rounded and its uncertainty increased slightly. The decrease above

3090 K is in sharp disagreement with the enthalpy data of [1981FIS/FIN], which indicate an essentially constant $C_{p,\mathrm{m}}$ of 142.3 J·K^{-1}·mol^{-1} above 2950 K. The reason for this discrepancy is not clear, but since for the purposes of this review, data for $C_{p,\mathrm{m}}$ (ThO$_2$, cr) are only required up to 3000 K, in order to process the vapour pressure data, we shall here restrict our treatment of the high temperature enthalpy and heat capacity data to this temperature, where the inconsistency is acceptable.

For this, we have made a simultaneous fit of the heat capacity and enthalpy data from 2300 to 3000 K for C_p and $H(T) - H(298.15\ \mathrm{K})$ to a cubic equation (for C_p), with the constraints that C_p (2300 K) and $H(2300\ \mathrm{K}) - H(298.15\ \mathrm{K})$ are identical to the values from our selected data below 2300 K (essentially the same as those of [1982GLU/GUR]). The fitting used the 15 C_p data points from [1996RON/HIE] and 13 data points for $H(T) - H(298.15\ \mathrm{K})$, 5 from [1961HOC/JOH] and 8 from [1981FIS/FIN].

The uncertainty in the measurements of [1981FIS/FIN] is estimated to be at least ±2%, since their calibration differed from a standard sample of NBS molybdenum by 1.5% even at 2500 K, and their errors are likely to increase with temperature. Their reproducibility for duplicate runs was about 0.5%. The uncertainty of the C_p measurements by [1996RON/HIE] is much more difficult to estimate, but from their reproducibility (in the small figure given in the paper), we estimate the uncertainty to be at least 6%.

The enthalpy data were therefore given a weighting factor of three in the fitting. The average deviation of the C_p data from the fit is +3.6%, with a standard deviation of ±3.9%, while for the enthalpy data, these values are −0.23% and ±0.85%, which reflect satisfactorily the relative accuracies of the two data sets.

The resulting fit to the heat capacity is shown in Figure VII-1, together with earlier assessments, which have fitted the enthalpy only. The corresponding enthalpy values are shown in Figure VII-2.

The heat capacity data above 2300 K have been refitted to the equation:

$$[C^{\circ}_{p,\mathrm{m}}]^{3000\ \mathrm{K}}_{2300\ \mathrm{K}}(\mathrm{ThO_2,cr},T) = 5.32988\times10^{3} - 2.9586\,T + 4.7187\times10^{-4}\,T^{2} - 4.9273\times10^{9}\,T^{-2}\quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

The Gibbs energy function values $\{(G_{\mathrm{m}}(T) - H_{\mathrm{m}}(298.15\ \mathrm{K}))/T\}$ for ThO$_2$(cr) derived from this fit have been used in the analysis of the vapour pressure data in Section VII.1.3.2.

Rounded values of the melting point and uncertainty measured by [1996RON/HIE] are accepted, as is the enthalpy of fusion estimated by [1982GLU/GUR]:

$$T_{\mathrm{fus}} = (3650 \pm 20)\ \mathrm{K}$$

$$\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}(\mathrm{ThO_2,\ cr,\ 3650\ K}) = (61.5 \pm 10.0)\ \mathrm{kJ\cdot mol^{-1}}.$$

Figure VII-1: Fit to C_p and $H(\mathrm{T}) - H(298.15\ \mathrm{K})$ for $ThO_2(cr)$ from 2300 to 3000 K. Heat capacity

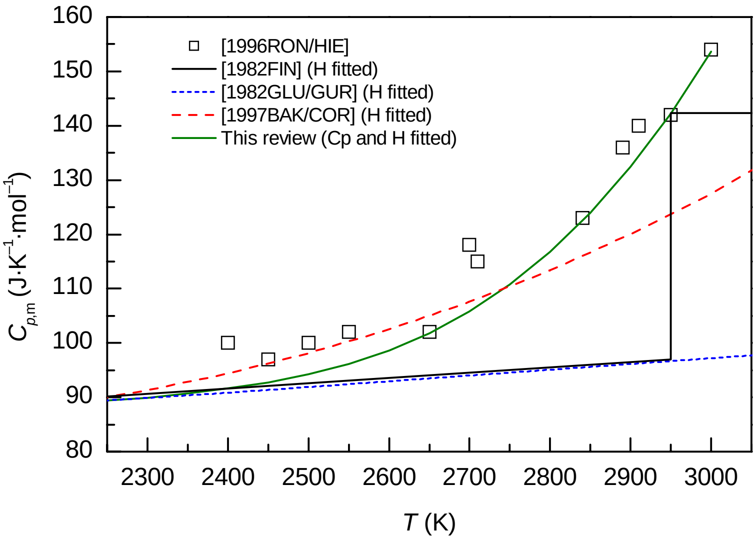
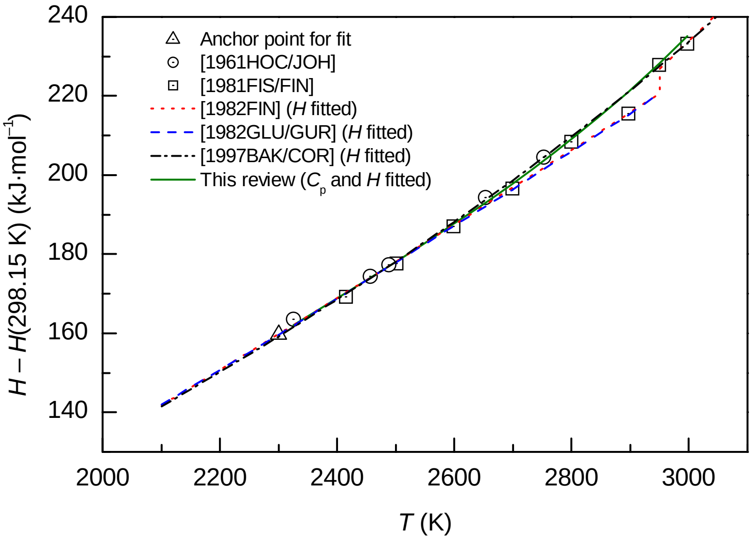


Figure VII-2: Fit to C_p and $H(T) - H(298.15\ \mathrm{K})$ for $ThO_2(cr)$ from 2300 to 3000 K. Enthalpy



VII.1.3 Thorium dioxide gas $ThO_2(g)$

VII.1.3.1 Standard entropy and heat capacity

The thorough study by Gabelnick *et al.* [1974GAB/REE] of the infrared spectra of ThO_2 condensed into argon matrices, gave values of 787.4 and 753.3 cm^{-1} respectively for the ν_1 and ν_3 vibration frequencies of $Th^{16}O_2$, confirming the earlier, less precise values of Linevsky [1963LIN]. These values have also been confirmed more recently by Kushto and Andrews [1999KUS/AND] in their study of the spectra of the molecules formed by the reaction of Th with NO(g). The O−Th−O interbond angle of (122.5 ± 2.0)°, deduced by Gabelnick *et al.* [1974GAB/REE] from the ratio of $\nu_3\ (Th^{18}O_2)/\nu_3\ (Th^{16}O_2)$, is preferred to the lower value of 106° from Linevsky [1963LIN], since the former study used an appreciably higher resolution spectrometer, and their normal co-ordinate analysis for the molecule gave an extremely consistent set of frequencies for the three isotopomeric thorium dioxide molecules. There are no measurements of the symmetrical ν_2 frequency, inactive in the infrared. We have adopted the value of (220 ± 30) cm^{-1} estimated by Glushko *et al.* [1982GLU/GUR] (uncertainty estimated by this review) as well as their estimates of r(Th–O) = (1.82 ± 0.05) Å, (based on the value for the ground-state of ThO(g), 1.840 Å) and the excited electronic levels of $ThO_2(g)$. The latter start at 20000 cm^{-1}, so have negligible contributions to the Gibbs energy function at temperatures of interest for the analysis of the vapour pressure measurements (up to 2865 K). The selected molecular parameters are therefore identical to those taken by [1982GLU/GUR]. Green [1980GRE] selected slightly different estimates of the interatomic distance (1.80 Å) and bending frequency (250 cm^{-1}) (and did not include any excited levels). The selected parameters give the selected values of the heat capacity and entropy at 298.15 K:

$$S^{\circ}_{m}(\mathrm{ThO_2, g, 298.15\ K}) = (281.7 \pm 3.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$C^{\circ}_{p,m}(\mathrm{ThO_2, g, 298.15\ K}) = (46.84 \pm 0.50)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

The heat capacities from 298.15 to 800 K are given by:

$$[C^{\circ}_{p,m}]^{800\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThO_2, g,}\ T) = 46.9010 + 2.01352\times10^{-2}\ T - 1.02652\times10^{-5}\ T^2 - 4.57730\times10^{5}\ T^{-2}\quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

VII.1.3.2 Enthalpy of formation

Rand [1975RAN] has reviewed the early measurements of the vaporisation of thoria. The first precise measurements were by Shapiro [1952SHA], weight loss of thoria-coated filaments, and Hoch and Johnston [1954HOC/JOH], using a tantalum effusion cell. The latters' results are much higher than those of most others. It was not until mass-spectrometric studies [1957ING/CHU], [1960HAS/MEL] showed that that the vapour over ThO_2(cr) contains appreciable amounts of ThO(g) and O(g) as well as ThO_2(g) that the vaporisation behaviour began to be understood. For example, the oxygen potential is so low in a tantalum container that the vapour in the study by

[1954HOC/JOH] consisted mainly of ThO(g) rather than $ThO_2(g)$, as noted in Section VII.1.1.2, so these results have been discounted. All the studies are summarised in Table VII-4, which also includes the second and third law values of $\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}$ (298.15 K) calculated using the selected thermal functions of $ThO_2(cr)$ and $ThO_2(g)$.

Table VII-4: Studies of the vaporisation of thoria.

Reference	Method and reaction	Corrected for $ThO(g)+O(g)$?	Temperature range (K)	$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}$ (298.15 K) (kJ·mol^{-1})	
				Second law	Third law
[1952SHA]	$ThO_2(cr) \rightleftharpoons ThO_2(g)$	No	2062 − 2257	752	773.3 ± 20.0
[1954HOC/JOH]	$ThO_2(cr) \rightleftharpoons ThO_2(g)$, but additional ThO(g) due to use of Ta container	—	2398 − 2676		715.9 ± 15.0 Results discounted
[1961DAR/MCC]	Mass-loss effusion & mass-spectrometry $ThO_2(cr) \rightleftharpoons ThO_2(g)$	No	2268 − 2593	731 ± 50	766.9 ± 15.0
[1963ACK/RAU]	Mass-loss effusion & mass-spectrometry $ThO_2(cr) \rightleftharpoons ThO_2(g)$	No	2180 − 2871	—	764.3 ± 12.0
[1963ACK/RAU]	Mass-loss effusion & mass-spectrometry $ThO_2(cr) \rightleftharpoons ThO_2(g)$	Yes, by this review	2180 − 2871	728 ± 25	770.0 ± 15.0
[1963VOR/DAN]	$ThO_2(cr) \rightleftharpoons ThO_2(g)$	No	1803 − 2233	—	746.7 ± 60.0
[1965SHC/SEM]	Mass-spectrometry $ThO_2(cr) \rightleftharpoons ThO_2(g)$	Yes, by authors	2573 − 3023	740	781.2 ± 16.0
[1973ACK/RAU2]	Mass-loss effusion & mass-spectrometry in $Th(l) + ThO_2(cr)$	—	2400 − 2800	No new data	No new data
[1974HIL/MUR]	Mass-loss effusion & mass-spectrometry $Th(g) + ThO_2(g) \rightleftharpoons 2\ ThO(g)$	—	2160 − 2176	—	770.6 ± 25.0
[1979BEL/SEM]	Mass spectrometry $ThO_2(cr) \rightleftharpoons ThO_2(g)$	Yes, by authors	2480 − 2860	746	—
[1980ACK/TET]	Transpiration $ThO_2 \rightleftharpoons ThO_2(cr)$	No	2400 − 2655	715	767.2 ± 25.0
[1980CAE/CAS]	Mass-spectrometry $ThO_2(cr) \rightleftharpoons ThO_2(g)$	Yes, by authors	2057 − 2421	817	759.2 ± 20.0
Selected values, see text	Total effective pressure	No			766.5 ± 10.0
	$ThO_2(cr) \rightleftharpoons ThO_2(g)$	Yes, by this review			771.4 ± 10.0

The investigation by Ackermann and Tetenbaum [1980ACK/TET] is useful in that the authors studied in detail the small range of non-stoichiometry in ThO_{2-x}, and measured the congruently vaporising composition and the partial pressures of O(g), ThO(g) and ThO_2(g) over non-stoichiometric ThO_{2-x} down to O/Th = 1.97, as a function of temperature around 2500 K. They indicate that the congruently vaporising composition is in fact very slightly hypostoichiometric, varying from $ThO_{1.999}$ at 2400 K to $ThO_{1.994}$ at 2800 K. This small hypostoichiometry will have a very small effect on the derived enthalpies of sublimation, and considering the large uncertainties of the values quoted in Table VII-4, has been ignored. They also measured the total vapour pressures, by a transpiration technique, at 2400, 2500 and 2655 K.

More recently Joseph *et al.* [2002JOS/SIV] have studied the laser induced vaporisation of liquid thoria at very high temperatures. They give values of the partial pressures of the Th(g), ThO(g), ThO_2(g) and O(g) at 5146 and 6253 K, but of course the relevant temperature of the sample in such experiments is difficult to establish reliably. Nevertheless, the extrapolation of these data down to the melting point of thoria (3650 K) gives a value in good agreement with the selected data, extrapolated upwards, so these data are probably reasonably reliable.

A noticeable feature of Table VII-4 is that for many of the studies there is a marked difference between the second and third-law enthalpies of sublimation, although there is insufficient information in many of the papers to give a reliable estimate of the uncertainties. The reason for this is quite unclear. As we have seen, the thermal functions of ThO_2(cr) are reasonably well-defined, even at temperatures up to 2800 K, as are the structure and two of the three vibration frequencies of ThO_2(g), at least when condensed in argon matrices. Reasonable uncertainties in the intermolecular distance and bending frequency lead to uncertainties of no more than 2 − 3 $J\cdot K^{-1}\cdot mol^{-1}$ in the Gibbs energy function, and thus differences of 6 − 9 $kJ\cdot mol^{-1}$ in the third-law enthalpy, appreciably smaller than the observed inconsistencies between many of the experimental second- and third-law enthalpies of sublimation. A theoretical study of ThO_2(g) to give a more reliable estimate of the bending frequency ν_2 would be very useful.

For the selected value of $\Delta_{\text{sub}}H^{\circ}_{\text{m}}$ (298.15 K), we have taken the weighted mean of the four values relating to the sublimation to ThO_2(g) alone (including [1974HIL/MUR]), for which $\Delta_{\text{sub}}H^{\circ}_{\text{m}}$ (298.15 K) = (771.4 ± 10.0) $kJ\cdot mol^{-1}$. This is confirmed by the fact that the difference between this and the weighted mean of the values relating to the sublimation to give the equilibrium composition of ThO_2(g), ThO(g) and O(g), $\Delta_{\text{sub}}H^{\circ}_{\text{m}}$ (298.15 K) = (766.5 ± 10.0) $kJ\cdot mol^{-1}$, is in satisfactory agreement with the difference (5.9 $kJ\cdot mol^{-1}$) calculated from the results of [1963ACK/RAU] in Table VII-4. However, in view of the disagreement between the second- and third-law enthalpies of sublimation, we have increased the uncertainty:

$$\mathrm{ThO_2(cr)} \rightleftharpoons \mathrm{ThO_2(g)}$$

$$\Delta_{\mathrm{sub}} H^{\mathrm{o}}_{\mathrm{m}}\,(298.15\ \mathrm{K}) = (771.4 \pm 15.0)\ \mathrm{kJ{\cdot}mol^{-1}}$$

leading to the selected enthalpy of formation:

$$\Delta_{\mathrm{f}} H^{\mathrm{o}}_{\mathrm{m}}\,(\mathrm{ThO_2, g, 298.15\ K}) = -(455.0 \pm 15.4)\ \mathrm{kJ{\cdot}mol^{-1}}$$

and, finally, to the selected value:

$$\Delta_{\mathrm{f}} G^{\mathrm{o}}_{\mathrm{m}}\,(\mathrm{ThO_2, g, 298.15\ K}) = -(462.1 \pm 15.4)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

VII.2 Thorium hydrogen compounds

VII.2.1 Solid thorium hydrides, ThH_2(cr) and $ThH_{3.75}$(cr)

There is little new information on the thermodynamics of the Th-H system since the thorough review by Flotow *et al.* [1984FLO/HAS], and the present review has accepted, with minor changes, their selected data.

VII.2.1.1 Phase diagram and structures

Flotow *et al.* [1984FLO/HAS] have given a phase diagram of the system up to 1100 K, which is based on the early work of Nottorf (reported in [1952NOT/WIL]) elaborated by [1951MAL/CAM], Peterson and colleagues [1959PET/WES], [1962PET/REX] and at higher temperatures, Catton and Satterwaithe [1977CAT/SAT]. Some of this work was done with thorium containing appreciable impurity levels, which, as indicated by the influence of the presence of ThO_2 on the Th-H equilibrium as studied by [1959PET/WES2], may have a noticeable effect, see below. Although general features of the system are not in doubt, the details of the phase boundaries of the two stable hydrides, ThH_2(cr) and $Th_{3.75}$(cr) are not known at all precisely.

Both phases have appreciable ranges of homogeneity, even at relatively modest temperatures, and hydrogen is appreciably soluble in α-Th above *ca.* 800 K. The dihydride has a face-centred tetragonal structure, space group *F4/mmm*, ZrH_2 type, with $a = (5.734 \pm 0.003)$ Å and $c = (4.965 \pm 0.003)$ Å for a high purity sample with H/Th = (1.997 ± 0.002) [1978FLO/OSB]. These lattice constants agree reasonably with earlier literature values, which in general relate to less pure or less stoichiometric samples. The dihydride can exist with a deficit or excess of hydrogen. Korst [1962KOR] has suggested that the face-centred tetragonal phase can have a composition as low as $ThH_{1.73}$ at room temperature and that a face centred cubic phase $ThH_{1.73}$(cr) with $a = (5.4893 \pm 0.0002)$ Å may be stable. However, Peterson and Westlake [1959PET/WES2] have shown that a hydride with a face-centred cubic structure with $a = 5.492$ Å could be formed in the presence of 4 and 6% ThO_2, so Korst's results were probably brought about by a ThO_2 or other impurity.

The higher hydride has an ideal composition of $ThH_{3.75}$(cr), but has an extensive range of hypostoichiometry above 600 K. Flotow and Osborne

[1978FLO/OSB] gave a lattice parameter of (9.116 ± 0.003) Å of the body-centred cubic cell, space group $I\bar{4}3d$, for a high purity sample with H/Th = (3.746 ± 0.003), again in reasonable agreement with earlier work. The lattice parameters for the corresponding thorium deuterides are similar to those of the corresponding hydrides [1952RUN/SHU], [1977CAT/SAT], [1977MUE/BEY].

VII.2.1.2 Thermodynamic data of thorium dihydride ThH_2(cr)

VII.2.1.2.1 Heat capacity and entropy

Miller *et al.* [1976MIL/CAT] measured the heat capacity of $ThH_{1.96}$(cr) from 1.4 to 20K, but the only complete study of the low temperature properties is by Flotow and Osborne [1978FLO/OSB], who, as noted in Appendix A, measured the heat capacity of a sample of ThH_2(cr) very close to the stoichiometric composition from 5 to 350 K. Their results are selected:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThH_2, cr, 298.15\ K}) = (36.71 \pm 0.07)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThH_2, cr, 298.15\ K}) = (50.73 \pm 0.10)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

There are no measurements of the heat capacity of ThD_2(cr) or ThT_2(cr), but Flotow *et al.* [1984FLO/HAS] have estimated the following values by modelling the heat capacity contributions from the lattice vibrations, represented by an Einstein function, conduction electrons and acoustic modes. This method had been shown to be valid for the deuterides of uranium, yttrium and zirconium.

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThD_2, cr, 298.15\ K}) = (47.67 \pm 0.47)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThD_2, cr, 298.15\ K}) = (55.72 \pm 0.56)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThT_2, cr, 298.15\ K}) = (54.30 \pm 0.54)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThT_2, cr, 298.15\ K}) = (60.46 \pm 0.60)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

These are the selected values.

There are no heat capacity measurements on ThH_2(cr), ThD_2(cr) or ThT_2(cr) above 350 K, but Flotow *et al.* [1978FLO/OSB], [1984FLO/HAS] have estimated the heat capacities of the three compounds up to 800 or 1000 K, by a similar method. These have been fitted to the equations below:

$$[C_{p,\mathrm{m}}]^{1000\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThH_2, cr}, T) = 8.295 + 0.1256\,T - 5.05319\times10^{-5}\,T^2 - 4.0410\times10^{5}\,T^{-2}\quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$[C_{p,\mathrm{m}}]^{800\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThD_2, cr}, T) = 31.417 + 0.1014\,T - 4.7403\times10^{-5}\,T^2 - 8.6714\times10^{5}\,T^{-2}\quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$[C_{p,\mathrm{m}}]^{1000\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThT_2, cr}, T) = 47.450 + 0.07015\,T - 2.9923\times10^{-5}\,T^2 - 1.0143\times10^{6}\,T^{-2}\quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

The data for the D and T compounds are given for information only.

VII.2.1.2.2 Enthalpy of formation

There is one thorough calorimetric study of the enthalpy of reaction of thorium with hydrogen, but at one temperature only, by Picard and Kleppa [1980PIC/KLE], who measured the partial molar enthalpy of solution $\Delta_{\text{sln}}H_{\text{m}}$ (H_2, 700 K), as a function of the H/Th ratio (from 0 to 2.003) in the solid. As discussed in Appendix A, they found that $\Delta_{\text{sln}}H_{\text{m}}$ (H_2) was relatively constant in the diphasic region between $0.03 < \text{H/Th} < 1.99$, (particularly up to H/Th = 1.0) but changed fairly sharply both at the lower phase boundary ($0.02 < \text{H/Th} < 0.03$) and in the $ThH_{2\pm x}$(cr) phase. Picard and Kleppa integrated the values of $\Delta_{\text{sln}}H_{\text{m}}$ (H_2) across the whole range from H/Th = 0 to 2, to obtain $\Delta_{\text{f}}H_{\text{m}}$ (ThH_2, cr, 700 K) $= -(145.6 \pm 0.8)$ kJ·mol^{-1}.

There are three studies of the equilibrium pressures of hydrogen in the diphasic region {Th(cr) + ThH_2(cr)}, by Nottorf, reported in [1952NOT/WIL] (773 to 1073 K), Mallett and Campbell [1951MAL/CAM] (924 to 1149 K) and Peterson and Rexer (773 to 1073 K). These studies are remarkably consistent, being almost indistinguishable. All authors found that the measured pressures in the diphasic {Th(cr) + ThH_2(cr)} region, were not constant but increased slowly but steadily with H/Th. This mirrors the behaviour of the partial molar enthalpy of reaction. There is a significant solubility of hydrogen in α-Th, and the dihydride is noticeably hypostoichiometric at these temperatures, so as noted by [1984FLO/HAS], the measured plateau pressures will not correspond to those calculated from the thermodynamic data for pure ThH_2(cr). Third-law calculations are thus not meaningful for these data, but the second-law values of $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (ThH_2, cr, 298.15 K), from the very consistent slopes of the plateau pressures, should give more reliable information of the enthalpy of formation of ThH_2(cr), for comparison with the more directly measured value from Picard and Kleppa [1980PIC/KLE]. This comparison, shown in Table VII-5, (where the uncertainties, estimated by this review, include those from the uncertainties in the heat capacity of ThH_2(cr) above 298.15 K), shows there is good agreement between the Gibbs energy and calorimetric data.

Table VII-5: Enthalpy of formation of ThH_2(cr) at 298.15 K from equilibrium and calorimetric data.

Reference	Temperature range (K)	$\log_{10} p_{\text{H}_2}$ /bar	$\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (ThH_2, cr, 298.15 K) (kJ·mol^{-1})
[1951MAL/CAM]	924 – 1149	$-7500/T + 6.4767$	$-(148.1 \pm 5.0)$
[1952NOT/WIL]	773 – 1073 [a]	$-7700/T + 6.665$	$-(150.3 \pm 5.0)$
[1962PET/REX]	773 – 1073	$-7609/T + 6.5939$ [b]	$-(148.6 \pm 2.6)$
[1980PIC/KLE]	700	Calorimetric	$-(145.0 \pm 2.0)$

a: Temperature range as given in [1984FLO/HAS].

b: Calculated by [1984FLO/HAS] from data in the paper.

The selected value is that from the calorimetric study [1980PIC/KLE], since that has an explicit integration of the partial molar enthalpy of solution across the whole region from H/Th = 0 to 2 and was carried out at the lowest temperature, where the effects of non-stoichiometry are smallest.

$$\Delta_f H_m^o(\text{ThH}_2, \text{cr}, 298.15\ \text{K}) = -(145.0 \pm 2.0)\ \text{kJ·mol}^{-1}$$

This gives

$$\Delta_f G_m^o(\text{ThH}_2, \text{cr}, 298.15\ \text{K}) = -(105.5 \pm 2.0)\ \text{kJ·mol}^{-1}.$$

There are no experimental data for the formation of ThD_2(cr) and ThT_2(cr), but from a consideration of their vibrational modes [1984FLO/HAS] have estimated the following differences for the enthalpies of formation of the isotopic compounds: $\Delta_f H_m^o(\text{ThH}_2, \text{cr}, 298.15\ \text{K}) - \Delta_f H_m^o(\text{ThD}_2, \text{cr}, 298.15\ \text{K}) = (2.05 \pm 0.41)\ \text{kJ·mol}^{-1}$ and $\Delta_f H_m^o(\text{ThH}_2, \text{cr}, 298.15\ \text{K}) - \Delta_f H_m^o(\text{ThT}_2, \text{cr}, 298.15\ \text{K}) = (2.47 \pm 0.63)\ \text{kJ·mol}^{-1}$. When combined with the data for ThH_2(cr), these give $\Delta_f H_m^o(\text{ThD}_2, \text{cr}, 298.15\ \text{K}) = -(147.1 \pm 2.0)\ \text{kJ·mol}^{-1}$, and $\Delta_f H_m^o(\text{ThT}_2, \text{cr}, 298.15\ \text{K}) = -(147.5 \pm 2.1)\ \text{kJ·mol}^{-1}$.

These values are given for information only.

VII.2.1.3 Thermodynamic data of $\text{ThH}_{3.75}$(cr)

VII.2.1.3.1 Heat capacity and entropy

There are two measurements of the heat capacity of the $\text{ThH}_{3.75}$(cr) phase up to 20 K, by Schmidt and Wolf [1975SCH/WOL] ($\text{ThH}_{3.75}$(cr), 2 to 12 K) and Miller *et al.* [1976MIL/CAT] ($\text{ThH}_{3.75}$ and $\text{ThD}_{3.75}$, 1.4 to 20 K). However, the only complete study of the low temperature properties is by Flotow and Osborne [1978FLO/OSB], who, as noted in Appendix A, measured the heat capacities of a sample of $\text{ThH}_{3.75}$(cr) very close to the stoichiometric composition, from 5 to 350 K and their results are selected:

$$C_{p,m}^o(\text{ThH}_{3.75}, \text{cr}, 298.15\ \text{K}) = (51.32 \pm 0.10)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$S_m^o(\text{ThH}_{3.75}, \text{cr}, 298.15\ \text{K}) = (54.42 \pm 0.11)\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

There are no measurements of the heat capacity of $\text{ThD}_{3.75}$(cr) or $\text{ThT}_{3.75}$(cr), but Flotow *et al.* [1984FLO/HAS] have estimated the following values by modelling the heat capacity contributions from the lattice vibrations, represented by an Einstein function, conduction electrons and acoustic modes. This method had been shown to be valid for the deuterides of uranium, yttrium and zirconium.

$$C_{p,m}^o(\text{ThD}_{3.75}, \text{cr}, 298.15\ \text{K}) = (69.71 \pm 0.70)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$S_m^o(\text{ThD}_{3.75}, \text{cr}, 298.15\ \text{K}) = (63.97 \pm 0.64)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$C_{p,m}^o(\text{ThT}_{3.75}, \text{cr}, 298.15\ \text{K}) = (81.49 \pm 0.81)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$S_m^o(\text{ThT}_{3.75}, \text{cr}, 298.15\ \text{K}) = (72.65 \pm 0.73)\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

These are the selected values.

There are no heat capacity measurements on $ThH_{3.75}$(cr) above 350 K, but Flotow *et al.* [1978FLO/OSB], [1984FLO/HAS] have estimated the heat capacities of $ThH_{3.75}$(cr), $ThD_{3.75}$(cr) and $ThT_{3.75}$(cr), up to 800 or 1000 K, as described above. These have been fitted to the equations below:

$$[C_{p,\mathrm{m}}]^{1000\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThH_{3.75}, cr}, T) = -7.426 + 0.237538\,T - 9.33488\times10^{-5}\,T^2 - 3.3555\times10^{5}\,T^{-2} \quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$[C_{p,\mathrm{m}}]^{800\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThD_{3.75}, cr}, T) = 28.708 + 0.21154\,T - 9.9891\times10^{-5}\,T^2 - 1.1718\times10^{6}\,T^{-2} \quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$[C_{p,\mathrm{m}}]^{800\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThT_{3.75}, cr}, T) = 59.036 + 0.15490\,T - 6.91848\times10^{-5}\,T^2 - 1.5622\times10^{6}\,T^{-2} \quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

The data for the D and T compounds are given for information only.

VII.2.1.3.2 Enthalpy of formation

There are no calorimetric studies involving $ThH_{3.75}$(cr) and the enthalpy of formation is derived from measurements of the hydrogen pressure in the {ThH_2(cr) + $ThH_{3.75}$(cr)} diphasic region by Nottorf, reported in [1952NOT/WIL] (473 to 623 K), and Caton and Satterthwaite [1977CAT/SAT] (823 to 973 K). However, the authors of both these papers emphasise that this equilibrium suffers severely from hysteresis, and the measured pressures, particularly for the study of [1977CAT/SAT], are probably not the equilibrium values. Moreover, both ThH_2(cr) and $ThH_{3.75}$(cr) are markedly non-stoichiometric at the higher temperatures used by [1977CAT/SAT], and their results are therefore given for information only. As for the calculations for the formation of the dihydride, third-law calculations are not meaningful for these data, but the second-law values, derived from the slopes of the measured pressures, should give more reliable information of the enthalpy of the Reaction (VII.1).

$$\frac{8}{7}\,\mathrm{ThH_2(cr)} + \mathrm{H_2(g)} \rightleftharpoons \frac{8}{7}\,\mathrm{ThH_{3.75}(cr)} \qquad \text{(VII.1)}$$

– see Table VII-6, in which the uncertainties are estimated by the review.

Table VII-6: Enthalpy of Reaction (VII.1).

Reference	Temperature range (K)	$\log_{10} p_{H_2}$ / bar	$\Delta_r H^\circ_m$ ((VII.1), 298.15 K) (kJ·mol^{-1})
[1952NOT/WIL]	473 – 623 [a]	$-4220/T + 6.625$	-80.4 ± 4.6
[1977CAT/SAT]	823 – 973	$-4182/T + 7.159$	-86.4 ± 9.2

a: Temperature range as given in [1984FLO/HAS].

The selected value is based on the data of Nottorf [1952NOT/WIL], which correspond more closely to equilibrium, and were measured at lower temperatures, where the effects of non-stoichiometry are smallest. Combined with the selected value for ThH_2(cr), this gives

$$\Delta_f H^o_m(\text{ThH}_{3.75}, \text{cr}, 298.15 \text{ K}) = -(215.4 \pm 8.0) \text{ kJ·mol}^{-1}$$

where the uncertainty has been increased to allow for uncertainties in the thermal functions and the lack of true equilibrium in the studies. This selection yields

$$\Delta_f G^o_m(\text{ThH}_{3.75}, \text{cr}, 298.15 \text{ K}) = -(142.9 \pm 8.0) \text{ kJ·mol}^{-1}.$$

There are no experimental thermodynamic data for the formation of $ThD_{3.75}$(cr) and $ThT_{3.75}$(cr), but from a consideration of their vibrational modes [1984FLO/HAS] have estimated the following differences for the enthalpies of formation of the isotopic compounds: $\Delta_f H^o_m(\text{ThH}_{3.75}, \text{cr}, 298.15 \text{ K}) - \Delta_f H^o_m(\text{ThD}_{3.75}, \text{cr}, 298.15 \text{ K}) = (4.48 \pm 0.84) \text{ kJ·mol}^{-1}$ and $\Delta_f H^o_m(\text{ThH}_{3.75}, \text{cr}, 298.15 \text{ K}) - \Delta_f H^o_m(\text{ThT}_{3.75}, \text{cr}, 298.15 \text{ K}) = (5.56 \pm 1.17) \text{ kJ·mol}^{-1}$. When combined with the data for $ThH_{3.75}$(cr), these give $\Delta_f H^o_m(\text{ThD}_{3.75}, \text{cr}, 298.15 \text{ K}) = -(221.9 \pm 8.0) \text{ kJ·mol}^{-1}$, and $\Delta_f H^o_m(\text{ThT}_{3.75}, \text{cr}, 298.15 \text{ K}) = -(221.0 \pm 8.1) \text{ kJ·mol}^{-1}$.

These values are given for information only.

VII.2.2 Thorium hydride gases, ThH_n(g)

VII.2.2.1 Thorium monohydride gas, ThH(g)

Souter *et al.* [1997SOU/KUS] have identified the ThH species (as well as other thorium hydrides) by examining the IR spectra of the products condensed from the reaction of laser-ablated thorium with H_2(g) in solid argon matrices. Isotopic substitution by deuterium confirmed the spectral assignments. Estimates of the vibration frequencies by DFT calculations gave values in close agreement with the experimental data: ω = 1485.2 cm^{-1}, r = 1.985 Å and a doublet ground state, see Appendix A. The value of the rotational constant B calculated from the interatomic distance is B = 4.2636 cm^{-1}. The other parameters required for the normal non-rigid rotator, anharmonic oscillator approximation were estimated from the values for other heavy metal monohydride gases given by Huber and Herzberg [1979HUB/HER]: $\omega x = (30 \pm 10) \text{ cm}^{-1}$, $\alpha = (0.15 \pm 0.05) \text{ cm}^{-1}$, $D = (2.0 \pm 1.0) \times 10^{-4} \text{ cm}^{-1}$. No excited electronic levels were included; this is therefore the major source of uncertainty in the calculated values of the thermal functions.

The calculated values at 298.15 K are:

$$C^o_{p,m}(\text{ThH}, \text{g}, 298.15 \text{ K}) = (29.6 \pm 4.0) \text{ J·K}^{-1}\text{·mol}^{-1}$$

$$S^o_m(\text{ThH}, \text{g}, 298.15 \text{ K}) = (233.5 \pm 5.0) \text{ J·K}^{-1}\text{·mol}^{-1}$$

with the uncertainties estimated by the review, and these are the selected values.

VII.2.2.2 Other thorium hydride gases, $ThH_2(g)$, $ThH_3(g)$, $ThH_4(g)$

Souter *et al.* [1997SOU/KUS] also identified ThH_2, ThH_3 and ThH_4 in their condensation products in solid argon matrices, and also made density functional theory calculations of the vibration frequencies for these gaseous species, with reasonable agreement. $ThH_2(g)$ has a bent C_{2v} structure with r(Th–H) = 2.040 Å, $ThH_3(g)$ is trigonal C_{3v} with r(Th–H) = 2.047 Å, and $ThH_4(g)$ tetrahedral T_d with r(Th–H) = 2.058 Å. Unfortunately, [1997SOU/KUS] do not give a complete set of the vibration frequencies for these molecules, but only those active in the infrared, so no further processing of these data is possible. Fuller details of the structures and a comparison of the experimental and calculated vibration frequencies are given in Appendix A.

VII.3 Aqueous thorium hydroxide complexes

VII.3.1 Discussion of experimental methods

There is only one stable oxidation state of thorium and the corresponding aqueous ion, Th^{4+}, is the least hydrolysed of the known M^{4+} ions. Both these facts make the experimental study of thorium hydrolysis simpler than that of U^{4+}, Np^{4+} and Pu^{4+}. Still, there are a number of problems encountered when exploring the hydrolytic behaviour of Th(IV) as exemplified by the many different, and sometimes contradictory, chemical models proposed for these reactions. Some of the problems are method-related and we will therefore begin this survey with a short methodological discourse.

The stoichiometry and equilibrium constants for hydrolysis reactions are in general formulated as:

$$m\mathrm{Th}^{4+} + n\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th}_m(\mathrm{OH})_n^{4m-n} + n\mathrm{H}^+ \qquad \text{(VII.2)}$$

There are a number of different experimental methods to determine the stoichiometry and equilibrium constants for Reaction (VII.2). *cf.* Section VII.3.4. The advantages and disadvantages of the most frequently used methods, potentiometry, liquid-liquid extraction and solubility, are briefly discussed in the following sections; for more details see the book by Rossotti and Rossotti [1961ROS/ROS].

VII.3.1.1 Potentiometric methods

The stoichiometry and equilibrium constant for Reaction (VII.2) are determined from the known analytical total concentrations of thorium, Th_{tot}, and protons, H_{tot}, in different test solutions, together with an experimental determination of the free hydrogen ion concentration, $-\log_{10}[H^+]$. The following equations are used, where $\overline{n}_{OH}$ denotes the average number of coordinated OH^- per Th(IV), equal to the number of protons released per Th(IV) in Eq. (VII.2). $^*\beta_{n,m}$ denotes the equilibrium constant for Reaction (VII.2). H_{tot} is often a negative quantity. Since the chemical reactions are written using H_2O and H^+ as components, this means that addition of hydroxide is most conveniently given as a negative quantity of H^+.

$$\mathrm{Th}_{tot} = [\mathrm{Th}^{4+}] + \sum m[\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}] = [\mathrm{Th}^{4+}] + \sum \frac{m^*\beta_{n,m}[\mathrm{Th}^{4+}]^m}{[\mathrm{H}^+]^n} \quad (\mathrm{VII.3})$$

$$\mathrm{H}_{\mathrm{tot}} = [\mathrm{H}^+] - \sum n[\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}] = [\mathrm{H}^+] - \sum \frac{n^*\beta_{n,m}[\mathrm{Th}^{4+}]^m}{[\mathrm{H}^+]^n} \quad (\mathrm{VII.4})$$

$$\bar{n}_{\mathrm{OH}} = \frac{[\mathrm{H}^+] - \mathrm{H}_{\mathrm{tot}}}{\mathrm{Th}_{\mathrm{tot}}} \quad (\mathrm{VII.5})$$

If $\bar{n}_{\mathrm{OH}}$ is independent of $\mathrm{Th}_{\mathrm{tot}}$ the system is mononuclear, if not, polynuclear complexes are formed. To determine the stoichiometry of the complexes and equilibrium constants of the system, it is necessary to vary the total concentration $\mathrm{Th}_{\mathrm{tot}}$ and $-\log_{10}[\mathrm{H}^+]$ over as large a range as possible; the available concentration range is limited by the low solubility of thorium hydrous oxides. It is not possible to decrease the total thorium concentration below approximately 0.1 mM, because protolytic impurities in the ionic medium used then results in a large error in $\bar{n}_{\mathrm{OH}}$. As the potentiometric method becomes inaccurate at higher acidities (where ($[\mathrm{H}^+] - \mathrm{H}_{\mathrm{tot}}$) is a relatively small difference between two large measured values), the $-\log_{10}[\mathrm{H}^+]$ range is limited to values greater than 2, the upper limit being given by the onset of precipitation of thorium hydroxide/hydrous oxide, at about $-\log_{10}[\mathrm{H}^+] = 4$, depending on the thorium concentration.

The analysis of the experimental data is complicated by the presence of several different species and the "best" chemical model, consistent with the experimental data and the estimated experimental uncertainty, is usually determined using least squares methods (*e.g.* [1964HIE/SIL], [1965BAE/MEY], [2000EKB/ALB]). Complexes that occur in small amounts are too often included in these models and they may be artefacts that represent methodological shortcomings rather than real chemical species. To spot these species it is necessary to make a speciation calculation using the deduced equilibrium constants to explore the concentrations of the species formed in the various test solutions. In addition to the mathematical/statistical analysis of the data one must always test if the proposed stoichiometry is consistent with known structural features of thorium hydroxide/oxide complexes. An additional complication occurs due to the fact that the potentiometric and other "classical" equilibrium analytical methods cannot distinguish the different origins of the protons released in Eq. (VII.2); they can come either from coordinated water or coordinated hydroxide, where $2\mathrm{OH}^- \equiv \mathrm{O}^{2-} + \mathrm{H_2O}$. Potentiometric methods are the most accurate for the evaluation of the stoichiometry and equilibrium constants for polynuclear complexes; mononuclear complexes are usually minor species in these studies.

VII.3.1.2 Liquid-liquid extraction methods

The distribution of a metal ion between an aqueous and an immiscible organic phase containing an organic ligand that can form uncharged complexes with the metal ion in the organic phase provides information on chemical equilibria in the aqueous phase. Measurements of this type can be made at such low total concentrations of the metal ion that precipitation of hydrous oxides can be avoided. However, in these systems, sorption of thorium on the container walls must be considered. An advantage of liquid-liquid extraction is the wide pH range that can be covered by these methods. Beta-diketones, like acetylacetone, and thenoyltrifluoroacetone (TTA), are often used as extractants. The interpretation of the experimental data is complicated by the fact that they can form both binary and ternary complexes in the aqueous phase; the latter are often neglected in the data analysis, *cf.* [1992ENG/ALB], [2000EKB/ALB]. This problem does not occur in solvent extraction with tri-*n*-butylphosphate, as in the study of [1984NAK/ZIM], where the extractant TBP and the extracted $Th(NO_3)_4 \cdot 2TBP$ complex are only present in the organic phase and do not affect the aqueous speciation. The precise determination of large and small distribution coefficients between the two phases may be a problem in this method, as is the sorption of metal ion on the container walls in experiments at tracer concentration levels. The applicability of liquid-liquid extraction methods to low thorium concentrations and over a wide pH range favours these methods for the determination of equilibrium constants for mononuclear complexes.

VII.3.1.3 Solubility methods

Solubility methods are, in principle, useful for investigation of hydrolysis and other equilibria. However, a requirement is that the activity and therefore the composition of the solid phase is constant when the concentrations of the ions in the test solutions vary. The X-ray powder pattern of the solid phase is often used to check this. This is an excellent method for investigating the bulk phase but, if it is not accompanied by a detailed quantitative diffraction pattern analysis, it provides no information on small amounts of microcrystalline or amorphous phases that may be present. As these phases have a higher solubility than the crystalline bulk phase, they will determine the solubility. Solubility should whenever possible be determined both from under- and over-saturation to ensure that true equilibrium, and not a mere steady-state, has been achieved. Hydrolysis equilibria of Th(IV) have been investigated using metastable hydrous oxides or hydroxide phases, solids that often are amorphous or have variable particle size. The particle or crystallite size of X-ray amorphous hydrous oxides is usually below 10 nm and the size distribution varies with preparative conditions and pretreatment. In this range the solubility increases dramatically with decreasing particle size [1967SCH], [2002FAN/NEC]. The ratio between surface and volume for a phase increases strongly with decreasing particle size. The change in Gibbs energy of a solid in a given solvent depends on the surface area and the interfacial surface tension, $\overline{\gamma}$, according to the expression:

$$\delta G(\text{surface}) = \bar{\gamma}\,\delta\mathcal{A} \qquad \text{(VII.6)}$$

where $\delta\mathcal{A}$ is the change in molar surface area, $\mathcal{A}$. According to Schindler [1967SCH] the variation in the solubility product with the change in surface area is equal to:

$$\log_{10} K_s\,(\mathcal{A}_1) = \log_{10} K_s(\mathcal{A}_2) + (2/3)\,\bar{\gamma}\,\{(\mathcal{A}_1 - \mathcal{A}_2)/\mathrm{R}T\ln(10)\} \qquad \text{(VII.7)}$$

Bruno [1989BRU] has tested this equation on the solubility of $UO_2(s)$ with different BET surfaces. He found that $\log_{10} K_s$ increased from -1.6 to 0.6 when the molar BET surface area increased from 54 $m^2 \cdot mol^{-1}$ to 8000 $m^2 \cdot mol^{-1}$ and that the value of $\bar{\gamma} = 2.1$ $J \cdot m^{-2}$ was in fair agreement with the corresponding value from contact angle measurements, $\bar{\gamma} = 1.7$ $J \cdot m^{-2}$. A more detailed discussion is given in Section VII.4.3.

It is often assumed that a solid that gives a sharp X-ray diffraction pattern does not contain small particles, but this is not always the case and the presence of small particles can accordingly result in an erroneous solubility product for the assumed crystalline phase. An example of the consequences is given in Section VII.4.3, Figure VII-20.

In addition, the particle size of the solid phase must be sufficiently large to allow the separation of the solid and aqueous phases and this is, in practice, difficult for small particles. This is probably the main reasons for the widely different solubility that is reported for Th(IV) hydrous oxide phases. The attainment of solubility equilibrium is often a slow process, in particular for crystalline thorium oxides [2001HUB/BAR], [2003NEC/ALT] and care must be taken to ensure that true equilibrium has been attained in the system. The solubility of hydrous thorium oxide is low at pH > 5, but sorption of thorium on the container walls is no problem as the thorium buffer capacity of the system is determined by the solid phase; the situation is different in liquid-liquid extraction where the thorium buffer capacity is low.

The measured solubility, s, of thorium in equilibrium with $Th(OH)_4(s)$ or $ThO_2(s)$ is given by:

$$s = [\mathrm{Th}^{4+}] + \Sigma m\left[\mathrm{Th}_m\left(\mathrm{OH}\right)_n^{4m-n}\right] = [\mathrm{Th}^{4+}] + \Sigma\frac{m\,{}^*\beta_{n,m}\left[\mathrm{Th}^{4+}\right]^m}{\left[\mathrm{H}^+\right]^n} \qquad \text{(VII.8)}$$

where $[Th^{4+}]$ is obtained from the solubility constant, ${}^*K_{s,0}$ for the reaction:

$$\mathrm{ThO_2(s)} + 4\mathrm{H}^+ \rightleftharpoons \mathrm{Th}^{4+} + 2\mathrm{H_2O(l)} \qquad \text{(VII.9)}$$

The solubility constant for the solid phase, assuming that its activity is constant, is:

$${}^*K_{s,0} = \frac{[\mathrm{Th}^{4+}]}{[\mathrm{H}^+]^4}. \qquad \text{(VII.10)}$$

Solubility measurements give no direct information on the speciation, but the method does provide information on the charge of the species present in solution as illustrated in the following example. The measured solubility, s, of thorium in equilibrium with $Th(OH)_4(s)$ is given by:

$$\begin{aligned} s = {} & ([\mathrm{Th}^{4+}] + 4[\mathrm{Th}_4(\mathrm{OH})_{12}^{4+}]) + ([\mathrm{Th(OH)}^{3+}] + 2[\mathrm{Th}_2(\mathrm{OH})_5^{3+}]) + ([\mathrm{Th(OH)}_2^{2+}] + \\ & 2[\mathrm{Th}_2(\mathrm{OH})_6^{2+}]) + ([\mathrm{Th(OH)}_3^{+}] + 2[\mathrm{Th}_2(\mathrm{OH})_7^{+}]) + ([\mathrm{Th(OH)}_4] + [\mathrm{Th}_m(\mathrm{OH})_{4m}]) \end{aligned} \qquad \text{(VII.11)}$$

where we have given the sum of concentrations of species with charges from 4+ to zero within separate parentheses; the list of possible species is not complete but the ones chosen arbitrarily in Eq. (VII.11) illustrate the principle.

After introducing the equilibrium constants for the formation of hydroxide complexes and ${}^*K_{s,0}$ in Eq. (VII.11) we obtain:

$$\begin{aligned} s = {} & ({}^*K_{s,0} + 4\,{}^*K_{s,0}^4\,{}^*\beta_{12,4})\,[\mathrm{H}^+]^4 + ({}^*K_{s,0}\,{}^*\beta_{1,1} + 2\,{}^*K_{s,0}^2\,{}^*\beta_{5,2})\,[\mathrm{H}^+]^3 \\ & + ({}^*K_{s,0}\,{}^*\beta_{2,1} + 2\,{}^*K_{s,0}^2\,{}^*\beta_{6,2})\,[\mathrm{H}^+]^2 + ({}^*K_{s,0}\,{}^*\beta_{3,1} + 2\,{}^*K_{s,0}^2\,{}^*\beta_{7,2})\,[\mathrm{H}^+] \\ & + ({}^*K_{s,0}\,{}^*\beta_{4,1} + m\,{}^*K_{s,0}^m\,{}^*\beta_{4m,m}) \end{aligned} \qquad \text{(VII.12)}$$

From Eq. (VII.12) we can see that the function $\log_{10} s$ *vs.* $-\log_{10}[\mathrm{H}^+]$ has two asymptotes with the slopes -4 and zero, respectively. (Polynuclear species with higher charge $z = (4m-n)$ which give slopes of $-z$ are not considered in this example.) In addition the solubility constant ${}^*K_{s,0}$ and the equilibrium constants ${}^*\beta_{n,1}$ can only be determined if one assumes that polynuclear complexes are not formed, or if there is independent information on their equilibrium constants, *e.g.* from potentiometric data.

For these reasons, hydrolysis constants simply fitted to solubility data for Th(IV) hydroxide or hydrous oxide or crystalline $ThO_2(cr)$, *e.g.*, those in [1964NAB/KUD], [1989MOO], are not reliable and usually in strong contradiction to values derived using other methods. Therefore the present review at first selects the hydrolysis constants from studies based on potentiometric and solvent extraction studies. In a second step the selected hydrolysis constants are used to re-evaluate the published solubility data at pH < 5, *i.e.*, to calculate the corresponding solubility constants. The recalculation of the pH-dependent solubility curves provides furthermore a test of the consistency of the selected data set, in particular for the neutral complexes predominant in the neutral and alkaline pH range.

VII.3.2 Ionic medium and ionic strength effects

The hydrolysis of Th(IV) at total concentrations larger than $0.1-1$ mM is dominated by the formation of polynuclear complexes that have high positive charges, *e.g.* $\mathrm{Th}_2(\mathrm{OH})_2^{6+}$ and $\mathrm{Th}_6(\mathrm{OH})_{15}^{9+}$. Hence electrostatic effects are expected to play an important role for the stability of these species as shown by the ionic strength dependence of the reaction:

$$2\mathrm{Th(OH)}^{3+} \rightleftharpoons \mathrm{Th}_2(\mathrm{OH})_2^{6+}\,. \qquad \text{(VII.13)}$$

Using the specific ion interaction theory (SIT) we find:

$$\begin{aligned}\log_{10} K^{\circ}\,(\mathrm{VII.13}) &= \log_{10} K\,(\mathrm{VII.13}) + \log_{10}\gamma_{\mathrm{Th_2(OH)_2^{6+}}} - 2\log_{10}\gamma_{\mathrm{Th(OH)^{3+}}}\\ &= \log_{10} K\,(\mathrm{VII.13}) - 18D + (\,\varepsilon(\mathrm{Th_2(OH)_2^{6+}},\mathrm{X^-}) - 2\,\varepsilon(\mathrm{Th(OH)^{3+}},\mathrm{X^-})\,)m_{\mathrm{X}} \quad (\mathrm{VII.14})\end{aligned}$$

where D is the Debye-Hückel term, ε the ion interaction coefficient and m_X the molality of the ionic medium anion X^-, for details *cf.* Appendix B. The value $\log_{10} K$ (VII.13) that determines the relative amounts of $Th(OH)^{3+}$ and $Th_2(OH)_2^{6+}$ increases by nearly four $\log_{10}$ units from $I = 0$ to $I = 3$ M *cf.* Eq. (VII.14). It is therefore not surprising to find different chemical models in systems at different ionic strength. Available experimental potentiometric data also show a pronounced difference in solubility, or ease of precipitation of hydrous oxides in different ionic media. The highest values of $\bar{n}_{OH}$ are found in perchlorate media and these data therefore provide the most accurate information on polynuclear complexes. In ionic media containing chloride and nitrate as counter-ions, one must consider the possibility that they can be components in ternary thorium hydroxide complexes, resulting in different Th/OH stoichiometry between these systems and those in perchlorate media. There is no information on the stoichiometry of such systems in the published literature, except in a large angle X-ray diffraction study by Johansson [1968JOH] and a High-Energy X-ray Scattering (HEXS) study by Wilson *et al.* [2007WIL/SKA].

Perchlorate, chloride and nitrate are the anions in the ionic media commonly used to investigate the hydrolysis of Th(IV). There is no evidence for complex formation between Th^{4+} and ClO_4^-. Chloride and nitrate complexes are discussed in Sections VIII.2.2.1 and X.1.3.3, respectively. Hence, it is necessary to discuss if and how these will affect the reported equilibrium constants for the Th(IV) hydroxide complexes. As discussed in Sections VIII.2.2.1 and X.1.3.3, the experimental data in the binary Th(IV) chloride and nitrate systems can be described with similar accuracy using both complexation and ion interaction models. When evaluating the hydrolysis data in chloride and nitrate ionic media, this review has used the ion interaction model with the interaction coefficients $\varepsilon(\mathrm{Th^{4+}},\mathrm{Cl^-}) = (0.25 \pm 0.03)\ \mathrm{kg\cdot mol^{-1}}$ and $\varepsilon(\mathrm{Th^{4+}},\mathrm{NO_3^-}) = (0.31 \pm 0.12)\ \mathrm{kg\cdot mol^{-1}}$, respectively. With this model no correction for the formation of thorium chloride and nitrate complexes is necessary (see Section VI.3).

In nitrate media there is strong evidence for the formation of thorium nitrate complexes as discussed in Section X.1.3.3 and results of large-angle X-ray diffraction studies of aqueous solution also demonstrate chemical bonding of NO_3^- to Th(IV) in hydroxide complexes [1968JOH2]:

$$\mathrm{Th^{4+}} + p\,\mathrm{NO_3^-} \rightleftharpoons \mathrm{Th(NO_3)}_p^{(4-p)} \quad (\mathrm{VII.15})$$

$$\mathrm{Th}_m\mathrm{(OH)}_n^{4m-n} + q\,\mathrm{NO_3^-} \rightleftharpoons \mathrm{Th}_m\mathrm{(OH)}_n\mathrm{(NO_3)}_q^{(4m-n-q)} \quad (\mathrm{VII.16})$$

Experimental hydrolysis constants in nitrate media are therefore conditional equilibrium constants $\log_{10} {}^{*}\beta_{n,m}^{cond}$ and refer to the reactions:

$$m\,\mathrm{Th(NO_3)}_p^{(4-p)} + n\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th}_m\mathrm{(OH)}_n\mathrm{(NO_3)}_q^{(4m-n-q)} + n\,\mathrm{H^+} + (mp-q)\,\mathrm{NO_3^-} \quad (\mathrm{VII.17})$$

with

$$\log_{10}{}^{*}\beta^{cond}_{n,m} = \log_{10}\frac{["(n,m)"]}{["\text{Th}"]^{m}[\text{H}^{+}]^{n}} = \log_{10}{}^{*}K\ (\text{VII.17}) - (mp-q)\log_{10}[\text{NO}_3^-] \quad (\text{VII.18})$$

where $["\text{Th}"] = [\text{Th}^{4+}] + \Sigma_p\,[\text{Th(NO}_3)_p^{(4-p)}]$

and $["(n,m)"] = [\text{Th}_m(\text{OH})_n^{4m-n}] + \Sigma_q\,[\text{Th}_m(\text{OH})_n(\text{NO}_3)_q^{(4m-n-q)}]$

are experimental equilibrium concentrations including nitrate complexes.

In the case of the non-hydrolysed thorium species we have the choice of using either the ion interaction model (with $\varepsilon(\text{Th}^{4+},\text{NO}_3^-)$ = (0.31 ± 0.12) kg·mol^{-1}) or calculating the free Th^{4+} concentration using the complex formation model and the corresponding equilibrium constants $\log_{10}\beta_p$ (VII.15) selected for Th(IV) nitrate complexes. However, there is no quantitative information on the ternary Th(IV)-hydroxide-nitrate complexes formed by Reactions (VII.16). Therefore it is more convenient to use the ion interaction model for both the Th^{4+} ion and the hydroxide complexes, *i.e.*, to use ion interaction coefficients $\varepsilon(\text{Th}^{4+},\text{NO}_3^-)$ and $\varepsilon(\text{Th}_m(\text{OH})_n^{4m-n},\text{NO}_3^-)$ which take implicit account of the formation of the complexes $\text{Th(NO}_3)_p^{(4-p)}$ and $\text{Th}_m(\text{OH})_n(\text{NO}_3)_q^{(4m-n-q)}$, respectively.

With this background we will now discuss various experimental studies of the hydrolysis of Th^{4+}.

VII.3.3 Discussion of the hydrolysis of Th^{4+} using potentiometric data

Baes and Mesmer [1976BAE/MES] have reviewed the hydrolysis of the Th^{4+} ion and discussed the potentiometric data from older publications. The selections of Baes and Mesmer [1976BAE/MES], together with the studies on which they were based, are discussed in detail in Appendix A; the present review agrees with most of their general conclusions. Thermodynamic data for the hydrolysis of Th^{4+} were also discussed by Fuger *et al.* [1992FUG/KHO], but no data were selected.

Potentiometric studies have been made under conditions where polynuclear complexes dominate and the information on mononuclear hydrolysis is therefore limited; accordingly the focus of the following discussion will be on polynuclear species. Publications on the hydrolysis of Th(IV) often discuss alternative chemical models that are used to describe the experimental findings; the choice of the "best" model is then made using a least-squares analysis. The different models are described and discussed in the Appendix A entries for the various publications. The uncertainty is in general given at the 3σ level, where σ is the estimated standard deviation in the least-squares analysis. The standard deviation is dependent on the weight of an individual determination, but also on the number of data points and their distribution. In general the individual data points are assigned unit weights, but the number and distribution of data points varies between different experiments. Hence, the standard deviations are not strictly comparable. In Table VII-7, we have only listed the "best" chemical model proposed in the available potentiometric studies or recalculated from the original data by Hietanen and Sillén [1968HIE/SIL] or Baes *et al.* [1965BAE/MEY], [1976BAE/MES] using appropriate least-squares analysis methods. The reported equilibrium constants are discussed in detail in the corresponding Appendix A entries and the evaluation of equilibrium constants at zero ionic strength with the SIT are presented in Section VII.3.4.

A number of papers give only qualitative information on the hydrolysis of thorium [1930CHA/SOU], [1947SCH/FAU], [1948SOU], [1954FAU], [1960MAT/ABR], [1962PRA/DEY], [1965HEN/TYR], [1966HEN/JOH], [1970SER/ALM], [1972PER], [1977MIL2]. Freezing point [1948SOU] or emf data in nitrate [1954FAU] and perchlorate [1947SCH/FAU] solutions were interpreted with the formation of $\mathrm{Th_4(OH)_8^{8+}}$ (or $\mathrm{Th_4O_4^{8+}}$) as the only or predominant complex. The equilibrium constants from the potentiometric studies in [1955PAN/HSE], [1971KIC/STE], [1972USH/SKO], [2003SAW/SHA], [2004BEN/BOU] are not accepted by the present review, because the studies were performed in solutions where the predominant species are polynuclear, a fact that the authors neglected when interpreting their data in terms of only mononuclear species (*cf.* Appendix A reviews of these papers).

Table VII-7: Equilibrium constants for the formation of Th(IV) hydroxide complexes determined by potentiometry.

Reference	Ionic medium	*t* (°C)	Proposed species $(n,m) = \mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$	Comments
[1954HIE]	1.0 M $\mathrm{NaClO_4}$	25	$\mathrm{Th\{(OH)_3Th\}}_n^{(4+n)+}$	"Core and link" model erroneous (*cf.* Appendix A)
[1954KRA/HOL]	1.0 M $\mathrm{NaClO_4}$	25	(1,1), (2,1), (2,2)	Graphical evaluation (not accepted)
[1965BAE/MEY]	1.0 M $\mathrm{NaClO_4}$	0	(1,1), (2,1), (2,2), (8,4) and (15,6)	
		25	(1,1), (2,1), (2,2),(8,4), and (15,6)	Experimental data at 25°C from [1954KRA/HOL]
		95	(1,1), (2,1), (2,2), (8,4),and (15,6)	
[1968HIE/SIL]	1.0 M $\mathrm{NaClO_4}$	25	(1,1), (2,1), (2,2), (8,4) and (15,6)	Reinterpretation of data in [1954HIE], [1954KRA/HOL] and [1965BAE/MEY]
[1968DAN/MAG]	4.0 M $\mathrm{NaClO_4}$	25	(1,2), (5,3), (4,2), (8,4), and (14,6)	Model not accepted by this review
[1991GRE/LAG2]	3.0 M $\mathrm{NaClO_4}$	25	(1,1), (2,2), (4,1), (8,4), (15,6) or (14,6), and (12,4)	

(Continued on next page)

Table VII-7 (continued)

Reference	Ionic medium	t (°C)	Proposed species $(n,m) = \mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$	Comments
[2000EKB/ALB]	1.0 M $NaClO_4$	15	(1,1), (2,1), (8,4), (15,6)	Further data are reported for (3,1) and (4,1) from a solvent extraction study with TTA (not accepted by this review)
		25	(1,1), (2,1), (8,4), (15,6)	
		35	(1,1), (2,1), (8,4), (15,6)	
[2003SAW/SHA]	1.0 M $NaClO_4$	25	(1,1), (3,1)	Polynuclear species are not considered
[2004BEN/BOU]	0.1 M $NaClO_4$	25	(2,1), (3,1), (4,1), and (7,2)	Polynuclear species other than (7,2) are not considered
[1968DAN/MAG]	4.0 M $NaNO_3$	25	(2,2), (6,3), (12,4)	(6,3) not reliable
[1971MIL2]	3.0 M $LiNO_3$	25	(2,2), {(3,3)}, (5,3)	Species {(*n*,*m*)} in parentheses are uncertain
	3.0 M KNO_3	25	{(2,1)}, (2,2), (3,2), (15,6)	
	1.5 M $Mg(NO_3)_2$	25	(2,2), (5,3), (15,6)	
[1982MIL/SUR2]	0.5 – 3 M $NaNO_3$	25	(2,2), (5,3), (15,6)	
[1983BRO/ELL]	0.1 M KNO_3	25	(1,1), (12,4), (15,6)	
[1976BAE/MES]	3.0 M (M)NO_3 M = Li, K, Mg	25	(2,2), (8,4), (15,6)	Reinterpretation of data in [1971MIL2]
[1968HIE/SIL]	3.0 M NaCl	25	different models tested (2,2), (3,2), (14,6)	Speciation model included in the selection of data
[1976BAE/MES]	3.0 M NaCl	25	(2,2), (3,2), (14,6)	Reinterpretation of data in [1968HIE/SIL]
[1981MIL2]	0.5 − 3.0 M NaCl	25	(2,2), (3,2)	No data for (14,6) because of rather limited pH range
	3.0 M LiCl	25	(2,2), (3,2)	
	3.0 M KCl	25	(2,2), (3,2)	
[1981SUR/MIL]	0.5 − 3.0 M LiCl	25	(2,2), (3,2)	See comment on [1981MIL2]
	0.5 − 3.0 M KCl	25	(2,2), (3,2)	
[1982SUR/MIL]	0.25 − 1.5 M $MgCl_2$	25	(2,2), (3,2)	See comment on [1981MIL2]
	0.25 − 1.5 M $CaCl_2$	25	(2,2), (3,2)	
	0.25 − 1.5 M $SrCl_2$	25	(2,2), (3,2)	
	0.25 − 1.5 M $BaCl_2$	25	(2,2), (3,2)	
[1959HIE/SIL2]	0.5 M $ThCl_4$ and 0.7 M $ThCl_4$+ 2.2 M NaCl	25	(1,2), (2,2)	Study in (Th,Na)Cl “self-media”
[1955PAN/HSE]	0.01 M $ThCl_4$ + 0 – 0.5 M $NaClO_4$	25	(1,1), (2,1)	Polynuclear species are not considered

(Continued on next page)

Table VII-7 (continued)

Reference	Ionic medium	t (°C)	Proposed species $(n,m) = \mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$	Comments
[1971KIC/STE]	0.7 mM $Th(NO_3)_4$ + 0.01 − 0.04 M Na(NO_3, Cl, ClO_4)	25	(1,1), (2,1), (3,1), (4,1)	"Self-media". Polynuclear species are not considered
[1972USH/SKO]	0.05 M Na(Cl, ClO_4)	25	(1,1), (2,1)	Polynuclear species are not considered

VII.3.3.1 Speciation model for Th(IV) hydroxide complexes in $NaClO_4$ media

The experimental data considered by this review are those from the potentiometric studies in [1954HIE], [1954KRA/HOL], [1965BAE/MEY], [1968DAN/MAG], [1991GRE/LAG2] and [2000EKB/ALB]. The experimental data from [1954HIE], [1954KRA/HOL], and [1965BAE/MEY] have been reinterpreted in [1968HIE/SIL]. As discussed in [1968HIE/SIL] (Table A-30, *cf.* Appendix A), there is not a large difference between the equilibrium constants for a certain study when evaluated with the least-squares program used by Sillén and colleagues (*e.g.* [1968HIE/SIL], [1991GRE/LAG2]) and that used by Kraus, Baes and Mesmer *et al.* (*e.g.* [1954KRA/HOL], [1965BAE/MEY], [1976BAE/MES]), as discussed in the various Appendix A entries. The experimental data from [1954KRA/HOL] and [1965BAE/MEY] are interpreted using the following species, where $(n,m) = \mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$: (1,1), (2,1), (2,2), (8,4), and (15,6) and that of [1954HIE] with the species (1,1), (2,2), (8,4) and (15,6). The first model is also found in measurements at 0 and 95°C in 1 M $NaClO_4$ [1965BAE/MEY]. Lefèbvre [1958LEF] reinterpreted the experimental data from [1954HIE], [1954KRA/HOL] with a model including the species (2,1), (2,2), (12,5) and $(n,7)$ with $n = 18-21$, which is not accepted by this review.

This review selects the chemical model with the following complexes and equilibrium constants $\log_{10}{}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ in 1 M $NaClO_4$ that is the average of the recalculated equilibrium constants in [1968HIE/SIL], given in Table A-30 (*cf.* Appendix A): $\log_{10}{}^{*}\beta_{1,1}(\mathrm{Th(OH)}^{3+}) = -(4.0 \pm 0.2)$, $\log_{10}{}^{*}\beta_{2,1}(\mathrm{Th(OH)}_2^{2+}) = -(7.7 \pm 0.5)$ $\log_{10}{}^{*}\beta_{2,2}(\mathrm{Th}_2(\mathrm{OH})_2^{6+}) = -(4.52 \pm 0.10)$, $\log_{10}{}^{*}\beta_{8,4}(\mathrm{Th}_4(\mathrm{OH})_8^{8+}) = -(19.0 \pm 0.2)$ $\log_{10}{}^{*}\beta_{15,6}(\mathrm{Th}_6(\mathrm{OH})_{15}^{9+}) = -(36.7 \pm 0.2)$. The uncertainty has been selected so that it spans the uncertainty interval of the data from [1954KRA/HOL], [1964HIE/SIL], as discussed in [1965BAE/MEY] and [1968HIE/SIL]. The complex (2,1) is a minor species and the uncertainty has therefore been substantially increased in this review as compared to the value in [1965BAE/MEY]. In addition, the complex (12,4) included in the models of [1991GRE/LAG2] in 3 M $NaClO_4$ and [1983BRO/ELL] in 0.1 M KNO_3 is selected by the present review. Justification for this comes from the evaluation of solubility studies with Th(IV) hydrous oxide in the range

$4 < -\log_{10}[H^+] < 5$ (*cf.* Section VII.4 and Appendix A entries for [1964NAB/KUD], [1987RYA/RAI] and [2000RAI/MOO]). Consistency between potentiometric models and these solubility studies can only be achieved if the complex $Th_4(OH)_{12}^{4+}$ is included. Extrapolation of the selected conditional equilibrium constants to zero ionic strength and the evaluation of ion interaction coefficients for Th(IV) hydroxide complexes in perchlorate media is discussed in Section VII.3.4, considering simultaneously the accepted data in different ionic media.

The chemical model proposed by Ekberg *et al.* [2000EKB/ALB] for 1 M $NaClO_4$ agrees well with the one from the Sillén and Oak Ridge groups, however some of the equilibrium constants deviate significantly. The value of $\log_{10}{}^*\beta_{1,1}$ is 0.7 units higher than that selected above, while the values of $\log_{10}{}^*\beta_{2,1}$ and $\log_{10}{}^*\beta_{15,6}$ are 0.9 and 2.8 units lower, respectively. There is only a small difference in the calculated value of $\bar{n}_{OH}$ if these constants are used instead of those selected in the present review, except in test solutions where polynuclear complexes are negligible. The best model found in 3 M $NaClO_4$ [1991GRE/LAG2] also includes the complexes (1,1), (2,2), (8,4), (15,6) or (14,6), and additionally the complex (12,4) which is predominant at pH > 4. The experiments by Danesi *et al.* [1968DAN/MAG] in 4 M $NaClO_4$ is interpreted by using a very different chemical model involving the species $(n, m) = Th_m(OH)_n^{4m-n}$: (1,2), (5,3), (4,2), (8,4) and (14,6). For reasons given in Appendix A the present review considers this study as less reliable than those in 1 and 3 M $NaClO_4$ and has therefore not included these data in the final selection.

VII.3.3.2 Speciation model for Th(IV) hydroxide complexes in nitrate media

The potentiometric studies in nitrate ionic media [1968DAN/MAG], [1971MIL2], [1982MIL/SUR2], [1983BRO/ELL] are more extensive than those in perchlorate media and cover a broad range of ionic strengths, *e.g.*, 0.5 to 3 M $NaNO_3$ [1982MIL/SUR2]. However, as indicated earlier, these data only cover values of $\bar{n}_{OH} < 0.6$, which makes the determination of complexes with $n/m > 1$ more uncertain than in perchlorate media. The following species have been suggested: in 0.5 to 3 M $NaNO_3$ [1982MIL/SUR2]: (2,2), (5,3) and (15,6); in 4 M $NaNO_3$ [1968DAN/MAG]: (2,2), (6,3) and (12,4). The data in [1968DAN/MAG] are considered less accurate by this review and have not been used. Data in KNO_3 media have been described with two different chemical models, in 3 M KNO_3 [1971MIL2]: (2,2), (3,2), (2,1) and (15,6), where the last two are classified as uncertain; in 0.1 M KNO_3 [1983BRO/ELL]: (1,1), (12,4) and (15,6). As the corresponding experimental data are judged to be satisfactory by this review, it is not possible to prefer one model to the other. Milić [1971MIL2] has also determined the speciation in 3 M $LiNO_3$ and 1.5 M $Mg(NO_3)_2$ where the chemical models are {(2,2), (5,3), (3,3)} and {(2,2), (5,3), (15,6)}, respectively; Milić considers the species (3,3) to be uncertain. These data underscore the difficulty to determine a proper chemical model for the hydrolysis of Th(IV). Several different models seem to describe experimental data in aqueous nitrate media reasonably well.

The equilibrium constants for the complexes (2,2), (5,3) and (15,6) in 3 M $LiNO_3$ and KNO_3 [1971MIL2] are in good agreement with those in 0.5 to 3 M $NaNO_3$ (*cf.* Section VII.3.4). However, Baes and Mesmer [1976BAE/MES] have shown that the potentiometric data of Milić [1971MIL2] in 3 M KNO_3, 3 M $LiNO_3$ and 1.5 M $Mg(NO_3)_2$ can as well be described with the model appropriate for $NaClO_4$ solution, including the species (2,2), (8,4) and (15,6). These stoichiometries correspond to structures of M(IV) complexes that have been found both in solution and solid state, while there is no structural evidence for trinuclear complexes. The present review therefore prefers the interpretation of [1976BAE/MES]. The equilibrium constants at zero ionic strength and ion interaction coefficients in nitrate media are evaluated in Section VII.3.4, considering simultaneously the selected conditional equilibrium constants in different ionic media.

VII.3.3.3 Speciation model for Th(IV) hydroxide complexes in chloride media

The earliest experimental data are from Hietanen and Sillén [1968HIE/SIL] in 3 M NaCl. They tested a number of different chemical models, all of which describe the experimental data with very nearly the same accuracy. Many of the species proposed occur in small amounts in the test solutions, *cf.* Appendix A, and this review suggests that most of them are artefacts, *i.e.*, parameters that just improve the fit of the experimental data. The stoichiometry of these species does not have an obvious relationship to the known coordination chemistry of Th(IV), *e.g.*, there are no known structures containing tri- and penta-nuclear complexes. However, the complex $Th_2(OH)_2^{6+}$ is a predominant complex in a large concentration range and the equilibrium constant is not strongly dependent on the selection of other species; accordingly, this review considers the complex (2,2) as well established.

Baes and Mesmer [1976BAE/MES] demonstrated that the speciation model selected for $NaClO_4$ solution {(2,2), (8,4), (15,6)} is not appropriate to describe the data of [1968HIE/SIL] in 3 M NaCl. The model proposed in [1976BAE/MES] for chloride solution includes the two dinuclear species, (2,2) = $Th_2(OH)_2^{6+}$ and (3,2) = $Th_2(OH)_3^{5+}$ and the hexanuclear complex (14,6) = $Th_6(OH)_{14}^{10+}$. This speciation model was confirmed later by Milić [1981MIL2] and Suranji and Milić [1981SUR/MIL] who performed potentiometric studies in various chloride media (0.5 − 3.0 M NaCl, LiCl and KCl [1981MIL2], [1981SUR/MIL] and 0.25 − 1.5 M MCl_2 in $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ [1982SUR/MIL]) and described their data with the formation of the dinuclear species, (2,2) and (3,2). The complex (14,6) is not important under the experimental conditions in [1981MIL2], [1981SUR/MIL], [1982SUR/MIL] ($[Th]_{tot}$ = 10 mM, pH < 3.2), *cf.* speciation calculations in the Appendix A review of [1968HIE/SIL].

The present review also selects the model {(2,2), (3,2), (14,6)} proposed in the review of Baes and Mesmer [1976BAE/MES]. The equilibrium constants at zero ionic strength and ion interaction coefficients in chloride media are evaluated in

Section VII.3.4, considering simultaneously the accepted equilibrium constants in different ionic media.

VII.3.3.4 Speciation model and equilibrium constants for Th(IV) hydroxide complexes in (Th, Na)Cl "self-media"

There is one experimental study [1959HIE/SIL2] made under rather extreme conditions (0.5 M $ThCl_4$ and 0.7 M $ThCl_4$ + 2.2 M NaCl); two complexes $Th_2(OH)^{7+}$ and $Th_2(OH)_2^{6+}$ were proposed and their equilibrium constants were practically the same in both media: $\log_{10}{}^*\beta_{1,2} = -(2.9 \pm 0.2)$ and $\log_{10}{}^*\beta_{2,2} = -(5.05 \pm 0.05)$, respectively. As discussed in Appendix A, the interpretation of the experimental data is straightforward and provides good evidence that these species are real chemical entities and not experimental artefacts. This review accepts the equilibrium constants proposed, but they cannot be extrapolated to zero ionic strength.

VII.3.4 Equilibrium constants for the hydrolysis of Th(IV) at 25°C

For the selection of data for polynuclear species, the equilibrium constants at 25°C accepted in the Appendix A reviews of the potentiometric studies in [1965BAE/MEY] (including the recalculated data from [1954KRA/HOL]), [1968HIE/SIL] (including the recalculated data from [1954HIE], [1954KRA/HOL]), [1968DAN/MAG], [1971MIL2], [1976BAE/MES], [1981MIL2], [1981SUR/MIL], [1982SUR/MIL], [1982MIL/SUR2], [1983BRO/ELL], [1991GRE/LAG2] and [2000EKB/ALB] have been used and converted from molar to molal values (except those in [1965BAE/MEY] which are already given in molal units). The selection of data is focused on complexes found to be major species in the potentiometric studies.

The selection of reliable data for mononuclear species $Th(OH)_n^{4-n}$ is difficult, because they are usually minor species under the conditions used in potentiometric studies. In addition, most equilibrium constants reported for mononuclear complexes have been determined in solutions where the predominant species are polynuclear, a fact that the authors in some cases have neglected when interpreting the data (*cf.* Appendix A reviews of [1955PAN/HSE], [1963BIL/FUR], [1964NAB/KUD], [1972USH/SKO], [1971KIC/STE], [1989MOO], [2003SAW/SHA], [2004BEN/BOU]). Therefore these potentiometric data cannot be accepted by this review.

The present review uses the SIT to evaluate the equilibrium constants at zero ionic strength, $\log_{10}{}^*\beta^{\circ}_{n,m}$ ((VII.19), 298.15 K), for the reactions:

$$m\mathrm{Th}^{4+} + n\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th}_m(\mathrm{OH})_n^{4m-n} + n\mathrm{H}^+ \qquad \text{(VII.19)}$$

They are related to the conditional constants $\log_{10}{}^*\beta_{n,m}$ in an electrolyte medium MX or MX_2 by:

$$\log_{10}{}^*\beta^{\circ}_{n,m} = \log_{10}{}^*\beta_{n,m} - \Delta z^2 D + \Delta\varepsilon(n,m)_X\, m_X - n\log_{10} a_w \qquad \text{(VII.20)}$$

with

$$\Delta\varepsilon(n,m)_{\mathrm{X}} = \varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}, \mathrm{X}^-) + n\,\varepsilon(\mathrm{H}^+, \mathrm{X}^-) - m\,\varepsilon(\mathrm{Th}^{4+}, \mathrm{X}^-) \qquad \text{(VII.21)}$$

m_{X} is the molal concentration of anion X in the ionic medium MX or MX_2. The activity of water a_{w} is taken from Table B-1. As only positively charged ions are involved in Reactions (VII.19) and the SIT does not account for interactions between ions of the same charge sign, $\Delta\varepsilon(n,m)$ depends only on the anion of the medium electrolyte (X = ClO_4^-, NO_3^- or Cl^-) but is independent of the cation (M = Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}). The interaction coefficients for H^+ are taken from the previous NEA-TDB reviews; the values selected for the Th^{4+} ion are discussed in Section VI.3:

$$\varepsilon(\mathrm{H}^+, \mathrm{ClO}_4^-) = (0.14 \pm 0.01)\ \mathrm{kg{\cdot}mol^{-1}} \quad \varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4^-) = (0.70 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{H}^+, \mathrm{NO}_3^-) = (0.07 \pm 0.01)\ \mathrm{kg{\cdot}mol^{-1}} \quad \varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = (0.31 \pm 0.12)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{H}^+, \mathrm{Cl}^-) = (0.12 \pm 0.01)\ \mathrm{kg{\cdot}mol^{-1}} \quad \varepsilon(\mathrm{Th}^{4+}, \mathrm{Cl}^-) = (0.25 \pm 0.03)\ \mathrm{kg{\cdot}mol^{-1}}.$$

If sufficient data at different ionic strengths are available, the linear SIT regression (VII.22) is used for the extrapolation to $I = 0$:

$$\log_{10} {}^*\beta_{n,m} - n\log_{10} a_w - \Delta z^2 D = \log_{10} {}^*\beta^{\circ}_{n,m} - \Delta\varepsilon(n,m)_{\mathrm{X}}\, m_{\mathrm{X}} \qquad \text{(VII.22)}$$

In cases where the data are available only at one ionic strength or if they are too scattered to allow the application of Eq. (VII.22), $\log_{10} {}^*\beta^{\circ}_{n,m}$ is instead calculated with Eq. (VII.20) by using an estimate of $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}, \mathrm{X}^-)$ and $\Delta\varepsilon(n,m)_{\mathrm{MX}}$. The estimation of unknown $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}, \mathrm{X}^-)$ values will be discussed in Section VII.3.6.1.

VII.3.4.1 Polynuclear Th(IV) hydroxide complexes

The selection of data for the polynuclear Th(IV) hydroxide species is based exclusively on potentiometric studies where these complexes have been identified as major species. In the following sections, equilibrium constants in perchlorate ($\mathrm{NaClO_4}$), nitrate ($\mathrm{LiNO_3}$, $\mathrm{NaNO_3}$, $\mathrm{KNO_3}$) and chloride (NaCl) media have been evaluated simultaneously by using the SIT regression according to Eq. (VII.22) to obtain the equilibrium constant $\log_{10} \beta^{\circ}_{n,m}$ at zero ionic strength and the value of $\Delta\varepsilon(n,m)_{\mathrm{X}}$ for X = ClO_4^-, NO_3^- and Cl^-. In a few cases we have used the equilibrium constants for minor species to estimate their ionic strength dependence and to show the charge and size systematics of ion interaction coefficients.

VII.3.4.1.1 Dinuclear complexes

- **$\mathrm{Th_2(OH)_2^{6+}}$**

The complex $\mathrm{Th_2(OH)_2^{6+}}$ was found to be a major species in potentiometric studies in 1.0 and 3.0 M $\mathrm{NaClO_4}$ [1965BAE/MEY], [1968HIE/SIL], [1991GRE/LAG2], 0.5−4.0 M $\mathrm{NaNO_3}$ [1982MIL/SUR2], [1968DAN/MAG], 3.0 M $\mathrm{LiNO_3}$, $\mathrm{KNO_3}$ and $\mathrm{Mg(NO_3)_2}$ [1971MIL2] and 3.0 M NaCl [1968HIE/SIL] and in numerous studies of

Milić *et al*. in various chloride media: 0.5 − 3.0 M NaCl, LiCl and KCl [1981MIL2], [1981SUR/MIL], 0.25 − 1.5 M MCl_2 (M = Mg, Ca, Sr and Ba) [1982SUR/MIL].

Considering only the data in nitrate media from [1968DAN/MAG], [1971MIL2] and [1982MIL/SUR2] which agree very well with each other, the extrapolation to I = 0 with the SIT yields $\log_{10} {}^*\beta^{\circ}_{2,2}(\mathrm{Th_2(OH)_2^{6+}}) = -(6.1 \pm 0.2)$ (Table VII-8). The same value is obtained, if the linear SIT regression is applied to the data in LiCl, NaCl and KCl media, which are nearly all from the same group of authors [1981MIL2] [1981SUR/MIL], as those in nitrate media. The equilibrium constants in MCl_2 media (M = Mg, Ca, Sr and Ba) [1982SUR/MIL] are not included in the final data selection, because at $I < 2$ M the complex $\mathrm{Th_2(OH)_2^{6+}}$ is a minor species and hence the extrapolation to $I = 0$ is uncertain. The value of $\log_{10} {}^*\beta^{\circ}_{2,2}(\mathrm{Th_2(OH)_2^{6+}}) = -(5.4 \pm 0.2)$ obtained from the equilibrium constants in $NaClO_4$ solution (Table VII-8) is significantly different. However, there is no reason to discard the results of [1965BAE/MEY], [1968HIE/SIL], and [1991GRE/LAG2]. Simultaneous evaluation of all reported equilibrium constants in these studies (Figure VII-3), *i.e.* in $NaClO_4$, MNO_3 and MCl media (M = Li, Na and K), leads to:

$$\log_{10} {}^*\beta^{\circ}_{2,2}(\mathrm{Th_2(OH)_2^{6+}}) = -(5.9 \pm 0.5),$$

$$\Delta\varepsilon(2,2)_{\mathrm{ClO_4^-}} = (0.10 \pm 0.14)\ \mathrm{kg\cdot mol^{-1}} \text{ and } \varepsilon(\mathrm{Th_2(OH)_2^{6+}}, \mathrm{ClO_4^-}) = (1.22 \pm 0.24)\ \mathrm{kg\cdot mol^{-1}}$$

$$\Delta\varepsilon(2,2)_{\mathrm{NO_3^-}} = (0.21 \pm 0.11)\ \mathrm{kg\cdot mol^{-1}} \text{ and } \varepsilon(\mathrm{Th_2(OH)_2^{6+}}, \mathrm{NO_3^-}) = (0.69 \pm 0.26)\ \mathrm{kg\cdot mol^{-1}}$$

$$\Delta\varepsilon(2,2)_{\mathrm{Cl^-}} = (0.14 \pm 0.15)\ \mathrm{kg\cdot mol^{-1}} \text{ and } \varepsilon(\mathrm{Th_2(OH)_2^{6+}}, \mathrm{Cl^-}) = (0.40 \pm 0.16)\ \mathrm{kg\cdot mol^{-1}}.$$

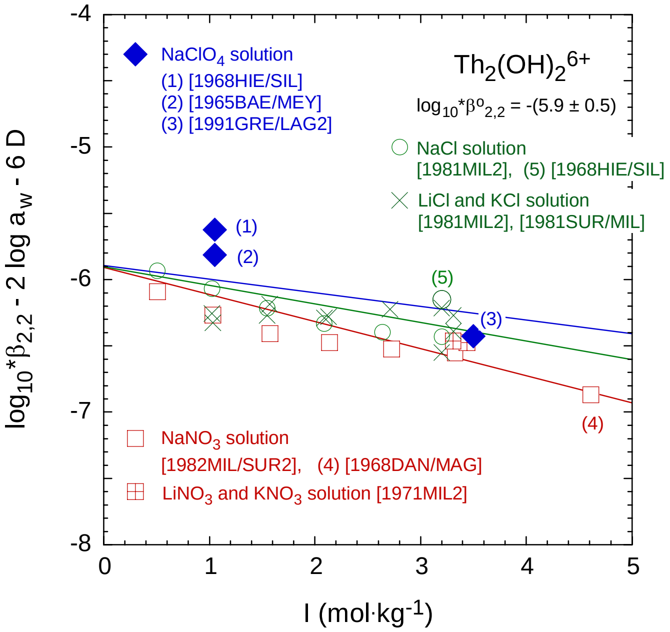
These values are selected by the present review. The uncertainties correspond to the 2σ level.

Table VII-8: Evaluation of $\log_{10} {}^*\beta^{\circ}_{2,2}(\mathrm{Th_2(OH)_2^{6+}})$ and Δε(2,2) by applying the SIT separately to equilibrium constants in perchlorate, nitrate and chloride media at 25°C.

Reference	Media	$\log_{10} {}^*\beta^{\circ}_{2,2}$	Δε(2,2) (kg·mol^{-1})
Perchlorate media		– 5.4 ± 0.2	0.29 ± 0.06
[1965BAE/MEY]	1.0 M $NaClO_4$ (Data from [1954KRA/HOL])		
[1968HIE/SIL]	1.0 M $NaClO_4$ (Data from [1954HIE])		
[1991GRE/LAG2]	3.0 M $NaClO_4$		
Nitrate media		– 6.1 ± 0.2	0.15 ± 0.04
[1982MIL/SUR2]	0.5 – 3.0 M $NaNO_3$		
[1968DAN/MAG]	4.0 M $NaNO_3$		
[1971MIL2]	3.0 M $LiNO_3$		
[1971MIL2]	3.0 M KNO_3		
Chloride media (MCl)		– 6.1 ± 0.2	0.08 ± 0.05
[1968HIE/SIL]	3.0 M NaCl		
[1981MIL2]	0.5 – 3.0 M NaCl		
[1981MIL2]	3.0 M LiCl		
[1981MIL2]	3.0 M KCl		
[1981SUR/MIL]	0.5 – 3.0 M LiCl		
[1981SUR/MIL]	0.5 – 3.0 M KCl		
Chloride media (MCl_2)		– 6.4 ± 0.2#	0.00 ± 0.06#
[1982SUR/MIL]	0.25 – 1.5 M $MgCl_2$		
[1982SUR/MIL]	0.25 – 1.5 M $CaCl_2$		
[1982SUR/MIL]	0.25 – 1.5 M $SrCl_2$,		
[1982SUR/MIL]	0.25 – 1.5 M $BaCl_2$		

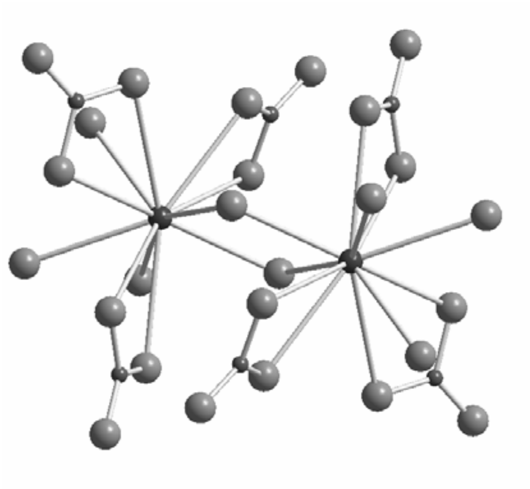
Not included in the final data selection, because $\mathrm{Th_2(OH)_2^{6+}}$ is a minor complex at $I < 2$ M; only the equilibrium constants at higher ionic strength are well established.

Figure VII-3: Application of the SIT to equilibrium constants reported for the reaction: $2Th^{4+} + 2H_2O(l) \rightleftharpoons Th_2(OH)_2^{6+} + 2H^+$ in perchlorate, nitrate and chloride (MCl, M = Li, Na, K) media at 25°C (data in $NaClO_4$ from [1968HIE/SIL], [1965BAE/MEY], [1991GRE/LAG2], in $NaNO_3$ from [1982MIL/SUR2], [1968DAN/MAG], in $LiNO_3$ and KNO_3 from [1971MIL2], in NaCl from [1981MIL2] and [1968HIE/SIL], and in LiCl and KCl from [1981MIL2], [1981SUR/MIL]).



The structure of the complex $Th_2(OH)_2^{6+}$ in the compound $Th_2(OH)_2(NO_3)_6(OH_2)_6$ (Figure VII-4) has been determined by Johansson [1968JOH]. The Th–Th distance is 3.99 Å, the Th–OH distances 2.33 and 2.39 Å. In addition there are three coordinated water at distances of 2.49, 2.53 and 2.57 Å. There are also three bidentate coordinated NO_3^- ions with an average Th–O distance of (2.65 ± 0.10) Å. This structure is used as a model for the interpretation of the solution structures of hydrolysed thorium solutions based on large angle X-ray scattering data as discussed in [1968JOH2]. In the test solutions where there is approximately one coordinated hydroxide per Th, Johansson finds a Th–Th distance of 3.94 Å and Th–O bond distances of about 2.50 Å. There is also evidence for coordinated nitrate groups. These data are not sufficient to provide a unique structure model but they are not inconsistent with the structure of the complex found in the solid state. In a recent study Wilson *et al.* [2007WIL/SKA] have determined the structure of $[Th_2(\mu\text{-}OH)_2(NO_3)_6(OH_2)_6]\cdot H_2O$, which is identical to that given by [1968JOH]. They have also determined the structures of two additional compounds $[Th_2(\mu\text{-}OH)_2(NO_3)_4(OH_2)_8](NO_3)_2$ and $[Th_2(\mu\text{-}OH)_2Cl_2(OH_2)_{12}]Cl_4{\cdot}2H_2O$ which also contain the "$Th_2(\mu\text{-}OH)_2$" unit.

Figure VII-4: Structure of $Th_2(OH)_2(NO_3)_6(OH_2)_6(cr)$.



- **$Th_2(OH)_3^{5+}$**

The complex $Th_2(OH)_3^{5+}$ has been observed as major species in chloride media, *i.e.*, in 3.0 M NaCl [1968HIE/SIL] 0.5 − 3.0 M NaCl, LiCl and KCl [1981MIL2], [1981SUR/MIL], and 0.25 − 1.5 M MCl_2 (M = Mg, Ca, Sr and Ba) [1982SUR/MIL]. It is also included in models for 3.0 M KNO_3 [1971MIL2] and 3.0 M $NaClO_4$ [1991GRE/LAG2], in the latter study only as a minor species.

Using the SIT for the extrapolation to zero ionic strength (Figure VII-5), the equilibrium constants in 0.5 − 3.0 M MCl media (M = Li, Na and K) from [1981MIL2], [1981SUR/MIL], [1968HIE/SIL] and those in 0.25 − 1.5 M MCl_2 media (M = Mg, Ca, Sr and Ba) from [1982SUR/MIL] lead to consistent $\log_{10}{}^*\beta^{\circ}_{3,2}$ and $\Delta\varepsilon(3,2)_{Cl^-}$ values (*cf.* Appendix A, review of [1981MIL2], [1981SUR/MIL], [1982SUR/MIL]) which are selected by this review:

$$\log_{10}{}^*\beta^{\circ}_{3,2}(Th_2(OH)_3^{5+}) = -(6.8 \pm 0.2).$$

$$\Delta\varepsilon(3,2)_{Cl^-} = (0.15 \pm 0.06)\ kg{\cdot}mol^{-1} \text{ and } \varepsilon(Th_2(OH)_3^{5+}, Cl^-) = (0.29 \pm 0.09)\ kg{\cdot}mol^{-1}.$$

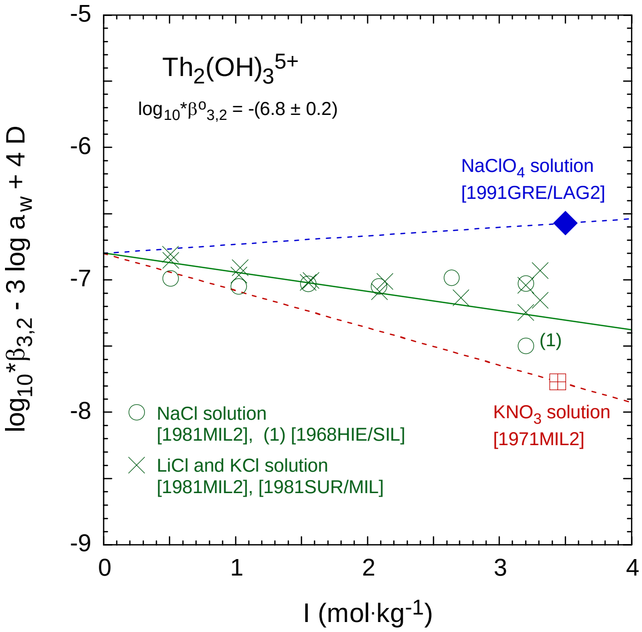
Combination of the selected equilibrium constant at $I = 0$ with the experimental values in 3.44 m KNO_3 and 3.50 m $NaClO_4$ (Figure VII-5) yields:

$$\Delta\varepsilon(3,2)_{ClO_4^-} = -(0.07 \pm 0.06)\ kg{\cdot}mol^{-1};\ \varepsilon(Th_2(OH)_3^{5+}, ClO_4^-) = (0.91 \pm 0.21)\ kg{\cdot}mol^{-1}$$

$$\Delta\varepsilon(3,2)_{NO_3^-} = (0.28 \pm 0.06)\ kg{\cdot}mol^{-1};\ \varepsilon(Th_2(OH)_3^{5+}, NO_3^-) = (0.69 \pm 0.25)\ kg{\cdot}mol^{-1}.$$

The uncertainties correspond to the 2σ level.

Figure VII-5: Application of the SIT to equilibrium constants reported for the reaction: $2Th^{4+} + 3H_2O(l) \rightleftharpoons Th_2(OH)_3^{5+} + 3H^+$ in perchlorate, nitrate and chloride (MCl, M = Li, Na, K) media at 25°C (data in $NaClO_4$ from [1991GRE/LAG2], in KNO_3 from [1971MIL2], in NaCl from [1981MIL2], [1968HIE/SIL], and in LiCl and KCl from [1981MIL2], [1981SUR/MIL]).



- **Other dinuclear complexes**

The dinuclear complexes $Th_2(OH)^{7+}$ proposed in [1959HIE/SIL2], [1968DAN/MAG] and $Th_2(OH)_4^{4+}$ proposed in [1968DAN/MAG] for a 4.0 M $NaClO_4$ medium are not selected by the present review.

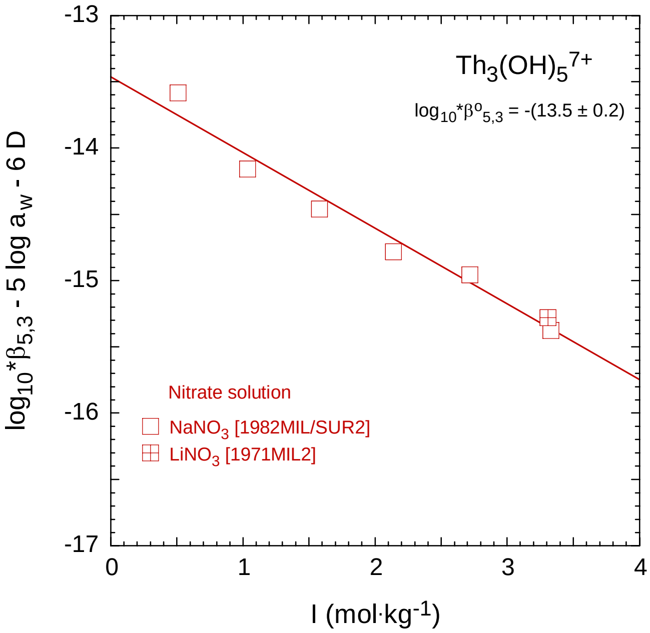
VII.3.4.1.2 Trinuclear complexes

- **$Th_3(OH)_5^{7+}$**

The complex $Th_3(OH)_5^{7+}$ has been included in models for nitrate media, *i.e.*, 0.5 − 3.0 M $NaNO_3$ [1982MIL/SUR2], 3.0 M $LiNO_3$ and 3.0 M $Mg(NO_3)_2$ [1971MIL2]. Extrapolation of the equilibrium constants in 0.5 to 3.0 M $NaNO_3$ [1982MIL/SUR2] and 3.0 M $LiNO_3$ [1971MIL2] to I = 0 with the SIT (Figure VII-6) leads to:

$\log_{10}{}^*\beta^{\circ}_{5,3}(\text{Th}_3(\text{OH})_5^{7+}) = -(13.5 \pm 0.2)$, $\Delta\varepsilon(5,3)_{\text{NO}_3^-} = (0.57 \pm 0.07)$ kg·mol^{-1} and $\varepsilon(\text{Th}_3(\text{OH})_5^{7+}, \text{NO}_3^-) = (1.15 \pm 0.37)$ kg·mol^{-1}.

Figure VII-6: Application of the SIT to equilibrium constants reported for the reaction: $3\text{Th}^{4+} + 5\text{H}_2\text{O(l)} \rightleftharpoons \text{Th}_3(\text{OH})_5^{7+} + 5\text{H}^+$ in nitrate media at 25°C, (data in $NaNO_3$ from [1982MIL/SUR2], in $LiNO_3$ from [1971MIL2]).



However, as shown by Baes and Mesmer [1976BAE/MES], the potentiometric data in 3.0 M $LiNO_3$ and 3.0 M $Mg(NO_3)_2$ [1971MIL2] can be described just as well with the model appropriate for $NaClO_4$ solution, including the species (2,2), (8,4) and (15,6). These stoichiometries correspond to structures that have been found both in solution and solid state. The stoichiometry (2,2) corresponds to structures that have been found in the solid state and solution [1968JOH], [1968JOH2] and the stoichiometry (8,4) has been found in solid state and solution for Zr(IV), an analogue to Th(IV), see Section VII.3.4.1.3 and Figure VII-8. There is no structural evidence for tri-nuclear Th(IV) hydroxide complexes. This review has therefore preferred the interpretation of [1976BAE/MES] of hydrolysis data from nitrate media and not selected the (5,3) species.

- **Other trinuclear complexes**

Other trinuclear complexes like $\mathrm{Th_3(OH)_3^{9+}}$ proposed in models for 3.0 M $\mathrm{LiNO_3}$ [1971MIL2] and 3.0 M NaCl [1968HIE/SIL], $\mathrm{Th_3(OH)^{11+}}$ in 3.0 M NaCl [1968HIE/SIL] or $\mathrm{Th_3(OH)_6^{6+}}$ in 4.0 M $\mathrm{NaNO_3}$ [1968DAN/MAG] are not considered to be well established.

VII.3.4.1.3 Tetranuclear complexes

- **$\mathrm{Th_4(OH)_8^{8+}}$**

The complex $\mathrm{Th_4(OH)_8^{8+}}$ was found to be a major species in the potentiometric studies in 1.0 M $\mathrm{NaClO_4}$ [1965BAE/MEY], [1968HIE/SIL], [2000EKB/ALB], 3.0 M $\mathrm{NaClO_4}$ [1991GRE/LAG2] and 4.0 M $\mathrm{NaClO_4}$ [1968DAN/MAG]. The conditional equilibrium constants determined in these studies are in reasonable agreement and the extrapolation to zero ionic strength with the SIT (Figure VII-7) yields:

$$\log_{10}{}^{*}\beta^{\circ}_{8,4}\,(\mathrm{Th_4(OH)_8^{8+}}) = -(20.4 \pm 0.4)$$

$\Delta\varepsilon(8,4)_{\mathrm{ClO_4^-}} = (0.01 \pm 0.08)\ \mathrm{kg\cdot mol^{-1}}$ and $\varepsilon(\mathrm{Th_4(OH)_8^{8+}}, \mathrm{ClO_4^-}) = (1.69 \pm 0.42)\ \mathrm{kg\cdot mol^{-1}}$. These values, with the uncertainties given as 2σ, are selected by the present review.

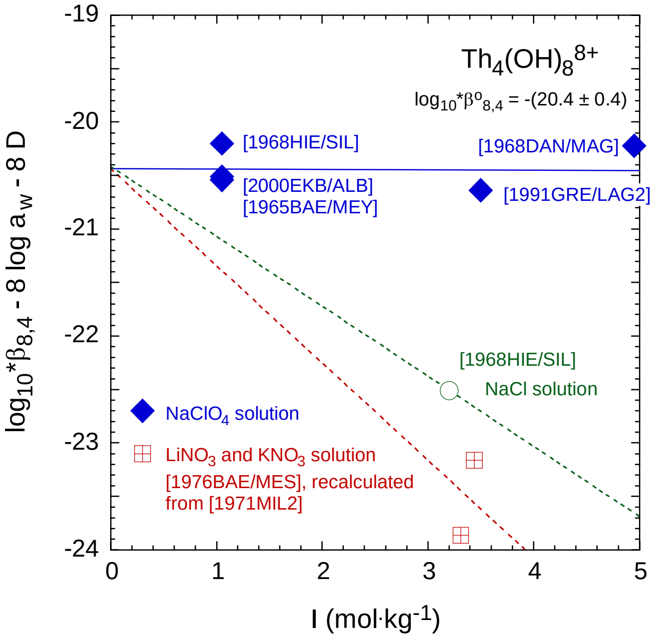
Hietanen and Sillén [1968HIE/SIL] tested different speciation models for their data in 3.0 M NaCl, including $\mathrm{Th_4(OH)_8^{8+}}$ as minor complex. The calculated value of $\log_{10}{}^{*}\beta_{8,4}$ is consistent for the different models. The value of $\log_{10}{}^{*}\beta_{8,4} = -(21.1 \pm 0.2)$ in 3 M NaCl can be used to evaluate the SIT coefficients

$$\Delta\varepsilon(8,4)_{\mathrm{Cl^-}} = 0.66 \pm 0.14\ \mathrm{kg\cdot mol^{-1}} \text{ and } \varepsilon(\mathrm{Th_4(OH)_8^{8+}}, \mathrm{Cl^-}) = (0.70 \pm 0.20)\ \mathrm{kg\cdot mol^{-1}}.$$

Baes and Mesmer [1976BAE/MES] re-evaluated the potentiometric data of Milić [1971MIL2] in 3.0 M $\mathrm{LiNO_3}$, 3.0 M $\mathrm{KNO_3}$ and 3.0 M $\mathrm{Mg(NO_3)_2}$ with the model selected for perchlorate media including the species (2,2), (8,4) and (15,6). The resulting standard deviations $\sigma(\bar{n}_{\mathrm{OH}})$ were found to be very small (0.0051, 0.0084 and 0.0029, respectively) and the calculated equilibrium constants for the complexes (2,2) and (15,6), which are also included in the models originally proposed by Milić [1971MIL2], differ only slightly from the $\log_{10}{}^{*}\beta_{2,2}$ and $\log_{10}{}^{*}\beta_{15,6}$ values calculated in [1971MIL2] in combination with the species (5,3) and (3,3) in 3 M $\mathrm{LiNO_3}$, (3,2) in 3 M $\mathrm{KNO_3}$ and (5,3) in 1.5 M $\mathrm{Mg(NO_3)_2}$. Therefore, the $\log_{10}{}^{*}\beta_{8,4}$ values proposed by [1976BAE/MES] appear also to be reasonable. In combination with $\log_{10}{}^{*}\beta^{\circ}_{8,4} = -(20.4 \pm 0.4)$ derived from the equilibrium constants in 1.0 to 4.0 M $\mathrm{NaClO_4}$, the equilibrium constants in 3.0 M $\mathrm{LiNO_3}$ and $\mathrm{KNO_3}$ proposed by [1976BAE/MES] lead to:

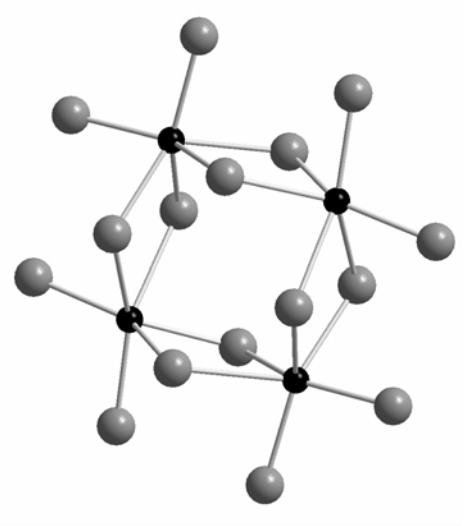
$$\Delta\varepsilon(8,4)_{\mathrm{NO_3^-}} = (0.91 \pm 0.14)\ \mathrm{kg\cdot mol^{-1}} \text{ and } \varepsilon(\mathrm{Th_4(OH)_8^{8+}}, \mathrm{NO_3^-}) = (1.59 \pm 0.51)\ \mathrm{kg\cdot mol^{-1}}.$$

Figure VII-7: Application of the SIT to equilibrium constants reported for the reaction: $4Th^{4+} + 8H_2O(l) \rightleftharpoons Th_4(OH)_8^{8+} + 8H^+$ in perchlorate, nitrate and chloride media at 25°C (data in $NaClO_4$ from [1968HIE/SIL], [1965BAE/MEY], [2000EKB/ALB], [1991GRE/LAG2], [1968DAN/MAG], data in $LiNO_3$ and KNO_3 recalculated by [1976BAE/MES] from [1971MIL2], and in NaCl from [1968HIE/SIL]).



There are no known structures of $Th_4(OH)_8^{8+}$, but in a large angle X-ray diffraction of a concentrated solution of hydrolysed Th(IV), Bacon and Brown [1969BAC/BRO] found a single large Th−Th interaction in the radial distribution curve that they interpreted as being due to a tetrahedral "Th_4" unit and suggested that the Th atoms are linked by six OH-groups along the tetrahedral sides, resulting in the stoichiometry $Th_4(OH)_6^{10+}$. A tetrahedral Th_4 arrangement is also found in the rather common "cubane"-type structure motifs and the data in [1969BAC/BRO] are also compatible with the complex $Th_4(\mu\text{-}OH)_4(OH)_4^{8+}$. A different geometry for Zr(IV) and Hf(IV) complexes with the stoichiometry $M_4(OH)_8^{8+}$ is found both in the solid state [1956CLE/VAU] and in solution [1960MUH/VAU] and in view of the chemical similarities between these ions and Th(IV), the $M_4(OH)_8^{8+}$ ion, with M = Zr or Hf, this may be an alternative structural model also for $Th_4(OH)_8^{8+}$. Muha and Vaughan [1960MUH/VAU] suggested a structure based on large angle X-ray scattering data, which consists of a square arrangement of the metal ions that are linked by four double hydroxide bridges as shown in Figure VII-8. The metal−metal and the metal−OH distances are 3.57 Å and 2.24 Å, respectively, both comparable with the typical Th−Th distance in polymers [1968JOH2] of about 3.95 Å and the Th−OH distance of about 2.50 Å, if consideration is taken of the difference in ionic radius of 0.2 Å between Th^{4+} and Zr^{4+} and Hf^{4+}. There is a second metal−metal distance at around 5 Å in this structure, *cf.* Figure VII-8. Åberg and Glaser [1993ABE/GLA] have studied solutions containing the tetramer $Zr_4(OH)_8^{8+}$ using ^{17}O and ^{1}H NMR spectroscopy. They observed an ^{17}O signal corresponding to 2O per Zr, that they assigned to a terminal water ligand, this review suggests that the signal refers to the bridging groups. The proton data indicate that there are two slowly exchanging protons per Zr and contrary to the suggestion in [1993ABE/GLA], this review suggests that they refer to the bridging hydroxide groups and that coordinated water molecules are in rapid exchange with the bulk solvent. The coordination number of Zr is at least six which should give the stoichiometry of the tetramer as $[Zr_4(OH)_8(OH_2)_{16}]^{8+}$.

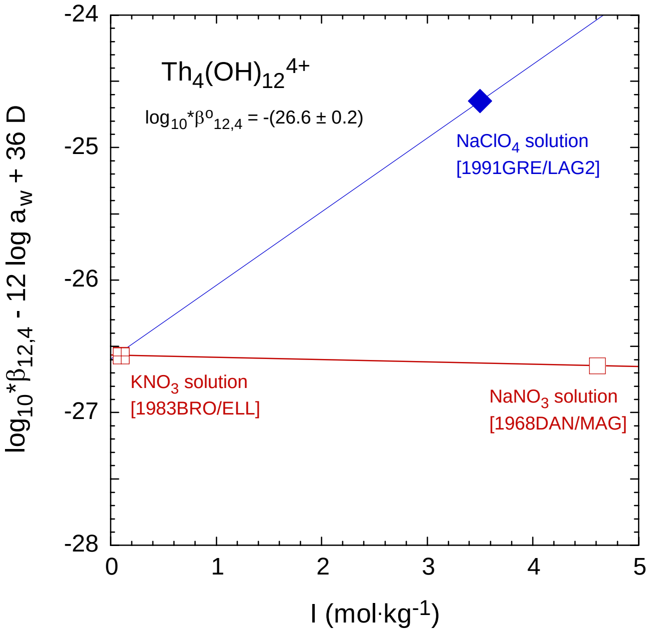
Figure VII-8: The structure of the $Zr_4(OH)_8^{8+}$ core in the crystal structures of zirconyl chloride and bromide octahydrates [1956CLE/VAU]. The hydrogen atoms cannot be located, but the bridges are formed by OH groups. The Zr ions (black) are coplanar.



- **$Th_4(OH)_{12}^{4+}$**

Equilibrium constants for the complex $Th_4(OH)_{12}^{4+}$ were first calculated by [1968DAN/MAG] ($\log_{10} {}^*\beta_{12,4} = -(37.21 \pm 0.06)$ in 4.0 M $NaNO_3$) and later by [1983BRO/ELL] ($\log_{10} {}^*\beta_{12,4} = -(30.55 \pm 0.03)$ in 0.1 M KNO_3) and [1991GRE/LAG2] ($\log_{10} {}^*\beta_{12,4} = -(34.9 \pm 0.1)$ in 3.0 M $NaClO_4$). It should be noted that this complex is predominant at pH values close to the onset of precipitation (pH 3.5−4.5). As potentiometric titrations are usually not continued up to pH values where precipitation occurs, it is not surprising that equilibrium constants for $\mathrm{Th_4(OH)_{12}^{4+}}$ are only reported in a few studies. On the other hand, this complex plays an important role in saturated solutions equilibrated with $\mathrm{Th(OH)_4}$(am) or $\mathrm{ThO_2}$(am, hyd). Its formation constant at $I = 0$ and ion interaction coefficients are therefore important for the reinterpretation made by this review of the solubility data in 0.1 and 0.5 M $\mathrm{NaClO_4}$ [1964NAB/KUD], [1987RYA/RAI], [1989MOO], in 0.1, 0.6, 1.0, 3.2 and 6.0 m NaCl [2000RAI/MOO], [1997RAI/FEL], [1991FEL/RAI] and in 1.0, 1.82 and 3.0 m $\mathrm{MgCl_2}$ [1997RAI/FEL] in the pH range 3.5 to 5.5 (*cf.* Section VII.4.1.1).

Figure VII-9: Application of the SIT to equilibrium constants reported for the reaction: $4\mathrm{Th^{4+}} + 12\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th_4(OH)_{12}^{4+}} + 12\mathrm{H^+}$ in perchlorate and nitrate media at 25°C (data in $\mathrm{NaClO_4}$ from [1991GRE/LAG2], data in $\mathrm{KNO_3}$ from [1983BRO/ELL], and in NaCl from [1968DAN/MAG]).



The application of the linear SIT regression to the equilibrium constants reported in [1968DAN/MAG], [1983BRO/ELL] and [1991GRE/LAG2] (Figure VII-9) yields:

$$\log_{10}{}^*\beta^o_{12,4}(\mathrm{Th_4(OH)_{12}^{4+}}) = -(26.6 \pm 0.2)$$

$$\Delta\varepsilon(12,4)_{\mathrm{ClO_4^-}} = -(0.56 \pm 0.06)\ \mathrm{kg \cdot mol^{-1}};\ \varepsilon(\mathrm{Th_4(OH)_{12}^{4+}}, \mathrm{ClO_4^-}) = (0.56 \pm 0.42)\ \mathrm{kg \cdot mol^{-1}}$$

$$\Delta\varepsilon(12,4)_{\mathrm{NO_3^-}} = (0.02 \pm 0.05)\ \mathrm{kg \cdot mol^{-1}};\ \varepsilon(\mathrm{Th_4(OH)_{12}^{4+}}, \mathrm{NO_3^-}) = (0.42 \pm 0.50)\ \mathrm{kg \cdot mol^{-1}}.$$

These values are selected by this review. As only these few data are available and the uncertainties given in the original papers, less than ±0.1 $\log_{10}$-units, seem to be underestimated, the uncertainty of $\log_{10}{}^{*}\beta^{\circ}_{12,4}$ is increased in the present review to ±0.2 $\log_{10}$-units.

VII.3.4.1.4 Hexanuclear complexes

The hexanuclear complexes derived from potentiometric studies have either the stoichiometry $\mathrm{Th_6(OH)_{15}^{9+}}$ (in 1.0 M $\mathrm{NaClO_4}$ [1965BAE/MEY], [1968HIE/SIL], [2000EKB/ALB], 0.1 M $\mathrm{KNO_3}$ [1983BRO/ELL], 3.0 M $\mathrm{KNO_3}$ [1971MIL2] and 0.5 − 3.0 M $\mathrm{NaNO_3}$ [1982MIL/SUR2]) or $\mathrm{Th_6(OH)_{14}^{10+}}$ (in 3.0 M NaCl [1968HIE/SIL]). This was confirmed by calculations of Baes and Mesmer [1976BAE/MES]. In a later study in 3.0 M $\mathrm{NaClO_4}$ [1991GRE/LAG2], it was not possible to decide which of these two hexanuclear complexes was formed. Both complexes improved the fits when included in different models. The equilibrium constant for the complex $\mathrm{Th_6(OH)_{15}^{9+}}$ which is also included in the model for 1.0 M $\mathrm{NaClO_4}$ can be used for the estimation of ion interaction coefficients in $\mathrm{NaClO_4}$ solution.

- **$\mathrm{Th_6(OH)_{15}^{9+}}$**

The application of the SIT to the reported $\log_{10}{}^{*}\beta_{15,6}$ values (Figure VII-10) shows that the equilibrium constant of [2000EKB/ALB] in 1.0 M $\mathrm{NaClO_4}$ is 2.5−3 $\log_{10}$-units lower than those of [1965BAE/MEY] and [1968HIE/SIL] in the same medium, while those of [1983BRO/ELL] and [1971MIL2] in 0.1 and 3.0 M $\mathrm{KNO_3}$ are 2−3 $\log_{10}$-units higher than the data of [1982MIL/SUR2] in 0.5−3.0 M $\mathrm{NaNO_3}$. The reason for these discrepancies is not clear. A simultaneous fit including all data in perchlorate and nitrate media leads to: $\log_{10}{}^{*}\beta^{\circ}_{15,6}(\mathrm{Th_6(OH)_{15}^{9+}}) = -(36.8 \pm 2.5)$, $\Delta\varepsilon(15,6)_{\mathrm{ClO_4^-}} = -(0.08 \pm 0.71)$ kg·mol^{-1} and $\Delta\varepsilon(15,6)_{\mathrm{NO_3^-}} = (1.39 \pm 0.32)$ kg·mol^{-1}. The large uncertainties (2σ) are mainly due to the equilibrium constants of [1983BRO/ELL] and [2000EKB/ALB]. If these values are excluded and the linear SIT extrapolation is applied in separate fits of: (a) the data of [1965BAE/MEY], [1968HIE/SIL] and [1991GRE/LAG2] in 1.0 and 3.0 M $\mathrm{NaClO_4}$ and (b) of those of [1982MIL/SUR2] in 0.5−3.0 M $\mathrm{NaNO_3}$, the following values are obtained (dashed lines in Figure VII-10): (a): $\log_{10}{}^{*}\beta^{\circ}_{15,6}(\mathrm{Th_6(OH)_{15}^{9+}}) = -(36.3 \pm 0.5)$ and $\Delta\varepsilon(15,6)_{\mathrm{ClO_4^-}} = -(0.07 \pm 0.14)$ kg·mol^{-1} (b): $\log_{10}{}^{*}\beta^{\circ}_{15,6}(\mathrm{Th_6(OH)_{15}^{9+}}) = -(37.4 \pm 0.6)$ and $\Delta\varepsilon(15,6)_{\mathrm{NO_3^-}} = (1.37 \pm 0.17)$ kg·mol^{-1}.

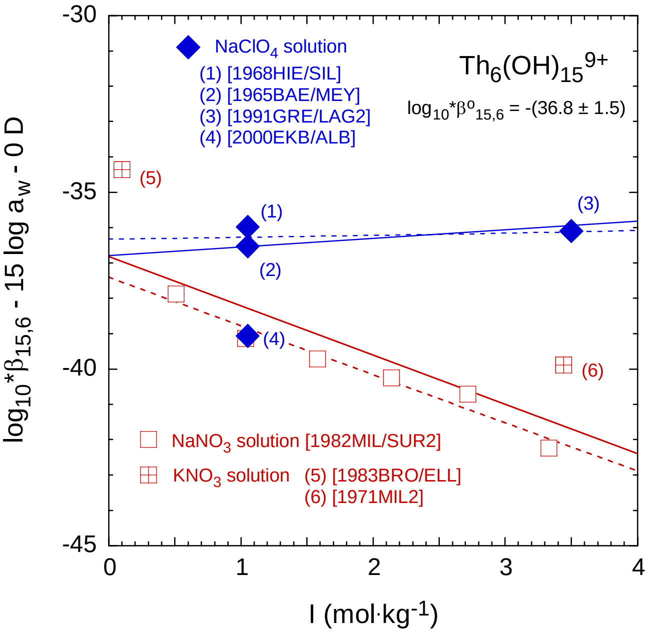
The present review selects the mean value of $\log_{10}{}^{*}\beta^{\circ}_{15,6}$ and excludes the data of [1983BRO/ELL] and [2000EKB/ALB] (solid lines in Figure VII-10), leading to following values:

$$\log_{10}{}^{*}\beta^{\circ}_{15,6}(\mathrm{Th_6(OH)_{15}^{9+}}) = -(36.8 \pm 1.5)$$

$$\Delta\varepsilon(15,6)_{\mathrm{ClO_4^-}} = -(0.25 \pm 0.40)\ \mathrm{kg\cdot mol^{-1}};\ \varepsilon(\mathrm{Th_6(OH)_{15}^{9+}}, \mathrm{ClO_4^-}) = (1.85 \pm 0.74)\ \mathrm{kg\cdot mol^{-1}}$$

$$\Delta\varepsilon(15,6)_{\mathrm{NO_3^-}} = (1.39 \pm 0.23)\ \mathrm{kg\cdot mol^{-1}};\ \varepsilon(\mathrm{Th_6(OH)_{15}^{9+}}, \mathrm{NO_3^-}) = (2.20 \pm 0.77)\ \mathrm{kg\cdot mol^{-1}}.$$

Figure VII-10: Application of the SIT to equilibrium constants reported for the reaction: $6Th^{4+} + 15H_2O(l) \rightleftharpoons Th_6(OH)_{15}^{9+} + 15H^+$ in perchlorate and nitrate media at 25°C (data in $NaClO_4$ from [1968HIE/SIL], [1965BAE/MEY], [2000EKB/ALB], [1991GRE/LAG2], in $NaNO_3$ from [1982MIL/SUR2] and in KNO_3 from [1971MIL2], [1983BRO/ELL]).



- **$Th_6(OH)_{14}^{10+}$**

The complex $Th_6(OH)_{14}^{10+}$ has been observed as a major species only in 3.0 M NaCl [1968HIE/SIL]. As mentioned above, it has been proposed as a possible species in 3.0 M $NaClO_4$ [1991GRE/LAG2] as an alternative to the complex $Th_6(OH)_{15}^{9+}$. The latter complex was selected both by Baes and Mesmer [1976BAE/MES] and the present review for the hydrolysis model in $NaClO_4$ media. In order to estimate the equilibrium constant at zero ionic strength, the expected ranges of the $\varepsilon(Th_6(OH)_{14}^{10+}, X^-)$ values have been estimated from Figure VII-13 in Section VII.3.6.1.

Using these estimates (Table VII-9) the conditional equilibrium constants in 3.0 M NaCl ($\log_{10}{}^*\beta_{14,6} = -(36.4 \pm 0.1)$ [1968HIE/SIL]) and 3.0 M $NaClO_4$ ($\log_{10}{}^*\beta_{14,6} = -(33.67 \pm 0.05)$ [1991GRE/LAG2]) lead to consistent values of $\log_{10}{}^*\beta^o_{14,6}(Th_6(OH)_{14}^{10+}) = -(36.7 \pm 1.0)$ and $-(36.9 \pm 1.1)$, respectively. The mean value, with an uncertainty covering the whole range of expectation, is selected by the present review:

$$\log_{10} {}^{*}\beta^{\circ}_{14,6}(\mathrm{Th_6(OH)_{14}^{10+}}) = -(36.8 \pm 1.2)$$

$$\varepsilon(\mathrm{Th_6(OH)_{14}^{10+}}, \mathrm{Cl^-}) = (0.8 \pm 0.3)\ \mathrm{kg{\cdot}mol^{-1}}$$

$$\varepsilon(\mathrm{Th_6(OH)_{14}^{10+}}, \mathrm{ClO_4^-}) = (2.2 \pm 0.3)\ \mathrm{kg{\cdot}mol^{-1}}.$$

Table VII-9: SIT coefficients $\varepsilon(\mathrm{Th_6(OH)_{14}^{10+}}, \mathrm{X^-})$ and $\varepsilon(\mathrm{Th_6(OH)_{15}^{9+}}, \mathrm{X^-})$ and $(\Delta\varepsilon)_X$ ($\mathrm{kg{\cdot}mol^{-1}}$) for the reaction $\mathrm{Th_6(OH)_{14}^{10+}} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th_6(OH)_{15}^{9+}} + \mathrm{H^+}$.

	$\mathrm{ClO_4^-}$	$\mathrm{NO_3^-}$	$\mathrm{Cl^-}$
$\varepsilon(\mathrm{Th_6(OH)_{14}^{10+}}, \mathrm{X^-})$	2.2 ± 0.3 [a]	2.9 ± 0.5 [a]	0.8 ± 0.3 [a]
$\varepsilon(\mathrm{Th_6(OH)_{15}^{9+}}, \mathrm{X^-})$	1.85 ± 0.74	2.20 ± 0.77	0.7 ± 0.3 [a]
$(\Delta\varepsilon)_X$	− 0.21 ± 0.3 [b]	− 0.63 ± 0.3 [b]	0.02 ± 0.3 [b]

a: Estimated from the correlations between $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}, \mathrm{X^-})$ and the charge $z = 4m–n$ of the thorium complex. (*cf.* Section VII.3.6.1, Figure VII-13).

b: Uncertainties of $\Delta\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}, \mathrm{X^-})$ for $z = 4m–n = 9$ and $z = 10$ are estimated from Figure VII-13 in Section VII.3.6.1. (Uncertainties calculated by error propagation would be much too large.)

- **Comments on the coexistence of $\mathbf{Th_6(OH)_{15}^{9+}}$ and $\mathbf{Th_6(OH)_{14}^{10+}}$**

Note that the present review has accepted the data interpretation based on models including (15,6) as the only hexanuclear complex in perchlorate and nitrate media and (14,6) in 3.0 M NaCl. As a consequence the question arises whether the selection of equilibrium constants for both complexes, $\log_{10} {}^{*}\beta^{\circ}_{15,6}(\mathrm{Th_6(OH)_{15}^{9+}})$ and $\log_{10} {}^{*}\beta^{\circ}_{14,6}(\mathrm{Th_6(OH)_{14}^{10+}})$, is consistent with the speciation models accepted for the evaluation of the original data in the corresponding media. Therefore, the conditional equilibrium constants for the reaction:

$$\mathrm{Th_6(OH)_{14}^{10+}} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th_6(OH)_{15}^{9+}} + \mathrm{H^+} \qquad \text{(VII.23)}$$

$$\log_{10} \beta\ \text{(VII.23)} = \log_{10}[\mathrm{H^+}] + \log_{10} \frac{[\mathrm{Th_6(OH)_{15}^{9+}}]}{[\mathrm{Th_6(OH)_{14}^{10+}}]}$$

$$= \log_{10} {}^{*}\beta^{\circ}_{15,6} - \log_{10} {}^{*}\beta^{\circ}_{14,6} - 18\,D - (\Delta\varepsilon)_X\ m_X \qquad \text{(VII.24)}$$

and the ratio $[\mathrm{Th_6(OH)_{15}^{9+}}]:[\mathrm{Th_6(OH)_{14}^{10+}}]$ are calculated for the different media and different ionic strengths. For this purpose the unknown SIT coefficients for (14,6) in perchlorate and nitrate media and for (15,6) in chloride media are estimated from the dependence of $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}, \mathrm{X^-})$ on the charge of the thorium species ($z = 4m-n$) (*cf.* Figure VII-13 in Section VII.3.6.1). The SIT coefficients and $\Delta\varepsilon(\mathrm{VII.23})_X$ values for the different anions $\mathrm{X^-}$ are given in Table VII-9.

As the speciation diagrams derived from the potentiometric data show the hexanuclear complexes as predominant species in the range $-\log_{10}[\mathrm{H^+}] = 3.5-4$, the ratio $[\mathrm{Th_6(OH)_{15}^{9+}}]:[\mathrm{Th_6(OH)_{14}^{10+}}]$ is calculated at $-\log_{10}[\mathrm{H^+}] = 3.8$. The results

$[\mathrm{Th_6(OH)_{15}^{9+}}]$:$[\mathrm{Th_6(OH)_{14}^{10+}}]$ = 1:6 in 3 M NaCl, 24:1 in 3 M $NaNO_3$ and 1:1 in 3 M $NaClO_4$ are consistent with the speciation models including (14,6) as predominant hexanuclear complex in 3 M NaCl [1968HIE/SIL], [1976BAE/MES] and (15,6) as predominant hexanuclear complex in 3 M $NaNO_3$ [1982MIL/SUR2], [1976BAE/MES]. It also explains why [1991GRE/LAG2] could interpret their data in 3 M $NaClO_4$ including either (15,6) or (14,6) in the speciation model. Lower ionic strength generally favours the formation of the complex (15,6) in all media. At I = 0.1 M the ratio $[\mathrm{Th_6(OH)_{15}^{9+}}]$:$[\mathrm{Th_6(OH)_{14}^{10+}}]$ at $-\log_{10}[\mathrm{H^+}]$ = 3.8 becomes 70:1 to 80:1 for the three media.

These calculations show that the present selection of standard state equilibrium constants for both complexes, $\log_{10}{}^*\beta^\circ_{15,6}(\mathrm{Th_6(OH)_{15}^{9+}})$ and $\log_{10}{}^*\beta^\circ_{15,6}(\mathrm{Th_6(OH)_{14}^{10+}})$, combined with reasonable estimates for the unknown SIT coefficients, does not create an inconsistency when both complexes are included in the calculations. The calculations are consistent with the speciation models accepted for the evaluation of the original data in the corresponding media. Moreover the present selections allow predictions for low ionic strength where, as expected, the calculated speciation for perchlorate, nitrate and chloride media is very similar.

A possible structure of the hexanuclear complexes might be based on the structure of $U_6(O)_4(OH)_4(SO_4)_6$(s) that contains a hexanuclear “$U_6(O)_4(OH)_4$” core to which sulphate ions are coordinated [1953LUN]. The uranium atoms have an approximately octahedral arrangement with bridging oxide and hydroxide ions located outside the triangular faces of an octahedron in such a way that each set of oxide and hydroxide ions form a tetrahedral arrangement around its centre.

VII.3.4.2 Mononuclear Th(IV) hydroxide complexes

Numerous authors have reported equilibrium constants for mononuclear Th(IV) hydroxide complexes $\mathrm{Th(OH)}_n^{4-n}$ with $n = 1-4$. The complex formally assigned the stoichiometry “Th(OH)$_4$(aq)” is probably not a monomer; the large charge and ionic radius of Th^{4+} require a higher coordination number than 4. In a mononuclear complex this can only be achieved by coordination of water. As coordinated water is a strong acid one should expect the formation of negatively charged complexes at high pH according to the reaction $\mathrm{Th(OH)_4(OH_2)}_n \rightleftharpoons \mathrm{Th(OH)_5(OH_2)}_{n-1}^- + \mathrm{H^+}$. However, a number of solubility studies with thorium hydroxide or ThO_2(am, hyd) [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [2002NEC/MUL] have shown that there is no evidence for the formation of anionic Th(IV) hydroxide complexes at high pH. As discussed in Appendix A, the equilibrium constants derived in [1954GAY/LEI] for the complexes $\mathrm{Th(OH)_5^-}$ and $\mathrm{Th(OH)_6^{2-}}$ (designated as $\mathrm{HThO_3^-}$ and $\mathrm{ThO_3^{2-}}$) are based on an erroneous (over)interpretation of solubility data in 0.38 – 0.87 M NaOH. A higher coordination number of Th(IV) in the polymers $[\mathrm{Th(OH)_4}]_m$ is achieved by bridge formation, *e.g.* the coordination number of Th is six in the tetramer $[\mathrm{Th(OH)_4}]_4 \equiv \mathrm{Th_4(OH)_{16}}$ with one of the M_4X_{16} type structures [1990WEL], p.201.

A very recent paper on the behaviour of Th(IV) in alkaline $CaCl_2$ solutions [2007BRE/ALT], which includes a solubility study with ThO_2(am, hyd) and EXAFS analysis of a Th(IV) solution in 4.5 M $CaCl_2$, indicates the formation of an aqueous Th(IV) complex with eight OH^- ligands stabilised by four associated Ca^{2+} ions. This ternary complex $Ca_4[Th(OH)_8]^{4+}$ causes a significant increase of the solubility in the range $11 < -\log_{10}[H^+] < 12$ in $CaCl_2$ solutions above 0.5 M. As this paper appeared at the final stage of the present review, it was not included in the data selection. However, a brief summary of the thermodynamic data is given in Appendix A.

The evaluation of equilibrium constants for mononuclear species $Th(OH)_n^{4-n}$ is difficult because they are usually minor species under the conditions used in potentiometric studies. In addition, most of the equilibrium constants reported for mononuclear complexes cannot be accepted by this review, because they were calculated from potentiometric or solubility data under conditions where polynuclear species are known to be predominant, a fact that the authors often neglected; in some cases they also proposed inadequate speciation schemes (*cf.* Appendix A reviews of [1954GAY/LEI], [1955PAN/HSE], [1963BIL/FUR], [1964NAB/KUD], [1967BIL/ING2], [1971KIC/STE], [1971USH/SKO], [1972USH/SKO], [1989MOO], [2003SAW/SHA], [2004BEN/BOU]). The solvent extraction studies with acetylacetone [1992ENG/ALB], [2000EKB/ALB] are well executed but when interpreting the data one is faced with the problem of the simultaneous formation of numerous binary complexes between Th^{4+} and the extractant and hydroxide in the aqueous phase and also the possible formation of ternary complexes; the latter have been neglected in [1992ENG/ALB], [2000EKB/ALB]. The equilibrium constants derived from cation exchange and colorimetric studies at low thorium concentrations [1967BER], [1986DAV/TOR2] deviate considerably from those determined by potentiometry. They are based on too many simplifying and erroneous assumptions which do not allow a reliable data evaluation. A new method is used by [2001MOU/AME], electrospray-ionisation mass spectrometry (ES-MS). It is not clear to this review how the concentrations determined using mass spectra can be used to represent the equilibrium concentrations. The mass spectra are determined by rapid evaporation of the solvent, but even so one can certainly expect a change in concentration of the solutes in these systems that are characterised by very rapid equilibria. The derived equilibrium constants for $Th(OH)_2^{2+}$ and $Th(OH)_3^{+}$ are more than two orders of magnitude greater than the values determined by potentiometric or solvent extraction methods and have therefore not been accepted by this review.

The selection of data for mononuclear species at 25°C is based on the potentiometric studies of [1954KRA/HOL] and [1954HIE] (recalculated in [1965BAE/MEY] and [1968HIE/SIL], respectively), [1983BRO/ELL], [1991GRE/LAG2] and [2000EKB/ALB] and in addition from the TBP extraction study of [1984NAK/ZIM]. Other values reported in the literature are listed in Table VII-10 to Table VII-13 for completeness. However, for the reasons pointed out in the corresponding Appendix A reviews, they are not reliable and are therefore not included in the selection of data. The values selected in the previous reviews of Baes and Mesmer [1976BAE/MES] and Neck and Kim [2001NEC/KIM] are shown for comparison and briefly discussed.

Table VII-10: Equilibrium constants $\log_{10} {}^*\beta_{1,1}$ (Th(OH)$^{3+}$) at 25°C (except otherwise stated) for the reaction $\mathrm{Th^{4+} + H_2O(l) \rightleftharpoons Th(OH)^{3+} + H^+}$ and values extrapolated to $I = 0$ with the SIT.

Method	Medium	$\log_{10} {}^*\beta_{1,1}$	$\log_{10} {}^*\beta^{\circ}_{1,1}$	Reference
pot	1.0 M $NaClO_4$	– 4.14 ± 0.04	– 2.96 ± 0.14	[1965BAE/MEY] ([1954KRA/HOL])
pot	1.0 M $NaClO_4$	– 3.71 ± 0.08	– 2.52 ± 0.16	[1968HIE/SIL] ([1954HIE])
pot	1.0 M $NaClO_4$	– 3.35 ± 0.06	– 2.16 ± 0.14	[2000EKB/ALB]
pot	3.0 M $NaClO_4$	– 4.20 ± 0.15	– 2.86 ± 0.48	[1991GRE/LAG2]
pot	0.10 M KNO_3	– 2.98 ± 0.01	– 2.32 ± 0.02	[1983BRO/ELL]
extr	0.50 M KNO_3 + 0.01 M $Th(NO_3)_4$ (I = 0.60 M)	– 3.28 ± 0.1	– 2.18 ± 0.16	[1984NAK/ZIM]
Further values not accepted by this review:				
pot	0.5 M $NaClO_4$	– 4.26	– 3.23	[1955PAN/HSE]
	0.3 M $NaClO_4$	– 4.12	– 3.21	
	0.1 M $NaClO_4$	– 4.00	– 3.35	
	0.05 M $NaClO_4$	– 3.92	– 3.41	
	"self-medium", I var.	– 3.77		
pot	dilute acids (I = 0.01–0.04 M)	– 3.61 ± 0.20	– 3.2 ± 0.2	[1971KIC/STE]
pot	0.05 M $Na(ClO_4/Cl)$	– 3.15 ± 0.07	– 2.64 ± 0.07	[1972USH/SKO]
pot	1.0 M $NaClO_4$	– 3.51 ± 0.03	– 2.32 ± 0.14	[2003SAW/SHA]
cix	0.5 M $NaClO_4$	11.64 ± 0.07^a	– 1.1 ± 0.1	[1967BER]
cix, col	I = 0.1 M, 20°C ($NaNO_3$, $NaClO_4$)	– 4.36 ± 0.14	– 3.7 ± 0.2	[1986DAV/TOR2]
dis	1.0 M $NaClO_4$	9.1 ± 3.1^a	– 3.5 ± 3.1	[1992ENG/ALB]
ES-MS	1.0 – 0.001 M $HClO_4$ extrapolated to I = 0		– 2.0 ± 0.2	[2001MOU/AME]
sol	0.1 M $NaClO_4$, 17°C	9.40 ± 0.24^a	– 3.8 ± 0.3	[1964NAB/KUD]
sol	0.1 M $NaClO_4$, 18°C	12.42 ± 0.02^a	– 0.7 ± 0.1	[1989MOO]
	0.5 M $NaClO_4$, 18°C	12.58 ± 0.02^a	– 0.2 ± 0.1	
review			– 3.2 ± 0.2	[1976BAE/MES]
review			– 2.2 ± 0.2	[2001NEC/KIM]
			– 2.5 ± 0.5	Present review

a: $\log_{10} \beta_{1,1}$ for the reaction: $\mathrm{Th^{4+} + OH^- \rightleftharpoons Th(OH)^{3+}}$

Table VII-11: Equilibrium constants $\log_{10} {}^*\beta_{2,1}(\mathrm{Th(OH)}_2^{2+})$ at 25°C for the reaction $\mathrm{Th}^{4+} + 2\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th(OH)}_2^{2+} + 2\mathrm{H}^+$ and values extrapolated to $I = 0$ with the SIT.

Method	Medium	$\log_{10} {}^*\beta_{2,1}$	$\log_{10} {}^*\beta^{\circ}_{2,1}$	Reference
pot	1.0 M $\mathrm{NaClO_4}$	– 7.85 ± 0.03	– 5.82 ± 0.14	[1965BAE/MEY] ([1954KRA/HOL])
pot	1.0 M $\mathrm{NaClO_4}$	– 8.6 ± 0.1	– 6.57 ± 0.17	[2000EKB/ALB]
Further values not accepted by this review:				
pot	0.5 M $\mathrm{NaClO_4}$	– 8.28	– 6.54	[1955PAN/HSE]
	0.3 M $\mathrm{NaClO_4}$	– 8.19	– 6.67	
	0.1 M $\mathrm{NaClO_4}$	– 8.14	– 7.05	
	0.05 M $\mathrm{NaClO_4}$	– 8.11	– 7.25	
	“self-medium”, I var.	– 8.09		
pot	dilute acids (I = 0.01–0.04 M)	– 7.62 ± 0.20	– 7.0 ± 0.2	[1971KIC/STE]
pot	0.05 M $\mathrm{Na(ClO_4/Cl)}$	– 6.56 ± 0.16	– 5.7 ± 0.2	[1972USH/SKO]
pot	0.1 M $\mathrm{NaClO_4}$	– 8.36 ± 0.11	– 7.3 ± 0.1	[2004BEN/BOU]
cix	0.5 M $\mathrm{NaClO_4}$	22.44 ± 0.10[a]	– 3.4 ± 0.2	[1967BER]
dis	1.0 M $\mathrm{NaClO_4}$	19.0 ± 2.7[a]	– 6.6 ± 2.7	[1992ENG/ALB]
ES-MS	1.0 – 0.001 M $\mathrm{HClO_4}$ extrapolated to $I = 0$		– 4.5 ± 0.5	[2001MOU/AME]
sol	$0.1 - 10^{-4}$ M $\mathrm{Th(NO_3)_4}$, 20°C	21.4[a]		[1963BIL/FUR]
sol	0.1 M $\mathrm{NaClO_4}$, 17°C	18.25 ± 0.37[a]	– 8.3 ± 0.4	[1964NAB/KUD]
sol	0.1 M $\mathrm{NaClO_4}$, 18°C	22.46 ± 0.15[a]	– 4.1 ± 0.2	[1989MOO]
	0.5 M $\mathrm{NaClO_4}$, 18°C	22.33 ± 0.15[a]	– 3.5 ± 0.2	
review			– 6.93 ± 0.2	[1976BAE/MES]
review			– 6.0 ± 0.6	[2001NEC/KIM]
			– 6.2 ± 0.5	Present review

a: $\log_{10} \beta_{2,1}$ for the reaction: $\mathrm{Th}^{4+} + 2\,\mathrm{OH}^- \rightleftharpoons \mathrm{Th(OH)}_2^{2+}$

Table VII-12: Equilibrium constants $\log_{10} {}^*\beta_{3,1}(\mathrm{Th(OH)}_3^{+})$ at 25°C for the reaction $\mathrm{Th}^{4+} + 3\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th(OH)}_3^{+} + 3\mathrm{H}^+$ and values extrapolated to $I = 0$ with the SIT. None of the reported values is accepted by the present review.

Method	Medium	$\log_{10} {}^*\beta_{3,1}$	$\log_{10} {}^*\beta^{\circ}_{3,1}$	Reference
pot	dilute acids (I = 0.01–0.04 M)	– 11.17 ± 0.20	– 10.4 ± 0.2	[1971KIC/STE]
pot	1.0 M $\mathrm{NaClO_4}$	– 10.75 ± 0.14	– 8.3 ± 0.2	[2003SAW/SHA]
pot	0.1 M $\mathrm{NaClO_4}$	– 11.63 ± 0.09	– 10.3 ± 0.1	[2004BEN/BOU]
cix	0.5 M $\mathrm{NaClO_4}$	33.06 ± 0.11[a]	– 6.2 ± 0.2	[1967BER]
dis	1.0 M $\mathrm{NaClO_4}$	26.2 ± 2.9[a]	– 12.8 ± 2.9	[1992ENG/ALB]
dis	1.0 M $\mathrm{NaClO_4}$	– 14.2 ± 3	– 11.8 ± 3	[2000EKB/ALB]

(Continued on next page)

Table VII-12 (Continued)

Method	Medium	$\log_{10}{}^{*}\beta_{3,1}$	$\log_{10}{}^{*}\beta^{\circ}_{3,1}$	Reference
ES–MS	1.0 – 0.001 M $HClO_4$ extrapolated to $I = 0$		– 7.5 ± 1	[2001MOU/AME]
sol	0.1 M $NaClO_4$, 17°C	26.74 ± 0.41 ^{a}	– 13.4 ± 0.4	[1964NAB/KUD]
sol	0.1 M $NaClO_4$, 18°C	34.36 ± 0.07 ^{a}	– 5.7 ± 0.1	[1989MOO]
	0.5 M $NaClO_4$, 18°C	34.42 ± 0.07 ^{a}	– 4.8 ± 0.1	
review/sol			≤ – 11.7	[1976BAE/MES]
review/estimate			– 11.0 ± 1.0	[2001NEC/KIM]

a: $\log_{10}\beta_{3,1}$ for the reaction: $Th^{4+} + 3OH^- \rightleftharpoons Th(OH)_3^+$.

Table VII-13: Equilibrium constants $\log_{10}{}^{*}\beta_{4,1}(Th(OH)_4(aq))$ at 25°C for the reaction $Th^{4+} + 4H_2O(l) \rightleftharpoons Th(OH)_4(aq) + 4H^+$ and values extrapolated to $I = 0$ with the SIT.

Method	Medium	$\log_{10}{}^{*}\beta_{4,1}$ or $\log_{10}\beta_{4,1}{}^{a}$	$\log_{10}{}^{*}\beta^{\circ}_{4,1}$	Reference
pot	dilute acids ($I = 0.01 - 0.04$ M)	– 14.43 ± 0.20)	– 13.7 ± 0.2	[1971KIC/STE]
pot	3.0 M $NaClO_4$	– 16.6 ± 0.1	– 13.6 ± 0.4	[1991GRE/LAG2]
pot	0.1 M $NaClO_4$	– 18.24 ± 0.13	– 16.9 ± 0.1	[2004BEN/BOU]
cix	0.5 M $NaClO_4$	43.51 ± 0.13^a	– 9.5 ± 0.2	[1967BER]
dis	1.0 M $NaClO_4$	– 19.4 ± 0.5	– 17.0 ± 0.5	[2000EKB/ALB]
dis	1.0 M $NaClO_4$	33.1 ± 3.0 ^{a}	– 19.7 ± 3.0	[1992ENG/ALB]
sol	0.1 M $NaClO_4$, 17°C	34.82 ± 0.44 ^{a}	– 19.1 ± 0.5	[1964NAB/KUD]
sol	0.1 M $NaClO_4$, 18°C	42.58 ± 0.08 ^{a}	– 11.3 ± 0.1	[1989MOO]
	0.5 M $NaClO_4$, 18°C	42.76 ± 0.08 ^{a}	– 10.2 ± 0.1	
review / sol			– 15.9 ± 0.3	[1976BAE/MES]
review / sol			– 17.5 ± 1.0	[2001NEC/KIM]
			– 17.4 ± 0.7 ^{b}	Present review

a: $\log_{10}\beta_{4,1}$ for the reaction: $Th^{4+} + 4OH^- \rightleftharpoons Th(OH)_4(aq)$.

b: Complex not established, but suggested for the geochemical modelling of solubility data in neutral and alkaline solutions.

VII.3.4.2.1 $Th(OH)^{3+}$

The conditional equilibrium constants reported for the complex $Th(OH)^{3+}$ are listed in Table VII-10. For better comparison they are extrapolated to zero ionic strength with the SIT using the following interaction coefficients for $Th(OH)^{3+}$, estimated from Figure VII-13 in Section VII.3.6.1:

$$\varepsilon(Th(OH)^{3+}, ClO_4^-) \approx \varepsilon(U(OH)^{3+}, ClO_4^-) = (0.48 \pm 0.08)\ kg{\cdot}mol^{-1},$$

$$\Delta\varepsilon(1,1)_{ClO_4^-} = -(0.08 \pm 0.13)\ kg{\cdot}mol^{-1},$$

$$\varepsilon(\mathrm{Th(OH)^{3+}, NO_3^-}) = (0.20 \pm 0.15)\ \mathrm{kg{\cdot}mol^{-1}},\ \ \Delta\varepsilon(1,1)_{\mathrm{NO_3^-}} = -(0.04 \pm 0.19)\ \mathrm{kg{\cdot}mol^{-1}}.$$

For the reasons pointed out in Appendix A, the present review accepts only the values from the potentiometric studies of [1965BAE/MEY] and [1968HIE/SIL] (recalculated from potentiometric data in [1954KRA/HOL] and [1954HIE], respectively), [1983BRO/ELL], [1991GRE/LAG2] and [2000EKB/ALB] and in addition from the TBP extraction study of [1984NAK/ZIM]. The $\log_{10} {}^{*}\beta^{\circ}_{1,1}$ values calculated from the accepted data vary from −2.96 to −2.16 and do not overlap within the reported uncertainty ranges (Table VII-10). It is evident that the reported statistical uncertainties are too small. Accordingly the deviations must arise from systematic errors which are, however, not evident from the published data. This review selects:

$$\log_{10} {}^{*}\beta^{\circ}_{1,1}\,(\mathrm{Th(OH)^{3+}}) = -(2.5 \pm 0.5).$$

In the review of Baes and Mesmer [1976BAE/MES] an equilibrium constant of $\log_{10} {}^{*}\beta^{\circ}_{1,1} = -(3.2 \pm 0.2)$ was selected from the value determined by [1971KIC/STE] in dilute solutions and that of [1965BAE/MEY] in 1 M NaClO$_4$. The ionic strength dependence of $\log_{10} {}^{*}\beta_{1,1}$ was described with the Pitzer and Brewer equation that differs from the SIT by using a slightly different Debye-Hückel term with a numerator $(1+\sqrt{I})$ instead of $(1+1.5\sqrt{I})$ (*cf.* Appendix A review of [1976BAE/MES]). The value of $\log_{10} {}^{*}\beta^{\circ}_{1,1} = -(2.2 \pm 0.2)$ selected in the review of Neck and Kim [2001NEC/KIM] is based exclusively on the data from [1983BRO/ELL], [1984NAK/ZIM] and [2000EKB/ALB].

VII.3.4.2.2 $\mathrm{Th(OH)_2^{2+}}$

The reported conditional equilibrium constants for the complex $\mathrm{Th(OH)_2^{2+}}$, either determined in dilute solutions or in NaClO$_4$ media (Table VII-11), are extrapolated to zero ionic strength with the SIT using $\varepsilon(\mathrm{Th(OH)_2^{2+}, ClO_4^-}) = (0.33 \pm 0.1)\ \mathrm{kg{\cdot}mol^{-1}}$ estimated in Section VII.3.6.1 and $\Delta\varepsilon(2,1)_{\mathrm{ClO_4^-}} = -(0.09 \pm 0.14)\ \mathrm{kg{\cdot}mol^{-1}}$. The $\log_{10} {}^{*}\beta^{\circ}_{2,1}$ values calculated from potentiometric studies range from −5.7 to −7.3 (Table VII-11), the results determined by other methods are even more scattered. For the reasons discussed in Appendix A, only the values from the potentiometric studies of [1965BAE/MEY] (recalculated from potentiometric data in [1954KRA/HOL]) and [2000EKB/ALB] in 1.0 M NaClO$_4$ are considered to be based on reliable experimental procedures and data evaluation. However, not even these two values overlap within the reported uncertainty ranges. This review therefore selects the mean value with the uncertainty covering the whole range of expectation of the two values from [1965BAE/MEY] and [2000EKB/ALB]:

$$\log_{10} {}^{*}\beta^{\circ}_{2,1}\,(\mathrm{Th(OH)_2^{2+}}) = -(6.2 \pm 0.5).$$

Baes and Mesmer [1976BAE/MES] selected $\log_{10} {}^{*}\beta^{\circ}_{2,1} = -(6.93 \pm 0.2)$ and specific interaction coefficients from the value of [1971KIC/STE] in dilute solutions and that of [1965BAE/MEY] in 1 M NaClO$_4$. The value of $\log_{10} {}^{*}\beta^{\circ}_{1,1} = -(6.0 \pm 0.6)$

selected in the review of Neck and Kim [2001NEC/KIM] is based on the values from [1965BAE/MEY] and [2000EKB/ALB] extrapolated to I = 0 with the SIT and on a correlation between $\log_{10} {}^*\beta^{\circ}_{2,1}$ and $\log_{10} {}^*\beta^{\circ}_{1,1}$.

VII.3.4.2.3 $Th(OH)_3^+$

The conditional equilibrium constants reported for the complex $Th(OH)_3^+$ are listed in Table VII-12 and extrapolated to zero ionic strength with the SIT using an estimated interaction coefficient of $\varepsilon(Th(OH)_3^+, ClO_4^-)$ = (0.15 ± 0.1) kg·mol^{-1} (*cf.* Section VII.3.6.1) and $\Delta\varepsilon(3,1)_{ClO_4^-} = -(0.13 \pm 0.14)$ kg·mol^{-1}. As discussed in Appendix A, none of the reported $\log_{10} {}^*\beta^{\circ}_{3,1}$ values, ranging from −13 to −7 (Table VII-12) is considered to be reliable. The equilibrium constants from the solvent extraction studies of [1992ENG/ALB], [2000EKB/ALB] have very large uncertainties (3 orders of magnitude); those from the potentiometric studies of [1971KIC/STE], [2003SAW/SHA], [2004BEN/BOU] are considerably overestimated, because the authors disregarded the formation of polynuclear species, which are known to be predominant under the experimental conditions in these studies. The equilibrium constants derived from solubility studies [1964NAB/KUD], [1989MOO], by cation exchange methods [1967BER] or by ES-MS are far out of the range of expectation.

In the review of Baes and Mesmer [1976BAE/MES] an upper limit of $\log_{10} {}^*\beta^{\circ}_{3,1} \leq -11.7$ was calculated from the solubility data of [1964NAB/KUD] while Neck and Kim [2001NEC/KIM] selected an estimated value of $\log_{10} {}^*\beta^{\circ}_{3,1} = -(11 \pm 1)$ in their review. The present review does not recommend an equilibrium constant for the complex $Th(OH)_3^+$ which is considered to be a minor species in both potentiometric and solubility studies.

VII.3.4.2.4 $Th(OH)_4(aq)$

The reported equilibrium constants for the neutral complex $Th(OH)_4(aq)$ and the corresponding values extrapolated to zero ionic strength with the SIT ($\Delta\varepsilon(4,1)_{ClO_4^-}$ = $-(0.14 \pm 0.11)$) are listed in Table VII-13. The equilibrium constants derived by solvent extraction at low Th concentrations [1992ENG/ALB], [2000EKB/ALB] are orders of magnitude lower than those estimated for $Th(OH)_4(aq)$ as a minor species in the potentiometric titrations [1971KIC/STE], [1991GRE/LAG2]. The values derived from the pH-independent solubility of $Th(OH)_4(am)$ or $ThO_2(am, hyd)$ in neutral to alkaline solutions-are usually described with the reaction:

$$Th(OH)_4(am) \text{ or } ThO_2(am, hyd) \rightleftharpoons Th(OH)_4(aq) \qquad (VII.25)$$

with

$$\log_{10}[Th(OH)_4(aq)] = \log_{10} K^{\circ}_{s,4}\,(VII.25) = \log_{10} {}^*K^{\circ}_{s,0} + \log_{10} {}^*\beta^{\circ}_{4,1} \qquad (VII.26)$$

The $\log_{10} {}^*\beta^{\circ}_{4,1}$ selected in the reviews [1976BAE/MES] and [2001NEC/KIM] are based on the solubility data of [1964NAB/KUD] and the more reliable data reported later in [1987RYA/RAI], [1989MOO], [1991FEL/RAI], respectively. The thorium concentration measured by Nabivanets and Kudritskaya [1964NAB/KUD] at pH 6−7 after centrifugation at 10000 rpm, $\log_{10}[\mathrm{Th}] = -6.3$, are two orders of magnitude higher than those determined at pH 6−14 after ultrafiltration (pore size 1.3−2 nm) [1987RYA/RAI], [1989MOO], [1991FEL/RAI] or ultracentrifugation at 90000 rpm (5×10^5 g) [2002NEC/MUL], [2004ALT/NEC]. The centrifugal force used by [1964NAB/KUD] is not sufficient to remove small Th(IV) polymers or colloids. The remaining thorium concentration is equal to that determined by [2002NEC/MUL], [2004ALT/NEC] in the supernatant solutions without removing polymeric or colloidal species.

The $\log_{10} {}^*\beta^{\circ}_{4,1}$ value calculated from $\log_{10}[\mathrm{Th(OH)_4(aq)}]$ according to Eq. (VII.26) depends on the solubility constant $\log_{10} {}^*K^{\circ}_{s,0}$. In Section VII.4.1.2 the pH-independent thorium concentrations determined in neutral to alkaline solutions after ultrafiltration [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [2002JER/VUO] or after ultracentrifugation [2002NEC/MUL], [2004ALT/NEC] are combined with the corresponding solubility constants $\log_{10} {}^*K^{\circ}_{s,0}$ calculated by this review from the solubility data at pH < 6 in these studies. The mean value of $\log_{10} {}^*\beta^{\circ}_{4,1}$ is selected and recommended as "working value" that can be used for geochemical modelling:

$$\log_{10} {}^*\beta^{\circ}_{4,1} = -(17.4 \pm 0.7).$$

This value is in the range of the results from the solvent extraction studies of [1992ENG/ALB] and [2000EKB/ALB]. However it is by no means established that the thorium concentration measured in solubility studies at pH 6−14 is actually caused by the mononuclear complex $\mathrm{Th(OH)_4(aq)}$. For the reasons discussed in Section VII.4.1.2, this review finds it more likely that the soluble uncharged species is one or more small (≤ 1.5 nm) polynuclear species $\mathrm{Th}_m\mathrm{O}_{mx}(\mathrm{OH})_{m(4-2x)}(\mathrm{aq})$, more simply written as $\mathrm{Th}_m(\mathrm{OH})_{4m}(\mathrm{aq})$, (*e.g.*, the tetranuclear species $\mathrm{Th_4O_4(OH)_8(aq)} = \mathrm{Th_4(OH)_{16}(aq)}$) with a diameter of about 1 nm. Accordingly the solubility in neutral to alkaline solutions is given by the reaction:

$$\mathrm{Th(OH)_4(am)\ or\ ThO_2(am,\ hyd)} \rightleftharpoons 1/m\ \mathrm{Th}_m(\mathrm{OH})_{4m}(\mathrm{aq}) \qquad \text{(VII.27)}$$

with $\log_{10} K^{\circ}_{s,(4m,m)} = -(6.3 \pm 0.8)$ if Th(IV) polymers or colloids are not removed and $\log_{10} K^{\circ}_{s,(4m,m)} = -(8.5 \pm 1.0)$ after 1.5−2 nm ultrafiltration or ultracentrifugation, *i.e.*, for a particle size below about 1.5 nm ($m < 10$), *cf.* Section VII.4.1.2.

VII.3.5 Enthalpies and entropies of Th(IV) hydrolysis reactions

VII.3.5.1 Temperature dependence of Th(IV) hydrolysis constants

The temperature dependence of Th(IV) hydrolysis constants has been investigated by Baes *et al.* [1965BAE/MEY] at 0, 25 and 95°C and Ekberg *et al.* [2000EKB/ALB] at 15, 25 and 35°C, both studies in 1 M $\mathrm{NaClO_4}$. Baes *et al.* [1965BAE/MEY] used $\Delta_r H_m$,

$\Delta_r S_m$ and $\Delta_r C_{p,m}$ when describing the temperature dependence; this is not justified as the experimental data were only available at three temperatures; Ekberg *et al.* [2000EKB/ALB] used the more reasonable approximation $\Delta_r C_{p,m} = 0$. The enthalpies of reaction:

$$m\,\mathrm{Th}^{4+} + n\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th}_m(\mathrm{OH})_n^{4m-n} + n\,\mathrm{H}^+ \qquad \text{(VII.28)}$$

$\Delta_r H_m$ (VII.28) calculated in these two studies are not consistent within the reported uncertainty ranges (Table VII-14). The reported entropies of reaction $\Delta_r S_m$ are even more discrepant. This is not surprising because the differences in the $\log_{10} {}^*\beta^{\circ}_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, 298.15 K) values of [1965BAE/MEY] and [2000EKB/ALB] and hence the Gibbs energies of reaction $\Delta_r G_m$ for the species (1,1), (2,1) and (15,6) are rather large.

Table VII-14: Thermodynamic data reported in [1965BAE/MEY] and [2000EKB/ALB]^a for Th(IV) hydroxide complexes in 1 M $\mathrm{NaClO_4}$ at 25°C.

Complex	$\Delta_r H_m$ (kJ·mol^{-1})	$\Delta_r S_m$ (J·K^{-1}·mol^{-1})	$\Delta_r C_{p,m}$ (J·K^{-1}·mol^{-1})	Reference
(1,1) = $\mathrm{Th(OH)^{3+}}$	25 ± 1	4 ± 5	937 ± 80	[1965BAE/MEY]
	38 ± 6	60 ± 20		[2000EKB/ALB]
(2,1) = $\mathrm{Th(OH)_2^{2+}}$	58 ± 1	46 ± 5	1272 ± 80	[1965BAE/MEY]
	36 ± 1	– 44 ± 4		[2000EKB/ALB]
(2,2) = $\mathrm{Th_2(OH)_2^{6+}}$	62 ± 1	119 ± 5	4 ± 80	[1965BAE/MEY]
(8,4) = $\mathrm{Th_4(OH)_8^{8+}}$	241 ± 1	446 ± 5	452 ± 80	[1965BAE/MEY]
	191 ± 3	280 ± 10		[2000EKB/ALB]
(15,6) = $\mathrm{Th_6(OH)_{15}^{9+}}$	454 ± 1	819 ± 5	1000 ± 80	[1965BAE/MEY]
	410 ± 60	600 ± 200		[2000EKB/ALB]

a: The data for $\mathrm{Th(OH)_3^+}$ and $\mathrm{Th(OH)_4(aq)}$ determined in [2000EKB/ALB] by liquid-liquid extraction are not accepted by this review (*cf.* Appendix A).

In Figure VII-11 the equilibrium constants reported in [1965BAE/MEY] and [2000EKB/ALB] for the complexes (1,1), (2,1), (2,2), (8,4) and (15,6) are plotted against $1/T$. The values at 25°C selected in the present review from data in perchlorate, nitrate and chloride media are included for comparison. Figure VII-11 indicates that most of the equilibrium constants and their temperature dependence determined in these two papers are in better agreement than the numerical $\Delta_r H_m$ and $\Delta_r S_m$ values in Table VII-14.

Figure VII-11: Temperature dependence of $\log_{10}{}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, 1.05 m NaClO$_4$).

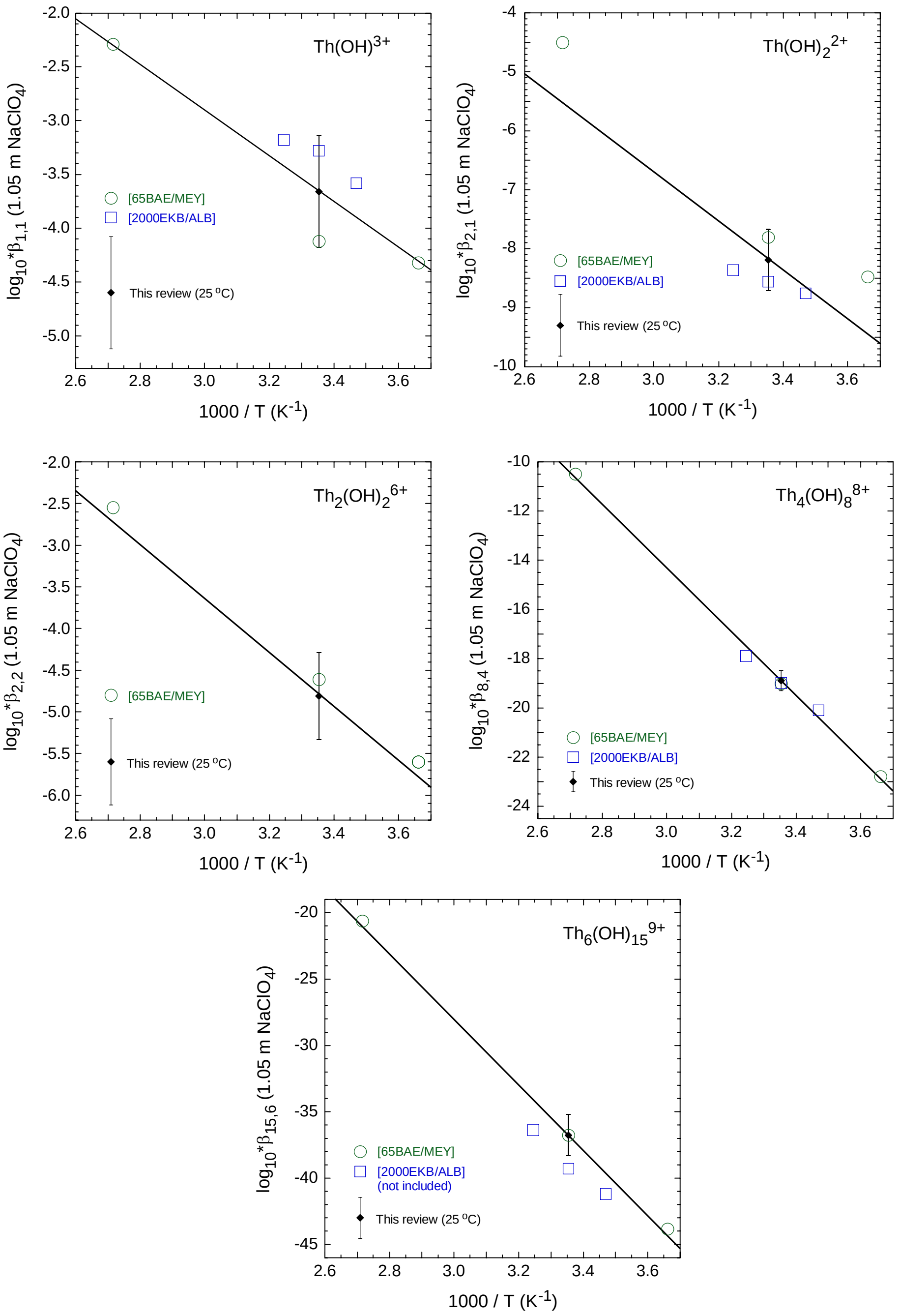


Table VII-15: Standard molar Gibbs energies, enthalpies and entropies for the reactions: $m\text{Th}^{4+} + n\text{H}_2\text{O(l)} \rightleftharpoons \text{Th}_m(\text{OH})_n^{4m-n} + n\text{H}^+$ at 25°C.

Complex	$\Delta_r G^\circ_m$ ^{a} (kJ·mol^{-1})	$\Delta_r H^\circ_m$ ^{b} (kJ·mol^{-1})	$\Delta_r S^\circ_m$ ^{c} (J·K^{-1}·mol^{-1})
Th(OH)^{3+}	14.3 ± 2.9	44.2 ± 6.3	100 ± 23
Th(OH)_2^{2+}	35.4 ± 2.9	85.7 ± 41.4	169 ± 139
$\text{Th}_2(\text{OH})_2^{6+}$	33.7 ± 2.9	58.3 ± 5.7	83 ± 22
$\text{Th}_4(\text{OH})_8^{8+}$	116.4 ± 2.3	243.0 ± 21.3	424 ± 72
$\text{Th}_6(\text{OH})_{15}^{9+}$	210.1 ± 8.6	472.8 ± 22.0	881 ± 79

a: Calculated from the selected $\log_{10} {}^*\beta^\circ_{n,m}$ values: $\Delta_r G^\circ_m(n,m) = -\text{R}T\ln(10)\ \log_{10} {}^*\beta^\circ_{n,m}$.

b: Calculated with Eq.(VII.30) and the $\Delta_r H_m(n,m)$ values derived from the temperature dependence of $\log_{10} {}^*\beta_{n,m}(\text{Th}_m(\text{OH})_n^{4m-n})$ in 1.05 m NaClO4, (Figure VII-11).

c: $\Delta_r S^\circ_m = (\Delta_r H^\circ_m - \Delta_r G^\circ_m) / T$

The equilibrium constants $\log_{10} {}^*\beta_{n,m}(\text{Th}_m(\text{OH})_n^{4m-n})$ in 1.05 m NaClO$_4$ increase with the temperature and for (n,m) = (2,2), (8,4) and (15,6) the linearity of the plots $\log_{10} {}^*\beta_{n,m}(T)$ *vs.* $1/T$, holds from 0 to 95°C. The values for the mononuclear complexes (1,1) and (2,1) are more scattered. Using the approximation $\Delta_r C_{p,\text{m}} = 0$, *i.e.*,

$$\Delta_r H_\text{m} = \text{R}T^2\ (\partial \ln {}^*\beta_{n,m} / \partial T)_\text{p} \qquad \text{(VII.29)}$$

the following enthalpies of reaction, $\Delta_r H_\text{m}$((VII.28), 1.05 m NaClO$_4$, 298.15 K) with the uncertainties covering the whole ranges of experimental data, are calculated from the slopes of the van't Hoff plots $(-\Delta_r H_\text{m}/\text{R}\ln(10))$ in Figure VII-11: $\Delta_r H_\text{m}(1,1) = (40.6 \pm 6.3)$ kJ·mol^{-1}, $\Delta_r H_\text{m}(2,1) = (79.6 \pm 41.4)$ kJ·mol^{-1}, $\Delta_r H_\text{m}(2,2) = (61.8 \pm 5.7)$ kJ·mol^{-1}, $\Delta_r H_\text{m}(8,4) = (247.5 \pm 21.3)$ kJ·mol^{-1} and $\Delta_r H_\text{m}(15,6) = (472.3 \pm 22.0)$ kJ·mol^{-1}.

For reasons of consistency, the equilibrium constants $\log_{10} {}^*\beta_{n,m}$ at 25°C calculated with the $\log_{10} {}^*\beta^\circ_{n,m}$ and $\Delta\varepsilon(n,m)_{\text{ClO}_4^-}$ values selected in the present review (Section VII.3.4) are used as fixed values. The corresponding standard state enthalpies of reaction are calculated with the equations given in Grenthe *et al.* [1997GRE/PLY2] (p. 397−424), applied to the Th(IV) hydrolysis reactions (VII.28):

$$\begin{aligned}\Delta_r H^\circ_\text{m}(n,m) &= \Delta_r H_\text{m}(n,m) + \text{R}T^2\ (\partial \ln\gamma_{(n,m)} / \partial T)_\text{p,m} + n\ \text{R}T^2\ (\partial \ln\gamma_{\text{H}^+} / \partial T)_\text{p,m} \\ &\quad - m\ \text{R}T^2\ (\partial \ln\gamma_{\text{Th}^{4+}} / \partial T)_\text{p,m} - n\ \text{R}T^2\ (\partial \ln a_\text{w} / \partial T)_\text{p,m} \\ &= \Delta_r H_\text{m}(n,m) - \Delta z^2(n,m)\,\text{A}_\text{L}(3/4)\,\sqrt{I_\text{m}}/(1 + 1.5\sqrt{I_\text{m}}) + \text{R}T^2\, m_\text{X}\,\Delta\varepsilon_\text{L}(n,m) \\ &\quad - n\ \text{R}T^2\ (\partial \ln a_w / \partial T)_\text{p,m}\end{aligned} \qquad \text{(VII.30)}$$

The temperature dependence of a_w, the activity of water, is known: $-\text{R}T^2\ (\partial \ln a_w / \partial T) = 0.033$ kJ·mol^{-1} for 1.05 m NaClO$_4$ [1991PIT] (*cf.* Table IX.14 in [1997GRE/PLY2]). However, for the activity coefficients of the highly charged Th(IV) species only the temperature dependence of the Debye-Hückel term can be calculated ($\text{A}_\text{L} = 4\,\text{R}T^2\,(\partial \text{A}_\phi/\partial T)_\text{p} = 1.986$ kJ·kg$^{1/2}$·mol$^{-3/2}$ at 25°C [1991PIT]); the temperature dependence of the ion interaction coefficients ($\Delta\varepsilon_L = (\partial\,\Delta\varepsilon\,/\,\partial T)_p$) is not known and a reasonable estimation is not possible. Neglecting this latter term (*i.e.*, using $\Delta\varepsilon_L(n,m) = 0$), the standard enthalpies of reaction $\Delta_r H^\circ_m$ ((VII.28), 298.15 K) and standard entropies of reaction $\Delta_r S^\circ_m$ ((VII.28), 298.15 K) are calculated and summarised in Table VII-15. It should be noted that the uncertainties in the experimental $\Delta_r H_m(n,m)$ values are larger than the terms for the conversion from 1.05 m $NaClO_4$ to $I = 0$.

VII.3.5.2 Calorimetric data

In general, data obtained by calorimetry are more precise than those from the temperature variation of equilibrium constants. However, Milić [1981MIL2] is the only author reporting calorimetric measurements on Th(IV) hydrolysis reactions and the study is limited to the formation of $Th_2(OH)_2^{6+}$ and $Th_2(OH)_3^{5+}$ in 0.5−3 M NaCl, 3 M LiCl and 3 M KCl at 25°C. The enthalpies of reaction determined in 3 M NaCl, 3 M LiCl and 3 M KCl show large differences and those in 0.5−3.0 M NaCl show an unexpectedly strong ionic strength dependence. The terms $\Delta z^2(n,m)\,A_L(3/4)\,\sqrt{I_m}/(1 + 1.5\sqrt{I_m})$ and $n\,RT^2\,(\partial \ln a_w\,/\,\partial T)_{p,m}$ are small (< 5 kJ·mol⁻¹) compared to the reported variation of $\Delta_r H_m$. Therefore, this review applies the SIT (*cf.* [1997GRE/PLY2]) to calculate $\Delta_r H^\circ_m(n,m)$ and $\Delta\varepsilon_L(n,m) = (\partial\,\Delta\varepsilon(n,m)\,/\,\partial T)_p$ from the data of Milić [1981MIL2]. The linear regression (Figure VII-12) according to Eq. (VII.31):

$$\Delta_r H_m(n,m) - \Delta z^2(n,m)\,A_L(3/4)\,\sqrt{I_m}/(1 + 1.5\sqrt{I_m}) - n\,RT^2\,(\partial \ln a_w\,/\,\partial T)_{p,m} = \Delta_r H^\circ_m(n,m) - \{RT^2\,\Delta\varepsilon_L(n,m)\}\,m_{Cl^-} \qquad \text{(VII.31)}$$

yields:

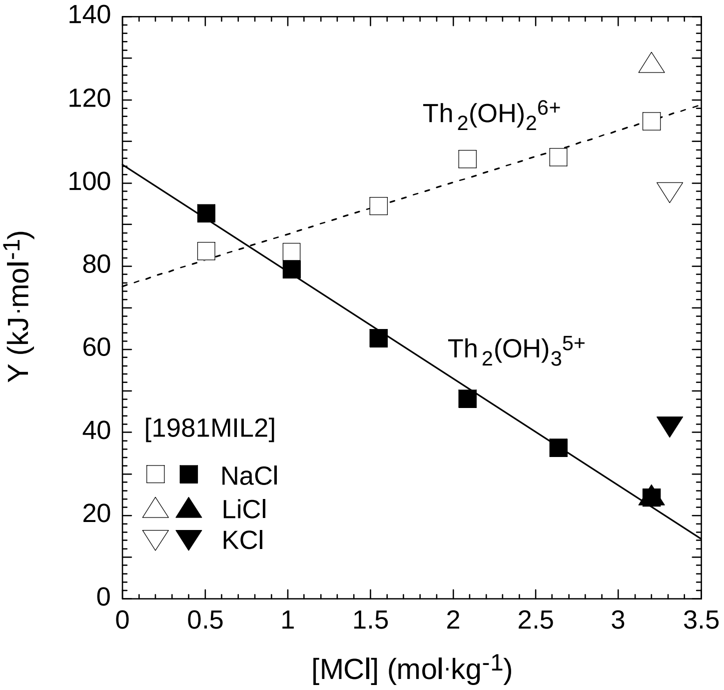
$$\Delta_r H^\circ_m(2,2) = (75.2 \pm 4.3)\ \text{kJ·mol}^{-1}; \qquad \Delta\varepsilon_L(2,2) = -(0.017 \pm 0.004)\ \text{kg·mol}^{-1}\text{·K}^{-1}$$

$$\Delta_r H^\circ_m(3,2) = (104.4 \pm 4.4)\ \text{kJ·mol}^{-1}; \qquad \Delta\varepsilon_L(3,2) = (0.035 \pm 0.005)\ \text{kg·mol}^{-1}\text{·K}^{-1}.$$

These values are not selected because no experimental details are reported in [1981MIL2] and possible errors and uncertainties cannot be estimated by this review. The reaction enthalpy for the formation of $Th_2(OH)_2^{6+}$ is in fair agreement with the value derived in Section VII.3.5.1 from the temperature dependence of $\log_{10}{}^*\beta_{2,2}$ in 1 M $NaClO_4$, but the $\Delta\varepsilon_L(m,n)$ values are large compared to the usual range (the temperature dependence of ion interaction coefficients is usually in the range $-0.005 < (\partial\varepsilon_{j,k}/\,\partial T)_p < 0.005$ kg·mol⁻¹·K⁻¹). The strong variation of the $\Delta_r H_m$ values in [1981MIL2] with the ionic strength and medium could partly be due to experimental artefacts (*cf.* Appendix A).

Figure VII-12: Application of the SIT to $\Delta_r H_m(n,m)$ values reported in [1981MIL2] for the reactions: $2Th^{4+} + 2H_2O(l) \rightleftharpoons Th_2(OH)_2^{6+} + 2H^+$ and $2Th^{4+} + 3H_2O(l) \rightleftharpoons Th_2(OH)_3^{5+} + 3H^+$ in 0.51−3.20 m NaCl, 3.20 m LiCl and 3.31 KCl at 25°C. The Y-values of the plotted data correspond to the following term:

$$\begin{aligned}Y &= \Delta_r H_m(n,m) - \Delta z^2(n,m)A_L(3/4)\sqrt{I_m} \,/\, (1+1.5\sqrt{I_m}) - nRT^2(\partial \ln a_w/\partial T)_{p,m}\\ &= \Delta_r H^o_m(n,m) - RT^2\ m_{Cl}\,\Delta\varepsilon_L(n,m)\end{aligned}$$



VII.3.6 Summary of selected data for Th(IV) hydroxide complexes

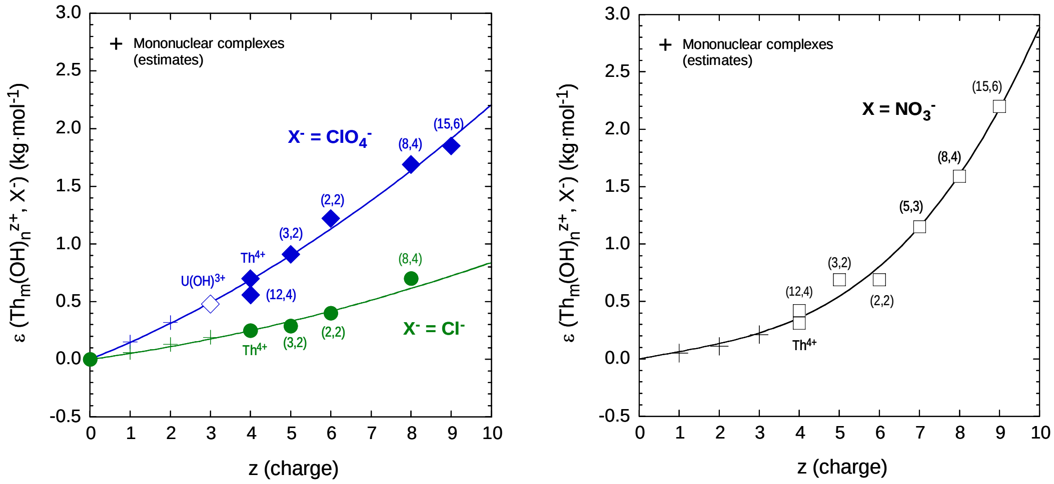
VII.3.6.1 Ion interaction (SIT) coefficients

For polynuclear Th(IV) hydroxide complexes which are found to be major species or at least species with significant contributions in potentiometric studies, $\Delta\varepsilon(n,m)$ values are derived in Section VII.3.4.1 by linear SIT regression from the conditional equilibrium constants $\log_{10} {}^*\beta_{n,m}(Th_m(OH)_n^{4m-n}$, 298.15 K) in perchlorate, nitrate and chloride media. The ion interaction coefficients for the Th(IV) hydroxide complexes $\varepsilon(Th_m(OH)_n^{4m-n}, X^-)$, with $X^- = ClO_4^-$, NO_3^- and Cl^- are calculated according to:

$$\Delta\varepsilon(n,m)_X = \varepsilon(Th_m(OH)_n^{4m-n}, X^-) + n\,\varepsilon(H^+, X^-) - m\,\varepsilon(Th^{4+}, X^-),$$

with auxiliary data for $\varepsilon(\mathrm{H}^+,\mathrm{X}^-)$ and the $\varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-)$ values selected in Section VI.3. In Figure VII-13 the evaluated SIT coefficients are plotted as a function of the charge $z = (4m\text{–}n)$. The regular variation of all values in perchlorate, chloride and nitrate media makes it possible to estimate unknown $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n},\mathrm{X}^-)$ values, *e.g.* for the mononuclear complexes (crosses in Figure VII-13), where the available experimental data are not sufficient for the evaluation by linear SIT regression. The value of $\varepsilon(\mathrm{U(OH)}^{3+},\mathrm{ClO}_4^-)$ from [1992GRE/FUG] is considered to be an analogue for $\varepsilon(\mathrm{Th(OH)}^{3+},\mathrm{ClO}_4^-)$. Assuming that interaction coefficients for neutral species ($z = 0$) are equal to zero, the curves start at $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_{n=4m}(\mathrm{aq}),\mathrm{X}^-) = 0$. For $\mathrm{X}^- = \mathrm{Cl}^-$ this is supported by the pH independent solubility in neutral and alkaline solution which is also independent of the chloride concentration in 0.5 and 5 M NaCl [2004ALT/NEC].

Figure VII-13: Ion interaction (SIT) coefficients $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n},\mathrm{X}^-)$ as a function of the charge of the thorium species ($z = 4m\text{–}n$).



The interaction coefficients evaluated in Section VI.3 and those for the mononuclear complexes estimated from Figure VII-13 are summarised in Table VII-16. For reasons of consistency, estimates of $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n},\mathrm{X}^-)$ for minor species in electrolyte media of anion X^- are included as well.

Table VII-16: Ion interaction coefficients selected for Th(IV) hydroxide complexes[#].

$Th_m(OH)_n^{4m-n}$	$\varepsilon(Th_m(OH)_n^{4m-n}, X^-)$ (kg·mol^{-1})		
	$X^- = ClO_4^-$	$X^- = NO_3^-$	$X^- = Cl^-$
Th^{4+}	0.70 ± 0.10	0.31 ± 0.12	0.25 ± 0.03
$Th(OH)^{3+}$	0.48 ± 0.08 [b]	0.20 ± 0.15 [a]	0.19 ± 0.05 [a]
$Th(OH)_2^{2+}$	0.33 ± 0.1 [a]	0.10 ± 0.15 [a]	0.13 ± 0.05 [a]
$Th(OH)_3^{+}$	0.15 ± 0.1 [a]	0.05 ± 0.15 [a]	0.06 ± 0.05 [a]
$Th(OH)_4(aq)$ or $(Th_m(OH)_{4m})_{1/m}(aq)$	0	0	0
$Th_2(OH)_2^{6+}$	1.22 ± 0.24	0.69 ± 0.26	0.40 ± 0.16
$Th_2(OH)_3^{5+}$	0.91 ± 0.21	0.69 ± 0.25	0.29 ± 0.09
$Th_3(OH)_5^{7+}$ [c]		1.15 ± 0.37	
$Th_4(OH)_8^{8+}$	1.69 ± 0.42	1.59 ± 0.51	0.70 ± 0.20
$Th_4(OH)_{12}^{4+}$	0.56 ± 0.42	0.42 ± 0.50	0.25 ± 0.20 [a]
$Th_6(OH)_{14}^{10+}$	2.2 ± 0.3 [a]	2.9 ± 0.5 [a]	0.83 ± 0.30 [a]
$Th_6(OH)_{15}^{9+}$	1.85 ± 0.74	2.20 ± 0.77	0.72 ± 0.30 [a]

#: The SIT coefficients selected in this table refer to a strict ion interaction approach where the effect of chloride or nitrate complexation is included in the interaction coefficients. Therefore these values must not be combined with the formation constants of chloride and nitrate complexes discussed in Sections VIII.2.2.1 and X.1.3.3.

a: Estimated from the correlations between $\varepsilon(Th_m(OH)_n^{4m-n}, X^-)$ and the charge of the complex (Figure VII-13).

b: $\varepsilon(U(OH)^{3+}, ClO_4^-)$ from [1992GRE/FUG]

c: This complex is not selected in the present review.

VII.3.6.2 Standard state equilibrium constants

Table VII-17 shows the equilibrium constants $\log_{10} {}^*\beta^\circ_{n,m}(Th_m(OH)_n^{4m-n}$, aq, 298.15 K) selected in the present review together with the $\Delta\varepsilon(n,m)$ values in perchlorate, nitrate and chloride ionic media. For complexes where $\Delta\varepsilon(n,m)$ cannot be calculated by linear regression, either because the species are of minor importance or because experimental data are available only at one ionic strength, $\Delta\varepsilon(n,m)$ is calculated with estimated $\varepsilon(Th_m(OH)_n^{4m-n}, X^-)$ values (Section VII.3.6.1). It should be noted that conditional equilibrium constants calculated with this data set for minor species, *e.g.* for $Th_4(OH)_8^{8+}$, $Th_4(OH)_{12}^{4+}$ or $Th_6(OH)_{15}^{9+}$ in 3 M NaCl, do not significantly affect the calculations with the "best model" for this medium. However, the estimates for $\varepsilon(Th_m(OH)_n^{4m-n}, X^-)$ are necessary for model calculations for conditions where the speciation is not directly available from potentiometric data. For instance in 0.1 − 0.5 M NaCl, depending on $[Th]_{tot}$ and pH, one would expect significant contributions of the species $Th_4(OH)_8^{8+}$, $Th_4(OH)_{12}^{4+}$ or $Th_6(OH)_{15}^{9+}$ (similar as in 0.1 − 0.5 M perchlorate or nitrate media). This is of particular importance for the evaluation of solubility data and predictions of solubilities.

Table VII-17: Selected equilibrium constants $\log_{10}{}^{*}\beta^{\circ}_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, aq, 298.15 K) and $\Delta\varepsilon(n,m)$ ($\mathrm{kg{\cdot}mol^{-1}}$) values for Th(IV) hydroxide complexes in perchlorate, nitrate and chloride ionic media[#].

Complex	$\log_{10}{}^{*}\beta^{\circ}_{n,m}$	$\Delta\varepsilon(n,m)_{\mathrm{ClO_4^-}}$	$\Delta\varepsilon(n,m)_{\mathrm{NO_3^-}}$	$\Delta\varepsilon(n,m)_{\mathrm{Cl^-}}$
(1,1) = $\mathrm{Th(OH)^{3+}}$	-2.5 ± 0.5	-0.08 ± 0.13 [a]	-0.04 ± 0.19 [a]	0.06 ± 0.06 [a]
(2,1) = $\mathrm{Th(OH)_2^{2+}}$	-6.2 ± 0.5	-0.09 ± 0.14 [a]	-0.07 ± 0.19 [a]	0.12 ± 0.06 [a]
(3,1) = $\mathrm{Th(OH)_3^{+}}$	–	-0.13 ± 0.14 [a]	-0.05 ± 0.19 [a]	0.17 ± 0.07 [a]
(4,1) = $\mathrm{Th(OH)_4(aq)}$ or $(\mathrm{Th}_m(\mathrm{OH})_{4m})_{1/m}$ (aq)	-17.4 ± 0.7 [b]	-0.14 ± 0.11	-0.03 ± 0.13	0.23 ± 0.05
(2,2) = $\mathrm{Th_2(OH)_2^{6+}}$	-5.9 ± 0.5	0.10 ± 0.14	0.21 ± 0.11	0.14 ± 0.15
(3,2) = $\mathrm{Th_2(OH)_3^{5+}}$	-6.8 ± 0.2	-0.07 ± 0.06	0.28 ± 0.06	0.15 ± 0.06
(8,4) = $\mathrm{Th_4(OH)_8^{8+}}$	-20.4 ± 0.4	0.01 ± 0.08	0.91 ± 0.14	0.66 ± 0.14
(12,4) = $\mathrm{Th_4(OH)_{12}^{4+}}$	-26.6 ± 0.2	-0.56 ± 0.06	0.02 ± 0.05	0.69 ± 0.23 [a]
(14,6) = $\mathrm{Th_6(OH)_{14}^{10+}}$	-36.8 ± 1.2	-0.04 ± 0.33 [a]	2.02 ± 0.52 [a]	1.01 ± 0.33 [a]
(15,6) = $\mathrm{Th_6(OH)_{15}^{9+}}$	-36.8 ± 1.5	-0.25 ± 0.40	1.39 ± 0.23	1.02 ± 0.34 [a]

#: The equilibrium constants and SIT coefficients selected in this table refer to a strict ion interaction approach where the effect of chloride or nitrate complexation is included in the interaction coefficients. Therefore these values must not be combined with the formation constants of chloride and nitrate complexes discussed in Sections VIII.2.2.1 and X.1.3.3.

a: Calculated with $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}, \mathrm{X^-})$ estimated in this review.

b: Equilibrium constants for the reactions: $\mathrm{Th^{4+} + 4H_2O(l) \rightleftharpoons (1/\mathit{m})Th_{\mathit{m}}(OH)_{4\mathit{m}}(aq) + 4H^+}$ calculated from the solubility of $\mathrm{Th(OH)_4(am) = ThO_2(am, hyd)}$ at pH 6 – 14: $\mathrm{Th(OH)_4(am) \rightleftharpoons (1/\mathit{m})Th_{\mathit{m}}(OH)_{4\mathit{m}}(aq)}$ with $m < 10$ after ultrafiltration or ultracentrifugation.

VII.3.6.3 Standard molar Gibbs energies, enthalpies and entropies

The selected equilibrium constants $\log_{10}{}^{*}\beta^{\circ}_{n,m}$ ((VII.2), 298.15 K) are used to calculate the corresponding standard Gibbs energies $\Delta_\mathrm{r}G^{\circ}_\mathrm{m}$ ((VII.2), 298.15 K) for the reactions:

$$m\mathrm{Th^{4+}} + n\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th}_m(\mathrm{OH})_n^{4m-n} + n\mathrm{H^+} \qquad \text{(VII.2)}$$

The enthalpies of reaction $\Delta_\mathrm{r}H_\mathrm{m}$ ((VII.2), 1.05 m $\mathrm{NaClO_4}$, 298.15 K) derived from the temperature dependence of the $\log_{10}{}^{*}\beta_{n,m}$ ((VII.2), 1.05 m $\mathrm{NaClO_4}$) values in [1965BAE/MEY], [2000EKB/ALB] are used to calculate $\Delta_\mathrm{r}H^{\circ}_\mathrm{m}$ ((VII.2), 298.15 K) and $\Delta_\mathrm{r}S^{\circ}_\mathrm{m}$ ((VII.2), 298.15 K) as described in Section VII.3.5.1.

The standard reaction data are combined with $\Delta_\mathrm{f}G^{\circ}_\mathrm{m}(\mathrm{Th^{4+}}$, 298.15 K) = $-(704.8 \pm 5.3)$ $\mathrm{kJ{\cdot}mol^{-1}}$, $\Delta_\mathrm{f}H^{\circ}_\mathrm{m}(\mathrm{Th^{4+}}$, 298.15 K) = $-(768.7 \pm 2.3)$ $\mathrm{kJ{\cdot}mol^{-1}}$ and $S^{\circ}_\mathrm{m}(\mathrm{Th^{4+}}$, 298.15 K) = $-(423.1 \pm 16.0)$ $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ selected in the present review and the auxiliary data for $\mathrm{H_2O(l)}$ and $\mathrm{H^+(aq)}$ in Table IV-1 to calculate the standard Gibbs energies of formation, $\Delta_\mathrm{f}G^{\circ}_\mathrm{m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, aq, 298.15 K), standard enthalpies of formation, $\Delta_\mathrm{f}H^{\circ}_\mathrm{m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, aq, 298.15 K), and standard entropies $S^{\circ}_\mathrm{m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, aq, 298.15 K) summarised in Table VII-18.

Table VII-18: Selected standard molar Gibbs energies, enthalpies and entropies of formation for Th(IV) hydroxide complexes. In order to maintain a high level of numerical consistency, more digits are given than is justified by the precision of the data.

Species	$\Delta_f G_m^o$ (kJ·mol^{-1})	$\Delta_f H_m^o$ (kJ·mol^{-1})	$\Delta_f S_m^o$ (J·K^{-1}·mol^{-1})	S_m^o (J·K^{-1}·mol^{-1})
Th^{4+}	− 704.783 ± 5.298	− 768.700 ± 2.300	− 214.379 ± 17.010	− 423.100 ± 16.000
$Th(OH)^{3+}$	− 927.653 ± 6.018	− 1010.330 ± 6.707	− 277.300 ± 29.586	− 252.765 ± 28.180
$Th(OH)_2^{2+}$	− 1143.673 ± 6.018	− 1254.660 ± 41.464	− 372.252 ± 146.233	− 114.459 ± 140.102
$Th(OH)_3^{+}$	No values selected			
$Th(OH)_4$(aq) or $(Th_m(OH)_{4m})_{1/m}$(aq)	− 1554.024 ± 6.638			
$Th_2(OH)_2^{6+}$	− 1850.168 ± 10.974	− 2050.760 ± 7.325	− 672.789 ± 40.684	− 623.716 ± 38.485
$Th_2(OH)_3^{5+}$	− 2082.171 ± 10.658			
$Th_4(OH)_8^{8+}$	− 4599.809 ± 21.317	− 5118.440 ± 23.204	− 1739.497 ± 101.251	− 708.329 ± 96.221
$Th_4(OH)_{12}^{4+}$	− 5512.980 ± 21.228			
$Th_6(OH)_{14}^{10+}$	− 7338.604 ± 32.523			
$Th_6(OH)_{15}^{9+}$	− 7575.744 ± 32.927	− 8426.850 ± 25.977	− 2854.623 ± 131.318	− 608.102 ± 124.441

VII.3.7 Ternary Th(IV) hydroxide complexes with organic ligands

Complex formation takes place by substitution of coordinated water by other ligands, L. In complexes where all water has not been replaced one must expect the formation of ternary complexes containing both coordinated L and hydroxide. One example is offered by the ternary Th(IV) hydroxide-carbonate complexes discussed in Section XI.1.3.2. Other examples are ternary complexes where L is a multidentate organic ligand like α-hydroxyacetate (glycolate) and 5-sulphosalicylate. The latter systems have been studied by Toraishi *et al.* [2002TOR/FAR] and [2003TOR/GRE]. These studies indicate the formation of a number of tetranuclear complexes containing both the organic ligand and hydroxide. In the first study there is also preliminary EXAFS data that indicate a Th−Th distance of 3.97 Å and based on this the authors suggested a "cubane" structure of a central "Th_4O_4" unit where the oxygen atom derives from the deprotonated OH-group in $HOCH_2COO^-$. Additional glycolate, hydroxide and fluoride ligands can coordinate to the Th-atoms in this unit [2003TOR/GRE]. The experimental data in [2003TOR/GRE] suggests the presence of hydroxide bridged cores "$Th(\mu\text{-}OH)_2Th$" and "$Th_4(\mu\text{-}OH)_4$" in the 5-sulphosalicylate system. The study also demonstrates that strong ternary and quarternary fluoride complexes may form even at very low fluoride concentrations.

This review does not include complexes with organic ligands and therefore the discussion of them is brief and no constants are included. However, the findings in [2002TOR/FAR] and [2003TOR/GRE] are important because they indicate that these complexes are very stable and ternary and quaternary complexes with other organic ligands should therefore not be neglected when discussing the speciation of thorium in systems that contain ligands with carboxylate and aromatic and aliphatic hydroxo groups, as is the case *e. g.* in humic and fulvic acids.

VII.4 Solubility of thorium oxides and hydroxides

There are numerous solubility studies performed with crystalline, microcrystalline or X-ray amorphous thorium oxides and hydroxides or hydrous oxides. Most of these studies were carried out by adding an appropriate amount of the solid to a test solution and achieving equilibrium from the direction of undersaturation [1954GAY/LEI], [1959HIG], [1961KOV/BAG2], [1964NAB/KUD], [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [1992BIS/KRA], [1992EWA/SMI], [1994OST/BRU], [1997RAI/FEL], [1998WIE/HEL], [2000FOU/VIN], [2000RAI/MOO], [2001HUB/BAR], [2002JER/VUO], [2002NEC/MUL], [2003NEC/ALT], [2004ALT/NEC]. Some of the reported solubility data were obtained after *in situ* precipitation of $\mathrm{Th(OH)_4(am)}$ [1959HIG] or after formation of (micro)crystalline $\mathrm{ThO_2(cr)}$ solids [1965BAE/MEY], [2000RAI/MOO], [2003NEC/ALT] in oversaturated solution. In both cases (solubility studies from under- and oversaturation) solid-liquid equilibrium is followed by measuring the thorium concentration and pH as a function of time. In equilibrium with Th oxide or hydroxide the total thorium concentration is given by:

$$\begin{aligned}[\mathrm{Th}]_{\mathrm{tot}} &= [\mathrm{Th}^{4+}] + \Sigma\, m[\,\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}\,] \\ &= {}^*K_{s,0}\ [\mathrm{H}^+]^4\ + \Sigma\, m\ \{{}^*\beta_{n,m}\,({}^*K_{s,0}\ [\mathrm{H}^+]^4)^m / [\mathrm{H}^+]^n\} \qquad \text{(VII.32)}\end{aligned}$$

where ${}^*K_{s,0}$ are the solubility constants for the reactions:

$$\mathrm{Th(OH)_4(cr)} + 4\mathrm{H}^+ \rightleftharpoons \mathrm{Th}^{4+} + 4\mathrm{H_2O(l)} \qquad \text{(VII.33)}$$

or

$$\mathrm{ThO_2(cr)} + 4\mathrm{H}^+ \rightleftharpoons \mathrm{Th}^{4+} + 2\mathrm{H_2O(l)} \qquad \text{(VII.34)}$$

and ${}^*\beta_{n,m}$ are the equilibrium constants for the hydrolysis species $\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$ discussed in Section VII.3.

Most of the results obtained in these solubility studies cannot be discussed and evaluated in a straightforward manner as shown in Section VII.3.1.3, several Appendix A entries and the following discussion. The pH-dependence of the measured solubility is often not in accord with that expected from the known hydrolysis behaviour of the Th^{4+} ion. Problems are caused for instance by the slow dissolution kinetics of crystalline $\mathrm{ThO_2(cr)}$ [2000RAI/MOO], [2001HUB/BAR], [2003NEC/ALT] and ageing or particle size effects in studies with amorphous thorium hydroxide or hydrous oxide. These effects will be discussed in more detail in the Sections VII.4.1.3 and VII.4.3. In addition, inhomogenous thorium oxyhydroxide phases and insufficient phase separation result in too high thorium concentrations that include contributions from polymeric or colloidal thorium species. Moreover sorption effects on filter material may lead to additional scattering of the solubility data.

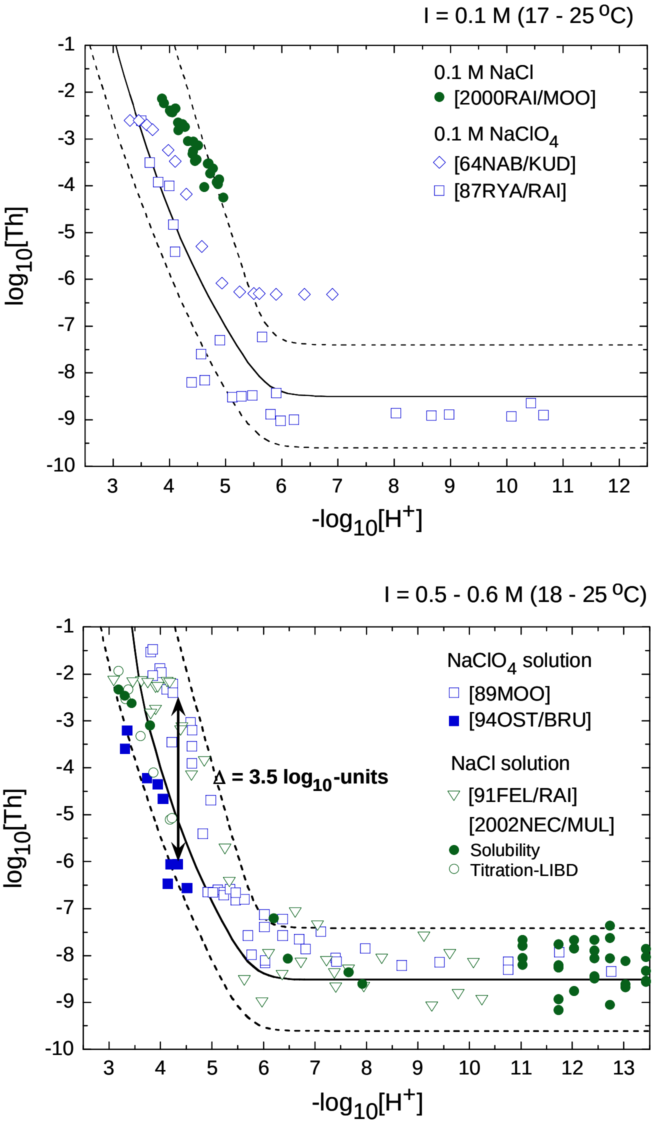
A second type of solubility data is based on studies where acidic thorium solutions are titrated at constant $[\mathrm{Th}]_{\mathrm{tot}}$ until the formation of a solid precipitate or colloids is observed. This non-equilibrium method gives the pH value when the solubility is exceeded for a given $[\mathrm{Th}]_{\mathrm{tot}}$. The sensitivity of the methods to detect the onset of precipitation was significantly improved throughout the last 80 years. In early studies like that of Britton [1925BRI], thorium solutions were titrated until precipitation was visible to the eye. Bilinski *et al.* [1963BIL/FUR], [1966BIL/BRA] used light scattering methods ("Tyndall effect") to detect the onset of precipitation or colloid formation while in more recent studies [2000BUN/KNO], [2002NEC/MUL], [2003NEC/ALT] the laser-induced breakdown detection method (LIBD) was used to detect the initial formation of colloids > 5 nm during coulometric titrations. These non-equilibrium methods overcome the problems of phase separation or ageing effects and give less scattered data. On the other hand, the results depend on the sensitivity of the detection method (for both $[\mathrm{Th}]_{\mathrm{tot}}$ and the minimum size of solid particles) and it is difficult to ascribe the results to a well-defined solid phase. Nevertheless, the results reported in all these papers, even the qualitative observations of [1925BRI], are comparable with those of the traditional solubility studies from undersaturation.

VII.4.1 Amorphous $\mathrm{Th(OH)_4(am)}$ or $\mathrm{ThO_2(am, hyd)}$

The X-ray amorphous Th(IV) precipitates, called either amorphous hydroxides "$\mathrm{Th(OH)_4(am)}$" or hydrous oxides "$\mathrm{ThO_2{\cdot}}x\mathrm{H_2O(am)}$" or "$\mathrm{ThO_2(am, hyd)}$" as in other NEA-TDB reviews, are not well-defined compounds (*cf.* [2003GUI/FAN]). The water content and the particle or crystallite size depend on the preparation method, pretreatment, alteration and temperature [1984GRE/LIE], [2000RAI/MOO], [2002NEC/MUL], [2003GUI/FAN]. Most of the amorphous precipitates used in solubility studies were not dried or heated at higher temperature but only washed with water. Östhols *et al.* [1994OST/BRU] and Neck *et al.* [2002NEC/MUL] used a precipitate dried at room temperature for one week in a vacuum desiccator. The resulting $\mathrm{ThO_2{\cdot}}x\mathrm{H_2O(am)}$ solid had a low degree of crystallinity (no characteristic XRD lines) and a water content of $x \approx 2.4-2.5$. Dzimitrowicz *et al.* [1985DZI/WIS] investigated Th(IV) precipitates prepared in a similar way. They were also X-ray amorphous; however, transmission electron microscopy (TEM) showed that they included small $\mathrm{ThO_2(cr)}$ crystallites (3 − 8 nm). The fact that the bulk phase is X-ray amorphous indicates that it consists mainly of a hydrated oxyhydroxide $\mathrm{ThO}_n\mathrm{(OH)}_{4-2n}{\cdot}x\mathrm{H_2O(am)}$ with $0 < n < 2$ rather than $\mathrm{ThO_2(s)}$.

Amorphous thorium oxyhydroxides with varying chemical composition, water content and particle size have also different thermodynamic properties. This may reflect the differences between reported solubility data. Typical examples of discrepancies between solubility data measured at the same ionic strength are shown in Figure VII-14.

Figure VII-14: Typical solubility data for $Th(OH)_4$(am) or ThO_2(am, hyd) at 17−25°C; a) $I = 0.1$ M [1964NAB/KUD], [1987RYA/RAI], [2000RAI/MOO]; b) $I = 0.5-0.6$ M [1989MOO], [1991FEL/RAI], [1994OST/BRU], [2002NEC/MUL]. The calculated solubility curves are based on the hydrolysis constants and ion interaction coefficients selected in this review and $\log_{10} {}^{*}K^{\circ}_{s,0} = (8.9 \pm 1.1)$. Solid lines: $\log_{10} {}^{*}K^{\circ}_{s,0} = 8.9$, dashed lines: $\log_{10} {}^{*}K^{\circ}_{s,0} = 7.8$ and 10.0.



In addition to systematic discrepancies in solubility up to 3 − 4 orders of magnitude, the different data sets are widely scattered. This is at least partly due to experimental problems with the phase separation procedures, *e.g.*, insufficient removal of colloids, and in particular at the low thorium concentrations at pH > 6, sorption effects on the filter material.

Figure VII-14 shows in addition that the solubility data of thorium hydroxide or hydrous oxide can be divided into two pH regions. At pH < 6, the thorium concentration shows a steep decrease with increasing pH while at pH 6 − 14 the thorium concentration remains at a constant level. In the following sections the published data are discussed and evaluated as follows:

1. The solubility data in the acidic solutions are used to calculate the solubility constant $\log_{10}{}^{*}K^{\circ}_{s,0}$ from each of the studies using the hydrolysis constants $\log_{10}{}^{*}\beta^{\circ}_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, aq, 298.15 K) and the ion interaction (SIT) coefficients $\varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-)$ and $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n},\mathrm{X}^-)$ selected in this review (Sections VII.3.6.1 and VII.3.6.2).
2. As none of the reported equilibrium constants for the formation of the neutral species $\mathrm{Th(OH)_4(aq)}$ (or $\mathrm{Th}_m(\mathrm{OH})_{4m}(\mathrm{aq})$) which is predominant in neutral to alkaline solutions, is free of ambiguities, the reported solubility data in that pH range are used to evaluate an "operational value" of $\log_{10}{}^{*}\beta^{\circ}_{4,1}$ that can be used for geochemical modelling.

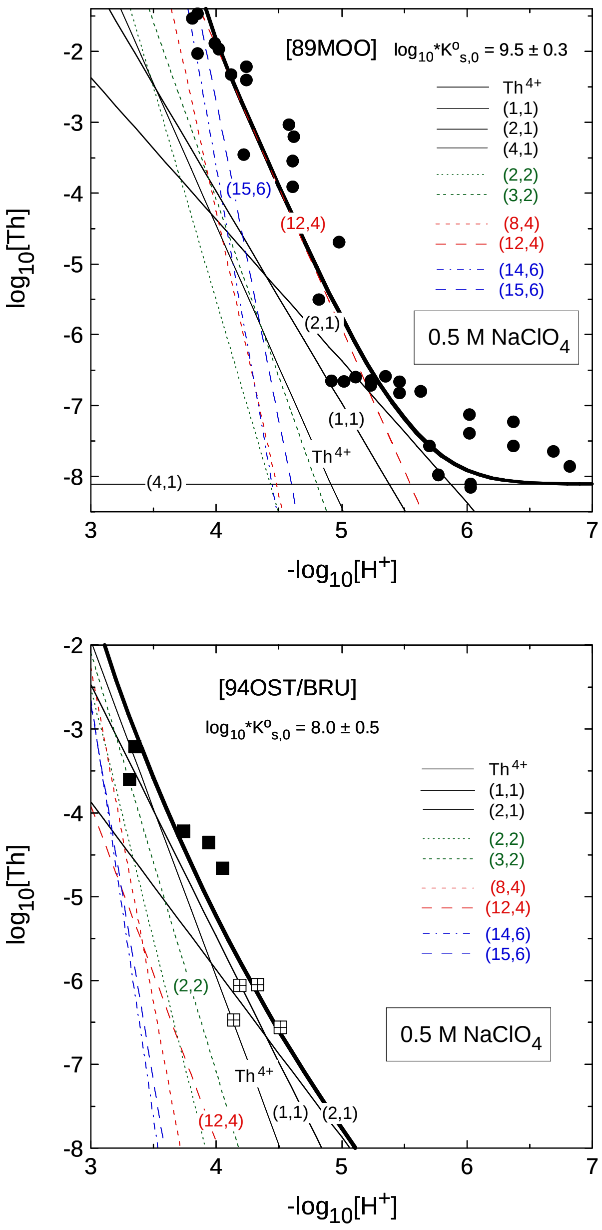
VII.4.1.1 Solubility of Th(OH)$_4$(am) or ThO$_2$(am, hyd) in acidic solutions

The literature data reported for the solubility of Th(OH)$_4$(am) or ThO$_2$(am, hyd) in acidic solution are used to calculate the solubility constant of the solid phase. As the numerous authors used different speciation schemes and hydrolysis constants and partly also different procedures for ionic strength correction, it does not make sense to compare the solubility constants given in the original papers; they have to be recalculated. For reasons of consistency, the values of $\log_{10}{}^{*}\beta^{\circ}_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, aq, 298.15 K) and the SIT coefficients $\varepsilon(\mathrm{Th}^{4+},\mathrm{X}^-)$ and $\varepsilon(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n},\mathrm{X}^-)$ selected by this review are used as fixed values. The only free parameter is then the solubility constant $\log_{10}{}^{*}K^{\circ}_{s,0}$ at zero ionic strength. For the reasons given above the solubility constants re-evaluated by this review can differ considerably from those given in the original papers (see Appendix A).

The re-evaluation of original experimental solubility data is illustrated in Figure VII-15 for the data of Moon [1989MOO] and Östhols *et al.* [1994OST/BRU], both at I = 0.5 M in NaClO$_4$ ionic medium. Besides the total thorium concentration (thick lines), Figure VII-15 also shows the speciation lines, *i.e.*, the thorium concentrations coming from the species (n,m) which are given by:

$$\begin{aligned}\log_{10}[\mathrm{Th}]_{(n,m)} &= \log_{10}(m[\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}])\\ &= \log_{10} m + \log_{10}{}^{*}\beta_{n,m} + m\log_{10}{}^{*}K_{s,0} + (4m-n)\cdot\log_{10}[\mathrm{H}^+] \qquad \text{(VII.35)}\end{aligned}$$

Figure VII-15: Solubility data for ThO_2(am, hyd) in 0.5 M $NaClO_4$ a) from [1989MOO] and b) from [1994OST/BRU] (filled squares: carbonate-free solution; open squares: under CO_2(g) atmosphere which has, however, no effect on the speciation at pH < 4.5). The solubility constant and aqueous speciation are calculated using the hydrolysis constants and SIT coefficients selected in the present review



Accordingly, the concentration lines of species with the same charge z = (4*m*–*n*) have the same slope (−z) in the plot of $\log_{10}[\mathrm{Th}]$ against $-\log_{10}[\mathrm{H}^+]$. If $\log_{10}{}^*K_{s,0}$ increases by 1 $\log_{10}$-unit the concentration of species (*n,m*) is increased by *m* $\log_{10}$-units (at given pH, ionic medium and ionic strength). As a consequence of relation (VII.35), the solubility constant calculated from the data of Moon [1989MOO] ($\log_{10}{}^*K^{\circ}_{s,0} = (9.5 \pm 0.3)$), is only 1.5 $\log_{10}$-units higher than that calculated from the data measured by [1994OST/BRU] ($\log_{10}{}^*K^{\circ}_{s,0} = (8.0 \pm 0.5)$), despite of the fact that the experimental thorium concentrations at pH 3−5 differ by 3−4 orders of magnitude. However, at the high thorium concentrations in the study of [1989MOO], polynuclear species are predominant in saturated solution, in particular the complex (12,4), whereas at the much lower saturation concentrations in the study of [1994OST/BRU] primarily mononuclear thorium species are formed in preference to the polynuclear hydroxide complexes.

The solubility constants $\log_{10}{}^*K^{\circ}_{s,0}$ recalculated in this way from the published original data at *I* = 0.01−4.0 M are summarised in Table VII-19. There is no obvious trend when $\log_{10}{}^*K^{\circ}_{s,0}$ is evaluated from data at low or high ionic strength indicating that the underlying hydrolysis constants and ion interaction coefficients include no systematic errors. The data measured by Östhols *et al.* [1994OST/BRU] and Neck *et al.* [2002NEC/MUL] with a precipitate dried at room temperature, $\log_{10}{}^*K^{\circ}_{s,0} = (8.0 \pm 0.5)$ and $\log_{10}{}^*K^{\circ}_{s,0} = (8.4 \pm 0.5)$, respectively, are 0.5−1.5 $\log_{10}$-units lower than the majority of the $\log_{10}{}^*K^{\circ}_{s,0}$ values calculated from solubility studies performed from oversaturation or from undersaturation with amorphous Th(IV) oxyhydroxide precipitates only washed with water ($\log_{10}{}^*K^{\circ}_{s,0} = 8.4-9.8$). The values calculated from data based on non-equilibrium methods (titration at constant $[\mathrm{Th}]_{\mathrm{tot}}$ until the pH of initial precipitation or colloid formation which is detected by light scattering [1966BIL/BRA] or LIBD [2002NEC/MUL]) are in the same range. The following mean value is calculated from the different papers re-evaluated in Table VII-19: $\log_{10}{}^*K^{\circ}_{s,0}(\mathrm{ThO_2(am,hyd)}) = (8.9 \pm 1.1)$ (or $\log_{10} K^{\circ}_{s,0}(\mathrm{ThO_2(am,hyd)}) = -(47.1 \pm 1.1)$).

Table VII-19: Solubility constants $\log_{10} {}^*K^{\circ}_{s,0}$ at zero ionic strength re-evaluated from solubility studies with $Th(OH)_4(am)$ or $ThO_2(am, hyd)$ at 17−25°C (based on $\log_{10} {}^*\beta^{\circ}_{n,m}(Th_m(OH)_n^{4m-n})$ values and SIT coefficients selected in the present review.)

Reference	Medium, t (°C)	$\log_{10} {}^*K^{\circ}_{s,0}$ ($ThO_2(am, hyd)$)
Solubility studies		
[1959HIG]	~ 0.01 M $NaNO_3$, r.t.	8.7 ± 0.4
[1964NAB/KUD]	0.1 M $NaClO_4$, 17°C	9.2 ± 0.4
[1987RYA/RAI]	0.1 M $NaClO_4$, 25°C	8.8 ± 0.5
[2000RAI/MOO]	0.1 M NaCl, 23°C	9.8 ± 0.3
[1989MOO]	0.5 M $NaClO_4$, 18°C	9.5 ± 0.3
[1994OST/BRU]	0.5 M $NaClO_4$, 25°C	8.0 ± 0.5 [a]
[2002NEC/MUL]	0.5 M NaCl, 25°C	8.4 ± 0.5 [a]
[1991FEL/RAI]	0.6 M NaCl/KCl, r.t.	9.4 ± 0.6
	1.2 M NaCl	9.3 ± 0.6
	3.0 M NaCl	9.2 ± 0.7
[1997RAI/FEL]	4.0 m NaCl, r.t.	8.3 ± 0.7
	6.0 m NaCl	8.1 ± 0.7
	1.0 m $MgCl_2$	8.8 ± 0.4
	1.8 m $MgCl_2$	7.8 ± 0.8 [b]
	3.0 m $MgCl_2$	8.0 ± 0.7 [b]
Studies based on titration until precipitation / colloid formation		
[1963BIL/FUR]	Dilute self–medium	
[1966BIL/BRA]	50% sea water (0.31 m NaCl), 20°C	8.7 ± 0.7
[2002NEC/MUL]	0.5 M NaCl, 25°C	8.4 ± 0.3

a: Solid dried at room temperature in a vacuum desiccator: $ThO_2{\cdot}xH_2O(s)$ with $x = 2.4 - 2.5$.

b: Data in ionic media far out of the validity range of the SIT.

VII.4.1.2 Solubility of $Th(OH)_4$(am) or ThO_2(am, hyd) in neutral and alkaline solution

The pH-independent solubility of $Th(OH)_4$(am) or ThO_2(am, hyd) in neutral to alkaline solutions is usually ascribed to the reaction:

$$Th(OH)_4(am) \text{ or } ThO_2(am, hyd) \rightleftharpoons Th(OH)_4(aq) \quad (VII.36)$$

with

$$\log_{10}[Th(OH)_4(aq)] = \log_{10} K^{\circ}_{s,4}\,(VII.36) = \log_{10} {}^*K^{\circ}_{s,0} + \log_{10} {}^*\beta^{\circ}_{4,1} \quad (VII.37)$$

if the ion interaction coefficients for neutral species are set equal to zero. The mean values of the experimental data determined in numerous studies are summarised in Table VII-20.

Table VII-20: Solubility of $Th(OH)_4(am)$ or $ThO_2(am, hyd)$ at 17−25°C in neutral and alkaline solutions; Column A: Data measured after ultrafiltration or ultracentrifugation; Column B: Data including colloidal or large polynuclear Th(IV) species (measured in the supernatant or after insufficient separation procedures).

Reference	Medium, t (°C)	$\log_{10} K^{\circ}_{s,4}$ or $\log_{10} K^{\circ}_{s,(4m,m)}$	
		A	B
[1954GAY/LEI]	0.01 − 0.87 M NaOH, 25°C		-5.7 ± 1.1
[1959HIG]	~ 0.01 M $NaNO_3$, r.t.		-6.8 ± 0.2
[1992EWA/SMI]	Dilute cement waters (pH 8−13), room temperature	-8.4 ± 0.3	
[2002JER/VUO]	0.1 M NaCl and synthetic groundwaters (I = 0.002 and 0.5 M), (20.5 – 23)°C	-9.5 ± 1.2	
[1964NAB/KUD]	0.1 M $NaClO_4$, 17°C		-6.3 ± 0.1
[1987RYA/RAI]	0.1 M $NaClO_4$, 25°C	-8.8 ± 0.4	
[1989MOO]	0.5 M $NaClO_4$, 18°C	-8.1 ± 0.3	
[2002NEC/MUL]	0.5 M NaCl, 25°C	-8.2 ± 0.9	-6.2 ± 0.5
[2004ALT/NEC]	0.5 and 5 M NaCl, and 0.25 and 2.5 M $MgCl_2$, 22°C	-8.5 ± 0.9	-6.3 ± 0.6
[1991FEL/RAI]	0.6 M NaCl/KCl, r.t.	-8.3 ± 1.0	
	1.2 M NaCl	-8.1 ± 0.9	
	3.0 M NaCl	-7.4 ± 1.0	

Column A shows data determined at pH 6−14 after ultrafiltration (pore size 1.3 −2 nm) [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [1992EWA/SMI], [2002JER/VUO] or ultracentrifugation at 90000 rpm (5×10^5 g) [2002NEC/MUL], [2004ALT/NEC]. The following mean value is obtained from the studies listed in Table VII-20: $\log_{10} K^{\circ}_{s,4}$ (VII.36) = −(8.5 ± 1.0).

The thorium concentrations in column B include contributions from colloidal or large polynuclear Th(IV) species. They were measured either in the supernatant [1954GAY/LEI], [2002NEC/MUL], [2004ALT/NEC] or after insufficient separation procedures. The thorium concentration measured by Nabivanets and Kudritskaya [1964NAB/KUD] at pH 6−7 after centrifugation at 10000 rpm, $\log_{10}[Th] = -6.3$, are two orders of magnitude higher. As shown in [2004ALT/NEC], the centrifugal force used by [1964NAB/KUD] is not sufficient to remove small Th(IV) polymers or colloids. The remaining thorium concentration is equal to that determined by [2002NEC/MUL], [2004ALT/NEC] in the supernatant solutions without removing polymeric or colloidal species. Similar values were reported by [1954GAY/LEI] in aliquots taken from the supernatant of their samples in 0.01 − 0.87 M NaOH ($\log_{10}[\mathrm{Th}] = -(5.7 \pm 1.1)$) and by [1959HIG] at pH 6 − 8 in 0.01 M $NaNO_3$. The latter author measured thorium concentrations of $\log_{10}[\mathrm{Th}] = -(6.8 \pm 0.2)$ after filtration with filter paper, which is also not sufficient to remove colloidal or large polynuclear species $\mathrm{Th}_m(\mathrm{OH})_{4m}(\mathrm{aq})$.

If the pH-independent thorium concentrations determined in neutral to alkaline solutions after ultrafiltration in [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [2002JER/VUO] or after ultracentrifugation [2002NEC/MUL], [2004ALT/NEC] is ascribed to Reaction (VII.36) and combined with the solubility constants $\log_{10} {}^{*}K^{\circ}_{s,0}$ calculated by this review from the data at pH < 6 in the corresponding solubility studies, we obtain the equilibrium constant $\log_{10} {}^{*}\beta^{\circ}_{4,1}$ (Table VII-21). This review selects the mean value of:

$$\log_{10} {}^{*}\beta^{\circ}_{4,1} = -(17.4 \pm 0.7).$$

The same value, but with a larger uncertainty, $\log_{10} {}^{*}\beta^{\circ}_{4,1} = -(17.4 \pm 1.5)$, is obtained from the mean values of all solubility data determined with $\mathrm{Th(OH)_4(am)}$ or $\mathrm{ThO_2(am, hyd)}$ at pH 6 − 14, ($\log_{10} K^{\circ}_{s,4} = -(8.5 \pm 1.0)$) and in acidic solutions ($\log_{10} {}^{*}K^{\circ}_{s,0} = (8.9 \pm 1.1)$, *cf.* Section VII.4.1.1).

Table VII-21: Equilibrium constants $\log_{10} K^{\circ}_{s,4}$ and $\log_{10} {}^{*}\beta^{\circ}_{4,1}$ at zero ionic strength re-evaluated by this review from solubility studies with $\mathrm{Th(OH)_4(am)}$ or $\mathrm{ThO_2(am, hyd)}$ at 17 − 25°C.

Reference	Medium	$\log_{10} K^{\circ}_{s,4}$	$\log_{10} {}^{*}K^{\circ}_{s,0}$	$\log_{10} {}^{*}\beta^{\circ}_{4,1}$
[1987RYA/RAI]	0.1 M $NaClO_4$	-8.8 ± 0.4	8.8 ± 0.5	-17.6 ± 0.6
[1989MOO]	0.5 M $NaClO_4$	-8.1 ± 0.3	9.5 ± 0.3	-17.6 ± 0.4
[1991FEL/RAI]	0.6, 1.2 and 3.0 M NaCl	-7.9 ± 1.0	9.3 ± 0.6	-17.2 ± 1.2
[2002NEC/MUL], [2004ALT/NEC]	0.5 and 5 M NaCl and 0.25 and 2.5 M $MgCl_2$	-8.5 ± 0.9	8.4 ± 0.5 –	-16.9 ± 1.0
[2002JER/VUO]	0.1 M NaCl and synthetic groundwaters (I = 0.002 and 0.5 M)	-9.5 ± 1.2	8.2 ± 0.6 [a]	-17.7 ± 1.3

a: Solubility constant from [1994OST/BRU], [2002NEC/MUL] for $\mathrm{ThO_2(am, hyd)}$ prepared in the same way.

The equilibrium constants $\log_{10} K^{\circ}_{s,4} = -(8.5 \pm 1.0)$ and $\log_{10} {}^{*}\beta^{\circ}_{4,1} = -(17.4 \pm 0.7)$ can be used as "operational values" for geochemical modelling. However it is by no means ascertained that the thorium concentration measured in solubility studies at pH 6 − 14 is actually due to the mononuclear complex $\mathrm{Th(OH)_4(aq)}$. This review finds it more likely that the soluble uncharged complex is one or more small (≤ 1.5 nm) polynuclear species $\mathrm{Th}_m\mathrm{O}_{mx}(\mathrm{OH})_{m(4-2x)}(\mathrm{aq})$, more simply written as

$Th_m(OH)_{4m}(aq)$, *e.g.*, tetranuclear species $Th_4O_4(OH)_8(aq)$ = $Th_4(OH)_{16}(aq)$ with a diameter of about 1 nm. Accordingly the solubility in neutral to alkaline solutions is given by the reaction:

$$\mathrm{Th(OH)_4(am)\ or\ ThO_2(am,\ hyd)} \rightleftharpoons 1/m\ \mathrm{Th}_m\mathrm{(OH)}_{4m}\mathrm{(aq)} \qquad \text{(VII.38)}$$

with $\log_{10} K^{\circ}_{s,(4m,m)} = -(6.3 \pm 0.8)$[1] if Th(IV) polymers or colloids are not removed and $\log_{10} K^{\circ}_{s,(4m,m)} = -(8.5 \pm 1.0)$ after 1.5−2 nm ultrafiltration or ultracentrifugation, *i.e.*, for a particle size ≤ 1.5 nm ($m < 10$).

VII.4.1.3 Ageing effects and selected data for ThO_2(am, hyd)

The effect of particle or crystallite size of ThO_2(am, hyd) is usually in the range of 2 to 20 nm and has a dramatic effect on the Gibbs energy and the solubility constant (*cf.* Section VII.4.3). As discussed above for the solubility data of [1994OST/BRU] and [2002NEC/MUL], drying of amorphous precipitates, *i.e.*, dehydration by condensation of smaller particles leads to larger and less hydrated particles with a smaller molar surface and hence to a bulk solid phase of lower Gibbs energy and solubility. Similarly, ageing effects observed for fresh amorphous precipitates may be interpreted in terms of increasing particle size by surface recrystallisation *via* local dissolution-precipitation equilibria (Ostwald ripening). As this effect seems to be kinetically favoured at higher aqueous thorium concentrations, it is expected to be more pronounced and faster at low pH than in neutral and alkaline solutions, where the aqueous thorium concentration is very low.

The effect of ageing of the solid phase, amorphous thorium hydroxide or hydrous oxide, on the measured thorium concentrations are best documented in the paper of Higashi [1959HIG] who measured the solubility from the direction of oversaturation after titration of 3×10^{-3} M thorium nitrate solutions from pH 2.5 to pH values in the range 4−8. Figure VII-16 shows the thorium concentrations measured after 1, 3, 7, and 100 days demonstrating the large solubility decrease as a result of ageing at pH < 6. The effect is more pronounced at lower pH and higher thorium concentrations in solution. A closer look at the solubility data determined by

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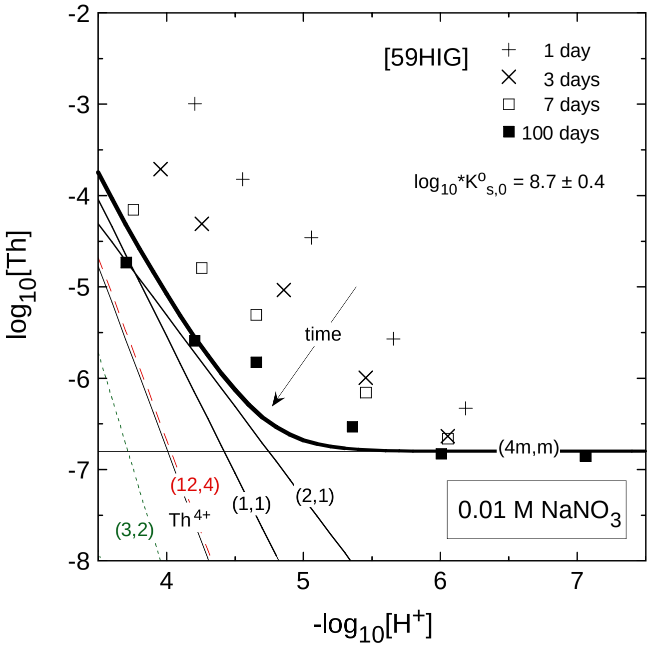
[1] If we ascribe the concentration of Th(IV) polymers or colloids to equilibrium (VII.38) with $1/m\ Th_m(OH)_{4m}(aq)$, more simply rewritten as ThO_2(coll, hyd), it is possible to calculate their formal molar standard Gibbs energy. However, this review does not select any thermodynamic data for these polymeric or colloidal species, since they are not well-defined compounds. With the mean value of $\log_{10} K^{\circ}_{s,0} = -(47.1 \pm 1.1)$ corresponding to $\Delta_f G^{\circ}_m$ (ThO_2, am, hyd, 298.15 K) = $-(1128.2 \pm 8.2)$ kJ·mol^{-1} and $\log_{10} K^{\circ}_{s,(4m,m)}$ (VII.38)= $-(6.3 \pm 0.8)$ we obtain $\Delta_f G^{\circ}_m$ (ThO_2, coll, hyd, 298.15 K) = $-(1092.3 \pm 9.3)$ kJ·mol^{-1}. Extending the application of Schindler's relation [1967SCH] discussed in Section VII.4.3 for crystalline, microcrystalline and amorphous thorium oxide and oxyhydroxides: $\Delta_f G^{\circ}_m$ (ThO_2, particle size d) = $-(1169.0 \pm 3.5) + 129/d$(nm) kJ·mol^{-1}, to these polymeric or colloidal Th(IV) hydroxide species, we can calculate their average particle diameter: $d = (1.7 \pm 0.2)$ nm. This means that the nuclearity of these species $Th_m(OH)_{4m}(aq)$ is in the range $10 < m < 50$.

[1991FEL/RAI] and [1997RAI/FEL] at pH < 5 in 0.6 − 6 m NaCl after relatively short equilibration time (< 10 days) and after more than 70 days reveals similar ageing effects. The corresponding solubility constants are listed in Table VII-22. For the low thorium concentrations at pH > 6, there is no clear variation of the solubility on equilibration.

Figure VII-16: Solubility of thorium hydroxide determined by Higashi [1959HIG] at room temperature from oversaturation after 1, 3, 7, and 100 days. The solubility and speciation lines are calculated with the hydrolysis constants and SIT coefficients selected in this review, $\log_{10}{}^{*}K^{\circ}_{s,0} = 8.7$ and $\log_{10} K_{s,(4m,m)} = -6.8$.



It is not possible to draw an exact borderline between the data for fresh and aged Th(IV) hydroxide or hydrous oxide, because this may also depend on washing procedures and storing time before the solids are used in the solubility experiments from undersaturation. Although the $\log_{10}{}^{*}K^{\circ}_{s,0}$ re-evaluated in Table VII-22 from experimental data measured after short and long equilibration times overlap, this review suggests that one might distinguish between the solubility constants derived from data measured after equilibration times < 25 days and > 70 days and ascribe them to fresh and aged ThO_2(am, hyd), respectively. Thus the following values are selected:

$$\log_{10}{}^{*}K^{\circ}_{s,0}\,(\mathrm{ThO_2(am,\ fresh,\ hyd)},\ 298.15\ \mathrm{K}) = (9.3 \pm 0.9)$$

$$\log_{10}{}^{*}K^{\circ}_{s,0}\,(\mathrm{ThO_2(am,\ aged,\ hyd)},\ 298.15\ \mathrm{K}) = (8.5 \pm 0.9).$$

The latter solubility constant, selected from data obtained after ageing for more than 2 months [1959HIG], [1991FEL/RAI], [1997RAI/FEL] or with a solid that was dried at room temperature [1994OST/BRU], [2002NEC/MUL] is recommended for modelling thorium solubilities in natural systems. For kinetic reasons discussed in Section VII.4.2.3 the thermodynamically stable $ThO_2(cr)$ is not expected to control the solubility in neutral and alkaline solutions.

Table VII-22: Solubility constants $\log_{10} {}^*K^\circ_{s,0}$ at zero ionic strength re-evaluated from solubility studies with fresh and aged or dried ThO_2(am, hyd) at 17−25°C (based on $\log_{10} {}^*\beta^\circ_{n,m}(\text{Th}_m(\text{OH})_n^{4m-n})$ values and SIT coefficients selected in the present review.)

Reference	Medium, t (°C)	$\log_{10} {}^*K^\circ_{s,0}$ (ThO_2, am, hyd)	
		Fresh (< 25 days)	Aged (> 70 days)
[1959HIG]	~ 0.01 M $NaNO_3$, r.t.	10 to 9	8.7 ± 0.4
[1964NAB/KUD]	0.1 M $NaClO_4$, 17°C	9.2 ± 0.4	
[1987RYA/RAI]	0.1 M $NaClO_4$, 25°C	8.8 ± 0.5	
[2000RAI/MOO]	0.1 M NaCl, 23°C	9.8 ± 0.3	
[1989MOO]	0.5 M $NaClO_4$, 18°C	9.5 ± 0.3	
[1991FEL/RAI]	0.6 M NaCl/KCl, r.t.	9.5 ± 0.5	9.1 ± 0.4
	1.2 M NaCl	9.5 ± 0.7	9.2 ± 0.4
	3.0 M NaCl	9.8 ± 0.4	8.9 ± 0.5
[1997RAI/FEL]	4.0 m NaCl, r.t.	8.6 ± 0.5	8.2 ± 0.5
	6.0 m NaCl	8.4 ± 0.6	8.0 ± 0.6
	1.0 m $MgCl_2$	8.8 ± 0.4	
			Dried solid [a]
[1994OST/BRU]	0.5 M $NaClO_4$, 25°C		8.0 ± 0.5
[2002NEC/MUL]	0.5 M NaCl, 25°C		8.4 ± 0.5

a: Solid dried at room temperature in a vacuum desiccator: $ThO_2{\cdot}xH_2O(s)$ with $x = 2.4 - 2.5$

VII.4.2 Anhydrous ThO_2(cr) and microcrystalline ThO_2(cr, hyd)

VII.4.2.1 Solubility constant of ThO_2(cr) calculated from thermodynamic data

The solubility constant of crystalline $ThO_2(cr)$ to give Th^{4+} can be calculated from the selected thermodynamic data for these species (Section VII.1.2), $\Delta_f G^\circ_m$(ThO_2, cr, 298.15 K) = −(1169.0 ± 3.5) kJ·mol^{-1} and $\Delta_f G^\circ_m$(Th^{4+}, 298.15 K) = −(704.8 ± 5.3) kJ·mol^{-1} (Section VI.1) and $\Delta_f G^\circ_m$ auxiliary data for $H_2O(l)$, OH^- or H^+.

The respective equilibrium constants for the reactions:

$$ThO_2(cr) + 2H_2O(l) \rightleftharpoons Th^{4+} + 4OH^- \quad \text{(VII.39)}$$

$$ThO_2(cr) + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O(l) \quad \text{(VII.40)}$$

are:

$$\log_{10} K^{\circ}_{s,0}\,(\text{ThO}_2,\ \text{cr},\ 298.15\ \text{K}) = -(54.24 \pm 1.11)$$

$$\log_{10} {}^{*}K^{\circ}_{s,0}\,(\text{ThO}_2,\ \text{cr},\ 298.15\ \text{K}) = (1.77 \pm 1.11).$$

These constants are about 7 $\log_{10}$-units lower than the values for ThO_2(am, hyd).

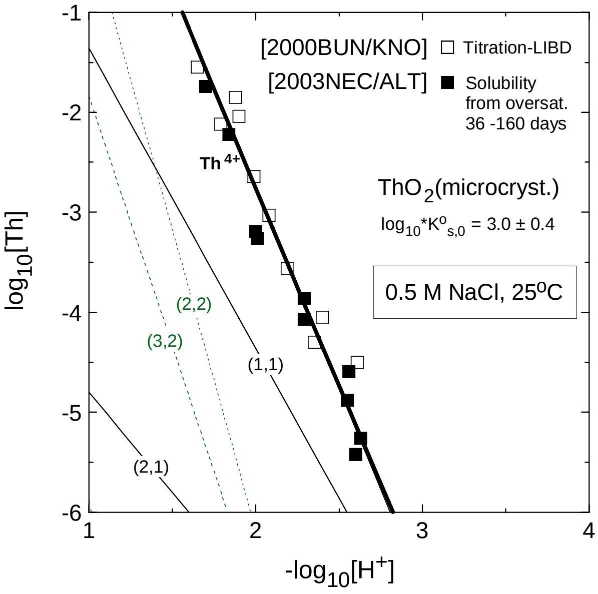
VII.4.2.2 Solubility of crystalline and microcrystalline ThO_2(cr) in acidic solution

Dissolution experiments with well-crystallised ThO_2(cr) are affected by the very slow dissolution kinetics [1984GRE/LIE], [2001HUB/BAR], [2003NEC/ALT]. Hubert *et al.* [2001HUB/BAR] investigated the dissolution kinetics of ThO_2(cr) at 25°C in 0.1 M $HClO_4$-$NaClO_4$ as a function of the calcination temperature and grain size. Using ThO_2(cr) prepared by heating thorium oxalate, hydroxide and nitrate at 900 and 1600°C, the thorium concentrations measured after 3 months at pH 1 − 3 were almost independent of pH. However, depending on the preparation of the solid, the measured value of $\log_{10}$[Th] varied from −4.0 to −5.5 and was correlated with the surface area of the solid [2001HUB/BAR]. The slow dissolution kinetics of ThO_2(cr) and its dependence on the preparation and pre-treatment of the solid was also observed in 7.5 M HNO_3 [1984GRE/LIE].

Dissolution experiments performed by Neck *et al.* [2003NEC/ALT] with crystalline ThO_2(cr) at pH 1.0 − 2.5 in 0.1 M and 0.5 M HCl/NaCl gave similar results as reported by [2001HUB/BAR]. Even after equilibration for more than one year, the thorium concentrations ($\log_{10}$[Th] = −4.6 to −5.2) were significantly below the expected equilibrium values and almost independent of pH (contrary to the expected slope of −4 for Th^{4+} as the predominant aqueous species). In analogous dissolution experiments with ThO_2(cr) at 23°C in 0.1 M HCl/NaCl, Rai *et al.* [2000RAI/MOO] measured somewhat higher thorium concentrations at pH 1.3 − 2.0. However, the corresponding solubility constants were also considered as lower limit for ThO_2(cr) ($\log_{10} {}^{*}K_{s,0} > 2.3$ at $I = 0.1$ M and $\log_{10} {}^{*}K^{\circ}_{s,0} > 1.0$ if converted to $I = 0$ with the SIT). Moreover, the thorium concentrations measured at pH 2 − 3 were independent of pH [2000RAI/MOO], similar as in [2003NEC/ALT]. Another unexpected observation was reported by Moon [1989MOO] for the solubility of crystalline ThO_2(cr) at pH 2 − 13 in 0.1 M $NaClO_4$: these results showed that $\log_{10}$[Th] decreased continuously as a function of pH, but approached more and more closely the thorium concentration in equilibrium with amorphous thorium hydroxide. At pH > 5 the data measured with ThO_2(cr) and $Th(OH)_4$(am) were identical. (An interpretation of this behaviour is presented in Section VII.4.3.2).

All these results indicate that solubility studies performed with ThO_2(cr) at 18 − 25°C from the direction of undersaturation have not reached equilibrium. On the other hand, equilibrium between crystalline and microcrystalline ThO_2(cr) and Th^{4+} was reached from the direction of oversaturation, both at 25°C [2003NEC/ALT] (Figure VII-17) and at 90°C [2000RAI/MOO] and 95°C [1965BAE/MEY] (Figure VII-18).

Figure VII-17: Solubility data from [2000BUN/KNO] and [2003NEC/ALT] for microcrystalline ThO_2(cr, hyd) at 25°C. The solubility constant and aqueous speciation are calculated using hydrolysis constants and SIT coefficients selected in the present review.[1]



Baes *et al.* [1965BAE/MEY] measured the solubility after adding crystalline ThO_2(cr) to acidic Th(IV) solutions in 1 M $NaClO_4$ at 95°C. Rai *et al.* [2000RAI/MOO] observed the transformation of an amorphous precipitate into a crystalline solid at 90°C and pH 1.5−3 in 0.1 M NaCl. They also observed that the unexpectedly high solubility data for ThO_2(cr) at pH 2.0−3.5, measured after equilibration at 23°C for more than two years, decreased after storing the samples for two weeks at 90°C and then readjusting the temperature to 23°C for one day. This observation was ascribed to the crystallisation of small amorphous fractions of the solid. The solubility data measured at 90°C from the direction of oversaturation show the expected dependence on pH, with a solubility about 2.2 $\log_{10}$-units higher than another set of data determined with ThO_2(cr)

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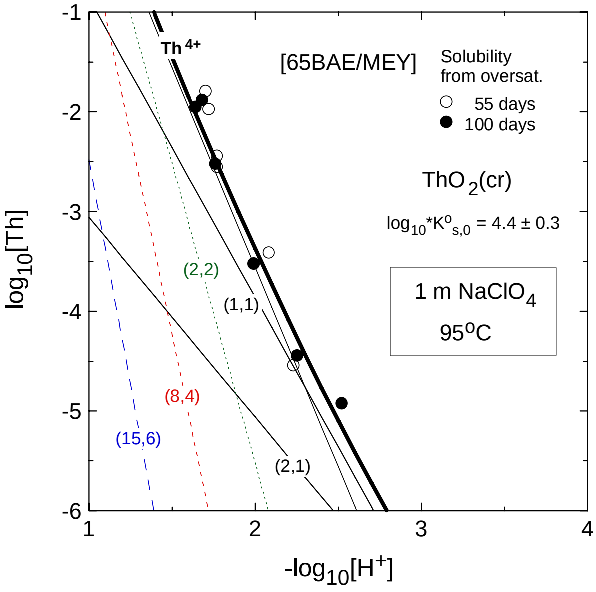
[1] All the hydroxide complexes were included in the calculations, but for these microcrystalline solids with very low solubility products, the concentrations of the species with high nuclearity (such as the (12,4) complex) are so low that they do not appear on this Figure.

from undersaturation [2000RAI/MOO]. In the studies of Bundschuh *et al.* [2000BUN/KNO] and Neck *et al.* [2003NEC/ALT], coulometric titration of Th(IV) solutions at pH = 1.5−2.5 (0.5 M HCl-NaCl) and 25°C led to the formation of small ThO_2 colloids which agglomerated to microcrystalline ThO_2(cr, hyd) precipitates. The size of the colloids, with a mean diameter of 16−23 nm, was determined by LIBD. XRD analysis of the microcrystalline thorium oxide phases formed in [2000RAI/MOO] at 90°C and in [2003NEC/ALT] at 25°C showed the ThO_2(cr) pattern with broadened lines.

Figure VII-18: Solubility data from [1965BAE/MEY] for ThO_2(cr) at 95°C. The solubility constant and aqueous speciation are calculated using hydrolysis constants selected in the present review for 1 M $NaClO_4$ at 95°C (*cf.* Section VII.3.5.1).



The solubility constants derived from the studies discussed in this section are summarised in Table VII-23. The $\log_{10} {}^*K^\circ_{s,0}$ values for microcrystalline ThO_2(cr, hyd) at 298.15 K are about one $\log_{10}$-unit higher than $\log_{10} {}^*K^\circ_{s,0}$ (ThO_2, cr, 298.15 K) = (1.8 ± 1.1) calculated from thermochemical data. This agreement is excellent if the effect of particle size on the solubility constant is taken into account (*cf.* Section VII.4.3). Similar differences are observed for the microcrystalline thorium oxide phases formed in solubility studies from oversaturation at 90°C [2000RAI/MOO] and 95°C [1965BAE/MEY] and the crystalline ThO_2(cr) used by [2000RAI/MOO] in solubility experiments from undersaturation at 90°C. The experimental solubility constant calculated from the study of [2000RAI/MOO] with crystalline ThO_2(cr) at 363 K, $\log_{10} {}^*K^{\circ}_{s,0}$ (ThO_2, cr, 363 K) = $-(0.2 \pm 0.4)$, and the calculated thermochemical value at 363 K, $\log_{10} {}^*K^{\circ}_{s,0}$ (ThO_2, cr, 363 K) = $-(1.9 \pm 1.1)$, are compatible if particle size effects are taken into account (*cf.* Appendix A). The latter value is calculated from the selected data for ThO_2(cr) and Th^{4+} according to Eq. (X.19) in [1997ALL/BAN] (Chapter X, p. 434), with a constant value of $\Delta_r C^{\circ}_{p,m} = -(135 \pm 15)$ J·K^{-1}·mol^{-1}.

Table VII-23: Solubility constants derived from solubility data from oversaturation for microcrystalline ThO_2(cr, hyd) and from undersaturation for ThO_2(cr) at pH < 2.5 and calculated value for anhydrous ThO_2(cr).

Medium	t (°C)	Method	$\log_{10} {}^*K_{s,0}$	$\log_{10} {}^*K^{\circ}_{s,0}$	Reference
1.0 M $NaClO_4$	95	sol, oversat.	4.4 ± 0.3	1.5 ± 0.4 [b]	[1965BAE/MEY]
0.1 m NaCl	90	sol, oversat.	3.5 ± 0.4 [a]	2.0 ± 0.4 [b]	[2000RAI/MOO]
	90	sol, undersat.	1.3 ± 0.4 [a]	-0.2 ± 0.4 [b]	
	23	sol, undersat.	≥ 2.3 [a]	≥ 1.0	
0.5 M NaCl	25	titr.-LIBD	5.4 ± 0.5	3.1 ± 0.5	[2000BUN/KNO],[2003NEC/ALT]
0.5 M NaCl	22	sol, oversat.	5.1 ± 0.4	2.8 ± 0.4	[2003NEC/ALT]
$I = 0$	25	calculated [c]		1.8 ± 1.1	This review, ThO_2(cr)
	90	calculated [c]		-1.9 ± 1.1	

a: Calculated from the experimental values of $\log_{10}[Th^{4+}]$ and pH (activity scale) given in [2000RAI/MOO] according to: $\log_{10} {}^*K_{s,0} = \log_{10}[Th^{4+}] + 4\,(pH + \log_{10}\gamma_{H^+})$, with $\log_{10}\gamma_{H^+} = -0.10$ at 23°C and – 0.12 at 90°C [b]. The uncertainty is given as 2σ.

b: Ionic strength corrections at 90 and 95°C are made with the SIT (*cf.* [1997GRE/PLY2] and [2003GUI/FAN]). The temperature derivatives of the activity of water and the SIT coefficients, $L_1 = -RT^2(\partial \ln a_w / \partial T) = 0.03$ kJ·mol^{-1} for 1.0 M $NaClO_4$ and 0.00 for 0.1 M NaCl, $\varepsilon_L(H^+, Cl^-) = (\partial(\varepsilon(H^+, Cl^-))/\partial T) = -(1.0 \pm 0.1) \times 10^{-3}$ kg·mol^{-1}·K^{-1} and $\varepsilon_L(H^+, ClO_4^-) = (0.9 \pm 0.2) \times 10^{-3}$ kg·mol^{-1}·K^{-1}, are taken from [1997GRE/PLY2]. The unknown values of $\varepsilon_L(Th^{4+}, Cl^-)$ and $\varepsilon_L(Th^{4+}, ClO_4^-)$ are set equal to zero within an uncertainty of $\pm 5 \times 10^{-3}$ kg·mol^{-1}·K^{-1}.

c: Calculated from standard state thermodynamic data selected in the present review for Th(cr), ThO_2(cr) and Th^{4+}.

Similar solubility constants were calculated by [2004HEI/HUB] from dissolution experiments with mixed Th(IV)-U(IV) oxides $Th_{1-x}U_xO_2$(cr) at $-\log_{10}[H^+]$ = 1, 2, 3 and 4 in 0.1 M HNO_3-KNO_3 media at room temperature (*cf.* Appendix A). However, solid solution phases are not within the scope of the present review.

VII.4.2.3 Discussion of solubility data for crystalline and microcrystalline ThO_2(cr) in neutral and alkaline solution

The reported experimental solubility data determined with ThO_2(cr) in near-neutral and alkaline solutions are listed in Table VII-24. The mean value of the experimental thorium concentrations determined by the different authors, $\log_{10}[\text{Th}] = -(9.3 \pm 1.4)$, is close to experimental values for amorphous hydroxides or hydrous oxides ($\log_{10} K^{\circ}_{s,4}$ (ThO_2, am, hyd) $= -(8.5 \pm 1.0)$). In addition, there is no clear effect of temperature. The same has been observed for solubility measurements with crystalline UO_2(cr) at 25°C [1995YAJ/KAW] and 100−300°C [1985PAR/POH], which are also independent of the temperature and close to the values for UO_2(am, hyd) [2001NEC/KIM], [2003GUI/FAN].

It is obvious that the measured solubility data do not refer to the reaction:

$$\text{ThO}_2(\text{cr}) + 2\text{H}_2\text{O(l)} \rightleftharpoons \text{Th(OH)}_4(\text{aq}) \qquad \text{(VII.41)}$$

All values in Table VII-24 are orders of magnitude higher than the expected thorium concentration of $\log_{10}[\text{Th(OH)}_4(\text{aq})] = \log_{10} K^{\circ}_{s,4}$ (ThO_2, cr) $= -(15.6 \pm 1.3)$, which results from the solubility constant $\log_{10} {}^{*}K^{\circ}_{s,0}$ (ThO_2, cr, 298.15 K) $= (1.8 \pm 1.1)$ (calculated from $\Delta_{\text{f}}G^{\circ}_{\text{m}}$ (ThO_2, cr, 298.15 K) $= -(1169.0 \pm 3.5)$ kJ·mol^{-1}) and $\log_{10} {}^{*}\beta^{\circ}_{4,1} = -(17.4 \pm 0.7)$ selected by this review.

Table VII-24: Solubility data for ThO_2(cr) in near-neutral and alkaline solutions (measured after ultrafiltration or ultracentrifugation).

Reference	Solid	Medium	t (°C)	$\log_{10}[\text{Th}]$
[2001HUB/BAR]	ThO_2(cr) prepared at 900 and 1600°C	0.1 M NaClO_4, pH 5.3 − 7.2	room temperature	
	a) from hydroxide			− 10.3 ± 0.2 [a]
	b) from nitrate			− 9.6 ± 0.4 [a]
	c) from oxalate			− 10.6 ± 0.6 [a]
[2000FOU/VIN]	ThO_2(cr) powder prepared from oxalate calcined up to 1600°C	synthetic granite waters pH 6.6 − 9.2	25 90	− 10.3 ± 0.7 − 8.3 ± 0.4
[1989MOO]	ThO_2(cr) prepared at 700°C from oxalate	0.1 M NaClO_4, pH 6 − 13	18	− 8.2 ± 0.3
[1998WIE/HEL]	ThO_2(microcryst.)	cement pore water pH 12.5 and 13.2	22 55	− 9.6 ± 0.4 − 10.0 ± 0.1
[2003NEC/ALT]	ThO_2(cr) (commercial, p.a.)	0.1 M NaCl-NaOH pH 11 − 13.5	22	− 9.3 ± 0.8
[2004ALT/NEC]	ThO_2(cr) (commercial, p.a.)	0.1 and 0.5 M NaCl and 0.25 and 2.5 M MgCl_2 saturated with Mg(OH)_2(cr), pH 9 − 11	22	− 9.0 ± 1.3

a: Measured after only 10 days, while the data of [1998WIE/HEL], [2000FOU/VIN] were measured after 25 and 31 days, respectively, and those of [2003NEC/ALT], [2004ALT/NEC] after 71 and 112 days.

These experimental findings may be caused by small amounts of more soluble amorphous material present in the crystalline solid [2000RAI/MOO], [2003RAI/YUI] (*cf.* discussion in Section VII.4.3). Another possible explanation is proposed in [2001NEC/KIM], [2002FAN/NEC]: The thermodynamic data for ThO_2(cr) determined by calorimetry refer to the crystalline "bulk", but what is relevant when this phase is in contact with water is the thermodynamics at the interface, *i.e.*, at the hydrated surface containing OH-groups.

There is a thermodynamic driving force for the transformation of "$Th(OH)_4$(am)" particles on the surface into the thermodynamically stable ThO_2(cr), a process enhanced by an increase in temperature, but solid-state transformations at room temperature are relatively slow and are not achieved in the time frames used in most solubility studies. The change in solubility due to particle growth is also enhanced by an increase in temperature.

VII.4.3 Discussion of particle size effects

VII.4.3.1 Particle size effect on thermodynamic data for ThO_2(s)

As stated above, the variation of the solubility of oxide / hydrous oxide phases can be a result of surface hydration or particle size variation (or a combination of both). In the model used to describe the effects of particle size on the solubility, one assumes that the solid has the same chemical composition as the bulk crystalline material, in this case ThO_2(cr). The difference between the molar Gibbs energy of small particles with a large molar surface area $\mathcal{A}$ and large particles with a much smaller molar surface area ($\mathcal{A} \rightarrow 0$) is given by [1967SCH]

$$\Delta_f G^\circ_m(\mathcal{A}) - \Delta_f G^\circ_m(\mathcal{A} \rightarrow 0) \;=\; RT \ln \frac{K^\circ_{s,0}(\mathcal{A})}{K^\circ_{s,0}(\mathcal{A} \rightarrow 0)} \;=\; \frac{2}{3}\,\bar{\gamma}\,\mathcal{A} \qquad \text{(VII.42)}$$

where $\bar{\gamma}$ denotes the mean free surface energy per unit surface area of the solid-liquid interface (interfacial tension) and $\mathcal{A}$ the surface area per mole of solid:

$$\mathcal{A} = \frac{\mathrm{M}\,\alpha}{\rho\, d} \qquad \text{(VII.43)}$$

M is the molecular weight and ρ the density of the solid, d describes the particle size and α is a geometrical factor which depends on the shape of the particles. For approximately spherical particles with diameter d the geometry factor is $\alpha \approx 6$. According to Schindler [1967SCH] the mean free surface energy of the solid-liquid interface can be estimated by Eq. (VII.44):

$$\bar{\gamma} = -\frac{3\,RT \ln K^\circ_{s,0}(\mathcal{A} \rightarrow 0)}{2\, N_A \sum 4\pi r_i^2} \qquad \text{(VII.44)}$$

where r_i are the ionic radii of the ions.

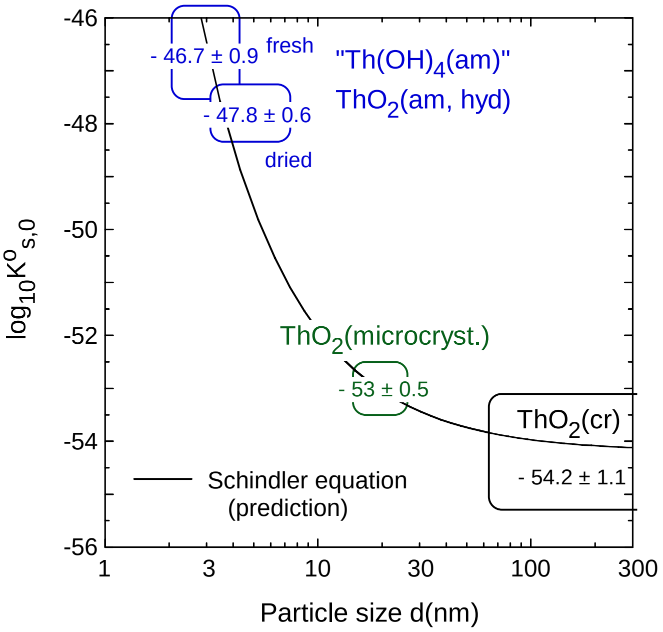
With the known data for crystalline $ThO_2(cr)$ ($\log_{10} K^{o}_{s,0}(\mathcal{A} \rightarrow 0) = -(54.2 \pm 1.1)$ calculated from thermochemical data, M = 264.04 g·mol^{-1}, ρ = 10.0 g·cm^{-3}), the ionic radii $r_{Th^{4+}} = 0.105$ nm, $r_{O^{2-}} = 0.140$ nm [1976SHA], and RT ln (10) = 5.708 kJ·mol^{-1} at 25°C, the interfacial tension $\overline{\gamma}$ is calculated to be 1.22 J·m^{-2} [2000BUN/KNO]. The relations between $\Delta_f G^{o}_{m}$ and $\log_{10} K^{o}_{s,0}$ of small ThO_2 particles (particle size d) and large crystals of $ThO_2(cr)$ are thus given by:

$$\Delta_f G^{o}_{m}(ThO_2, \text{particle size } d) = -(1169.0 \pm 3.5) + \frac{129}{d(\text{nm})} \quad \text{kJ·mol}^{-1} \qquad \text{(VII.45)}$$

$$\log_{10} K^{o}_{s,0}(ThO_2, \text{particle size } d) = -(54.2 \pm 1.1) + \frac{22.6}{d(\text{nm})} \qquad \text{(VII.46)}$$

The variation of $\log_{10} K^{o}_{s,0}(ThO_2)$ with the particle size d predicted by Schindler's Equation (VII.46) is illustrated in Figure VII-19 and compared with experimental data for crystalline and microcrystalline thorium oxides and amorphous oxyhydroxides.

Figure VII-19: Effect of particle size on the solubility constant of $ThO_2(cr)$ predicted with the equation of Schindler [1967SCH] and experimental data for microcrystalline $ThO_2(cr, hyd)$, and X-ray amorphous $ThO_2(am, aged, hyd)$ and $ThO_2(am, fresh, hyd)$ or “$Th(OH)_4(am)$”.



Titration-LIBD experiments at pH = 1.5−2.5 led to the formation of small thorium dioxide colloids (16−23 nm) [2000BUN/KNO], [2003NEC/ALT], which agglomerated to microcrystalline ThO_2(cr, hyd) [2003NEC/ALT]. The solubility products calculated for the ThO_2 colloids and the agglomerated precipitate are $\log_{10} K^{\circ}_{s,0} = -(52.9 \pm 0.5)$ and $-(53.2 \pm 0.4)$, respectively. Transmission electron microscopy investigations on X-ray amorphous Th(IV) precipitates dried at room temperature demonstrates the presence of small ThO_2(cr) crystallites in the range of 3−8 nm [1985DZI/WIS]. Applying Eq. (VII.46) to the solubility product determined for such dried oxyhydroxides ($\log_{10} K^{\circ}_{s,0} = -(47.8 \pm 0.6)$ [1994OST/BRU], [2002NEC/MUL]) leads to a calculated particle size of 3.0−4.5 nm. The increase in $\log_{10} K^{\circ}_{s,0}$ of about 1.2 and 6.4 $\log_{10}$-units, respectively, compared to the thermochemical value for crystalline thorium dioxide ($\log_{10} K^{\circ}_{s,0}$ (ThO_2, cr) = $-(54.2 \pm 1.1)$) is in excellent agreement with with Schindler's equation (Figure VII-19). For fresh amorphous precipitates, with $\log_{10} K^{\circ}_{s,0}$ (ThO_2(am, fresh, hyd)) = $-(46.7 \pm 0.9)$ (*cf.* Section VII.4.1.3), one would expect a somewhat smaller particle or crystallite size in the range of 2.6−3.8 nm. Accordingly the experimental solubility data for Th(IV) oxides/hydroxides could be ascribed to ThO_2(cr) as the only solid phase with the differences in $\log_{10} K^{\circ}_{s,0}$ arising from the difference in particle or crystallite size.

VII.4.3.2 Examples of unexpected solubility behaviour caused by particle size effects

In the following examples the "unexpected" pH dependence observed in numerous experimental studies is discussed in terms of a particle size distribution.

Example 1 (Figure VII-20): Moon [1989MOO] measured the solubility of crystalline ThO_2(cr) at pH 2−13 in 0.1 M $NaClO_4$; $\log_{10}$[Th] decreased continuously but approached more and more closely the thorium concentration in equilibrium with amorphous thorium hydroxide. At pH > 5 the data measured with ThO_2(cr) and $Th(OH)_4$(am) were identical. Similar observations are known for U(IV) oxide from the studies of Parks and Pohl [1985PAR/POH] with crystalline UO_2(cr) at 100−300°C and from Rai *et al.* [2003RAI/YUI] for microcrystalline UO_2(cr) precipitated at 90°C from aqueous U(IV) solutions. At pH < 1.5 the experimental data were close to values expected for UO_2(cr) while at pH > 2 the measured U(IV) concentration approached that of UO_2(am, hyd).

Example 2 (Figure VII-21): Another unexpected effect is the inverse sigmoid-like solubility curves observed for numerous experimental data obtained with amorphous ThO_2(am, hyd) [1964NAB/KUD], [1991FEL/RAI], [1997RAI/FEL], [2002NEC/MUL]. Contrary to the expected increase of solubility at low pH, one observes an almost constant solubility at decreasing pH (from pH 4 to pH 1).

In Figure VII-20 and Figure VII-21 the solubility is calculated on the assumption that the solid phases used in the studies of Moon [1989MOO], typically with 1 g crystalline ThO_2(cr) in 100 mL solution, and Neck *et al.* [2002NEC/MUL], with *ca*. 200 mg dried amorphous ThO_2(am, hyd) in 50 mL solution, have a certain size distribution. The calculations are performed dividing the solid into 4 particle size fractions (< 5 nm, 5 − 10 nm, 10 − 30 nm, and > 30 nm) with the respective solubility constants of $\log_{10} K^{o}_{s,0} = -(47 \pm 1), -(51 \pm 1), -(52.7 \pm 1.0)$, and $-(54 \pm 1)$ according to Eq. (VII.46). We may assume that the largest part of the crystalline oxide used by [1989MOO] consists of crystallites > 30 nm and that the solid contains only small fractions of smaller particles. According to the TEM study of [1985DZI/WIS] an amorphous precipitate dried at room temperature as used by [2002NEC/MUL] consists mainly of fractions in the range < 5 and 5 − 10 nm. The size fraction distributions used for the calculations in Figure VII-20 and Figure VII-21 are given in Table VII-25. The pH-dependent solubility is calculated for each of the 4 particle size fractions. The horizontal part of these curves at low pH indicates that the corresponding fraction is completely dissolved for the given amount of solid in the experiments. The total thorium concentration is given by the sum of the contributions of the different fractions.

Figure VII-20: Effect of different solubility limiting particle size fractions along an experimental solubility curve determined with crystalline ThO_2(cr) (1 g /100 mL solution) [1989MOO]. The particle size fraction distribution assumed for the calculation is given in Table VII-25. The solubility curves for the different fractions approach constant values at low pH when the corresponding fraction is completely dissolved.

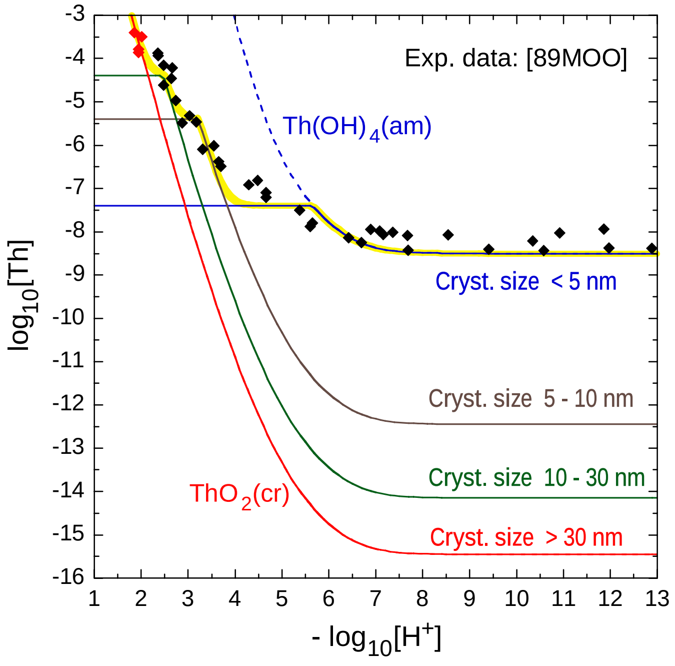


Figure VII-21: Effect of different solubility limiting particle size fractions along an experimental solubility curve determined with ThO_2(am, hyd) (200 mg / 50 mL solution) [2002NEC/MUL]. The particle size fraction distribution assumed for the calculation is given in Table VII-25. The solubility curves for the different fractions approach constant values at low pH when the corresponding fraction is completely dissolved.

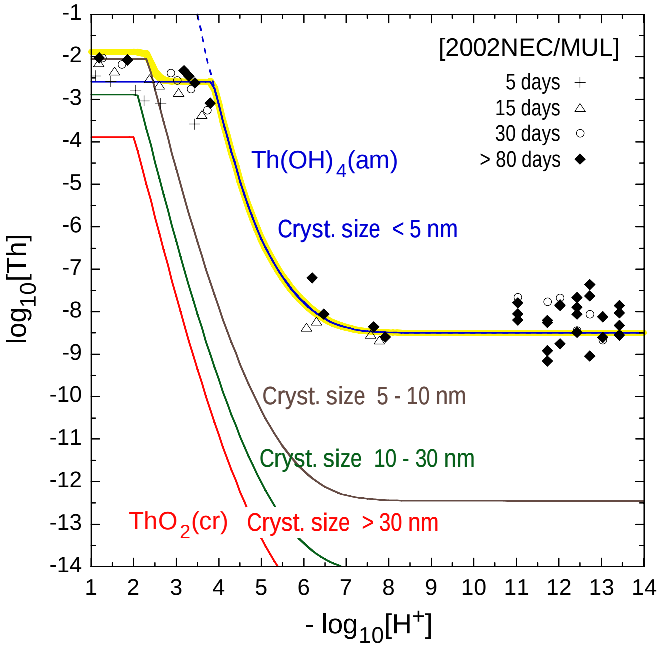


Table VII-25: Size fraction distributions assumed for the calculations in Figure VII-20 and Figure VII-21.

Size fraction	$\log_{10} K^{o}_{s,0}$	Example 1	Example 2
		ThO_2(cr); 10g·L^{-1} *	ThO_2(am, hyd); 4g·L^{-1} *
> 30 nm	− 54 ± 1	99.9%	< 1%
10 − 30 nm	− 52.7 ± 1	0.1%	10%
5 − 10 nm	− 51 ± 1	0.01%	70%
< 5 nm	− 47 ± 1	10^{-4}%	20%

*: The g·L^{-1} values give the solid/solution ratios in the experiments.

According to the solubility calculation for crystalline ThO_2(cr) (Figure VII-20), only the data at the lowest pH values actually refer to crystalline ThO_2(cr). With increasing pH, the total solubility is given by the small fractions of smaller particles. At pH > 5, the solubility is determined by the ppm fraction of particles < 5 nm, equal to

"$Th(OH)_4$(am)". The corresponding solubility calculation for amorphous ThO_2(am, hyd) (Figure VII-21) explains why the total solubility at low pH deviates from the curve for "$Th(OH)_4$(am)" (dashed line). The fraction of particles < 5 nm determines the solubility over almost the whole pH range. However, at low pH this fraction is completely dissolved and smaller fractions of larger particles become solubility limiting.

It should be emphasised that the calculations shown in the two examples above are not considered to reflect exactly the experimental conditions and particle/crystallite size distributions in these studies. However, they point out important problems in the interpretation of solubility data for oxides or oxyhydroxides of tetravalent metal ions:

1. The particle or crystallite size of hydrous oxides or hydroxides of tetravalent metal ions is usually small (2−20 nm) so that there is a dramatic effect on the Gibbs energy and the solubility constant. The differences in particle or crystallite size can explain at least semi-quantitatively the differences between the thermodynamic properties of Th(IV) oxides and hydroxides or oxyhydroxides. The molar surface of amorphous oxyhydroxides (agglomerates of small particles) is much larger than that of crystalline oxides composed of larger particles. Accordingly their water content must be larger as well, because the Gibbs energy change for surface hydration is negative.

2. Heating or drying of amorphous precipitates leads to dehydration by condensation of smaller particles. This process yields larger particles and hence a "more crystalline and less hydrous" bulk solid phase of lower Gibbs energy and solubility. Ageing effects observed for fresh amorphous precipitates, connected with a significant decrease of the solubility, may be interpreted in terms of increasing particle size *via* dissolution-precipitation equilibria. This effect is more pronounced at higher aqueous thorium concentrations, *i.e.*, at low pH as a result of faster recrystallisation kinetics. In neutral and alkaline solutions, the aqueous thorium concentration is extremely low so that crystallisation *via* solution, *i.e.*, the formation of pure ThO_2(cr), is hindered by kinetic restraints.

3. Th(IV) oxide or oxyhydroxide solids used in solubility studies are usually not perfectly homogeneous with regard to their particle or crystallite size, but have a certain size distribution. Example 1 (Figure VII-20) shows that even very small fractions of small particles determine the solubility in the neutral and alkaline pH range. Example 2 (Figure VII-21) shows that small fractions of larger crystallites included in amorphous hydroxide or hydrous oxide might be formed by recrystallisation *via* dissolution-precipitation processes at low pH and high thorium concentrations, resulting in deviations from the expected pH-dependence, in this case at low pH. These particle size effects underline that it is hardly possible to determine reliable hydrolysis constants from the observed pH-dependence of solubility data determined with thorium oxides and oxyhydroxides.

VIII Thorium Group 17 (halogens) compounds and complexes

VIII.1 Fluorine compounds and complexes

VIII.1.1 Solid and gaseous thorium fluorides

VIII.1.1.1 ThF(g), ThF_2(g), ThF_3(g)

These species are considered together since their data are linked by two mass-spectrometric studies, which thus involve some uncertainties in absolute pressures.

VIII.1.1.1.1 Standard entropy and heat capacity

The thermal functions of ThF(g), ThF_2(g) and ThF_3(g) were calculated assuming the molecular parameters shown in Appendix E, Table E-1. These are based on the parameters selected by [1977WAG/SCH], in turn derived principally from the estimates by [1973KRA/MOR]. No electronic contributions have been included, leading to considerable uncertainties in the thermal functions, especially for the monofluoride. The selected values, with uncertainties estimated by this review, are:

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThF, g, 298.15\ K}) = (257.3 \pm 12.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThF, g, 298.15\ K}) = (34.7 \pm 6.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThF_2, g, 298.15\ K}) = (295.2 \pm 10.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThF_2, g, 298.15\ K}) = (52.4 \pm 5.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThF_3, g, 298.15\ K}) = (339.3 \pm 10.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThF_3, g, 298.15\ K}) = (73.3 \pm 5.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

VIII.1.1.1.2 Enthalpies of formation

Zmbov [1969ZMB], [1970ZMB] has studied the reaction of ThF_4(g) with Ca(g) to give both ThF_3(g) and ThF_2(g) from 1288 to 1341 K, while Lau *et al.* [1989LAU/BRI] have studied four equilibria between ThF(g), ThF_2(g), ThF_3(g) and ThF_4(g) with Ba(g) and BaF(g) at broad ranges of temperature around 2000 K. The data from both mass-spectrometric studies are summarised in Table VIII-1, where the enthalpies of the reactions at 298.15 K derived from both second and third-law analyses are given. The auxiliary data for Ba(g), Ca(g) and BaF(g) and CaF(g) are taken from the assessments by Glushko *et al.* [1981GLU/GUR].

Of necessity, the pressures for most of these reactions were derived from mass-spectrometric intensities, leading to some uncertainties in the absolute pressures. However, the reactions involved are isomolecular, so the intensity factors, at least, will cancel out to a first approximation. We note that, for reasons not stated, [1989LAU/BRI] consider only their second-law enthalpy values.

Table VIII-1: Enthalpies of the reactions involving ThF(g), ThF_2(g) and ThF_3(g).

Temperature range / K	$\Delta_r H_m^o$ (298.15 K) (kJ·mol^{-1}) Second-law	Third-law	Reference
	$ThF_3(g) + CaF(g) \rightleftharpoons ThF_4(g) + Ca(g)$		
1288 – 1341	49.4	127.3	[1969ZMB]*, [1970ZMB]*
	$ThF_2(g) + 2CaF(g) \rightleftharpoons ThF_4(g) + 2Ca(g)$		
1288 – 1341	– 20.6	185.8	[1969ZMB]*, [1970ZMB]*
	$Th(g) + BaF(g) \rightleftharpoons ThF(g) + Ba(g)$		
2169 – 2337	– 82.5 ± 7.6	– 94.3 ± 0.9	[1989LAU/BRI]
	$ThF(g) + BaF(g) \rightleftharpoons ThF_2(g) + Ba(g)$		
2108 – 2342	– 138.9 ± 8.8	– 97.3 ± 3.6	[1989LAU/BRI]
	$ThF_2(g) + BaF(g) \rightleftharpoons ThF_3(g) + Ba(g)$		
1777 – 2273	– 85.7 ± 3.4	– 71.6 ± 1.1	[1989LAU/BRI]
	$ThF_3(g) + BaF(g) \rightleftharpoons ThF_4(g) + Ba(g)$		
1612 – 1832	– 97.3 ± 3.9	– 111.1 ± 1.2	[1989LAU/BRI]

*: discounted

Derived second law enthalpies are also somewhat uncertain in Zmbov's study, due to the rather narrow temperature range – indeed it will be seen that his second and third-law analyses are completely different, and these results have been discounted.

From the data of [1989LAU/BRI], we have four semi-independent measurements to define the three enthalpies of formation of ThF(g), ThF_2(g), ThF_3(g), as shown in Table VIII-2. We have used a least-square analysis to find the optimal solutions to the over-determined sets of linear equations, using either the second-law or the third-law enthalpies, with the results shown in Table VIII-3.

The selected values are rounded from the second-law values, since the conversion from intensities to absolute pressures is uncertain:

$$\Delta_f H_m^o(\text{ThF, g, 298.15 K}) = (30 \pm 15)\ \text{kJ·mol}^{-1}$$

$$\Delta_f H_m^o(\text{ThF}_2\text{, g, 298.15 K}) = -(590 \pm 20)\ \text{kJ·mol}^{-1}$$

$$\Delta_f H_m^o(\text{ThF}_3\text{, g, 298.15 K}) = -(1165 \pm 15)\ \text{kJ·mol}^{-1}.$$

The uncertainties have been increased from the purely statistical values to allow for the uncertainties in the thermal functions (especially for ThF(g)).

Table VIII-2: Sums of various enthalpies involving the enthalpies of formation of ThF(g), ThF_2(g) and ThF_3(g).

Reference	Expression	$\Delta_r H^\circ_m$ (298.15 K) (kJ·mol^{-1})	
		Second-law	Third-law
[1989LAU/BRI]	ThF(g)	9.5 ± 12.8	– 2.3 ± 13.2
[1989LAU/BRI]	– ThF(g) + ThF_2(g)	– 648.9 ± 12.1	– 607.3 ± 9.1
[1989LAU/BRI]	– ThF_2(g) + ThF_3(g)	– 595.7 ± 9.0	– 581.6 ± 8.4
[1989LAU/BRI]	ThF_3(g)	– 1143.4 ± 13.8	– 1129.6 ± 13.2

Table VIII-3: Derived enthalpies of formation, $\Delta_f H^\circ_m$ (298.15 K) (kJ·mol^{-1}).

Species	Second-law	Third-law	Selected
ThF(g)	32.4	13	30 ± 15
ThF_2(g)	−593.6	−579	−590 ± 20
ThF_3(g)	−1166.3	−1145	−1165 ± 15

These values are a little different from those reported by [1989LAU/BRI] ((24.3 ± 8.0), −(597.9 ± 10.0) and −(1171.5 ± 12.0) kJ·mol^{-1}), who analysed the over-determined set of equations in a different manner. They result in the selected values:

$$\Delta_f G^\circ_m (\text{ThF, g, 298.15 K}) = -(0.8 \pm 15.4)\ \text{kJ·mol}^{-1}$$

$$\Delta_f G^\circ_m (\text{ThF}_2\text{, g, 298.15 K}) = -(601.9 \pm 20.2)\ \text{kJ·mol}^{-1}$$

$$\Delta_f G^\circ_m (\text{ThF}_3\text{, g, 298.15 K}) = -(1159.8 \pm 15.3)\ \text{kJ·mol}^{-1}.$$

VIII.1.1.2 ThF_4(cr)

VIII.1.1.2.1 Structure

Like the other lanthanide and actinide tetrafluorides, ThF_4(cr) possesses monoclinic symmetry, space group $C^6_{2h}-C2/c$, [1949ZAC]. The structure was refined by Benner and Müller [1990BEN/MUL], using single crystals. The reported lattice parameters are: a = (13.049 ± 0.003) Å, b = (11.120 ± 0.002) Å, c = (8.538 ± 0.002) Å, β = (126.31 ± 0.01)°.

VIII.1.1.2.2 Heat capacity and entropy

The measurements of the heat capacity of a very pure sample of ThF_4(cr) by Lohr *et al.* [1954LOH/OSB] provide the selected values of the heat capacity and standard entropy:

$$C^\circ_{p,m} (\text{ThF}_4\text{, cr, 298.15 K}) = (110.71 \pm 0.13)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$S^\circ_m (\text{ThF}_4\text{, cr, 298.15 K}) = (142.06 \pm 0.17)\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

There are no published experimental data on the heat capacities above 298.15 K, but [1977WAG/SCH] give values based on preliminary high temperature enthalpy measurements by Dworkin from 1200 to 1420 K. We have refitted these so that they reproduce more precisely the value of $C^{\mathrm{o}}_{p,\mathrm{m}}$(298.15 K) measured by [1954LOH/OSB] and these are the selected values:

$$[C^{\mathrm{o}}_{p,\mathrm{m}}]^{1383\,\mathrm{K}}_{298.15\,\mathrm{K}}(\mathrm{ThF_4,\ cr,}\ T) = 121.734 + 9.064\times10^{-3}\,T - 2.8574\times10^{-7}\,T^2 - 1.21821\times10^{6}\,T^{-2}\quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Rand [1975RAN] has summarised the consistent direct measurements of the melting point (1383 ± 3) K, which is also consistent with the vapour pressure studies of [1958DAR/KEN] and [1980NAG/BHU2], see Section VIII.1.1.3.2.

The enthalpy of fusion selected by [1983FUG/PAR], based on unpublished data by Dworkin, has been adopted. This is close to that suggested by [1975RAN], based on values for the enthalpy of fusion of $\mathrm{Li_3ThF_7}$ and $\mathrm{UF_4}$.

$$\Delta_{\mathrm{fus}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{ThF_4,\ cr,\ 1383\ K}) = (41.84 \pm 5.00)\ \mathrm{kJ\cdot mol^{-1}}.$$

As seen below, this is consistent with the measured vapour pressures of the crystal and liquid. The heat capacity of the liquid selected by [1975RAN] and [1983FUG/PAR] has also been retained:

$$[C^{\mathrm{o}}_{p,\mathrm{m}}]^{1800\mathrm{K}}_{1383\mathrm{K}}(\mathrm{ThF_4,\ l}) = (138.9 \pm 10.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

VIII.1.1.2.3 Enthalpy of formation

There is only one direct determination of the enthalpy of formation, by van Deventer *et al.* [1970DEV/RUD], who measured the heat of combustion of thorium (99% pure) in fluorine to be $\Delta_{\mathrm{f}}H^{\mathrm{o}}_{\mathrm{m}}(\mathrm{ThF_4,\ cr,\ 298.15\ K}) = -(2110.8 \pm 5.0)\ \mathrm{kJ\cdot mol^{-1}}$. This result is a little less precise than many other fluorine combustions, perhaps due to problems in identifying the amount of unburnt thorium in the combustion. As noted below this is noticeably more negative than (and does not overlap with) the values derived from the Gibbs energy measurements discussed in the next paragraphs.

The Gibbs energy of formation of $\mathrm{ThF_4}$(cr) has been measured by several investigators. Darnell [1960DAR] has measured the equilibrium pressures of $\mathrm{SiF_4}$(g) for the reaction, $\mathrm{ThF_4(cr) + SiO_2(cr) \rightleftharpoons ThO_2(cr) + SiF_4(g)}$ from 871 to 1077 K. As noted in Appendix A, there are two minor problems with interpreting these data. In order to achieve reasonable times for equilibration, Darnell had to use finely powdered and probably amorphous silica. However, the Gibbs energies of the polymorphs of silica do not differ greatly and we have taken the phases to be α- or β-quartz according to the temperature.

A more serious problem is that $\mathrm{ThF_4}$(cr) and $\mathrm{SiO_2}$(cr) are not truly equilibrium phases, since $\mathrm{ThOF_2}$(cr) is a stable phase in this system, although its preparation needs temperatures of 1173 – 1273 K [1958EYE]. Darnell in fact found traces of $\mathrm{ThOF_2}$(cr) in his quenched samples. However, the pressures in two measurements of the reverse reaction (ThO_2(cr) reacting with SiF_4(g)) were in good accord with those of the forward reaction. Moreover, Darnell reports that in unpublished work, he has also measured the pressures of SiF_4(g) in the reaction of SiO_2(cr) and $ThOF_2$(cr), which are lower than those in the current study. The reaction involved was therefore probably that postulated by the author, $ThOF_2$(cr) not being formed for kinetic reasons.

The data have been processed by the third-law method to give the value for $\Delta_f H_m^o$ (ThF_4, cr, 298.15K) given in Table VIII-4, where the uncertainty has been increased to allow for the two factors mentioned above.

Table VIII-4: Enthalpy of formation of ThF_4(cr) at 298.15 K. Uncertainties include those of the auxiliary data.

Reference	Method and Reaction	Temperature range (K)	$\Delta_f H_m^o$ (ThF_4, cr, 298.15 K) (kJ·mol^{-1})
[1960DAR]	emf		
	$ThF_4(cr) + SiO_2(cr) \rightleftharpoons ThO_2(cr) + SiF_4(g)$	871 − 1077	− 2093.3 ± 10.9
[1966HEU/EGA]	emf		
	$Th(cr) + 2MgF_2(cr) \rightleftharpoons ThF_4(cr) + 2Mg(cr)$	873	− 2091.7 ± 2.4
	$Th(cr) + 4/3AlF_3(cr) \rightleftharpoons ThF_4(cr) + 4/3Al(cr)$	873	− 2097.0 ± 1.7
	$Th(cr) + 2NiF_2(cr) \rightleftharpoons ThF_4(cr) + 2Ni(cr)$	873	− 2072.5 ± 16.0
[1970DEV/RUD]	Calorimetric, $Th(cr) + 2F_2(g) \rightarrow ThF_4(cr)$	298.15	− 2110.8 ± 5.0
[1971TAN/YAM]	emf		
	$Th(cr) + 4/3AlF_3(cr) \rightleftharpoons ThF_4(cr) + 4/3Al(cr)$	873	− 2097.0 ± 1.7
	$Th(cr) + 4/3UF_3(cr) \rightleftharpoons ThF_4(cr) + 4/3U(cr)$	873	− 2103.6 ± 6.3
	$Th(cr) + 4UF_4(cr) \rightleftharpoons ThF_4(cr) + 4UF_3(cr)$	873	− 2106.2 ± 18.1
[1973SKE/PAT]	emf		
	$Th(cr) + 2NiF_2(cr) \rightleftharpoons ThF_4(cr) + 2Ni(cr)$	961 − 1076	− 2081.1 ± 18.1

There are three studies of $\Delta_f G_m$ (ThF_4, cr) derived using emf cells with a single crystal CaF_2 solid electrolyte. Single crystals are required for the electrolyte to minimise the interaction with ThF_4(cr). Heuss and Egan [1966HEU/EGA] and Tanaka *et al.* [1971TAN/YAM] made measurements only at 873 K, but with various counter electrodes (see Table VIII-4), whereas Skelton and Patterson [1973SKE/PAT] made measurements from 961 to 1076 K, but only against a Ni|NiF_2 electrode.

The results of the processing of these data by the third-law method are given in Table VIII-4. The auxiliary data were taken from [1989COX/WAG] (Al(cr), AlF_3(cr), Mg(cr), MgF_2(cr), SiO_2(cr), SiF_4(g)), the NEA-TDB reviews (Th and U species) and Table IV-1 (Ni(cr) and NiF_2(cr)).

It is clear that all the Gibbs energy measurements give an enthalpy of formation noticeably more positive than the calorimetric value, as pointed out by [1975RAN] and [1977WAG/SCH]. The Gibbs energies of formation derived from a Ni|NiF$_2$ counter electrode are also more positive than those based on Mg|MgF$_2$, Al|AlF$_3$ and the uranium fluoride electrodes (which are all reasonably consistent with the value based on the reaction with silica). However, there may be experimental problems with the use of a Ni|NiF$_2$ counter electrode, since the well-known extremely slow reaction of nickel with fluorinating agents indicates the formation of a protective layer of some kind and/or very slow diffusion of fluorine in NiF$_2$(cr). Thus the data derived from the data involving a Ni|NiF$_2$ electrode have been discounted.

The selected value is a rounded value consistent with the calorimetric and other Gibbs energy values:

$$\Delta_f H^o_m (\text{ThF}_4, \text{cr}, 298.15 \text{ K}) = -(2100.0 \pm 10.0) \text{ kJ·mol}^{-1},$$

which yields

$$\Delta_f G^o_m (\text{ThF}_4, \text{cr}, 298.15 \text{ K}) = -(2005.7 \pm 10.0) \text{ kJ·mol}^{-1}.$$

VIII.1.1.3 ThF$_4$(g)

VIII.1.1.3.1 Standard entropy and heat capacity

The electron diffraction study of ThF$_4$ vapour by Ezhov *et al.* [1969EZH/AKI] first demonstrated that ThF$_4$(g) has a tetrahedral structure, with r(Th–F) = (2.14 ± 0.01) Å. This has been confirmed by subsequent spectroscopic and theoretical studies, [1981DYK/JOS] and [2000GAG/SKY]. The latter have made density functional calculations of the structures and vibration frequencies of gaseous tetrahalide ThX$_4$ molecules. The calculated frequencies agreed reasonably well with experimental data for the two vibrations which are available ([1961BUC/BER], [1996KON]). The selected vibration frequencies are the two experimental values (ν_3 = 520(3), ν_4 = 116(3) cm^{-1}, plus the calculated values using B3LYP density functional, as suggested by [2000GAG/SKY] (ν_1 = 581.6(1), ν_2 = 109.3(2) cm^{-1}), where the numbers in parentheses are the degeneracy of the vibrations. These values for ν_1 and ν_2 are preferred to those selected by Konings and Hildenbrand [1998KON/HIL], which predate the density functional calculations.

The calculated values for the entropy and heat capacity of ThF$_4$(g) at 298.15 K from these molecular parameters are:

$$S^o_m (\text{ThF}_4, \text{g}, 298.15 \text{ K}) = (353.0 \pm 2.0) \text{ J·K}^{-1}\text{·mol}^{-1}$$

$$C^o_{p,m} (\text{ThF}_4, \text{g}, 298.15 \text{ K}) = (93.4 \pm 2.0) \text{ J·K}^{-1}\text{·mol}^{-1}$$

and these are the selected values. The input data used are given in Table E-1.

The heat capacity (in J·K^{-1}·mol^{-1}) up to 1300 K has been fitted to the equation:

$$[C^{\circ}_{p,\mathrm{m}}]^{1300\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThF_4, g}, T) = 102.950 + 7.4305 \times 10^{-3}\,T - 2.91682 \times 10^{-6}\,T^2 - 1.02068 \times 10^{6}\,T^{-2}\quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

VIII.1.1.3.2 Enthalpy of formation

There are three studies of the vapour pressures of ThF_4(cr) and ThF_4(l), which are summarised in Table VIII-5.

Darnell and Keneshea [1958DAR/KEN] studied the vapour pressures of the solid by Knudsen effusion and of the liquid by the boiling point method. They also determined by mass-spectrometric analysis that the principal vaporising species was monomeric ThF_4(g). Lau *et al.* [1989LAU/BRI] studied just the sublimation of the solid, by torsion effusion. The calculated pressures from these two investigations agree to within a few percent in the range where they overlap. The pressures measured by Nagarajan *et al.* [1980NAG/BHU2] on the solid and the liquid, by transpiration and the boiling point method are about 20% higher than the two other studies.

Table VIII-5: Enthalpy of vaporisation of ThF_4(cr) and ThF_4(l).

Method	Temperature range (K)	$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}$ (298.15 K) ($\mathrm{kJ{\cdot}mol^{-1}}$)	Reference
Effusion	1055 − 1297	351.3 ± 2.8	[1958DAR/KEN]
Boiling point	1437 − 1595	352.5 ± 2.2	
Transpiration	1293 − 1375	347.0 ± 0.8	[1980NAG/BHU2]
Transpiration, Boiling point	1394 − 1554	347.5 ± 1.0	
Torsion-effusion	1068 − 1201	351.2 ± 0.68	[1989LAU/BRI]

These data were analysed by the third-law method, using the thermal functions for ThF_4 discussed above, to give the results shown in Table VIII-5.

The selected enthalpy for the reaction of sublimation, $ThF_4(s) \rightleftharpoons ThF_4(g)$, is based on the weighted mean of the three studies, which are compared in Figure VIII-1:

$$\Delta_{\mathrm{sub}}H^{\circ}_{\mathrm{m}}(\mathrm{ThF_4, g, 298.15\ K}) = (349.3 \pm 2.0)\ \mathrm{kJ{\cdot}mol^{-1}}$$

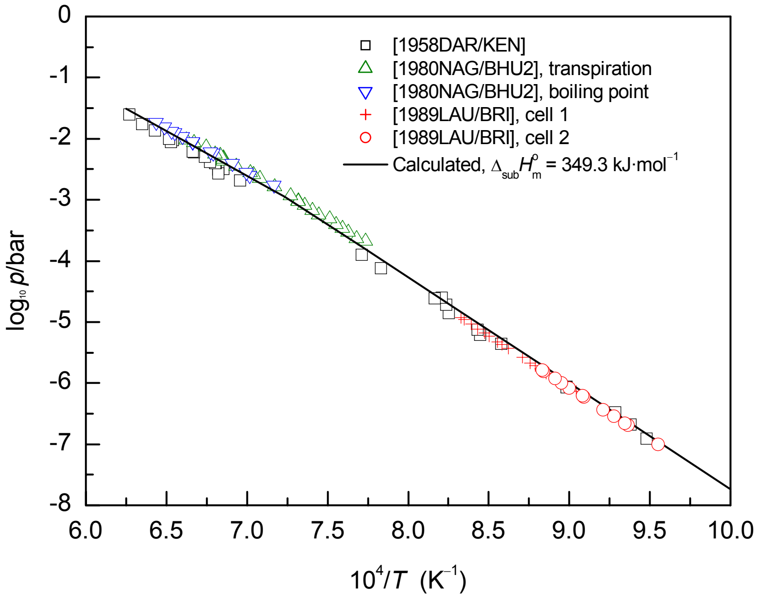
where the uncertainty has been increased to allow for uncertainties in the thermal functions. The derived enthalpy of formation of ThF_4(g) is thus:

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{ThF_4, g, 298.15\ K}) = -(1750.7 \pm 10.2)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

The pressures for the liquid are calculated with an estimated enthalpy of fusion of 41.84 $\mathrm{kJ{\cdot}mol^{-1}}$, as noted above. Thus the selected value for the Gibbs energy of formation is:

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{ThF_4, g, 298.15\ K}) = -(1719.3 \pm 10.2)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

Figure VIII-1: Vapour pressure of ThF_4(cr) and ThF_4(l).



VIII.1.1.4 ThOF(g)

This species was observed by Lau *et al.* [1989LAU/BRI] in their mass-spectrometric study of the lower fluorides of thorium, owing to the presence of oxygen impurity in their samples.

VIII.1.1.4.1 Standard entropy and heat capacity

The thermal functions of ThOF(g) were calculated assuming the molecular parameters shown in Table E-1. These are based on the parameters estimated by [1989LAU/BRI] (but with corrected moments of inertia), which are the same as those estimated for UOF(g) by Glushko *et al.* [1982GLU/GUR]. The ground state degeneracy was taken to be 6, as for ThF_3(g); no other electronic contributions have been included, leading to appreciable uncertainties in the thermal functions:

$$S^{\circ}_{m}\text{(ThOF, g, 298.15 K)} = (310.9 \pm 10.0)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$C^{\circ}_{p,m}\text{(ThOF, g, 298.15 K)} = (49.5 \pm 5.0)\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

VIII.1.1.4.2 Enthalpy of formation

Lau *et al.* [1989LAU/BRI] have studied the gaseous reaction ThO(g) + BaF(g) $\rightleftharpoons$ ThOF(g) + Ba(g) mass-spectrometrically from 1970 to 2277 K. Since the partial pressures of the species were derived from mass-spectrometric intensities, there is some uncertainty in the absolute pressures, even for this isomolecular reaction. The derived values of $\Delta_r H_m$(298.15 K) for the above reaction are calculated to be $-(20.6 \pm 4.1)$ kJ·mol^{-1} and $-(5.4 \pm 1.6)$ kJ·mol^{-1} from second- and third-law analyses respectively, where the uncertainties are the statistical values only. The thermal functions for Ba(g) and BaF(g) were taken from Glushko *et al.* [1981GLU/GUR], and their enthalpies of formation from Table IV-1. The derived values of $\Delta_f H^\circ_m$(ThOF, g, 298.15 K) are then $-(556.3 \pm 11.1)$ kJ·mol^{-1} and $-(541.0 \pm 10.4)$ kJ·mol^{-1}. The selected value is rounded from the mean, with an increased uncertainty to allow for experimental errors:

$$\Delta_f H^\circ_m(\text{ThOF, g, 298.15 K}) = -(550 \pm 12)\ \text{kJ·mol}^{-1}.$$

This value is somewhat different from that given by [1989LAU/BRI], $-(539.7 \pm 8.0)$ kJ·mol^{-1}, due principally to a different value for $\Delta_f H^\circ_m$(ThO, g, 298.15 K). The corresponding selected value for the Gibbs energy of formation is:

$$\Delta_f G^\circ_m(\text{ThOF, g, 298.15 K}) = -(566.2 \pm 12.4)\ \text{kJ·mol}^{-1}.$$

VIII.1.1.5 ThOF$_2$(cr)

VIII.1.1.5.1 Structure

The structure of ThOF$_2$(cr) has been determined by D'Eye [1958EYE] to be orthorhombic, with lattice parameters, a = (14.098 ± 0.100) Å, b = (4.049 ± 0.005) Å, c = (7.268 ± 0.005) Å, space group D^3_{6h}-$P6_3/mcm$, rather than hexagonal LaF$_3$ type, as originally reported by Zachariasen [1949ZAC]. D'Eye suggests that the deviation from hexagonal symmetry is due to the ordering of the oxygen and fluorine atoms.

VIII.1.1.5.2 Enthalpy of formation

The stability of ThOF$_2$(cr) can be derived from the measurements of the pressures of ThF$_4$(g) in the decomposition reaction 2ThOF$_2$(cr) $\rightleftharpoons$ ThO$_2$(cr) + ThF$_4$(g), by Darnell [1960DAR2], (mass-loss effusion, 1109 to 1286 K) and Lau *et al.* [1989LAU/HIL] (torsion effusion, 1088 to 1248 K). These studies give consistent pressures, and since they have relatively short temperature ranges, have been combined and processed by the second-law method to give the selected value:

$$\Delta_f H^\circ_m(\text{ThOF}_2\text{, cr, 298.15 K}) = -(1663.8 \pm 7.8)\ \text{kJ·mol}^{-1}$$

which corresponds to an enthalpy of formation of $-(0.6 \pm 7.8)$ kJ·mol^{-1} from ThO$_2$(cr) and ThF$_4$(cr), for 1 mole of ThOF$_2$. No correction was applied for the solubility of ThF$_4$ in ThO$_2$(cr), which may be as large as 15−20 mol% [1958EYE], [1960DAR2] at 1273 K, but the uncertainty has been increased to allow for this possibility.

VIII.1.1.5.3 Entropy

The second-law processing of the combined studies of the decomposition pressure noted above ([1960DAR2], [1989LAU/HIL]) also provides a value of the standard entropy of

$ThOF_2$(cr), for which no other experimental determination is available. The derived value:

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThOF_2, cr, 298.15\ K}) = (107.7 \pm 5.1)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

is therefore selected; it corresponds to an entropy of formation of (3.65 ± 5.10) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ from ThO_2(cr) and ThF_4(cr), indicating that this is the main contribution to the stability of ThO_2(cr). The selection yields:

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{ThOF_2,cr, 298.15\ K}) = -(1589.2 \pm 7.9)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

VIII.1.1.5.4 Heat capacity

The high temperature heat capacity has been estimated to be the mean of those for ThO_2(cr) and ThF_4(cr). This approximation may be less satisfactory at high temperatures, and this uncertainty has been included in the uncertainties for the derived enthalpy of formation and entropy of $ThOF_2$(cr) quoted above.

$$[C_{p,\mathrm{m}}]^{1500\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThOF_2, cr}, T) = 96.656 + 7.700 \times 10^{-3}\,T - 2.295 \times 10^{-7}\,T^2 - 1.1333 \times 10^{6}\,T^{-2}\quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

VIII.1.2 Aqueous thorium fluoride complexes

VIII.1.2.1 Formation constants of thorium fluoride complexes, ThF_n^{4-n}

Thorium(IV) forms strong complexes with fluoride. Complexes with the stoichiometry ThF_n^{4-n} with *n* ranging from 1 to 6 have been reported, *cf.* Table VIII-6. Thorium(IV) forms a sparingly soluble solid, ThF_4(cr, hyd), at moderately low fluoride concentrations ($\sim 10^{-4}$ M); this complicates the experimental determination of the equilibrium constants using methods such as potentiometry and liquid-liquid extraction. On the other hand it opens up the possibility of using solubility experiments to determine the equilibrium constants. Th(IV) is strongly hydrolysed and most experimental studies have therefore been made in acid solution in order to avoid this complication. Two sets of experimental data will be discussed. The first has been obtained at constant ionic strength using liquid-liquid extraction, potentiometry and solubility methods; the second comprises solubility data obtained in systems where the ionic strength varies. The accuracy of the equilibrium constants obtained from the former data is in general high, while the equilibrium constants from the latter are much more uncertain, as they are strongly dependent on the method used to estimate activity coefficients, especially if the ionic strength is relatively high.

In the studies using liquid-liquid extraction methods, the distribution of trace amounts of Th(IV) between an aqueous and an organic phase containing thenoyltrifluoroacetone (TTA) or dinonyl naphtalene sulphonic acid (DNNS) as extracting ligands has been measured at different fluoride concentrations. In most cases the hydrogen ion concentration has been constant and sufficiently large to prevent hydrolysis. The potentiometric studies have been made using a fluoride selective electrode to measure the concentration of [F^-]; this method requires a moderately high total concentration of Th, 0.1 − 10 mM, and is therefore more likely to result in the precipitation of $ThF_4 \cdot xH_2O$. The studies in [1949DOD/ROL], [1950DAY/STO], [1951ZEB/ALT], [1969NOR], [1971KLO/MUK], [1975PAT/RAM], [1976CHO/UNR], [1981SMI/MES] have been conducted at relatively high acidities (0.3 to 13 M [H^+]) where HF(aq) is the dominant fluoride species. In the potentiometric studies $ThF_4 \cdot xH_2O$(s) was precipitated at the highest fluoride and thorium concentrations used in the experiments *cf.* the potentiometric studies of [1970BAU] and [1990SAW/CHA2]. There is even a risk of precipitation at the low concentrations used in the liquid-liquid distribution measurements, *e.g.*, in the study of Norén [1969NOR], see comments in Appendix A. Based on the evaluation of the different studies in Appendix A (summarised in Table VIII-6) and the results obtained by recalculating the concentration equilibrium constants to zero ionic strength (Table VIII-7) this review has only considered equilibrium constants for the complexes ThF^{3+}, ThF_2^{2+} and ThF_3^+ that are based on liquid-liquid distribution and potentiometric data. Because of precipitation of $ThF_4 \cdot xH_2O$(s), it is not possible to obtain reliable equilibrium constants for the complexes ThF_n^{4-n} with $n > 3$ from these data. Equilibrium constants for complexes with $n \geq 4$ can only be obtained from solubility experiments; there is, however, only one study [1981SMI/MES] at constant ionic strength in addition to a study by Felmy and Rai [1993FEL/RAI] where the ionic strength varies.

There are ten studies [1949DOD/ROL], [1950DAY/STO], [1951ZEB/ALT], [1969NOR], [1970BAU], [1971KLO/MUK], [1975PAT/RAM], [1976CHO/UNR], [1981SMI/MES], [1990SAW/CHA2] that report the formation constants of ThF^{3+}, eight of ThF_2^{2+} [1949DOD/ROL], [1950DAY/STO], [1951ZEB/ALT], [1969NOR], [1970BAU], [1971KLO/MUK], [1981SMI/MES], [1990SAW/CHA2], six of ThF_3^+ [1949DOD/ROL], [1970BAU], [1971KLO/MUK], [1981SMI/MES], [1990SAW/CHA2], [1993FEL/RAI], three of ThF_4(aq) [1970BAU], [1981SMI/MES], [1990SAW/CHA2], and only one [1993FEL/RAI] for ThF_5^- or ThF_6^{2-} (Table VIII-6). For reasons given in Appendix A, the solubility study in [1959TAN/LU5] has not been accepted by this review. Most experimental studies have been made at such high hydrogen ion concentrations that it is not possible to reach the fluoride concentrations necessary for the formation of the higher ThF_n^{4-n} complexes. As indicated in Appendix A, the equilibrium constant for ThF_4(aq) reported in [1970BAU], [1990SAW/CHA2] is unreliable due to the suspected precipitation of ThF_4(cr, hyd). In order to obtain a reliable value for the equilibrium constant for the formation of ThF_4(aq), this review reinterpreted the solubility data reported in [1981SMI/MES] and [1993FEL/RAI], *cf.* Appendix A, with a NONLINT-SIT code (described in Appendix D). The selected equilibrium constants for ThF^{3+}, ThF_2^{2+} and ThF_3^+ from Table VIII-7 and the selected ion interaction parameters from Table VIII-8 were used as fixed parameters and the $\Delta_f G_m^\circ / RT$ values for ThF_4(aq) and ThF_4(cr, hyd) were determined. Attempts to evaluate the equilibrium constants for ThF_5^- or ThF_6^{2-} were made from correlations of equilibrium constants of Th- and U(IV) fluoride complexes (*cf.* Section VIII.1.2.1.4), and by reinterpretation of the solubility data in relatively concentrated fluoride solutions from [1993FEL/RAI] (see Section VIII.1.2.1.3). The selected ion interaction parameters from

Table VIII-8 and the selected equilibrium constants in Table VIII-7 were used as fixed parameters; these values are substantially different from those used by [1993FEL/RAI] in their original interpretation using the Pitzer model.

The experimental equilibrium constants from the various studies and their source are listed in Table VIII-6. The calculated equilibrium constants at zero ionic strength based on these literature data are discussed below and are summarised in Table VIII-7. Table VIII-6 demonstrates that the agreement of the experimental values is excellent in the cases where the experimental conditions are the same, indicating both a high accuracy and the absence of systematic errors. The uncertainty in the calculated equilibrium constants at zero ionic strength is much larger than the experimental values but this is a result of the uncertainties in the interaction coefficients.

The equilibrium constants $\log_{10} {}^{*}\beta_{n}^{\circ}$ (VIII.1) refer to the reaction:

$$\mathrm{Th^{4+}} + n\mathrm{HF(aq)} \rightleftharpoons \mathrm{ThF}_{n}^{4-n} + n\mathrm{H^{+}} \qquad \text{(VIII.1)}$$

By combining these values with the $\log_{10} \beta_{1}^{\circ}$ (VIII.2) = (3.18 ± 0.02) (Table IV-2) for the protonation of fluoride:

$$\mathrm{H^{+}} + \mathrm{F^{-}} \rightleftharpoons \mathrm{HF(aq)} \qquad \text{(VIII.2)}$$

this review has calculated $\log_{10} \beta_{n}^{\circ}$ (VIII.3) values for n = 1 – 3 that are given in Table VIII-7.

$$\mathrm{Th^{4+}} + n\mathrm{F^{-}} \rightleftharpoons \mathrm{ThF}_{n}^{4-n} \qquad \text{(VIII.3)}$$

Table VIII-6: Equilibrium constants for formation of aqueous Th^{4+} complexes with F^{-}.

$\log_{10} {}^{*}\beta_{n}$	Medium	Concentration (Molarity) of metal (M), ligand (L), H^{+} (H)	t (°C)	Method	References
		$\mathrm{Th^{4+}} + \mathrm{HF(aq)} \rightleftharpoons \mathrm{ThF^{3+}} + \mathrm{H^{+}}$			
4.70	0.5 M $NaClO_4$	n.a.	25	dis	[1951ZEB/ALT]
4.63	0.5 M $HClO_4$	M = 10^{-6}, L ≤ 0.002, H = 0.5	25	dis	[1950DAY/STO]
4.65 ± 0.05	0.5 M Na,$HClO_4$	M ≤ 0.005, L ≤ 0.018, H = 0.3	25	red	[1949DOD/ROL]
4.43 ± 0.02	2.0 M H(ClO_4,Cl)	M = trace, L≤ 0.01, H=2	25	dis	[1975PAT/RAM]
4.52 ± 0.05	3 M (H,Na)(ClO_4,F)	M≤ 0.03,L<3,H≤ 1	25	ise-F	[1971KLO/MUK]
4.68 ± 0.02	4 M $HClO_4$	M = 0.18 M, L≤ 4.5×10^{-3}, H = 4 M	20	ise-F	[1969NOR][a]
4.60 ± 0.05		M = 0.18 M, L≤ 4.5×10^{-3}, H = 4 M	20	dis	
4.65 ± 0.02	1.0 M $HClO_4$		10	dis	[1976CHO/UNR]
4.49 ± 0.03	1.0 M $HClO_4$		25	dis	[1976CHO/UNR]
4.33 ± 0.02	1.0 M $HClO_4$		55	dis	[1976CHO/UNR]
4.73 ± 0.02	1.0 M $HClO_4$	M = 0.001 M, L>0.008 M, H = 1 M	3	pot	[1976CHO/UNR]
4.51 ± 0.02	1.0 M $HClO_4$	M = 0.001 M, L>0.008 M, H = 1 M	25	pot	[1976CHO/UNR]

(Continued on next page)

Table VIII-6 (continued)

$\log_{10}{}^{*}\beta_n$	Medium	Concentration (Molarity) of metal (M), ligand (L), H^+ (H)	t (°C)	Method	References
4.45 ± 0.05	1.0 M $HClO_4$	M = 0.001 M, L>0.008 M, H = 1 M	47	pot	[1976CHO/UNR]
3.8	4 M HNO_3	M≤ 0.66 M, L≤ 0.38 M, H = 4 M	25	sol	[1981SMI/MES]
3.7	4 M HNO_3	M≤ 0.52 M, L≤ 0.30 M, H = 4 M	50	sol	[1981SMI/MES]
3.3	4 M HNO_3	M≤ 0.58 M, L≤ 0.24 M, H = 4 M	100	sol	[1981SMI/MES]
3.2	8 M HNO_3	M≤ 0.47 M, L≤ 0.10 M, H = 8 M	25	sol	[1981SMI/MES]
2.9	8 M HNO_3	M≤ 0.34 M, L≤ 0.099 M, H = 8 M	50	sol	[1981SMI/MES]
2.9	8 M HNO_3	M≤ 0.50 M, L≤ 0.18 M, H = 8 M	100	sol	[1981SMI/MES]
2.7	13 M HNO_3	M≤ 0.43 M, L≤ 0.53 M, H = 13 M	25	sol	[1981SMI/MES]
2.8	13 M HNO_3	M≤ 0.42 M, L≤ 0.04 M, H = 13 M	50	sol	[1981SMI/MES]
2.7	13 M HNO_3	M≤ 0.51 M, L≤ 0.05 M, H = 13 M	100	sol	[1981SMI/MES]
		$Th^{4+} + F^- \rightleftharpoons ThF^{3+}$			
8.03	$I = 0$	n.a.	25	est	[1982WAG/EVA][b]
8.46	$I = 0$	n.a.	5	est	[1970BAU]
8.44	$I = 0$	n.a.	25	est	[1970BAU]
8.32	$I = 0$	n.a.	45	est	[1970BAU]
8.11	0.01 M NH_4NO_3	$M \le 3.8\times10^{-4}, L \le 2.7\times10^{-4}, H = 1.2\times10^{-3}$	5	ise-F	[1970BAU]
8.08	0.01 M NH_4NO_3	$M \le 3.8\times10^{-4}, L \le 2.7\times10^{-4}, H = 9.4\times10^{-4}$	25	ise-F	[1970BAU]
7.95	0.01 M NH_4NO_3	$M \le 3.8\times10^{-4}, L \le 2.7\times10^{-4}, H = 1.5\times10^{-3}$	45	ise-F	[1970BAU]
5.92	varied (H,Na,Ca)F,$Th(NO_3)_4$	M≤0.5,L≤0.45,H=0.45	25	sol	[1959TAN/LU5]
7.61 ± 0.01	1 M NaF, $HClO_4$	M≤ 0.02, L≤ 0.048,H = 0.48	23	ise-F	[1990SAW/CHA2]
		$Th^{4+} + 2HF(aq) \rightleftharpoons ThF_2^{2+} + 2H^+$			
7.46	0.5 M $NaClO_4$	n.a.	25	dis	[1951ZEB/ALT]
7.49	0.5 M $HClO_4$	M = 10^{-6}, L≤ 0.002, H = 0.5	25	dis	[1950DAY/STO]
7.46 ± 0.05	0.5 M Na,$HClO_4$	M≤ 0.005, L≤ 0.018, H = 0.3	25	red	[1949DOD/ROL]
7.26 ± 0.14	3 M (H, Na)(ClO_4,F)	M≤ 0.03, L<3,H≤ 1	25	ise-F	[1971KLO/MUK]
7.65 ± 0.03	4 M $HClO_4$	M = 0.18 M, L≤ 4.5×10^{-3},H = 4 M	20	ise-F	[1969NOR][a]
6.8	4 M HNO_3	M≤ 0.66 M, L≤ 0.38 M,H = 4 M	25	sol	[1981SMI/MES]
6.6	4 M HNO_3	M≤ 0.52 M, L≤ 0.30 M,H = 4 M	50	sol	[1981SMI/MES]
6.0	4 M HNO_3	M≤ 0.58 M, L≤ 0.24 M,H = 4 M	100	sol	[1981SMI/MES]
5.9	8 M HNO_3	M≤ 0.47 M, L≤ 0.10 M,H = 8 M	25	sol	[1981SMI/MES]
5.4	8 M HNO_3	M≤ 0.34 M, L≤ 0.099 M,H = 8 M	50	sol	[1981SMI/MES]
5.5	8 M HNO_3	M≤ 0.50 M, L≤ 0.18 M,H = 8 M	100	sol	[1981SMI/MES]
5.4	13 M HNO_3	M≤ 0.43 M, L≤ 0.53 M,H = 13 M	25	sol	[1981SMI/MES]
5.8	13 M HNO_3	M≤ 0.42 M, L≤ 0.04 M,H = 13 M	50	sol	[1981SMI/MES]
5.5	13 M HNO_3	M≤ 0.51 M, L≤ 0.05 M,H = 13 M	100	sol	[1981SMI/MES]

(Continued on next page)

Table VIII-6 (continued)

$\log_{10} {}^*\beta_n$	Medium	Concentration (Molarity) of metal (M), ligand (L), H^+ (H)	t (°C)	Method	References
$Th^{4+} + 2F^- \rightleftharpoons ThF_2^{2+}$					
14.23	$I = 0$	n.a.	25	est	[1982WAG/EVA][b]
15.01	$I = 0$	n.a.	5	est	[1970BAU]
15.06	$I = 0$	n.a.	25	est	[1970BAU]
14.80	$I = 0$	n.a.	45	est	[1970BAU]
14.40	0.01 M NH_4NO_3	$M \leq 3.8\times10^{-4}, L \leq 2.7\times10^{-4}, H=1.2\times10^{-3}$	5	ise-F	[1970BAU]
14.44	0.01 M NH_4NO_3	$M \leq 3.8\times10^{-4}, L \leq 2.7\times10^{-4}, H=9.4\times10^{-4}$	25	ise-F	[1970BAU]
14.15	0.01 M NH_4NO_3	$M \leq 3.8\times10^{-4}, L \leq 2.7\times10^{-4}, H=1.5\times10^{-3}$	45	ise-F	[1970BAU]
8.68	varied (H,Na,Ca)F,Th(NO_3	$M \leq 0.5, L \leq 0.45, H=0.45$	25	sol	[1959TAN/LU5]
13.42 ± 0.05	1 M NaF, $HClO_4$	$M \leq 0.02, L \leq 0.048, H=0.48$	23	ise-F	[1990SAW/CHA2]
$Th^{4+} + 3HF(aq) \rightleftharpoons ThF_3^+ + 3H^+$					
8.97 ± 0.06	0.5 M Na,$HClO_4$	$M \leq 0.005, L \leq 0.018, H = 0.3$	25	red	[1949DOD/ROL]
8.9 ± 0.03	3M(H,Na)(ClO_4,F)	$M \leq 0.03, L<3, H \leq 1$	25	ise-F	[1971KLO/MUK]
9.0	4 M HNO_3	$M \leq 0.66$ M, $L \leq 0.38$ M, H = 4 M	25	sol	[1981SMI/MES]
8.6	4 M HNO_3	$M \leq 0.52$ M, $L \leq 0.30$ M, H = 4 M	50	sol	[1981SMI/MES]
8.2	4 M HNO_3	$M \leq 0.58$ M, $L \leq 0.24$ M, H = 4 M	100	sol	[1981SMI/MES]
8.2	8 M HNO_3	$M \leq 0.47$ M, $L \leq 0.10$ M, H = 8 M	25	sol	[1981SMI/MES]
7.5	8 M HNO_3	$M \leq 0.34$ M, $L \leq 0.099$ M, H = 8 M	50	sol	[1981SMI/MES]
7.9	8 M HNO_3	$M \leq 0.50$ M, $L \leq 0.18$ M, H = 8 M	100	sol	[1981SMI/MES]
8.2	13 M HNO_3	$M \leq 0.43$ M, $L \leq 0.53$ M, H = 13 M	25	sol	[1981SMI/MES]
9.1	13 M HNO_3	$M \leq 0.42$ M, $L \leq 0.04$ M, H = 13 M	50	sol	[1981SMI/MES]
8.5	13 M HNO_3	$M \leq 0.51$ M, $L \leq 0.05$ M, H = 13 M	100	sol	[1981SMI/MES]
$Th^{4+} + 3F^- \rightleftharpoons ThF_3^+$					
18.89	$I = 0$	n.a.	25	est	[1982WAG/EVA][b]
19.82	$I = 0$	n.a.	5	est	[1970BAU]
19.81	$I = 0$	n.a.	25	est	[1970BAU]
19.53	$I = 0$	n.a.	45	est	[1970BAU]
19.04	0.01 M NH_4NO_3	$M \leq 3.8\times10^{-4}, L \leq 2.7\times10^{-4}, H=1.2\times10^{-3}$	5	ise-F	[1970BAU]
19.01	0.01 M NH_4NO_3	$M \leq 3.8\times10^{-4}, L \leq 2.7\times10^{-4}, H=9.4\times10^{-3}$	25	ise-F	[1970BAU]
18.70	0.01 M NH_4NO_3	$M \leq 3.8\times10^{-4}, L \leq 2.7\times10^{-4}, H=1.5\times10^{-3}$	45	ise-F	[1970BAU]
17.65 ± 0.20	1 M NaF, $HClO_4$	$M \leq 0.02, L \leq 0.048, H = 0.48$	23	ise-F	[1990SAW/CHA2]

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Table VIII-6 (continued)

$\log_{10} {}^*\beta_n$	Medium	Concentration (Molarity) of metal (M), ligand (L), H^+ (H)	t (°C)	Method	References
$Th^{4+} + 4HF(aq) \rightleftharpoons ThF_4 + 4H^+$					
10.4	4 M HNO_3	M≤ 0.66 M, L≤ 0.38 M,H = 4 M	25	sol	[1981SMI/MES]
9.8	4 M HNO_3	M≤ 0.52 M, L≤ 0.30 M,H = 4 M	50	sol	[1981SMI/MES]
9.8	4 M HNO_3	M≤ 0.58 M, L≤ 0.24 M,H = 4 M	100	sol	[1981SMI/MES]
10.1	8 M HNO_3	M≤ 0.47 M, L≤ 0.10 M,H = 8 M	25	sol	[1981SMI/MES]
9.2	8 M HNO_3	M≤ 0.34 M, L≤ 0.099 M,H = 8 M	50	sol	[1981SMI/MES]
10.1	8 M HNO_3	M≤ 0.50 M, L≤ 0.18 M,H = 8 M	100	sol	[1981SMI/MES]
11.0	13 M HNO_3	M≤ 0.43 M, L≤ 0.53 M,H = 13 M	25	sol	[1981SMI/MES]
12.6	13 M HNO_3	M≤ 0.42 M, L≤ 0.04 M,H = 13 M	50	sol	[1981SMI/MES]
11.6	13 M HNO_3	M≤ 0.51 M, L≤ 0.05 M,H = 13 M	100	sol	[1981SMI/MES]
$Th^{4+} + 4F^- \rightleftharpoons ThF_4$					
22.24	$I = 0$	n.a.	25	est	[1982WAG/EVA][b]
23.23	$I = 0$	n.a.	5	est	[1970BAU]
23.17	$I = 0$	n.a.	25	est	[1970BAU]
23.33	$I = 0$	n.a.	45	est	[1970BAU][c]
22.37	0.01 M NH_4NO_3	M≤ 3.8×10^{-4}, L≤ 2.7×10^{-4},H = 1.2×10^{-3}	5	ise-F	[1970BAU]
22.29	0.01 M NH_4NO_3	M≤ 3.8×10^{-4}, L ≤ 2.7×10^{-4},H = 9.4×10^{-3}	25	ise-F	[1970BAU]
22.41	0.01 M NH_4NO_3	M≤ 3.8×10^{-4}, L ≤ 2.7×10^{-4},H = 1.5×10^{-3}	45	ise-F	[1970BAU][c]
23.67 ± 0.11	1 M NaF, $HClO_4$	M≤ 0.02, L≤ 0.048,H = 0.48	23	ise-F	[1990SAW/CHA2]
$Th^{4+} + 5F^- \rightleftharpoons ThF_5^-$					
24.76	$I = 0$	M≤ 1×10^{-5}, L≤ 1,pH = 4.2 − 6.5	25	sol	[1993FEL/RAI]
$Th^{4+} + 6F^- \rightleftharpoons ThF_6^{2-}$					
25.56	$I = 0$	M≤ 1×10^{-5}, L≤ 1,pH = 4.2 − 6.5	25	sol	[1993FEL/RAI]

a: The equilibrium constants at 20 and 25°C do not differ significantly, due to the small enthalpy of reaction.

b: Assessment.

c: The author states that the values are not reliable.

n. a.: not available.

Table VIII-7: Calculated values at 25ºC of $\log_{10}\beta_n^o(\mathrm{Th}^{4+} + n\mathrm{F}^- \rightleftharpoons \mathrm{ThF}_n^{4-n})$ and $\log_{10}{}^*\beta_n^o(\mathrm{Th}^{4+} + n\mathrm{HF(aq)} \rightleftharpoons \mathrm{ThF}_n^{4-n} + n\mathrm{H}^+)$ based on SIT model calculations/ reinterpretations by this review of data from various sources (see text for details).

I_c	I_m	$\log_{10}{}^*\beta_1$	$\log_{10}{}^*\beta_1^o$	$\log_{10}\beta_1$	$\log_{10}\beta_1^o$	Reference
0.5	0.513	4.7	5.71 ± 0.07		8.89 ± 0.07	[1951ZEB/ALT]
0.5	0.513	4.63	5.64 ± 0.07		8.82 ± 0.07	[1950DAY/STO]
0.5	0.513	4.65	5.66 ± 0.07		8.84 ± 0.07	[1949DOD/ROL]
2	2.204	4.43	5.66 ± 0.29		8.84 ± 0.29	[1975PAT/RAM]
3	3.503	4.52	5.74 ± 0.46		8.92 ± 0.46	[1971KLO/MUK]
4	4.868	4.68	5.85 ± 0.63		9.03 ± 0.63	[1969NOR]
1	1.05	4.49	5.64 ± 0.14		8.82 ± 0.14	[1976CHO/UNR](dis)
1	1.05	4.51	5.66 ± 0.14		8.84 ± 0.14	[1976CHO/UNR] (pot)
1	1.05			7.6 ± 0.01	9.00 ± 0.14	[1990SAW/CHA2]
4	4.557	3.8	5.40 ± 1.06		8.58 ± 1.06	[1981SMI/MES]
			5.69 ± 0.13		8.87 ± 0.15	Selected [a]
I_c	I_m	$\log_{10}{}^*\beta_2$	$\log_{10}{}^*\beta_2^o$	$\log_{10}\beta_2$	$\log_{10}\beta_2^o$	Reference
0.5	0.513	7.46	9.16 ± 0.08		15.52 ± 0.08	[1951ZEB/ALT]
0.5	0.513	7.49	9.19 ± 0.08		15.55 ± 0.08	[1950DAY/STO]
0.5	0.513	7.46	9.16 ± 0.08		15.52 ± 0.08	[1949DOD/ROL]
3	3.503	7.26	9.34 ± 0.52		15.70 ± 0.52	[1971KLO/MUK]
4	4.868	7.65	9.67 ± 0.72		16.03 ± 0.72	[1969NOR]
1	1.051			13.42±0.05	15.84 ± 0.16	[1990SAW/CHA2]
4	4.557	6.8	9.30 ± 1.10		15.66 ± 1.10	[1981SMI/MES]
			9.27 ± 0.13		15.63 ± 0.23	Selected [a]
I_c	I_m	$\log_{10}{}^*\beta_3$	$\log_{10}{}^*\beta_3^o$	$\log_{10}\beta_3$	$\log_{10}\beta_3^o$	Reference
0.5	0.513	8.97	10.99 ± 0.08		20.53 ± 0.09	[1949DOD/ROL]
3	3.503	8.9	11.27 ± 0.54		20.81 ± 0.54	[1971KLO/MUK]
1	1.051			17.65±0.20	20.66 ± 0.23	[1990SAW/CHA2]
4	4.557	9.0	11.65 ± 1.07		21.19 ± 1.07	[1981SMI/MES]
			11.13 ± 0.14		20.67 ± 0.16	Selected [a]
I_c	I_m	$\log_{10}{}^*\beta_4$	$\log_{10}{}^*\beta_4^o$	$\log_{10}\beta_4$	$\log_{10}\beta_4^o$	Reference
4	4.557	10.4	13.37 ± 0.57		26.09 ± 0.57	[1981SMI/MES]
0	0				25.58 ± 0.18	This review [b]
					25.58 ± 0.18	Selected
I_c	I_m				$\log_{10}\beta_5^o$	
0	0				26.61 ± 2.62	Estimated [c]
I_c	I_m				$\log_{10}\beta_6^o$	
0	0				28.70 ± 2.81	Estimated [c]
0	0				29.23 ± 0.62	This review (not selected) [b]

a: Average values based on the data in solutions with ionic strength less than 4 M; the values at $I_c > 4$ M are in good agreement with the other values but have larger uncertainties.

b: Based on reinterpretations of the data reported by [1993FEL/RAI] using the NONLINT-SIT code (see text for details).

c: Extrapolated values based on correlations between $\log_{10}\beta_1^o$ through $\log_{10}\beta_4^o$ for Th-F/U(IV)-F complexes (see text for details); these values are not selected but provided for information only.

Table VIII-8: SIT ion-interaction parameters used by this review in developing the thorium-fluoride system model.

Species	Ion interaction coefficients (kg·mol^{-1})		References
	ε_1	ε_2	
H^+ - ClO_4^-	0.14 ± 0.02	0.00	Table B-4
Th^{4+} - ClO_4^-	0.7 ± 0.1	0.00	This review
ThF^{3+} - ClO_4^-	0.48 ± 0.08	0.00	This review [a]
ThF_2^{2+} - ClO_4^-	0.3 ± 0.1	0.00	This review [a]
ThF_3^+ - ClO_4^-	0.1 ± 0.1	0.00	This review [a]
Na^+ - F^-	0.02 ± 0.02	0.00	Table B-5
NH_4^+ - F^-	0.03 ± 0.02	0.00	This review [b]
NH_4^+ - NO_3^-	−0.075 ± 0.001	0.057 ± 0.004	Table B-6
H^+ - NO_3^-	0.07 ± 0.01	0.00	Table B-4
Th^{4+} - NO_3^-	0.31 ± 0.12	0.00	This review
ThF^{3+} - NO_3^-	0.25 ± 0.20	0.00	This review [c]
ThF_2^{2+} - NO_3^-	0.15 ± 0.20	0.00	This review [c]
ThF_3^+ - NO_3^-	0.0 ± 0.2	0.00	This review [c]
Na^+ - ThF_6^{2-}	−0.30 ± 0.06	0.00	Table B-5 [d]
NH_4^+ - ThF_6^{2-}	−0.30 ± 0.06	0.00	Table B-5 [d]

a: Assumed to be identical to the ion interaction parameters for the corresponding U(IV) fluoride complexes reported in [2003GUI/FAN].

b: Assumed to be identical to the value of $\varepsilon(K^+, F^-)$ reported in [2003GUI/FAN].

c: Estimated from correlations presented in Figure VI-4, which are assumed to hold also for cationic complex ions.

d : Assumed to be identical to the value of $\varepsilon(Na^+, UO_2F_4^{2-})$ reported in [2003GUI/FAN].

VIII.1.2.1.1 Formation constants of ThF^{3+}, ThF_2^{2+}, and ThF_3^+

The calculated $\log_{10} {}^*\beta_1^{\circ}$ (VIII.1) values at 25°C from [1949DOD/ROL], [1950DAY/STO], [1951ZEB/ALT], [1975PAT/RAM], [1971KLO/MUK], [1969NOR], [1976CHO/UNR] are very similar (varying from 5.64 to 5.85). However, the standard deviation in these values depends on the magnitude of the ionic strength correction that increases with increasing ionic strength; they are much higher in studies conducted at relatively high ionic strength. For example, the $\log_{10} {}^*\beta_1^{\circ}$ values at 25°C calculated from data at the ionic strength 0.51 and 4.87 m are (5.71 ± 0.07) [1951ZEB/ALT] and (5.85 ± 0.63) [1969NOR] respectively. The agreement between the estimated equilibrium constants is much better than the uncertainty estimate, indicating that the uncertainty of the interaction coefficients may be overestimated. Based on the calculated values of equilibrium constants in Table VIII-7 from studies at ionic strength less than 4 m, this review selects the following unweighted average values:

$$\log_{10} {}^*\beta_1^{\circ}\,(\text{VIII.1}) = (5.69 \pm 0.13)$$

$$\log_{10} \beta_1^\circ \text{(VIII.3)} = (8.87 \pm 0.15).$$

The corresponding values at the ionic strength of 4.87 m from Norén [1969NOR], converted to zero ionic strength with the SIT, are $\log_{10} {}^*\beta_1^\circ$ (VIII.1) = 5.85 and $\log_{10} \beta_1^\circ$ (VIII.3) = 9.03, and those from the solubility study of Smith and Mesmer [1981SMI/MES], $\log_{10} {}^*\beta_1^\circ$ (VIII.1) = 5.40 and $\log_{10} \beta_1^\circ$ (VIII.3) = 8.58, are in good agreement with the selected values.

The values of $\log_{10} \beta_2^\circ$ calculated from the conditional equilibrium constants in [1949DOD/ROL], [1950DAY/STO] [1951ZEB/ALT], [1971KLO/MUK], and [1990SAW/CHA2] are very similar and vary from 15.52 to 15.84. Based on these data (Table VIII-7) from studies at an ionic strength less than 4 m, this review selects the following unweighted values:

$$\log_{10} {}^*\beta_2^\circ \text{(VIII.1)} = (9.27 \pm 0.13)$$

$$\log_{10} \beta_2^\circ \text{(VIII.3)} = (15.63 \pm 0.23).$$

The corresponding values calculated from the conditional equilibrium constants at an ionic strength of 4.56 m [1981SMI/MES] are $\log_{10} {}^*\beta_2^\circ$ (VIII.1) = 9.30 and $\log_{10} \beta_2^\circ$ (VIII.3) = 15.66, both in good agreement with the selected values, while the values from Norén [1969NOR], $\log_{10} {}^*\beta_2^\circ$ (VIII.1) = 9.67 and $\log_{10} \beta_2^\circ$ (VIII.3) = 16.03 differ somewhat from the selected values.

The values of $\log_{10} \beta_3^\circ$ (VIII.3) from [1949DOD/ROL], [1971KLO/MUK], and [1990SAW/CHA2] vary from 20.53 to 20.81. Based on data (Table VIII-7) at ionic strength less than 4 m, this review selects the following unweighted average values:

$$\log_{10} {}^*\beta_3^\circ \text{(VIII.1)} = (11.13 \pm 0.14)$$

$$\log_{10} \beta_3^\circ \text{(VIII.3)} = (20.67 \pm 0.16).$$

The corresponding values recalculated to $I = 0$ from the data of Smith and Mesmer [1981SMI/MES] at the ionic strength 4.56 m, $\log_{10} {}^*\beta_3^\circ$ (VIII.1) = 11.65 and $\log_{10} \beta_3^\circ$ (VIII.3) = 21.19, differ significantly from the selected values.

VIII.1.2.1.2 Formation constants of ThF_4(aq)

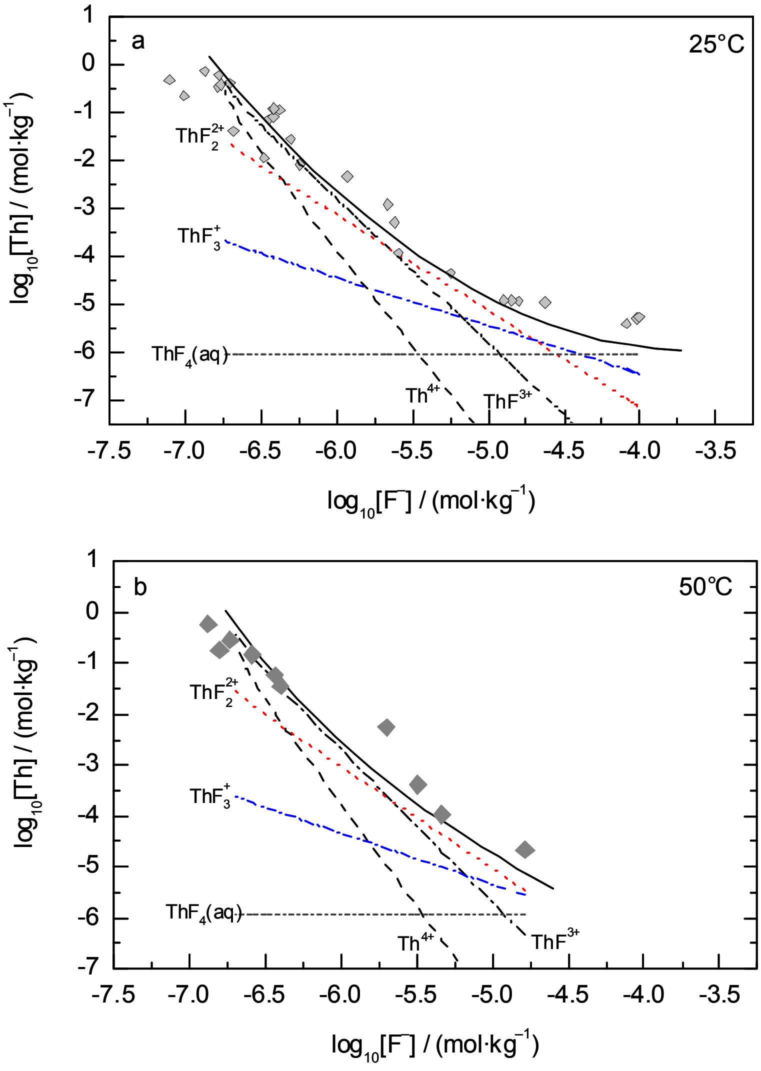
As discussed earlier, only the solubility studies can provide information on the equilibrium constant $\log_{10} \beta_4^\circ$ (VIII.3). In two solubility studies, [1981SMI/MES] and [1993FEL/RAI], the raw experimental data are listed. The [1981SMI/MES] study was conducted at high ionic strength (4.56 m) and in acidic solutions where several Th-F$^-$ complexes may be important. It is uncertain if the SIT model is applicable at these high ionic strengths, especially since reliable values for SIT ion-interaction parameters for the HNO_3 media used in this study are not available. For this reason these data were not used when selecting the equilibrium constants $\log_{10} \beta_n^\circ$, $n = 1-3$. This review has used the data in the careful study reported in [1981SMI/MES] for validation purposes, even though they are not ideal for determining the $\log_{10} \beta_4^\circ$ value. Figure VIII-2-a shows a comparison of the experimental data from [1981SMI/MES] and the calculated solubility at 25°C using the equilibrium constants selected by this review, including the solubility product to be discussed later (Section VIII.1.3.1.3). For comparison, Figure VIII-2-b shows experimental and calculated solubility at 50°C. One conclusion from this comparison is that the stability of $ThF_4(aq)$ decreases relative to that of the lower complexes with increasing temperature.

Felmy and Rai [1993FEL/RAI] used the aqueous phase data reported in [1982WAG/EVA] to interpret their data. The values of $\log_{10}\beta_1^\circ$, $\log_{10}\beta_2^\circ$ and $\log_{10}\beta_3^\circ$ (8.03, 14.23, and 18.89, respectively, assessed by [1982WAG/EVA]) differ considerably from those selected in the present review. The experimental data of [1993FEL/RAI] in relatively dilute NaF and NH_4F solutions (< 0.01 M) were therefore reinterpreted and used to calculate $\Delta_f G_m^\circ / RT$ (ThF_4, aq). This was done using the NONLINT-SIT code (Appendix D) where average $\Delta_f G_m^\circ / RT$ (ThF^{3+}) = −418.293, $\Delta_f G_m^\circ / RT$ (ThF_2^{2+}) = − 547.422, and $\Delta_f G_m^\circ / RT$ (ThF_3^+) = −672.591 were used as fixed parameters; these values were calculated from the selected equilibrium constant $\log_{10}\beta_1^\circ$ (VIII.3) = (8.87 ± 0.15), $\log_{10}\beta_2^\circ$ (VIII.3) = (15.63 ± 0.23), and $\log_{10}\beta_3^\circ$ (VIII.3) = (20.67 ± 0.16) from this review, together with the selected auxiliary data reported in Chapter IV. The ion interaction parameters (Table VIII-8) $\varepsilon_1(Na^+,F^-)$ = (0.02 ± 0.02) $kg\cdot mol^{-1}$ [1992GRE/FUG] and $\varepsilon_1(NH_4^+,F^-)$ = (0.03 ± 0.02) $kg\cdot mol^{-1}$, assumed to be identical to that for $\varepsilon(K^+,F^-)$, were kept constant in this procedure. The least squares fit provided values of $\Delta_f G_m^\circ / RT$ (ThF_4, aq) = − (797.469 ± 0.416) and $\log_{10}\beta_4^\circ$ (VIII.3) = (25.58 ± 0.18) and values of $\Delta_f G_m^\circ / RT$ (ThF_4, cr, hyd) = −(811.684 ± 0.348) and − (812.026 ± 0.846) from solubility data in NaF and NH_4F systems, respectively. The values of $\Delta_f G_m^\circ / RT$ (ThF_4, cr, hyd) thus determined are close to the value selected by this review, − (811.860 ± 0.915), and also close to the value for $\Delta_f G_m^\circ / RT$ (ThF_4, cr) = − (809.10 ± 4.03) (see Section VIII.1.1.2.3). This review has therefore selected the equilibrium constant

$$\log_{10}\beta_4^\circ = (25.58 \pm 0.18).$$

Figure VIII-2 shows that ThF^{3+} or ThF_2^{2+} are dominant at low fluoride concentrations and $ThF_4(aq)$ becomes important only at relatively high fluoride concentrations, while in Figure VIII-3 $ThF_4(aq)$ is the dominant species in all the solutions. The calculated values of $\Delta_f G_m^\circ / RT$ (ThF_4, cr, hyd) based on $\Delta_f G_m^\circ / RT$ (ThF_4, aq) = − (797.469 ± 0.416) are similar (see Section VIII.1.3.1) for these three different chemical systems (solubility studies in HNO_3, NH_4F, and NaF) and thus the value of $\log_{10}\beta_4^\circ$ of (25.58 ± 0.18) provides close agreement between the predicted and experimental solubilities for ThF_4(cr, hyd) (Figure VIII-2 and Figure VIII-3).

Figure VIII-2: Observed [1981SMI/MES] and calculated solubility of ThF_4(cr, hyd) at 25°C (a) and 50°C (b) in 4.6 m HNO_3 as a function of the free fluoride ion concentration. The solid line depicts predicted total thorium concentration and the other lines depict predicted concentrations of different thorium species as marked, based on NONLINT-SIT calculations with the ion interaction parameters (Table VIII-8) and thermodynamic data (Table VIII-9) selected in this review.[1]



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[1] The goodness of fit is not significantly affected if the ThF_6^{2-} species is included in the model.

Figure VIII-3: Observed [1993FEL/RAI] and predicted solubility of ThF_4(cr, hyd) at 25°C in NH_4F solutions (a) and NaF solutions (b) using the thermodynamic data reported in Table VIII-8 and Table VIII-9 and as described in the main text. The solid line depicts predicted total thorium concentration and the other lines depict predicted concentrations of different thorium species as marked (Note: The goodness of fit is not significantly changed if ThF_6^{2-} species are included or excluded from the model).

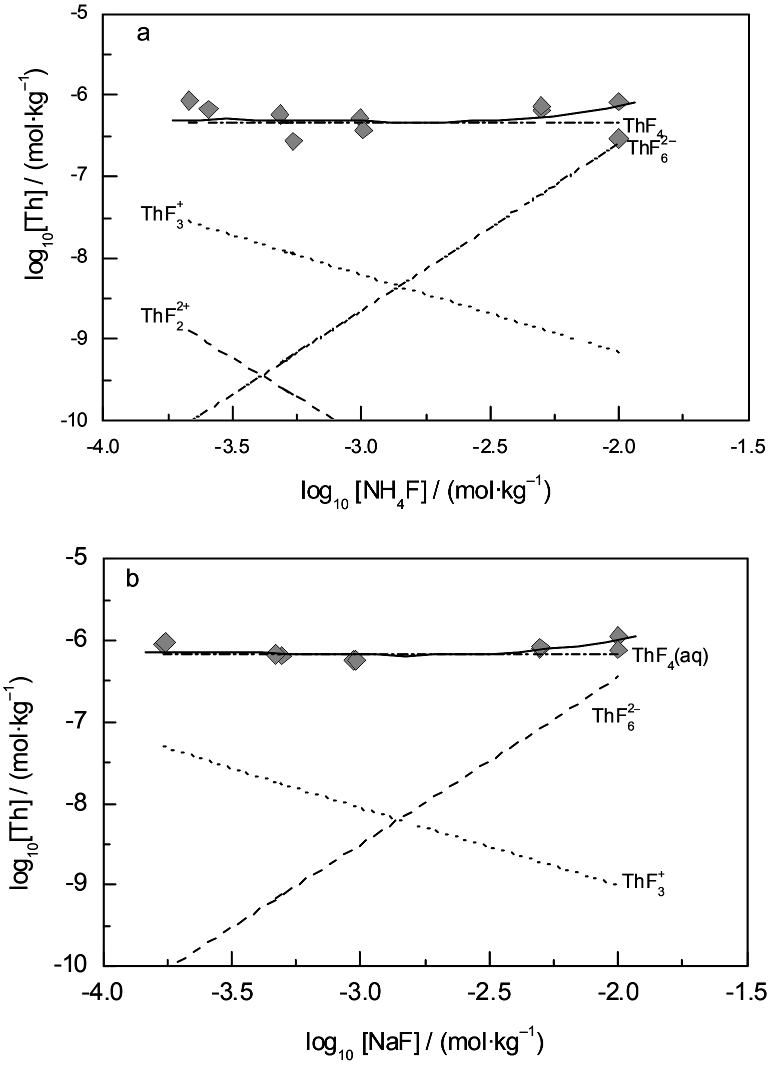


Table VIII-9: Molar Gibbs energies of formation at 25°C used in modelling the Th-fluoride system.

Species^a	$\Delta_f G_m^o / RT$ ^{b}	$\Delta_f G_m^o$ (kJ·mol^{-1})	Reference
Th^{4+}	-284.305 ± 2.137	-704.783 ± 5.298	This review
ThF^{3+}	$-418.293 \pm 0.350^*$	$-1036.936 \pm 0.868^*$	This review
ThF_2^{2+}	$-547.422 \pm 0.530^*$	$-1357.043 \pm 1.314^*$	This review
ThF_3^+	$-672.591 \pm 0.370^*$	$-1667.334 \pm 0.917^*$	This review
ThF_4(aq)	$-797.469 \pm 0.416^*$	$-1976.903 \pm 1.031^*$	This review^c
ThF_6^{2-}	$-1032.982 \pm 1.420^*$	$-2560.733 \pm 3.520^*$	This review^c
ThF_4(cr, hyd)	$-811.860 \pm 0.915^*$	$-2012.578 \pm 2.268^*$	This review$^{c,\,d}$
$ThF_4·NaF·H_2O$(cr)	$-1139.40 \pm 1.248^*$	$-2824.540 \pm 3.094^*$	This review^c
$ThF_4·NH_4F$(cr)	$-968.952 \pm 1.816^*$	$-2402.004 \pm 4.502^*$	This review^c

a: The values for other species [F^-, HF(aq), HF_2^-, H_2O, OH^-, Na^+, NH_4^+ and NO_3^-] used in modelling are those in Table IV-1.

b: The NONLINT-SIT model uses average $\Delta_f G_m^o / RT$ of different species and calculates uncertainties based on the experimental data, as described in Appendix D (see values for the $\Delta_f G_m^o$ column).

c: Based on reinterpretation of [1993FEL/RAI] data using the SIT model.

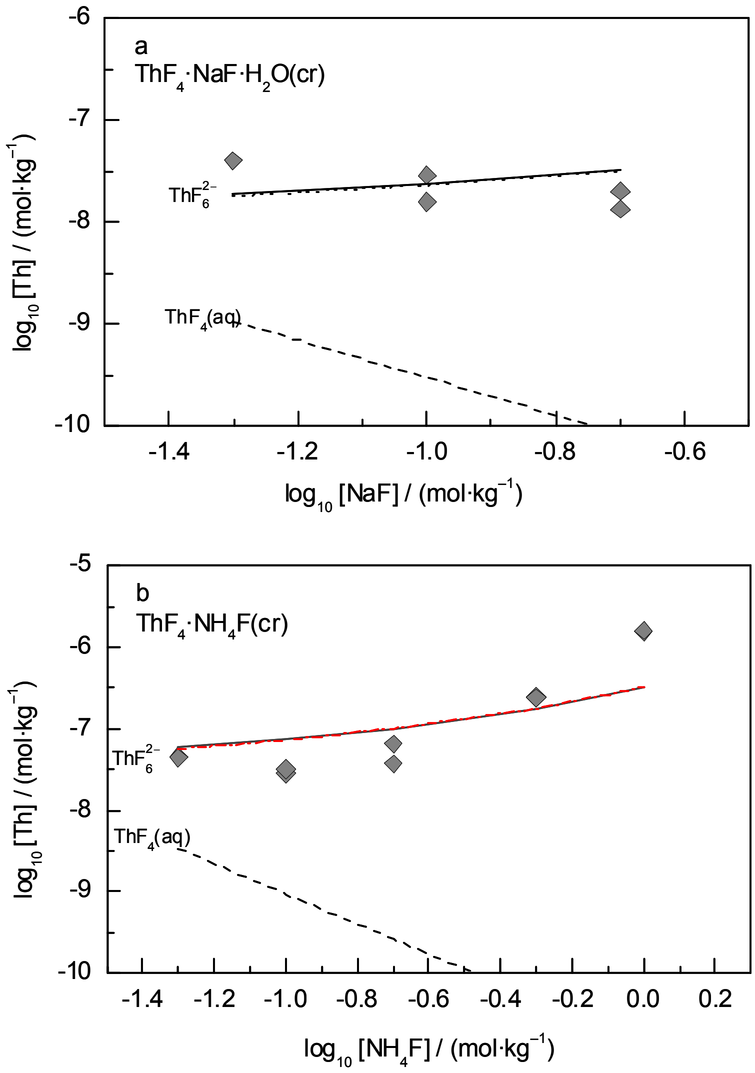
d: Based on an average value from the solubility data of [1993FEL/RAI] in NaF and NH_4F solutions and consistent with the solubility data of [1981SMI/MES] in relatively concentrated HNO_3 solutions (see text for details). The value does not include the water of hydration.

*: These uncertainties do not include those in $\Delta_f G_m^o$ (Th^{4+}, 298.15 K) and $\Delta_f G_m^o$ (F^-, 298.15 K).

VIII.1.2.1.3 Formation constants of ThF_5^- and ThF_6^{2-}

Only one study [1993FEL/RAI] has been made in a relatively high fluoride concentration range where the complexes ThF_5^- and/or ThF_6^{2-} might be formed. Because of the limited experimental information for these species, two different approaches were used to estimate/determine thermodynamic data. These included reinterpretation of solubility data of [1993FEL/RAI] and estimates based on correlations (see Section VIII.1.2.1.4) between Th(IV)-F and U(IV)-F complexes. The data for the solubility of $ThF_4·NaF·H_2O$(cr) in NaF and of $ThF_4·NH_4F$(cr) in NH_4F solutions [1993FEL/RAI] were reinterpreted using the NONLINT-SIT fitting code, keeping the $\Delta_f G_m^o / RT$ values for ThF^{3+}, ThF_2^{2+}, ThF_3^+, and ThF_4(aq) fixed at the values selected in this review; the values of ion interaction parameter $\varepsilon_1(Na^+, F^-)$ and $\varepsilon_1(NH_4^+, F^-)$ were also kept constant (Table VIII-8). Several different attempts were made to simultaneously fit the $\Delta_f G_m^o / RT$ values of the solid phases ThF_4(cr, hyd) (Figure VIII-3) and $ThF_4·NaF·H_2O$(cr) and $ThF_4·NH_4F$(cr) (Figure VIII-4) and of the ThF_5^- and/or ThF_6^{2-} complexes, along with ion interaction parameters for NH_4^+ - ThF_6^{2-}. The result of these calculations is best discussed by comparing the experimental data with those calculated using the selected $\Delta_f G_m^o / RT$ values (Table VIII-9) and ion interaction parameters (Table VIII-8) as shown in Figure VIII-4. The solubility is low and the total concentration of fluoride is therefore very close to the free fluoride concentration. The experimental data show a nearly constant aqueous thorium concentration (Figure VIII-4-a) or a nearly constant concentration followed by an increase in concentration with increasing fluoride concentration (Figure VIII-4-b), which is consistent with a solubility reaction of these solid phases ($ThF_4 \cdot MF$) involving ThF_6^{2-} species. The solubility reactions involving ThF_4(aq) or ThF_5^-, the only other possible significant species in these high fluoride solutions, would result in a decrease in the thorium concentrations of two and one order of magnitude, respectively, with an increase in concentration of NaF or NH_4F of a factor of ten. Changes in the ionic medium will affect the solubility (the increase in thorium concentrations with the increase in NH_4F concentration, Figure VIII-4-b, is due to this effect); the present review took this into account and tested models that included the negatively charged complexes. The "best" of these models that included ThF_6^{2-} (with $\Delta_f G_m^o / RT$ (ThF_6^{2-}) = − (1032.982 ± 1.420) and $\log_{10} \beta_6^o$ = (29.23 ± 0.62)) is shown in Figure VIII-3 and Figure VIII-4, and it is obvious that ThF_6^{2-} becomes dominant only at relatively high fluoride concentrations (> ~0.02 M). The modelling runs also showed that ThF_5^- was not the dominant species in any of these systems and it was not possible to estimate the $\Delta_f G_m^o / RT$ value for this species with any degree of certainty. The modelling of these solubility data with average values of $\log_{10} \beta_5^o$ = 26.61 and $\log_{10} \beta_6^o$ = 28.70, estimated from correlations of constants for Th-F/U(IV)-F complexes (Figure VIII-5), also showed that ThF_5^- never becomes dominant in these systems. The value of $\log_{10} \beta_6^o$ = (29.23 ± 0.62) obtained from reinterpretation of solubility data of [1993FEL/RAI] looks reasonable, being within the range of the values $\log_{10} \beta_6^o$ = (28.70 ± 2.81) estimated from correlations of Th-F/U(IV)-F complexes (Figure VIII-5). Although it can be used for scoping studies, this value was not selected because of a number of assumptions made and difficulties encountered in interpreting these data, and because no other supporting experimental information is available.

Figure VIII-4: Observed [1993FEL/RAI] and predicted solubilities of thorium double salts in NaF and NH_4F solutions at 25ºC using the thermodynamic data reported in Table VIII-8 and Table VIII-9. The solid line depicts predicted total thorium concentration and the other lines depict predicted concentrations of different thorium species as marked (a) $ThF_4{\cdot}NaF{\cdot}H_2O(cr)$ and (b) $ThF_4{\cdot}NH_4F(cr)$.

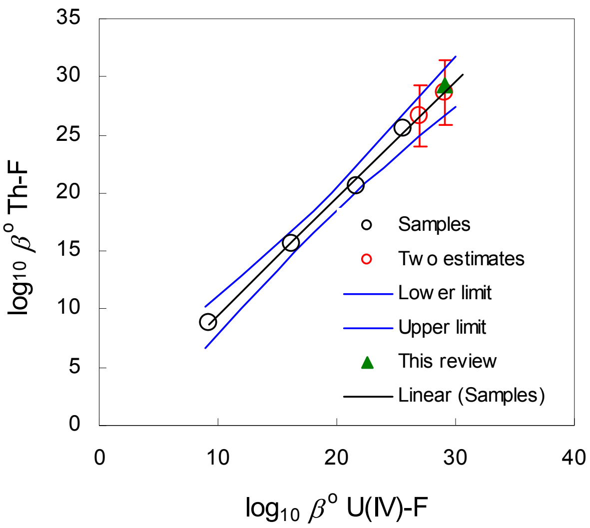


VIII.1.2.1.4 Comparison with U(IV)-fluoride complexes

The experimental data discussed in the previous sections provide reliable estimates of the equilibrium constants for the complexes ThF_n^{4-n}, n = 1 – 3 and a good estimate for $\mathrm{ThF_4}$(aq). There is evidence for the formation of anionic complexes at fluoride concentrations higher than ~ 0.02 M, and a value of the equilibrium constant for ThF_6^{2-} is available for scoping studies.

It is well known that different actinide ions have very similar properties when they are in the same oxidation state; this review has therefore compared the selected and estimated equilibrium constants for the Th(IV) and U(IV) fluoride complexes in Figure VIII-5. The figure underscores the large similarity in the chemical properties of the two systems, and also the consistency of the experimental observations and the evaluation procedure used.

Figure VIII-5: Comparison of $\log_{10}\beta_n^{\mathrm{o}}$ for the UF_6^{2-} and ThF_6^{2-} complexes. The values at the 95% confidence interval for the higher Th-F species, $\log_{10}\beta_5^{\mathrm{o}}$ = (26.61 ± 2.62) and $\log_{10}\beta_6^{\mathrm{o}}$ = (28.70 ± 2.81), were predicted from an extrapolation of the regression of the values of $\log_{10}\beta_1^{\mathrm{o}}$ to $\log_{10}\beta_4^{\mathrm{o}}$. The experimental value of $\log_{10}\beta_6^{\mathrm{o}}$ = (29.23 ± 0.62) for ThF_6^{2-}, based on the analyses of literature data (Section VIII.1.2.1.3), falls within the predicted envelope[1].



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[1] The extrapolated values are slightly different ($\log_{10}\beta_5^{\mathrm{o}}$ = (26.38 ± 2.56) and $\log_{10}\beta_6^{\mathrm{o}}$ = (28.41 ± 2.75)) when the regression is forced through zero.

VIII.1.2.2 Enthalpies and entropies of reaction for Th(IV) fluoride complexes

Calorimetry provides the most accurate information of the enthalpy of reaction, and the only studies of this type from Grant *et al.* [1989GRA/KIN] and Ahrland *et al.* [1990AHR/HEF] are therefore selected as the most accurate sources. The enthalpies of reaction determined using the van't Hoff equation [1970BAU], [1976CHO/UNR] and [1981SMI/MES] are much less accurate, *cf.* Table VIII-10.

$$\mathrm{Th}^{4+} + n\mathrm{F}^- \rightleftharpoons \mathrm{ThF}_n^{4-n} \qquad \text{(VIII.4)}$$

Table VIII-10: Molar enthalpy and entropy of Reactions (VIII.4).

Reaction	Ionic medium	$\Delta_r H_m$ (kJ·mol^{-1})	$\Delta_r S_m$ (J·K^{-1}·mol^{-1})	Reference
$\mathrm{Th}^{4+} + \mathrm{F}^- \rightleftharpoons \mathrm{ThF}^{3+}$	1.00 M $HClO_4$	1.0 ± 1.3	146 ± 5	[1976CHO/UNR]$^{(a)}$
	1.00 M $HClO_4$	2.3 ± 0.8	151 ± 6	[1976CHO/UNR]$^{(b)}$
	0.01 M NH_4NO_3	– 5.0	163	[1970BAU]
	0.50 M $NaClO_4$	1.6 ± 0.3	150 ± 1	[1989GRA/KIN]
	4.00 M $HClO_4$	– 2.4 ± 0.1	149 ± 4	[1990AHR/HEF]
$\mathrm{Th}^{4+} + 2\mathrm{F}^- \rightleftharpoons \mathrm{ThF}_2^{2+}$	0.01 M NH_4NO_3	– 8.3	293	[1970BAU]
	4.00 M $HClO_4$	– 3.3 ± 0.4	269 ± 5	[1990AHR/HEF]
$\mathrm{Th}^{4+} + 3\mathrm{F}^- \rightleftharpoons \mathrm{ThF}_3^{+}$	0.01 M NH_4NO_3	– 11.6	373	[1970BAU]
$\mathrm{Th}^{4+} + 4\mathrm{F}^- \rightleftharpoons \mathrm{ThF}_4\mathrm{(aq)}$	0.01 M NH_4NO_3	– 15.5	431	[1970BAU]

a: solvent extraction

b: potentiometry

The calorimetric values of the enthalpy and entropy for the reaction $\mathrm{H}^+ + \mathrm{F}^- \rightleftharpoons \mathrm{HF(aq)}$ are in good agreement with the values selected in this review. The enthalpies of reaction for the formation of the various fluoride complexes are small, indicating that the equilibrium constants do not vary much with the temperature. As discussed above, this review is not confident about the quality of the equilibrium data reported by [1970BAU]; for this reason and because of the very limited temperature range used to determine the enthalpy of reaction, this review has not accepted the enthalpies and entropies of reaction proposed by [1970BAU]. The data from [1976CHO/UNR] are in reasonable agreement with the calorimetric data. The experimental enthalpy of reaction does not refer to zero ionic strength, but to the actual ionic medium used in the experiment. It is not possible to extrapolate these data to zero ionic strength based on the available information. The difference in the enthalpy of reaction is surprisingly large between the two calorimetric studies, but this is possibly due to the different ionic media. This review finds no reason to select one over the other and the selected value is therefore the average of the two, where the uncertainty is the deviation from the mean in the two studies. This review has used this average as an estimate of the enthalpy of reaction for the formation of ThF^{3+} at zero ionic strength and has accordingly selected:

$$\Delta_{\mathrm{r}} H^{\circ}_{\mathrm{m}}\,((\mathrm{VIII.4}),\ n = 1) = -(0.4 \pm 2.0)\ \mathrm{kJ\cdot mol^{-1}}.$$

The value selected by this review for the enthalpy of reaction for ThF_2^{2+} was taken from [1990AHR/HEF]:

$$\Delta_{\mathrm{r}} H^{\circ}_{\mathrm{m}}\,((\mathrm{VIII.4}),\ n = 2) = -(3.3 \pm 0.4)\ \mathrm{kJ\cdot mol^{-1}}.$$

VIII.1.2.3 Summary of selected values for the aqueous thorium fluoride species

The $\Delta_{\mathrm{f}} G^{\circ}_{\mathrm{m}}$ values for the selected Th-F species are reported in Table VIII-11 and the equilibrium constants for the important reactions involving these species are reported in Table VIII-12.

Table VIII-11: Summary of selected $\Delta_{\mathrm{f}} G^{\circ}_{\mathrm{m}}$ values for the aqueous Th-F species

Species	$\Delta_{\mathrm{f}} G^{\circ}_{\mathrm{m}}$ ($\mathrm{kJ\cdot mol^{-1}}$)
Th^{4+}	-704.783 ± 5.298
ThF^{3+}	-1036.936 ± 5.411
ThF_2^{2+}	-1357.043 ± 5.631
ThF_3^{+}	-1667.334 ± 5.763
$\mathrm{ThF_4(aq)}$	-1976.903 ± 6.066

Table VIII-12: Summary of selected equilibrium constants for reactions involving aqueous Th-F species

Species	$\log_{10} \beta^{\circ}$
$\mathrm{Th}^{4+} + \mathrm{F}^- \rightleftharpoons \mathrm{ThF}^{3+}$	8.87 ± 0.15
$\mathrm{Th}^{4+} + 2\mathrm{F}^- \rightleftharpoons \mathrm{ThF}_2^{2+}$	15.63 ± 0.23
$\mathrm{Th}^{4+} + 3\mathrm{F}^- \rightleftharpoons \mathrm{ThF}_3^{+}$	20.67 ± 0.16
$\mathrm{Th}^{4+} + 4\mathrm{F}^- \rightleftharpoons \mathrm{ThF_4(aq)}$	25.58 ± 0.18

VIII.1.3 Other solid thorium fluoride compounds

Thorium readily forms fluoride compounds from aqueous solutions at relatively low fluoride concentrations; these solid phases can be used for solubility experiments and thereby provide information of the speciation in the aqueous phase. At fluoride concentrations between 0.0001 M and 0.01 M, the hydrated crystalline $\mathrm{ThF_4}$ designated here as $\mathrm{ThF_4}$(cr, hyd) is easily formed [1993FEL/RAI]. At higher fluoride concentrations, crystalline double salts are formed. The nature of these salts is dependent on the fluoride concentrations and the associated alkali metal. In the NaF media, crystalline double salts of the composition $\mathrm{ThF_4\cdot NaF\cdot H_2O(cr)}$ and $\mathrm{ThF_4\cdot 3NaF(cr)}$ are reported [1993FEL/RAI]. In the $\mathrm{NH_4F}$ media, crystalline double salts of the composition $\mathrm{ThF_4\cdot NH_4F(cr)}$ [1993FEL/RAI], and $\mathrm{ThF_4\cdot (NH_4F)_3(cr)}$ and $\mathrm{ThF_4\cdot (NH_4F)_4(cr)}$ [1969RYA/PEN], [1971PEN/RYA] are reported. Although several additional double salts in the $Th(NO_3)_4$-MF-H_2O, (M = K, NH_4, Na) systems are reported to precipitate from aqueous solutions ([1959TAN/LU4], [1959TAN/LU6]), no definitive characterisation or thermodynamic data for these compounds are available.

There are several studies that report the solubility product of ThF_4(cr, hyd), and these studies are discussed in the previous section and in Section VIII.1.3.1.3. The data in Table VIII-13 have been used to determine the solubility product for the reaction:

$$ThF_4(cr, hyd) + 4H^+ \rightleftharpoons Th^{4+} + 4HF(aq).$$

As the water of hydration is not part of the structure of ThF_4(cr, hyd), *cf.* Section VIII.1.3.1.3, this review has calculated the selected Gibbs energy of formation from the selected solubility and NEA auxiliary data (Tables IV-1 and IV-2) to give $\Delta_f G^o_m$ (ThF_4, cr, hyd, 298.15 K) = −(2012.6 ± 6.1) $kJ\cdot mol^{-1}$.

Table VIII-13: Solubility products of ThF_4(cr, hyd) at 25°C according to the reaction: $ThF_4(cr, hyd) + 4H^+ \rightleftharpoons Th^{4+} + 4HF(aq)$.

Medium	$\log_{10} {}^*K_s$	$\log_{10} {}^*K^o_s$ [a]	Reference
0.5 M $NaClO_4$	−14.7	−16.74 ± 0.07[b]	[1949DOD/ROL]
3 M $NaClO_4$	−15.17	−17.68 ± 0.45[b]	[1971KLO/MUK]
4 M HNO_3	−16.25 ± 0.40	−18.90 ± 0.50[c]	[1981SMI/MES]
$I = 0$ (NaF)	−16.30	−19.04 ± 0.15[c]	[1993FEL/RAI]
$I = 0$ (NH_4F)	−16.30	−19.18 ± 0.37[c]	[1993FEL/RAI]
$I = 0$		−19.11 ± 0.40	Selected [d]

a: Values calculated in this review.

b: Calculated from $\log_{10} K^o = [\log_{10} K - \Delta z^2 D + \Delta\varepsilon I_m] \pm [\sigma\Delta\varepsilon I_m]$ using the appropriate ion-interaction parameters reported in Table VIII-8.

c: Determined from reinterpretation of the data reported in the quoted reference with NONLINT-SIT fitting code and the thermodynamic data reported in Table VIII-8 and Table VIII-9.

d: An average of NaF and NH_4F system values, selected in this review, for details see Section VIII.1.3.1.3.

Only one study [1993FEL/RAI] reports the solubility products of some of the double salts ($ThF_4\cdot NaF\cdot H_2O$(cr), $ThF_4\cdot NH_4F$(cr)). Since the solubility product is dependent on the aqueous phase model used for interpretations, it is necessary to reinterpret the literature data in order to obtain solubility product values that are consistent with the aqueous phase model recommended in this review. Discussed below are the solubility products of several different solid phases as reported in the literature and reinterpreted in this review. The equilibrium constants from [1959TAN/LU5] and [1962NIK/LUK] are not accepted by this review for reasons given in Appendix A.

VIII.1.3.1 Solid ThF_4(cr, hyd)

VIII.1.3.1.1 Structure

The early investigations by Chauvenet [1911CHA] indicated the existence of di-, tetra- and octahydrates of thorium fluoride. Later studies by Asker *et al.* [1952ASK/SEG], D'Eye and Booth [1955EYE/BOO], [1957EYE/BOO], and Gagarinskii and Mashirev [1959GAG/MAS2] showed that a compound of composition $ThF_4{\cdot}2.5-3.0\ H_2O$(cr) is formed by air-drying a fresh precipitate obtained by addition of aqueous hydrofluoric acid to a thorium nitrate solution. This hydrate was shown [1955EYE/BOO] to be pseudo-tetragonal. Although an unambiguous indexing could not be obtained, the compound does not appear to be isomorphous with orthorhombic $UF_4{\cdot}2.5H_2O$(cr). A lower hydrate, $ThF_4{\cdot}0.5-2.0H_2O$(cr), indexed on the basis of an orthorhombic cell, is isolated when the precipitate is allowed to stand 48 hours with the mother liquor.

According to D'Eye and Booth [1955EYE/BOO], $ThF_4{\cdot}0.5H_2O$(cr) forms upon dehydration of the higher hydrates at 323−353 K under a pressure of 10^{-5} torr. Other low hydrates were obtained [1957EYE/BOO] by boiling anhydrous ThF_4(cr) with water.

VIII.1.3.1.2 Dehydration and hydration reactions

As briefly discussed in Appendix A, Gagarinskii and Mashirev [1959GAG/MAS2] showed that samples of thorium fluoride hydrates with compositions $ThF_4{\cdot}2.5H_2O$(cr) and $ThF_4{\cdot}0.5H_2O$(cr) could be dehydrated without apparent loss of structure, and report the enthalpies of rehydration to be $-(8.673 \pm 0.017)$ and $-(4.912 \pm 0.021)$ $\text{kJ}\cdot\text{mol}^{-1}$ respectively. This review notes, however, that there is considerable doubt as to the identity and thermodynamic stability of the phases involved in these apparently reversible dehydration-hydration reactions. For these reasons, these values are given for information only, although they are not incompatible with the small difference between the value $\Delta_f G^\circ_m$(ThF_4, cr, 298.15 K) = $-(2005.7 \pm 10.0)$ $\text{kJ}\cdot\text{mol}^{-1}$ and that, $\Delta_f G^\circ_m$(ThF_4, cr, hyd, 298.15 K) = $-(2012.6 \pm 6.4)$ $\text{kJ}\cdot\text{mol}^{-1}$, obtained from solubility data and discussed below.

VIII.1.3.1.3 Solubility and Gibbs energy

A number of papers [1949DOD/ROL], [1962NIK/LUK], [1971KLO/MUK], [1981SMI/MES], [1993FEL/RAI] have reported a solubility product for ThF_4(cr, hyd) at different ionic strengths and in different ionic media (Table VIII-13).

The solubility product for Reaction (VIII.5)

$$ThF_4(\text{cr, hyd}) + 4H^+ \rightleftharpoons Th^{4+} + 4HF(\text{aq}) \qquad \text{(VIII.5)}$$

from [1949DOD/ROL], [1962NIK/LUK] and [1971KLO/MUK] is significantly larger than those from [1981SMI/MES] and [1993FEL/RAI]. These studies are discussed in

Appendix A and for reasons given there they are not accepted by this review. The data from [1993FEL/RAI] were reinterpreted as described in the previous section using solubility data for ThF_4(cr, hyd) and the NONLINT-SIT fitting code *cf.* Appendix D.

The solubility data of ThF_4(cr, hyd) in NaF and NH_4F solutions [1993FEL/RAI] and in 4 M HNO_3 solutions at 25°C and 50°C [1981SMI/MES] were reinterpreted using NONLINT-SIT and data reported in Table VIII-8 and Table VIII-9 to determine $\Delta_f G^\circ_m / RT$ for ThF_4(cr, hyd). The $\Delta_f G^\circ_m / RT$ (ThF_4, cr, hyd) values thus determined from the NaF, NH_4F, HNO_3 at 25°C, and HNO_3 at 50°C systems were $-(811.684 \pm 0.348)$, $-(812.026 \pm 0.846)$, $-(811.372 \pm 2.460)$ and $-(811.146 \pm 2.320)$, respectively. The solubility products calculated from these $\Delta_f G^\circ_m / RT$ values, using the auxiliary thermodynamic data reported in this review, are given in Table VIII-13. These values are in good agreement and the average ${}^*K^\circ_{s,0}$ based on NaF and NH_4F systems, together with the selected equilibrium constants for the complexes, provides a close agreement between the predicted and the observed thorium concentrations as a function of F^- concentrations (Figure VIII-2 and Figure VIII-3). This review selects a value of $\Delta_f G^\circ_m / RT$ (ThF_4(cr, hyd)) $= -(811.860 \pm 0.915)$, based on the average value from NaF and NH_4F systems investigated by [1993FEL/RAI]. The NaF and NH_4F system studies [1993FEL/RAI] were conducted in relatively low ionic strength solutions where the ion-interaction parameters other than the bulk electrolyte are not needed for the dominant species observed in this system; therefore the $\Delta_f G^\circ_m / RT$ value for ThF_4(cr, hyd) from these data are probably more precise than those from [1981SMI/MES]. These $\Delta_f G^\circ_m / RT$ values exclude the water of hydration, of course. The value of $\Delta_f G^\circ_m / RT$ (ThF_4, cr, hyd) $= -(811.860 \pm 0.915)$ at 25°C gives the selected value:

$$\log_{10} {}^*K^\circ_s \text{ (VIII.5)} = -(19.11 \pm 0.40)$$

as compared to the value of -16.30 reported by [1993FEL/RAI] based on the Pitzer model and the equilibrium constants for the complexes assessed by [1982WAG/EVA]. This difference is mainly due to differences in the values of equilibrium constants of fluoride complexes of thorium used, primarily β_4, in the interpretations.

As noted in Section VIII.1.1.2.1, ThF_4(cr) crystallises in the monoclinic space group *C*2/*c* [1990BEN/MUL]. The structure consists of a three-dimensional network of ThF_8 polyhedra where each fluoride acts as a bridge between two Th^{4+}; there is no space in this structure for coordinated or interstitial water. Accordingly we suggest that the hydrated ThF_4(cr, hyd) has the same structure as the anhydrous compound and that the water is sorbed on the surface of the microcrystalline particles. Hence, the properties of the sorbed water are not too different from those of pure water. This suggestion is supported by the fact that the Gibbs energy of formation of the hydrated phases (excluding that of the water of hydration) calculated from the solubility is very similar to that of ThF_4(cr), especially considering the large uncertainty in the assessed value for the latter ($\Delta_f G^\circ_m$ (ThF_4, cr, hyd, 298.15 K) = $-(2012.6 \pm 6.4)$ kJ·mol^{-1}; $\Delta_f G^\circ_m$ (ThF_4, cr, 298.15 K) $= -(2005.7 \pm 10.0)$ kJ·mol^{-1}).

VIII.1.3.2 $ThF_4{\cdot}NH_4F(cr)$

The data on the solubility of $ThF_4{\cdot}NH_4F(cr)$ in NH_4F solutions [1993FEL/RAI] was used in conjunction with the aqueous phase model discussed in this review containing ThF^{3+}, ThF_2^{2+}, ThF_3^+, $ThF_4(aq)$, and ThF_6^{2-} and an estimated value of $\varepsilon_1(NH_4^+, ThF_6^{2-}) = -(0.30 \pm 0.06)$ kg·mol^{-1} (Table VIII-8 and Table VIII-9) to determine $\Delta_f G_m^o / RT$ ($ThF_4{\cdot}NH_4F$, cr) = −(968.952 ± 1.816). Figure VIII-4-b compares the experimental data and a chemical model that includes ThF_6^{2-}. The agreement is not impressive, but the changes in thorium concentrations with the changes in MF concentrations are predicted well enough (also see Figure VIII-4-a and Section VIII.1.2) to conclude that negatively charged complexes (ThF_6^{2-}) are formed. However, no equilibrium constant for ThF_6^{2-} has been selected.

These data, when combined with other auxiliary data, provide a $\log_{10} K^o$ value of −(36.829 ± 0.790) based on the SIT model; the value of $\log_{10} K^o = -33.898$ found in [1993FEL/RAI] was based on the Pitzer model for Reaction (VIII.6).

$$ThF_4{\cdot}NH_4F(cr) \rightleftharpoons Th^{4+} + 5F^- + NH_4^+ \qquad \text{(VIII.6)}$$

Since both values are based on the same experimental data and the solubility study was conducted at relatively low ionic strengths where both the Pitzer and the SIT models should be in good agreement, the major difference in these values is as a result of the differences in values for equilibrium constants of aqueous complexes, particularly for ThF_6^{2-}, used in interpretation of data.

VIII.1.3.3 $ThF_4{\cdot}NaF{\cdot}H_2O(cr)$

The data on the solubility of $ThF_4{\cdot}NaF{\cdot}H_2O(cr)$ in NaF solutions [1993FEL/RAI] were used in conjunction with the aqueous phase model (Table VIII-9) including an estimated value of $\varepsilon_1(Na^+, ThF_6^{2-}) = -(0.30 \pm 0.06)$ kg·mol^{-1} recommended in this review (Table VIII-8) to determine $\Delta_f G_m^o / RT$ ($ThF_4{\cdot}NaF{\cdot}H_2O$, cr) = − (1139.400 ± 1.248). There is a close agreement between the experimental and predicted aqueous thorium concentrations as a function of NaF concentrations (Table VIII-4-a). The predictions also show that one of the major species in this system is ThF_6^{2-}. These data, when combined with other auxiliary data (Table IV-1), provide a $\log_{10} K^o$ (VIII.7) value of − (37.33 ± 0.54) based on the SIT model as opposed to a value of −34.03 from [1993FEL/RAI] based on the Pitzer model for the reaction:

$$ThF_4{\cdot}NaF{\cdot}H_2O(cr) \rightleftharpoons Th^{4+} + 5F^- + Na^+ + H_2O(l). \qquad \text{(VIII.7)}$$

As discussed earlier, the observed large difference in the standard state equilibrium constants based on the SIT and Pitzer models must result primarily from the differences in the standard state equilibrium constants for the major aqueous species used in these interpretations. Of course, the activity coefficients for the species involved, in particular that for the Th^{4+} ion, are also different in the two models (*cf.* Section VI.3.2).

VIII.2 Chlorine compounds and complexes

VIII.2.1 Solid and gaseous thorium chloride compounds

VIII.2.1.1 $ThCl_2$(cr), $ThCl_3$(cr)

The experimental results on the existence of the lower thorium chlorides, $ThCl_2$(cr) and $ThCl_3$(cr) are quite contradictory.

Hayek *et al.* [1951HAY/REH] obtained products with compositions close to $ThCl_2$ and $ThCl_3$ from the reaction of thorium metal with gaseous chlorine in stoichiometric quantities while Jantsch and Homayr [1954JAN/HOM] reported the formation of $ThCl_3$ as a result of the reduction of $ThCl_4$ with aluminium and also, which is more surprising, from the thermal decomposition of $ThCl_4$ at 673 K. As noted by Rand [1975RAN], contamination by oxygen and silica may have been serious in these experiments.

Rand [1975RAN] notes that Dock [1965DOC] reported the formation of phases of composition close to $ThCl_2$ and $ThCl_3$, with complicated X-ray patterns, as a result of the annealing of thorium metal-$ThCl_4$ mixtures at 923 − 1073 K in tantalum containers. However, these results were subsequently described by the same group [1973CHI/FUL] as anomalous and probably caused by inadvertent contamination by oxygen or moisture.

Based on potentiometric and coulometric measurements, Smirnov *et al.* [1983SMI/KUD] reported that, in the system thorium metal-fused alkali salts, the oxidation state of thorium was non-integral varying between 2 and 4, depending on the ionic composition of the melt, the concentration of dissolved thorium and the temperature. These results followed earlier similar conclusions by the same group of authors who also reported [1983KUD/SMI] a decrease in the magnetic susceptibility, attributed to the formation of diamagnetic Th(II), in the reaction of metallic thorium with molten potassium chloride containing thorium tetrachloride.

However, all of the emf results by Chiotti and Dock [1975CHI/DOC], Yoshida *et al.* [1967YOS/OYA], and Srinivasan and Flengas [1964SRI/FLE] failed to identify lower oxidation states of thorium in the Th-$ThCl_4$ system. The voltametric determinations by Martinot [1986MAR4] also showed no evidence of the existence of Th(II) in the eutectic system, even as an intermediate species.

In addition, Chiotti *et al.* [1973CHI/FUL] showed that the Th-$ThCl_4$ system was a simple eutectic system and that the only species identified by X-ray in this system were metallic thorium and the two modifications of $ThCl_4$. In one experiment only, [1973CHI/FUL] observed a few extraneous lines due to $ThOCl_2$ as the result of contamination by oxygen or moisture.

There is thus little or no conclusive evidence for the formation of any stable solid thorium chlorides other than $ThCl_4$(cr).

VIII.2.1.2 ThCl(g), $ThCl_2$(g), $ThCl_3$(g)

These species are considered together since their data are linked by a mass-spectrometric study, which thus involves some uncertainties in absolute pressures.

VIII.2.1.2.1 Standard entropy and heat capacity

The thermal functions of ThCl(g), $ThCl_2$(g) and $ThCl_3$(g) were calculated assuming the molecular parameters shown in Table E-1. These are based on the parameters selected by [1977WAG/SCH], in turn derived principally from the estimates by [1973KRA/MOR]. No electronic contributions have been included, leading to considerable uncertainties in the thermal functions, especially for the monochloride. The selected values, with uncertianties estimated by this review, are:

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThCl, g, 298.15\ K}) = (269.2 \pm 12.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThCl, g, 298.15\ K}) = (36.4 \pm 6.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThCl_2, g, 298.15\ K}) = (317.1 \pm 10.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThCl_2, g, 298.15\ K}) = (55.3 \pm 5.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThCl_3, g, 298.15\ K}) = (369.7 \pm 10.0\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThCl_3, g, 298.15\ K}) = (78.0 \pm 5.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

VIII.2.1.2.2 Enthalpies of formation

Lau and Hildenbrand [1990LAU/HIL] have studied three equilibria between ThCl(g), $ThCl_2$(g), $ThCl_3$(g) and $ThCl_4$(g) which are summarised in Table VIII-14, where the enthalpies of the given reactions at 298.15 K derived from both second and third law analyses are given. The auxiliary data for Ca(g) and CaCl(g) are taken from the assessments by Glushko *et al.* [1981GLU/GUR].

Table VIII-14: Enthalpies of the reactions involving ThCl(g), $ThCl_2$(g) and $ThCl_3$(g) and $ThCl_4$(g).

Reaction	Temperature range (K)	$\Delta_r H^{\circ}_{\mathrm{m}}$ (298.15 K) ($\mathrm{kJ{\cdot}mol^{-1}}$)	
		Second law	Third law
Th(g) + CaCl(g) $\rightleftharpoons$ ThCl(g) + Ca(g)	2181 − 2478	− 73.9 ± 7.6	− 83.5 ± 0.6
ThCl(g) + CaCl(g) $\rightleftharpoons$ $ThCl_2$(g)+ Ca(g)	2113 − 2296	− 144.6 ± 10.5	− 130.5 ± 1.5
$ThCl_2$(g) + CaCl(g) $\rightleftharpoons$ $ThCl_3$(g) + Ca(g)	2003 − 2203	− 109.1 ± 7.2	− 101.4 ± 1.0

Of necessity, the pressures for these reactions were derived from mass-spectrometric intensities, leading to uncertainties in the absolute pressures, even though the intensity factors in the conversion will approximately cancel for these isomolecular reactions. It will be seen that the agreement between the second and third-law analyses is mostly quite reasonable. From these data, the enthalpies of formation of ThCl(g), $ThCl_2$(g) and $ThCl_3$(g) can be calculated in sequence, the uncertainties necessarily increasing in this order, as shown in Table VIII-15.

The selected values, which are based on the second-law values, are thus:

$$\Delta_f H_m^\circ(\text{ThCl, g, 298.15 K}) = (247 \pm 20)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{ThCl}_2\text{, g, 298.15 K}) = -(179 \pm 22)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{ThCl}_3\text{, g, 298.15 K}) = -(569 \pm 25)\ \text{kJ}\cdot\text{mol}^{-1}.$$

The uncertainties have been increased from the purely statistical values to allow for the uncertainties in the thermal functions and the conversion from mass-spectrometric intensities to pressures for the third-law values.

Table VIII-15: Derived enthalpies of formation, $\Delta_f H_m^\circ$ (298.15 K) ($kJ\cdot mol^{-1}$).

Species	Second law	Third Law	Selected
ThCl(g)	246.9 ± 10.9	237.3 ± 7.9	247 ± 20
$ThCl_2$(g)	− 178.9 ± 16.0	− 174.4 ± 9.5	− 179 ± 22
$ThCl_3$(g)	− 569.2 ± 18.3	− 557.0 ± 10.8	− 569 ± 25

These values are somewhat different from those reported by [1990LAU/HIL] ((228.9 ± 8.0), −(194.6 ± 10.0) and −(579.9 ± 12.0) $kJ\cdot mol^{-1}$), but the precise values of the thermal functions used by these authors are not entirely clear.

The above selections result in:

$$\Delta_f G_m^\circ(\text{ThCl, g, 298.15 K}) = (215.7 \pm 20.3)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{ThCl}_2\text{, g, 298.15 K}) = -(191.3 \pm 22.2)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{ThCl}_3\text{, g, 298.15 K}) = -(563.8 \pm 25.2)\ \text{kJ}\cdot\text{mol}^{-1}.$$

VIII.2.1.3 $ThCl_4$(cr)

VIII.2.1.3.1 Enthalpy of formation

The tetragonal β form ($I4_1/amd$) of this compound, with lattice parameters a = 8.486 Å and c = 7.465 Å [1969MUC/SMI], normally found at room temperature, is in fact metastable below 679 K. The stable low temperature phase, also tetragonal ($I4_1/a$), with lattice parameters a = (6.408 ± 0.001) Å and c = (12.924 ± 0.003) Å, can only be obtained if extreme care is taken in cooling the sample [1974MAS/JHA]; note the structures were erroneously interchanged in [1983FUG/PAR], p.16. The β form is isomorphous with the other actinide tetrachlorides [1968BRO]. As this is the form normally obtained at room temperature, we will consider the values for this polymorph as the standard data for $ThCl_4$(cr).

The enthalpy of formation of thorium tetrachloride involves the enthalpy of dissolution of thorium metal and of thorium tetrachloride in HCl solutions.

If one notes, for information only, the very early results by [1910WAR] and [1911CHA], obtained on impure material, the enthalpy of solution of thorium metal in HCl according to reaction:

$$\alpha\text{-Th} + 4H^+ \rightleftharpoons Th^{4+} + 2H_2(g) \qquad \text{(VIII.8)}$$

has been measured in two studies, with excellent agreement. Eyring and Westrum [1950EYR/WES] reported a value of $-(760.2 \pm 0.8)$ kJ·mol^{-1} for Reaction (VIII.8) above, using 6.004 M HCl - 0.005 M Na_2SiF_6 as the dissolution medium, while [1969SMI/THA] obtained $-(761.1 \pm 1.7)$ kJ·mol^{-1}, using 6.06 M HCl - 0.005 M Na_2SiF_6.

These two teams also measured the enthalpy of solution of β-$ThCl_4$ in the same medium (containing Na_2SiF_6) they used for the dissolution of the metal and reported $-(186.52 \pm 0.33)$ kJ·mol^{-1} [1950EYR/WES] and $-(186.8 \pm 1.4)$ kJ·mol^{-1} [1969SMI/THA]. Eyring and Westrum [1950EYR/WES] reported the enthalpy of solution of β-$ThCl_4$ in 6.004 M HCl to be $-(185.27 \pm 0.25)$ kJ·mol^{-1}, establishing as $-(1.25 \pm 0.42)$ kJ·mol^{-1} the effect of the presence of 0.005 M Na_2SiF_6 in that medium. The enthalpy of solution of β-$ThCl_4$ in 6.00 M HCl was reported by [1973FUG/BRO] as $-(188.3 \pm 0.4)$ kJ·mol^{-1}. This result gives a third access to the enthalpy of formation of β-$ThCl_4$ through the use of the enthalpy of solution of the metal. For this calculation we have used, for the dissolution of the metal, the value $-(759.4 \pm 1.3)$ kJ·mol^{-1} obtained by averaging the values of [1950EYR/WES] and [1969SMI/THA] after correcting for the presence of Na_2SiF_6. The data used in the calculation of the enthalpy of formation of β-$ThCl_4$ are assembled in Table VIII-16.

Table VIII-16: Data used in the evaluation of the enthalpy of formation of β-$ThCl_4$.

HCl concentration (mol·dm^{-3})	(mol·kg^{-1})	$\Delta_f H_m$ (HCl, partial) (kJ·mol^{-1})	Enthalpy of solution (kJ·mol^{-1})		$\Delta_f H^o_m$ ($ThCl_4$, β) (kJ·mol^{-1})	References
			Th(cr)	β-$ThCl_4$		
6.004 [a]	6.8563	−153.386 ± 0.110	−760.2 ± 0.8	−186.52 ± 0.33	−1187.2 ± 1.0	[1950EYR/WES]
6.06 [a]	6.9297	−153.227 ± 0.110	−761.1 ± 1.7	−186.8 ± 0.8	−1186.2 ± 2.0	[1969SMI/THA]
6.00	6.8510	−153.400 ± 0.110	−759.4 ± 1.3 [b]	−188.3 ± 0.4	−1184.7 ± 1.4	[1973FUG/BRO]
				Weighted average	−1186.3 ± 1.3	

a: Containing 0.005 M Na_2SiF_6.

b: Calculated from [1950EYR/WES] and [1969SMI/THA] and corrected for the absence of Na_2SiF_6.

The selected value:

$$\Delta_f H_m^\circ(\text{ThCl}_4, \beta, 298.15\ \text{K}) = -(1186.3 \pm 1.3)\ \text{kJ}\cdot\text{mol}^{-1}$$

is the weighted mean of the values arising from the measurements of [1950EYR/WES], [1969SMI/THA], and [1973FUG/BRO]. The selected auxiliary values for the partial molar enthalpy of the chloride ion in the media are given in Table VIII-16.

The enthalpy of solution of $ThCl_4$(cr) in *ca.* 16000 H_2O was given at 288 K as − 237.2 kJ·mol^{-1} by Chauvenet [1911CHA]. As discussed in Appendix A, use of the constants for the hydrolysis of the thorium ion selected in this review (Table VII-15) and of that for the formation of the first thorium chloride complex (Section VIII.2.2) leads to a dissolution reaction that can be written as:

$$\begin{aligned}&\text{ThCl}_4(\text{cr}) + 0.5780\ (\text{H}_2\text{O in } ca.\ 16000\ \text{H}_2\text{O(l)}) \rightleftharpoons \\ &\quad (0.2893\ \text{Th}^{4+} + 0.4602\ \text{Th(OH)}^{3+} + 0.0589\ \text{Th(OH)}_2^{2+} + 0.1916\ \text{ThCl}^{3+} + \\ &\quad 3.8084\ \text{Cl}^- + 0.5780\ \text{H}^+) \quad \text{in } ca.16000\text{H}_2\text{O(l)} \qquad \text{(VIII.9)}\end{aligned}$$

accepting the result of Chauvenet as valid for 298.15 K.

To process Chauvenet's experimental value, we have therefore used the following auxiliary data: the enthalpy effect corresponding to the formation at infinite dilution of the various thorium hydrolytic species adopted in Table VII-15; $\Delta_f H_m^\circ(\text{Th}^{4+}$, 298.15 K$) = -(768.7 \pm 2.3)$ kJ·mol^{-1}, assumed to be valid for the dilute medium used, and $\Delta_f H_m(\text{Cl}^-$, *ca.* 4000 H_2O, 298.15 K$) = -(166.854 \pm 0.100)$ kJ·mol^{-1}. Also required is the enthalpy at infinite dilution of the reaction $\text{Th}^{4+} + \text{Cl}^- \rightleftharpoons \text{ThCl}^{3+}$, for which this review has not selected a value. However, [1968OHA/MOR] have suggested that this enthalpy effect is very small, and for the current comparison, we have used the value of (0.16 ± 2.00) kJ·mol^{-1} derived from the data given by [1982WAG/EVA], the uncertainty being conservatively estimated by this review. These values lead to $\Delta_f H_m^\circ(\text{ThCl}_4$, cr, 298.15 K$) = -(1173.5 \pm 5.0)$ kJ·mol^{-1}, where the uncertainty does not include the unknown uncertainty of Chauvenet's determination. This result, given for information only, is to be compared with $\Delta_f H_m^\circ(\text{ThCl}_4$, cr, 298.15 K$) = -(1186.3 \pm 1.3)$ kJ·mol^{-1} adopted above.

VIII.2.1.3.2 Entropy

There are no experimental data for the heat capacity and therefore entropy of β-$ThCl_4$ and we have accepted the estimated value of the entropy of Konings [2004KON], based on a systematic set of lattice and electronic contributions to the entropies of the oxides, fluorides and chlorides of the actinide elements, as described in Appendix A.

The selected value is thus:

$$S_m^\circ(\text{ThCl}_4, \beta, 298.15\ \text{K}) = (183.5 \pm 5.0)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The selected high temperature heat capacities are the estimates by Rand [1975RAN], which were also accepted by [1977WAG/SCH] and [1983FUG/PAR].

$$[C^{\circ}_{p,\mathrm{m}}]^{1043\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThCl_4}, \beta, T) = 120.293 + 23.2672\times10^{-3}\,T - 6.1505\times10^{5}\,T^{-2} \quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThCl_4}, \beta, 298.15\ \mathrm{K}) = (120.3 \pm 6.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$[C^{\circ}_{p,\mathrm{m}}]^{1500\mathrm{K}}_{1043\mathrm{K}}(\mathrm{ThCl_4}, \mathrm{l}) = (167.4 \pm 10.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}},$$

where the uncertainties are estimated by this review.

Chiotti *et al.* [1966CHI/GAR] have observed a transition in $\mathrm{ThCl_4(cr)}$ at (679 ± 2) K, with an enthalpy change of (5.0 ± 1.5) $\mathrm{kJ\cdot mol^{-1}}$, and fusion at (1042 ± 2) K with an enthalpy of fusion of (61.5 ± 2.6) $\mathrm{kJ\cdot mol^{-1}}$. The melting point is in excellent agreement with the value deduced from the vapour pressure data by both [1939FIS/GEW2] and [1979SIN/PRA], (1043 ± 2) K. However, the vapour pressure data (see Section VIII.2.1.4.2) correspond to an appreciably smaller enthalpy of fusion than that measured directly by [1966CHI/GAR]. It is to be noted that their samples were heated in tantalum containers, so the possibility of some reduction cannot be excluded.

The selected values are:

$$\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}(\mathrm{ThCl_4}, \mathrm{cr}, 629\ \mathrm{K}) = (5.0 \pm 1.5)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_{\mathrm{fus}}H^{\circ}_{\mathrm{m}}(\mathrm{ThCl_4}, \mathrm{cr}, 1043\ \mathrm{K}) = (61.5 \pm 5.0)\ \mathrm{kJ\cdot mol^{-1}}.$$

The selected values give for the Gibbs energy of formation:

$$\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{ThCl_4}, \beta, 298.15\ \mathrm{K}) = -(1092.3 \pm 2.0)\ \mathrm{kJ\cdot mol^{-1}}.$$

VIII.2.1.4 $\mathrm{ThCl_4(g)}$

VIII.2.1.4.1 Standard entropy and heat capacity

Bazhanov *et al.* [1990BAZ/EZH] studied the electron diffraction of $\mathrm{ThCl_4(g)}$ concluding that the molecule is an undistorted tetrahedron, with r(Th–Cl) = 2.567 Å. Only one vibration frequency of $\mathrm{ThCl_4(g)}$ has been measured, by [1961BUC/BER], who found ν_3 = 335(3) $\mathrm{cm^{-1}}$. As for $\mathrm{ThF_4(g)}$, we have accepted this, plus the calculated values for the remaining three frequencies using the B3LYP density functional, as suggested by [2000GAG/SKY] (ν_1 = 340.3(1), ν_2 = 62.0(2), ν_4 = 61.8(3) $\mathrm{cm^{-1}}$), where the numbers in parentheses are the degeneracy of the vibrations. The agreement between the calculated and experimental value of ν_3 is very good, 330 *vs*. 335 $\mathrm{cm^{-1}}$, and the calculated values for ν_1, ν_2 and ν_4 are preferred to the estimates selected by Konings and Hildenbrand [1998KON/HIL], which predate the density functional calculations.

The calculated values for the entropy and heat capacity of $\mathrm{ThCl_4(g)}$ at 298.15 K are:

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThCl_4}, \mathrm{g}, 298.15\ \mathrm{K}) = (403.4 \pm 4.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThCl_4}, \mathrm{g}, 298.15\ \mathrm{K}) = (101.4 \pm 3.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

and these are the selected values. The input data used are given in Table E-1.

VIII.2.1.4.2 Enthalpy of formation

The vapour pressures of $ThCl_4(cr)$ and $ThCl_4(l)$ have been measured by a number of investigators, as summarised in Table VIII-17. These data have been analysed by the third-law method, to give the results shown in the Table VIII-17. For the measurements of [1979SIN/PRA], the data measured by the two techniques were consistent, and were thus combined.

Table VIII-17: Vapour pressure data for the vaporisation of $ThCl_4(cr)$ and $ThCl_4(l)$.

Method	Temperature range (K)	$\Delta_{sub}H^{o}_{m}$ (298.15 K) (kJ·mol^{-1})	Reference
Boiling point $ThCl_4(cr)$	974 − 1036	233.94 ± 1.80	[1939FIS/GEW2]
Boiling point $ThCl_4(l)$	1052 − 1186	231.88 ± 1.26	[1939FIS/GEW2]
Boiling point $ThCl_4(cr)$	953 − 1025	235.39 ± 2.12	[1963YEN/LI]
Boiling point $ThCl_4(cr)$	933 − 1043	234.49 ± 2.03	[1966SU/NOV]
Knudsen effusion	671 − 882	230.47 ± 1.56	[1972KNA/MUL2]
Mass–spectrometric effusion	559 − 702	225.54 ± 9.51	[1974BIN/SCH2]
Transpiration, $ThCl_4(cr)$	880 − 1024	235.06 ± 0.43	[1979SIN/PRA]
Boiling point, $ThCl_4(cr)$	923 − 1043		
Transpiration, $ThCl_4(l)$	1055 − 1126	233.83 ± 1.53	[1979SIN/PRA]
Boiling point, $ThCl_4(l)$	1045 − 1161		
Torsion effusion, $ThCl_4(cr)$	685 − 775	236.50 ± 1.01	[1990LAU/HIL]

There is relatively good agreement between most of the data, except those of [1972KNA/MUL2] and [1974BIN/SCH2], which give somewhat higher pressures, as shown in Figure VIII-6. The selected enthalpy of sublimation is therefore based on the weighted mean of the concordant studies:

$$\Delta_{sub}H^{o}_{m}(ThCl_4, 298.15\ K) = (234.9 \pm 5.0)\ kJ\cdot mol^{-1}$$

where the uncertainty has been increased substantially from the statistical 2σ value (± 0.35 kJ·mol^{-1}) to allow for uncertainties in the thermal functions of both the condensed and gaseous phases.

The derived enthalpy of formation of $ThCl_4(g)$ is thus:

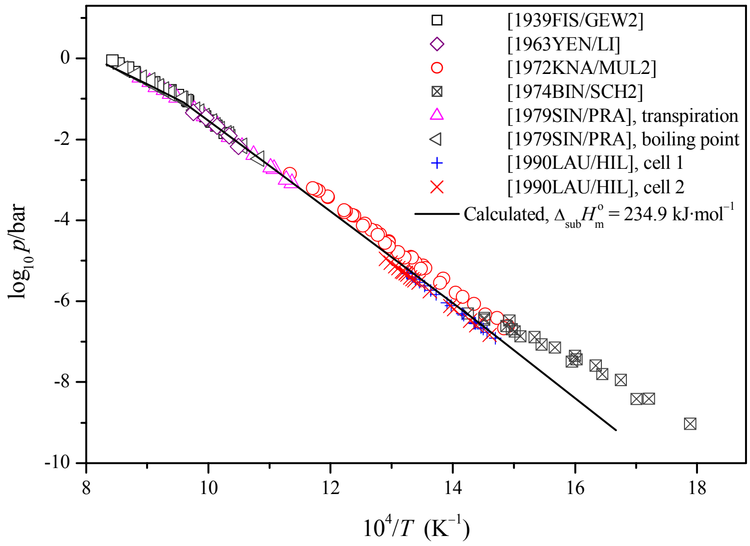
$$\Delta_{f}H^{o}_{m}(ThCl_4, g, 298.15\ K) = -(951.4 \pm 5.2)\ kJ\cdot mol^{-1}$$

yields:

$$\Delta_{f}G^{o}_{m}(ThCl_4, g, 298.15\ K) = -(923.0 \pm 5.3)\ kJ\cdot mol^{-1}.$$

The calculated vapour pressures of $ThCl_4(cr)$ and $ThCl_4(l)$ are included on Figure VIII-6.

Figure VIII-6: Vapour pressure of $ThCl_4$(cr) and $ThCl_4$(l).



VIII.2.1.5 $ThCl_4$ hydrates

The enthalpies of solution in water of the thorium tetrachloride di-, tetra-, hepta- and octahydrate were reported at 288 K by Chauvenet [1911CHA] as − 171.88, − 109.75, − 61.5, and − 47.91 kJ·mol^{-1}, respectively. As discussed in Appendix A, comparison of these values with the enthalpy of solution of the anhydrous salt reported for similar conditions by the same author, − 237.2 kJ·mol^{-1}, leads to the values:

$$\Delta_f H^{\circ}_{m}(\mathrm{ThCl_4{\cdot}2H_2O, cr, 298.15\ K}) = -(1822.4 \pm 12.0)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H^{\circ}_{m}(\mathrm{ThCl_4{\cdot}4H_2O, cr, 298.15\ K}) = -(2456.2 \pm 12.0)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H^{\circ}_{m}(\mathrm{ThCl_4{\cdot}7H_2O, cr, 298.15\ K}) = -(3361.9 \pm 12.0)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_f H^{\circ}_{m}(\mathrm{ThCl_4{\cdot}8H_2O, cr, 298.15\ K}) = -(3661.3 \pm 12.0)\ \mathrm{kJ{\cdot}mol^{-1}}$$

which are the selected values. The large uncertainty limits suggested by this review are to allow for the lack of experimental details in the values reported by Chauvenet and for the assumptions made in the calculations.

VIII.2.1.6 $ThOCl_2$(cr)

Thorium oxide dichloride, like other actinide oxide dichlorides, possesses orthorhombic symmetry, space group *Pbam*. Its lattice parameters have been obtained by Bagnall *et al.* as a = (15.494 ± 0.008) Å, b = (18.095 ± 0.008) Å, c = (4.078 ± 0.002) Å [1968BAG/BRO].

Yen *et al.* [1963YEN/LI] studied the phase diagram of the ThO_2-$ThCl_4$ system in order to prove the existence of $ThOCl_2$(cr) and to demonstrate that the compound could be obtained from the reaction of ThO_2 with $ThCl_4$. A eutectic at 988 K (*ca.* 55 K lower than the melting point of pure $ThCl_4$(cr)) was observed from 50 − 100 mol% $ThCl_4$, and presumed to be between $ThOCl_2$(cr) and $ThCl_4$(cr), but the details of the other parts of the phase diagram are not clear.

VIII.2.1.6.1 Enthalpy of formation

Chauvenet [1911CHA] has measured the enthalpy of solution of $ThOCl_2$(cr) in water to be − 117.78 kJ·mol^{-1}, presumably for similar conditions (probably 288 K, 1 mol thorium per *ca.* 16000 mol H_2O) as those used for other halides and related compounds reported in the same publication.

As discussed in Appendix A, use of the adopted constants for the hydrolysis of the thorium ion (Table VII-15) indicates that, in the resulting solution, the largest part of the thorium is found as polymeric hydroxide species, with appearance of a very small amount of precipitate of $Th(OH)_4$(am). Under these circumstances, these results will not be considered further.

Yen *et al.* [1963YEN/LI] measured the enthalpies of solution of $ThCl_4$(cr) and $ThOCl_2$(cr) in 0.1 M NaOH according to reactions:

$$\begin{aligned}\text{ThOCl}_2(\text{cr}) + \{2\text{NaOH}+\text{H}_2\text{O}\}\quad (\text{in NaOH·550 H}_2\text{O}) \rightarrow \\ \{\text{Th(OH)}_4(\text{ppt}) + 2\text{NaCl}\}\quad (\text{in NaOH·550H}_2\text{O})\end{aligned} \qquad \text{(VIII.10)}$$

and

$$\begin{aligned}\text{ThCl}_4(\text{cr}) + 4\text{NaOH}\quad (\text{in NaOH·550 H}_2\text{O}) \rightarrow \\ \{\text{Th(OH)}_4(\text{ppt}) + 4\text{NaCl}\}\quad (\text{in NaOH·550H}_2\text{O})\end{aligned} \qquad \text{(VIII.11)}$$

and reported the values $\Delta_r H_m$ (VIII.10) = −(129.33 ± 1.38) kJ·mol^{-1} and $\Delta_r H_m$ (VIII.11) = − (336.64 ± 2.03) kJ·mol^{-1}.

The authors ran both experiments under the same conditions using the same experimental assembly, in order to obviate the uncertainties associated with the formation of the thorium hydroxide precipitate. The difference of the two enthalpies of Reactions (VIII.10) and (VIII.11) above leads to the enthalpy of formation of $ThOCl_2$(cr), through the use of

$$\Delta_f H_m^\circ(\text{ThCl}_4, \beta, 298.15\text{ K}) = -(1186.3 \pm 1.3)\ \text{kJ·mol}^{-1},$$

and of the subsidiary data for the enthalpies of formation given below, from [1989COX/WAG], together with the enthalpies of dilution from Parker [1965PAR]:

$$\Delta_f H_m^\circ(\text{H}_2\text{O, NaOH·550H}_2\text{O}, 298.15\text{ K}) = -(285.83 \pm 0.04)\ \text{kJ·mol}^{-1},$$

$$\Delta_f H_m^\circ(\text{NaCl, NaOH·550H}_2\text{O}, 298.15\text{ K}) = -(407.07 \pm 0.06)\ \text{kJ·mol}^{-1},$$

$$\Delta_f H_m^\circ(\text{NaOH, NaOH·550H}_2\text{O}, 298.15\text{ K}) = -(469.91 \pm 0.04)\ \text{kJ·mol}^{-1}.$$

The derived value, $\Delta_f H^\circ_m$ ($ThOCl_2$, cr, 298.15 K) = −(1233.5 ± 2.8) kJ·mol^{-1}, overlaps, within the combined uncertainties, the results obtained by from the disproportionation of $ThOCl_2$(cr) as discussed below.

Additional values for the stability of $ThOCl_2$(cr) can be derived from the measurements of the pressures of $ThCl_4$(g) in the decomposition reaction: $2ThOCl_2(cr) \rightleftharpoons ThO_2(cr) + ThCl_4(g)$, by Yen *et al.* [1963YEN/LI], (boiling point method, 1040 to 1163 K) and Knacke *et al.* [1972KNA/MUL] (mass-loss effusion, 819 to 1006 K). These studies give consistent pressures, and since they have relatively short, non overlapping temperature ranges, they have been combined and processed together by the second-law method to give the value in Table VIII-18. The heat capacity of $ThOCl_2$(cr) was assumed to be half the sum of those of ThO_2(cr) and $ThCl_4$(cr):

$$[C^\circ_{p,m}]^{1200\,K}_{298.15\,K}(ThOCl_2, cr, T) = 95.936 + 1.4804 \times 10^{-2}\,T + 3.739 \times 10^{-7}\,T^2 - 8.317 \times 10^5\,T^{-2} \quad J \cdot K \cdot mol^{-1}$$

In addition, Korshunov and Drobot [1971KOR/DRO] have attempted to measure the $Cl_2(g)/O_2(g)$ ratio in equilibrium with $ThCl_4$(cr) and $ThOCl_2$(cr) by a circulation method. Their results supposedly for the equilibrium constant of the reaction:

$$ThCl_4(cr) + 0.5O_2(g) \rightleftharpoons ThOCl_2(cr) + Cl_2(g) \qquad (VIII.12)$$

refitted by the Review, are represented by the equation $\log_{10} K_p / \text{bar}^{0.5} = -603/T - 0.495$, and hence $\Delta_r G_m$ ((VIII.12), 820 K) = 11544 + 9.47 T J·mol^{-1}. These equations are slightly different from those given by [1971KOR/DRO].

These data have also been processed by the second law, and the derived $\Delta_f H^\circ_m$ ($ThOCl_2$, cr, 298.15 K) is included in Table VIII-18.

Table VIII-18: Derived values of $\Delta_f H^\circ_m$ ($ThOCl_2$, cr, 298.15 K).

Reference	Method	Temperature range (K)	$\Delta_f H^\circ_m$ ($ThOCl_2$, cr, 298.15K) (kJ·mol^{-1})
[1963YEN/LI]	Calorimetric	298.15	−(1233.5 ± 2.8)
[1963YEN/LI]	$2ThOCl_2(cr) \rightleftharpoons ThO_2(cr) + ThCl_4(g)$ boiling point method	1040 − 1163	− 1229.1 ± 3.1
[1972KNA/MUL]	$2ThOCl_2(cr) \rightleftharpoons ThO_2(cr) + ThCl_4(g)$ mass-loss effusion	819 − 1006	
[1971KOR/DRO]	$ThCl_4(cr) + 0.5O_2(g) \rightleftharpoons ThOCl_2(cr) + Cl_2(g)$ gas circulation	743 − 895	− 1164.6 ± 1.9

It is seen that the derived value of the enthalpy of formation from the study by [1971KOR/DRO] is discrepant. Moreover, since Reaction (VIII.12) involves the net formation of 0.5 mole of gas, it would be expected to have a positive rather than a negative entropy. It is probably relevant that [1971KOR/DRO] stated that their equilibria were established very slowly, and it seems likely from all the evidence that their data do not refer to the equilibrium situation.

The selected value is the weighted mean of the values of [1963YEN/LI] and [1972KNA/MUL]:

$$\Delta_f H_m^o (\text{ThOCl}_2, \text{cr}, 298.15\text{ K}) = -(1231.5 \pm 2.1)\text{ kJ·mol}^{-1}$$

which corresponds to an enthalpy of formation of $\Delta_f H_m^o = -(25.15 \pm 2.10)$ kJ·mol^{-1} from ThO_2(cr) and $ThCl_4$(cr), for 1 mole $ThOCl_2$(cr).

VIII.2.1.6.2 Entropy and Gibbs energy of formation

The second-law processing of the combined studies of the decomposition pressure noted above ([1963YEN/LI], [1972KNA/MUL]) also provides a value of the standard entropy of $ThOCl_2$(cr), for which no other experimental determination is available. The derived value:

$$S_m^o (\text{ThOCl}_2, \text{cr}, 298.15\text{ K}) = (116.9 \pm 2.9)\text{ J·K}^{-1}\text{·mol}^{-1}$$

is therefore selected; it corresponds to an entropy of formation of $-(7.5 \pm 3.8)$ J·K^{-1}·mol^{-1} from ThO_2(cr) and $ThCl_4$(cr), for 1 mol of $ThOCl_2$(cr).

The considerable stability of $ThOCl_2$ with respect to $ThCl_4$(cr) and ThO_2(cr) has been utilised by Corbett *et al.* [1986COR/SMI] to reduce the impurity level of oxygen in impure metallic thorium by equilibrating it with $ThCl_4$(l) at 1133 to 1173 K. However, they found that the lowest level of oxygen attainable by this technique was much higher than the theoretical value, assuming no solution phases were formed. The selected Gibbs energy of formation is:

$$\Delta_f G_m^o (\text{ThOCl}_2, \text{cr}, 298.15\text{ K}) = -(1153.6 \pm 2.3)\text{ kJ·mol}^{-1}.$$

VIII.2.2 Aqueous thorium chlorine compounds

VIII.2.2.1 Aqueous thorium chloride complexes

The aqueous thorium chloride complexes are much weaker than the corresponding fluoride complexes, as they are for the corresponding complexes of uranium(IV), Grenthe *et al.* [1992GRE/FUG], neptunium, and plutonium(IV), Lemire *et al.* [2001LEM/FUG] and Guillaumont *et al.* [2003GUI/FAN]. Grenthe *et al.* [1992GRE/FUG] (p. 192, 197) pointed out that it is very difficult to distinguish between complex formation and activity factor variations in systems where weak complexes are formed, especially when using "standard" solution chemical methods such as potentiometry, ion-exchange and liquid-liquid extraction. The reason is that in order to obtain a significant formation of weak complexes it is necessary to make very large changes in the composition of the test solutions used to explore the chemistry of these systems, which in turn results in significant changes in activity coefficients of the aqueous species. In order to address this difficulty, experiments have often been conducted using a constant ionic medium, but this is not enough to ensure that the activity coefficients of reactants and products remain constant as the ligand concentration is varied. The variation of the activity coefficients at constant ionic strength can be significant as is evident from the specific ionic interaction model when the ligand concentration is no longer small in comparison with the anion of the ionic medium, or when there is a substantial variation in the ratio Na^+/H^+ in the ionic medium. Nevertheless, the authors of the previous reviews of the NEA series on the chemical thermodynamics of actinides and other elements of importance in radioactive waste management did choose the complex formation model. For consistency, the authors of the present volume have done the same (Section VIII.2.2.1.2), but have in addition studied how well experimental observations can be explained using only activity factors based on the specific ion-interaction model with the parameters selected in this review (Section VIII.2.2.1.1).

VIII.2.2.1.1 Ion interaction model

The ion interaction model was used to reinterpret experimental data from [1950DAY/STO] and [1952WAG/STO] without including chloride complexes. Details of the interpretation are given in Appendix A. In both studies the distribution coefficient, D, of Th(IV) between an organic phase containing an extraction ligand and an aqueous phase was measured as a function of the concentration of chloride. These data were reinterpreted with two slightly different mathematical approaches, both based on the SIT, and should accordingly provide similar results. In the first (more traditional) approach the thorium species in the aqueous and organic phases were treated as trace components and the activity coefficients of the species in the organic phase were considered to be constant. The SIT coefficient $\varepsilon(Th^{4+},Cl^-)$ can then be derived by linear regression when $\log_{10}D$ is plotted *vs.* m_{Cl^-} (see the Appendix A entry of [1950DAY/STO]). The second approach, based on the NONLINT-SIT code (Appendix D), accounts for the activity changes in the organic phase as a result of changes in the concentration of thorium and includes all of the appropriate SIT ion-interaction parameters to fit the data. Table VIII-19 gives values of $\varepsilon(Th^{4+},Cl^-)$ obtained with these two different approaches at different ionic strengths from [1950DAY/STO] and [1952WAG/STO] and Figures presented in Appendix A show experimental and calculated values of $1/D$ from these investigations as a function of the chloride concentration in a set of experiments in $(H^+,Na^+)(ClO_4^-,Cl^-)$ media where the ionic strength has been kept constant at 0.5, 0.7, 1.0, 2.0, 4.0 and 6.0 M. The curves have been calculated assuming that the variation in the experimental distribution coefficients is due only to activity factor variations. These are well described using the selected ion interaction parameter $\varepsilon(Th^{4+},Cl^-) = 0.25\ kg\cdot mol^{-1}$ from this review.

The agreement between the two methods is satisfactory. This is important as it indicates that the deviations from ideality in experimental data can be well described using the ion interaction model alone; this fact has been used when interpreting the experimental hydrolysis data in chloride ionic media as discussed in Section VII. However, as the actinide chloride systems in previous volumes of this series have been interpreted using chloride complexes, this review will follow their example. The following figures (Figure VIII-7 and Figure VIII-8) provide comparisons of the ion interaction and complex formation models using the experimental data at 4.0 M from [1952WAG/STO]. These comparisons and others reported in Appendix A, [1952WAG/STO], show that the experimental data are well represented by both models up to chloride concentrations of about 3.0 m.

Table VIII-19: SIT coefficients $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ based on a reanalysis of literature data from [1950DAY/STO] and [1952WAG/STO] for the extraction of thorium from $(\mathrm{H}^+,\mathrm{Na}^+)(\mathrm{Cl}^-,\mathrm{ClO}_4^-)$ solutions using the strict ion interaction approach, *i.e.* without assuming the formation of chloride complexes. The calculations were performed with the NONLINT-SIT code and alternatively by linear regression in plots of $\log_{10} D$ *vs.* m_{Cl^-} − see the Appendix A entry for [1950DAY/STO].

Ionic strength (M)	Source of data	Best fit $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ (kg·mol^{-1}) [a]	
		NONLINT– SIT	SIT (linear regression) [b]
0.5	[1950DAY/STO]	0.20 ± 0.12	0.09 ± 0.04
0.5	[1952WAG/STO]	– 0.04 ± 0.16	– 0.09 ± 0.16
0.7	[1952WAG/STO]	0.08 ± 0.10	0.07 ± 0.10
1.0	[1952WAG/STO]	0.13 ± 0.16	0.15 ± 0.05
2.0	[1952WAG/STO]	0.23 ± 0.12	0.27 ± 0.02
4.0	[1952WAG/STO]	0.26 ± 0.22	0.32 ± 0.02
6.0	[1952WAG/STO]	0.25 ± 0.10	0.24 ± 0.02

a: NEA value for this parameter is (0.25 ± 0.03).

b: calculated fom $\log_{10} D$ *vs.* m_{Cl^-}; see Appendix A entry for [1950DAY/STO].

VIII.2.2.1.2 Complexation model

The equilibrium constants for the chloride complexes of U(IV), Np(IV) and Pu(IV) were evaluated in [1992GRE/FUG], [2001LEM/FUG] and [2003GUI/FAN]. The equilibrium constants for the reaction:

$$\mathrm{M}^{4+} + \mathrm{Cl}^- \rightleftharpoons \mathrm{MCl}^{3+} \qquad \text{(VIII.13)}$$

at zero ionic strength and the interaction term Δε were determined using experimental data at different ionic strength. The same method was used to test the chloride complexation model for the Th(IV)-Cl$^-$ system. For reasons given in Appendix A, the data from [1964NAB/KUD2] and [1976SOU/SHA] (Table VIII-20) are not accepted by this review.

Figure VIII-7: Evaluation of TTA solvent extraction data for Th^{4+} in 4.0 M (H, Na)ClO_4-(H, Na)Cl [1952WAG/STO] using alternatively the chloride complexation approach and the ion interaction approach with (fixed) SIT coefficients selected by this review (simple calculation for I_m = constant in comparison with calculation accounting for changes in I_m). The full drawn curve is calculated using a model with four chloride complexes from [1952WAG/STO] and the other curves using the SIT-model assuming a constant value of the ionic strength (dotted curve) and by taking the variation of the ionic strength into account (dashed curve). *D* is the experimental distribution coefficient.

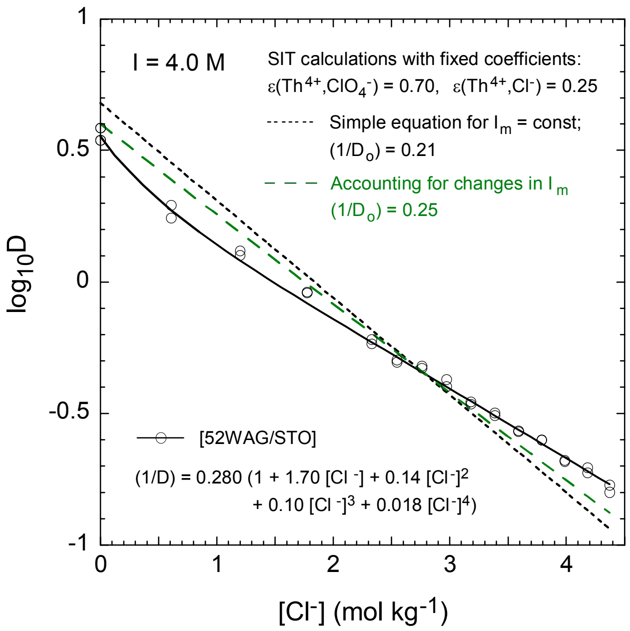


Figure VIII-8: Reinterpretation of data reported by [1952WAG/STO] for the extraction of thorium from chloride-perchlorate solutions at I = 4.0 M, using the strict ion interaction approach without chloride complexes. The calculations were performed with the NONLINT-SIT code. The SIT ion-interaction parameters used for these calculations included $\varepsilon(\mathrm{H^+,Cl^-})$ = 0.12 kg·mol^{-1}; $\varepsilon(\mathrm{H^+,ClO_4^-})$ = 0.14 kg·mol^{-1}; $\varepsilon(\mathrm{Th^{4+},\ Cl^-})$ = 0.25 kg·mol^{-1}; $\varepsilon(\mathrm{Th^{4+},ClO_4^-})$ = 0.70 kg·mol^{-1}; $\varepsilon(\mathrm{Na^+,\ Cl^-})$ = 0.03 kg·mol^{-1}; $\varepsilon(\mathrm{Na^+,ClO_4^-})$ = 0.01 kg·mol^{-1}; and $\varepsilon(\mathrm{Na^+,\ OH^-})$ = 0.04 kg·mol^{-1} taken from Appendix B (full curve) or the value $\varepsilon(\mathrm{Th^{4+},Cl^-})$ = (0.259 ± 0.222) kg·mol^{-1} fitted from the data (dashed curve). Changes in aqueous thorium concentrations as a function of chloride concentrations (a) or in 1/D (b) as a function of chloride concentrations are depicted and show that the data can be well predicted by the ion-interaction model up to chloride concentrations of about 3.0 m.

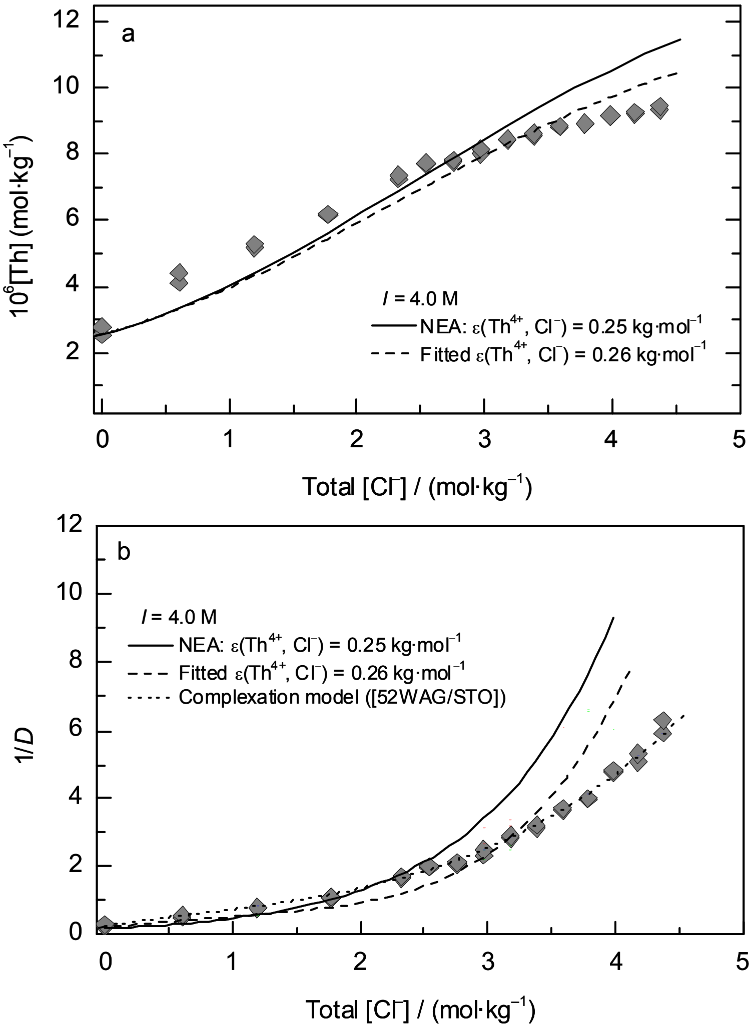


Table VIII-20: Experimental equilibrium data for the reaction $Th^{4+} + Cl^- \rightleftharpoons ThCl^{3+}$. These data, with the exception of [1964NAB/KUD2] and [1976SOU/SHA], have been described using the SIT model that results in $\log_{10} \beta_1^\circ = (1.70 \pm 0.10)$ and $\Delta\varepsilon = -(0.11 \pm 0.05)$ kg·mol^{-1} (see text for details).

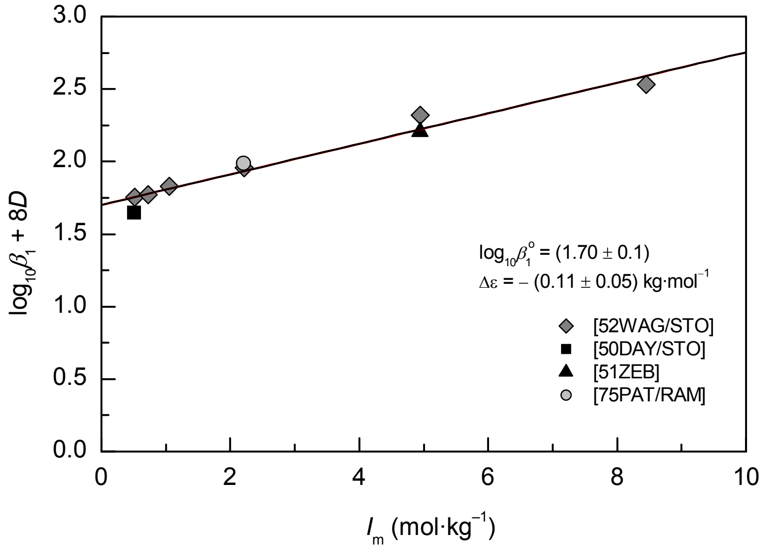
Method	Ionic medium	t (° C)	$\log_{10} \beta_1$	Reference
dis (TTA)	I = 0.50 M $H^+(Cl^-, ClO_4^-)$	25	0.246	[1950DAY/STO]
dis (TTA)	$[H^+]$ = 0.100 M	25	0.114	[1951ZEB/ALT]
	I = 4.00 M $Na^+(Cl^-, ClO_4^-)$			
pot	I = 0.50 M	25	0.447	[1968OHA/MOR]
	I = 1.00 M		0.778	
dis (DNNS)	$[H^+]$ = 2.00	25	0.114	[1975PAT/RAM]
	I = 2.00 M $H^+(Cl^-, ClO_4^-)$			
	Not constant	25	0.447	[1976SOU/SHA]
dis (TTA)	$[H^+]$ = 0.20 M	25		[1952WAG/STO]
	I = 0.50 M $(H^+, Na^+)(Cl^-, ClO_4^-)$		0.350	
	I = 0.70 M		0.250	
	I = 1.00 M		0.185	
	I = 2.00 M		0.083	
	$[H^+]$ = 0.32 M			
	I = 4.00 M		0.230	
	I = 6.00 M		0.322	

Using the experimental data of [1950DAY/STO], [1951ZEB/ALT], [1952WAG/STO] and [1975PAT/RAM], *cf.* Table VIII-20, values of

$$\log_{10} \beta_1^\circ = (1.70 \pm 0.10) \text{ and } \Delta\varepsilon = -(0.11 \pm 0.05) \text{ kg·mol}^{-1}$$

were calculated with specific ion interaction equation as shown in Figure VIII-9, and these are the selected values. These values are very similar to those obtained for U(IV), $\log_{10} \beta_1^\circ = (1.72 \pm 0.13)$ and $\Delta\varepsilon = -(0.29 \pm 0.08)$ kg·mol^{-1}; Np(IV), $\log_{10} \beta_1^\circ = (1.5 \pm 0.3)$ and $\Delta\varepsilon = -(0.15 \pm 0.18)$ kg·mol^{-1} and Pu(IV), $\log_{10} \beta_1^\circ = (1.81 \pm 0.27)$ and $\Delta\varepsilon = -(0.09 \pm 0.07)$ kg·mol^{-1}, indicating that the interactions between all tetravalent actinides and chloride ions are very similar.

Figure VIII-9: Extrapolation to $I = 0$ of experimental data for the formation of $ThCl^{3+}$ using the specific ion interaction equation. The data refer to mixed perchlorate/chloride media and are taken from [1950DAY/STO], [1951ZEB/ALT], [1952WAG/STO] and [1975PAT/RAM].



Equilibrium constants for the formation of $ThCl_n^{4-n}$, $n = 2-4$ have been reported by [1952WAG/STO] and [1951ZEB/ALT]. However, these constants have been obtained under conditions where a very large part of the perchlorate ion in the ionic medium has been replaced by chloride and these constants are according to the present review merely fitting parameters that have no chemical meaning; they are therefore not selected but for the purpose of completeness they are listed in Table VIII-21.

No higher chloride complexes have been selected for U(IV), Np(IV) and Pu(IV) in previous volumes in this series.

The only experimental data for the enthalpy and entropy of reaction in the aqueous Th^{4+}-Cl^- system are given by [1968OHA/MOR]; for reasons given in Appendix A these data are not accepted by this review.

Table VIII-21: Equilibrium constants for the reactions $\mathrm{Th^{4+}} + n\mathrm{Cl^-} \rightleftharpoons \mathrm{ThCl}_n^{4-n}$; $n = 2-4$ from [1952WAG/STO] and [1951ZEB/ALT] in chloride-perchlorate media and from [1964NAB/KUD2] in HCl-HNO$_3$ media.

Reaction	Ionic strength	t (°C)	$\log_{10}\beta_n$	Reference
$\mathrm{Th^{4+} + 2Cl^- \rightleftharpoons ThCl_2^{2+}}$	2.00 M	25	−1.00	[1952WAG/STO]
	4.00 M		−0.85	
	6.00 M		−0.26	
	4.00 M	25	−0.90	[1951ZEB/ALT]
	4.00 M H(Cl$^-$, NO$_3^-$)	25	−0.80	[1964NAB/KUD2]
$\mathrm{Th^{4+} + 3Cl^- \rightleftharpoons ThCl_3^{+}}$	2.00	25	−0.70	[1952WAG/STO]
	4.00		−1.0	
	6.00		−0.46	
	4.00	25	−1.43	[1951ZEB/ALT]
	4.00 M H(Cl$^-$, NO$_3^-$)	25	−0.85	[1964NAB/KUD2]
$\mathrm{Th^{4+} + 4Cl^- \rightleftharpoons ThCl_4(aq)}$	4.00	25	−1.74	[1952WAG/STO]
	4.00 M H(Cl$^-$, NO$_3^-$)	25	−1.46	[1964NAB/KUD2]
$\mathrm{Th^{4+} + 5Cl^- \rightleftharpoons ThCl_5^{-}}$	4.00 M H(Cl$^-$, NO$_3^-$)	25	−2.46	[1964NAB/KUD2]

The following equilibrium constant and molar standard Gibbs energy of formation have been selected by this review:

$$\log_{10}\beta_1^{\circ} = (1.70 \pm 0.10);\ \Delta_f G_m^{\circ}(\mathrm{ThCl^{3+}}, 298.15\ \mathrm{K}) = -(845.704 \pm 5.330)\ \mathrm{kJ\cdot mol^{-1}}$$

However, an equally good description may be obtained by using the SIT model (strict ion interaction approach excluding the formation of chloride complexes) in particular in perchlorate-chloride mixtures of high ionic strength and chloride concentration. Fitting the data at I = 2.0 through 6.0 M yields $\varepsilon(\mathrm{Th^{4+}, Cl^-})$ values very close to the value of $\varepsilon(\mathrm{Th^{4+}, Cl^-}) = (0.25 \pm 0.03)\ \mathrm{kg\cdot mol^{-1}}$ selected by this review, *cf.* Table VIII-19.

At low ionic strength and chloride concentrations up to 0.5 M, the experimental data are described somewhat better with the chloride complexation model and the interaction coefficients $\varepsilon(\mathrm{Th^{4+}, Cl^-}) = \varepsilon(\mathrm{Th^{4+}, ClO_4^-}) = (0.70 \pm 0.10)\ \mathrm{kg\cdot mol^{-1}}$ and $\varepsilon(\mathrm{ThCl^{3+}, Cl^-}) = \varepsilon(\mathrm{ThCl^{3+}, ClO_4^-}) = (0.62 \pm 0.11)\ \mathrm{kg\cdot mol^{-1}}$.

Johansson *et al.* [1991JOH/MAG] have used large angle X-ray scattering data (LAXS) to study the coordination sphere of Th(IV) in concentrated thorium chloride solutions. The models used to interpret the LAXS data indicated weak coordination of chloride at the highest chloride concentrations (above 7 m). In a similar study using EXAFS, Hennig *et al.* [2005HEN/TUT] obtained more clear evidence for the coordination of chloride; the authors even made an attempt to estimate the equilibrium constant for the formation of ThCl^{3+} (obtaining β_1 = 0.14 M^{-1}), but in view of the high ionic strength used this value cannot be used to estimate equilibrium constants at lower ionic strength.

VIII.2.2.2 Aqueous thorium chlorate complexes

There is only one experimental determination of the equilibrium constant for the reaction:

$$\mathrm{Th^{4+} + ClO_3^- \rightleftharpoons ThClO_3^{3+}}$$

determined using liquid-liquid extraction in a 0.5 M $\mathrm{H(ClO_4,ClO_3)}$ ionic medium, [1950DAY/STO]. The experimental value $\log_{10} \beta_1 = 0.26$ (reported without an uncertainty estimate) is accepted by this review.

However, the chlorate complexes are weak and the experimental data can alternatively be explained as due to activity coefficient variations based on ion-interaction parameters reported in Table VIII-22, rather than complex formation (Figure VIII-10).

Table VIII-22: SIT ion interaction parameters used to reinterpret [1950DAY/STO] data in 0.5 M $\mathrm{HClO_3}$-$\mathrm{HClO_4}$ mixtures (ion interaction approach without assuming the formation of chlorate complexes).

Species	ε ($\mathrm{kg{\cdot}mol^{-1}}$)	Reference
$\mathrm{H^+, ClO_4^-}$	0.14 ± 0.02	Appendix B
$\mathrm{H^+, ClO_3^-}$	0.14 ± 0.02	This review [a]
$\mathrm{Th^{4+}, ClO_4^-}$	0.70 ± 0.10	This review
$\mathrm{Th^{4+}, ClO_3^-}$	0.22 ± 0.08	This review [b]

a: Assumed to be identical to that selected by NEA-TDB for $\mathrm{H^+}$- $\mathrm{ClO_4^-}$.

b: Value fitted from [1950DAY/STO] data using NONLINT-SIT (see Figure VIII-10).

Using the complex formation approach, the equilibrium constant at zero ionic strength calculated using the SIT model and the following interaction parameters $\varepsilon(\mathrm{Th^{4+}, ClO_3^-}) = \varepsilon(\mathrm{Th^{4+}, ClO_4^-}) = (0.70 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$, $\varepsilon(\mathrm{H^+, ClO_3^-}) = \varepsilon(\mathrm{H^+, ClO_4^-}) = (0.14 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}$ and $\varepsilon(\mathrm{ThClO_3^{3+}, ClO_4^-}) = (0.62 \pm 0.11)\ \mathrm{kg{\cdot}mol^{-1}}$ is:

$$\log_{10} \beta_1^{\circ} = (1.55 \pm 0.13)$$

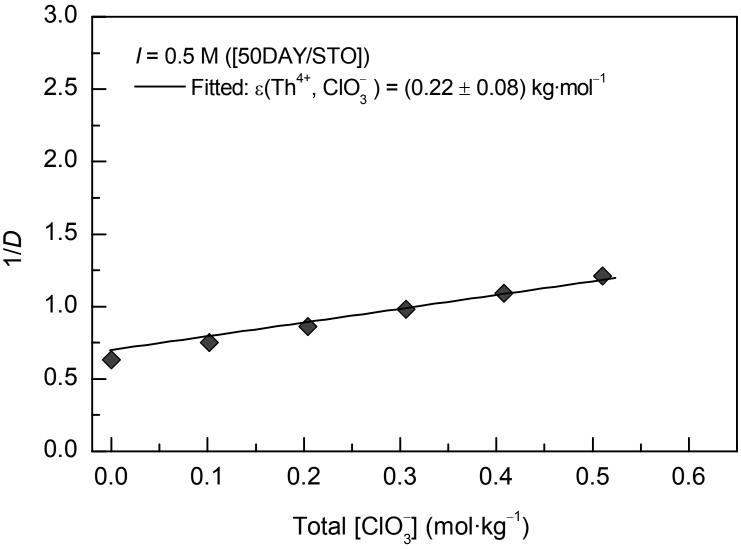
and this value is selected by this review.

The corresponding selected value for the Gibbs energy of formation is:

$$\Delta_f G_m^{\circ}(\mathrm{ThClO_3^{3+}}, 298.15\ \mathrm{K}) = -(721.53 \pm 5.51)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

Figure VIII-10, based on ion interaction parameters reported in Table VIII-22, shows the alternative description without the assumption of complex formation.

Figure VIII-10: Experimental and predicted (NONLINT-SIT) values of 1/*D* *vs.* total ClO_3^- concentration at an ionic strength 0.51 m from [1950DAY/STO]. The predicted line is based on ion-interaction parameters reported in Table VIII-22.



Although an independently confirmed value for the SIT ion-interaction parameter for $\varepsilon(Th^{4+}, ClO_3^-)$ is not available, the fitted value (Table VIII-22) is close to $\varepsilon(Th^{4+}, Cl^-)$ = (0.25 ± 0.03) kg·mol^{-1} given in Table A-8 and describes the experimental data very well (Figure VIII-10) for chlorate concentrations up to 0.5 m without assuming the formation of chlorate complexes. However, in order to be consistent with the previous volumes of this series, this review has used the complex formation model to select the equilibrium constant of $ThClO_3^{3+}$.

VIII.3 Bromine compounds and complexes

VIII.3.1 Solid and gaseous thorium bromides

VIII.3.1.1 ThBr(g), $ThBr_2$(g), $ThBr_3$(g)

These species are considered together since their data are linked by a mass-spectrometric study, resulting in some uncertainties in the absolute pressures.

VIII.3.1.1.1 Standard entropy and heat capacity

The thermal functions of ThBr(g), $ThBr_2$(g) and $ThBr_3$(g) were calculated assuming the molecular parameters shown in Table E-1. These are based on the parameters selected by [1977WAG/SCH], in turn derived principally from the estimates by [1973KRA/MOR]. No electronic contributions have been included, leading to considerable uncertainties in the thermal functions, especially for the monobromide. The selected values, with uncertainties estimated by this review, are:

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThBr, g, 298.15\ K}) = (281.1 \pm 12.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThBr, g, 298.15\ K}) = (37.4 \pm 6.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$S^{\circ}_{\mathrm{m}}(\mathrm{ThBr_2, g, 298.15\ K}) = (339.1 \pm 10.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThBr_2, g, 298.15\ K}) = (56.7 \pm 5.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$S^{\circ}_{\mathrm{m}}(\mathrm{ThBr_3, g, 298.15\ K}) = (405.3 \pm 10.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThBr_3, g, 298.15\ K}) = (80.8 \pm 5.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

VIII.3.1.1.2 Enthalpies of formation

Lau and Hildenbrand [1990HIL/LAU] have studied four equilibria between ThBr(g), $ThBr_2$(g), $ThBr_3$(g) and $ThBr_4$(g), in both the absence and presence of aluminium, which are summarised in Table VIII-23, where the enthalpies of the given reactions at 298.15 K derived only from the second-law analyses are given, since [1990HIL/LAU] indicate that the given ‘equilibrium’ constants are only proportional to the true constants, especially for the reactions involving Al(g). The auxiliary data for Al(g) and AlBr(g) are taken from the assessments by Glushko *et al.* [1981GLU/GUR], except that the enthalpy of formation of AlBr(g) has been taken to be $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (AlBr, g, 298.15 K) = (12.6 ± 7.5) $\mathrm{kJ{\cdot}mol^{-1}}$, from the later work of Hildenbrand and Lau [1989HIL/LAU].

Table VIII-23: Enthalpies of the reactions involving ThBr(g), $ThBr_2$(g) and $ThBr_3$(g) and $ThBr_4$(g).

Reaction	Temperature range (K)	$\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ (298.15 K) ($\mathrm{kJ{\cdot}mol^{-1}}$) Second law
$\mathrm{Th(g) + Br(g) \rightleftharpoons ThBr(g)}$	1986 − 2455	350.1 ± 8.2
$\mathrm{Th(g) + ThBr_2(g) \rightleftharpoons 2\ ThBr(g)}$	1986 − 2455	89.1 ± 3.9
$\mathrm{ThBr_2(g) + AlBr(g) \rightleftharpoons ThBr_3(g) + Al(g)}$	1696 − 1935	− 56.5 ± 5.1
$\mathrm{ThBr_3(g) + AlBr(g) \rightleftharpoons ThBr_4(g) + Al(g)}$	1696 − 1935	− 91.6 ± 5.5

With these data, we have four semi-independent measurements to define the three enthalpies of formation of ThBr(g), $ThBr_2$(g), $ThBr_3$(g), as shown in Table VIII-24. We have used a least-square analysis to find the optimal solutions to the over-determined set of linear equations, with the results shown in Table VIII-25. These second law values, in fact, form a very consistent set, and are the basis for the selected values:

$$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}(\mathrm{ThBr, g, 298.15\ K}) = (365 \pm 20)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}(\mathrm{ThBr_2, g, 298.15\ K}) = (40 \pm 20)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}(\mathrm{ThBr_3, g, 298.15\ K}) = -(334 \pm 15)\ \mathrm{kJ\cdot mol^{-1}}.$$

Table VIII-24: Sums of various enthalpies involving the enthalpies of formation of $\mathrm{ThBr(g)}$, $\mathrm{ThBr_2(g)}$ and $\mathrm{ThBr_3(g)}$.

Reference	Expression			$\Delta H_{\mathrm{m}}^{\circ}$ (298.15 K) ($\mathrm{kJ\cdot mol^{-1}}$)
				Second-law
[1990HIL/LAU]	$\mathrm{ThBr(g)}$			363.7 ± 10.2
[1990HIL/LAU]	2 $\mathrm{ThBr(g)}$	– $\mathrm{ThBr_2(g)}$		691.1 ± 3.9
[1990HIL/LAU]		– $\mathrm{ThBr_2(g)}$	+ $\mathrm{ThBr_3(g)}$	−374.0 ± 6.5
[1990HIL/LAU]			– $\mathrm{ThBr_3(g)}$	−333.2 ± 6.8

Table VIII-25: Derived enthalpies of formation, $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ (298.15 K) ($\mathrm{kJ\cdot mol^{-1}}$).

Species	Second law	Selected
$\mathrm{ThBr(g)}$	365.0	365 ± 20
$\mathrm{ThBr_2(g)}$	39.5	40 ± 20
$\mathrm{ThBr_3(g)}$	−333.9	−334 ± 15

The uncertainties have been increased from the purely statistical values to allow for the uncertainties in the thermal functions.

These values are somewhat different from those reported by [1990HIL/LAU], who analysed the over-determined set of equations in a different manner. Moreover the precise values of the thermal functions used by these authors are not entirely clear.

The corresponding selected values for the Gibbs energy of formation are:

$$\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{ThBr, g, 298.15\ K}) = (319.6 \pm 20.3)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{ThBr_2, g, 298.15\ K}) = (0.0 \pm 20.2)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{ThBr_3, g, 298.15\ K}) = -(371.1 \pm 15.3)\ \mathrm{kJ\cdot mol^{-1}}.$$

VIII.3.1.2 $\mathrm{ThBr_2(cr)}$, $\mathrm{ThBr_3(cr)}$

Evidence for the existence and properties of the lower thorium bromides $\mathrm{ThBr_3(cr)}$ and $\mathrm{ThBr_2(cr)}$ is limited.

Hayek *et al.* [1951HAY/REH] reported the synthesis of these compounds by direct reaction of the elements in the proper stoichiometric ratios. They describe

$ThBr_3$(cr) (analysed as $ThBr_{2.80}$) as a black compound with brown glints, similar to ThI_3(cr). The compound is pyrophoric and evolves hydrogen upon dissolution in water.

$ThBr_3$(cr) is reported to disproportionate under dynamic vacuum at 868 K into the dibromide and the tetrabromide. Freed from the tetrabromide by sublimation at 903 K, the dibromide samples (analysed as $ThBr_{2.11}$), also evolve hydrogen when dissolved in water. The compound is reported to disproportionate into the metal and $ThBr_4$ at 913 K. No structural data on the lower bromides were given by [1951HAY/REH].

Shchukarev *et al.* [1956SHC/NOV] reported the reduction of the tetrabromide to the tribromide by hydrogen at 633 K in the absence of moisture, according to the reaction,

$$ThBr_4(cr) + \tfrac{1}{2}H_2(g) \rightleftharpoons ThBr_3(cr) + HBr(g) \qquad \text{(VIII.14)}$$

and gave the calculated thermodynamic data for this reaction: $\Delta_r H_m$((VIII.14), 633 K) = (10.0 ± 2.0) $kJ\cdot mol^{-1}$ and $\Delta_r S_m$((VIII.14), 633 K) = $-$(9.6 ± 1.3) $J\cdot K^{-1}\cdot mol^{-1}$. However, the entropy change for this reaction involving the formation of HBr(g) at the expense of $0.5H_2$(g) would be expected to be highly positive (the value for the corresponding reaction involving uranium is *ca.* +80 $J\cdot K^{-1}\cdot mol^{-1}$) [2003GUI/FAN], so the data of Shchukarev *et al.* [1956SHC/NOV] have been discounted.

VIII.3.1.3 $ThBr_4$(cr)

As shown by the results of Mason *et al.* [1974MAS/JHA2], the tetragonal β form of this compound, although normally found at room temperature, (with lattice parameters a = (8.934 ± 0.003) Å, c = (7.964 ± 0.001) Å, space group $I4_1/amd$, [1974MAS/JHA2]), is in fact metastable below (699 ± 5) K. These authors showed that the low temperature phase, also tetragonal with a = (6.737 ± 0.001) Å, c = (13.601 ± 0.003) Å, space group $I4_1/a$, [1974MAS/JHA2], can only be obtained if care is taken in cooling or annealing the sample. These results are in disagreement with earlier data of Scaife [1966SCA] who reported the low-temperature form to be orthorhombic. The tetragonal β form is isomorphous with protactinium tetrabromide and with the actinide tetrachlorides [1968BRO]. As this form is normally obtained at room temperature, we will consider the related values as standard data.

VIII.3.1.3.1 Enthalpy of formation

The enthalpies of solution of $ThBr_4$(β) in (1.00 ± 0.01) and (6.00 ± 0.05) M HCl have been measured at (298.15 ± 0.05) K as $-$(283.2 ± 1.3) $kJ\cdot mol^{-1}$ and $-$(233.9 ± 0.8) $kJ\cdot mol^{-1}$, respectively [1973FUG/BRO]. Values for the enthalpy of formation of the compound are obtained from the $\Delta_f H_m$(Th^{4+}, 1.00 M HCl) = $-$(769.877 ± 1.600) $kJ\cdot mol^{-1}$ and $\Delta_f H_m$(Th^{4+}, 6.00 M HCl) = $-$(758.957 ± 1.600) $kJ\cdot mol^{-1}$ (see Chapter VI), and the partial molar enthalpies of formation of hydrobromic acid, assumed to be the same in HCl solutions as in HBr solutions of the same molality, $\Delta_f H_m$(HBr, partial, 1.00 M HCl) = $-$(119.395 ± 0.150) $kJ\cdot mol^{-1}$, and $\Delta_f H_m$(HBr, partial, 6.00 M HCl) =

– (109.554 ± 0.200) kJ·mol^{-1} [2000RAN/FUG]. The values obtained are – (964.257 ± 2.100) kJ·mol^{-1} and −(963.273 ± 2.000) kJ·mol^{-1} for the enthalpy of formation of $ThBr_4(\beta)$ from the 1 M and the 6 M HCl cycles, respectively. The average of these values from two cycles, not entirely independent, yields $\Delta_f H^\circ_m$ ($ThBr_4$, β, 298.15 K) = −(963.8 ± 2.0) kJ·mol^{-1}.

In his early study covering a large number of halides and oxyhalides of thorium and their hydrates, Chauvenet [1911CHA] reported a value of −293.67 kJ·mol^{-1} for the enthalpy of solution of $ThBr_4$(cr) in *ca.* 16000 H_2O, probably at 288 K. Use, as discussed in Appendix A, of the values adopted by this review (Table VII-15) for the hydrolysis of the thorium ion and of that for the formation of the first thorium bromide complex (Section VIII.2.2) leads to a dissolution reaction that can be written as:

$$\begin{aligned}&ThBr_4\text{ (cr)} + 0.6190\ H_2O\text{ (in } ca.\ 16000\ H_2O(l)) \rightleftharpoons\\ &\quad (0.3352\ Th^{4+} + 0.4982\ Th(OH)^{3+} + 0.06040\ Th(OH)_2^{2+} + 0.1062 ThBr^{3+} +\\ &\quad 3.8938\ Br^- + 0.6190\ H^+)\text{ in } ca. 16000 H_2O(l)\end{aligned} \qquad \text{(VIII.15)}$$

Use of the enthalpy of solution experimentally measured by Chauvenet (assumed to be valid at 298.15 K), of $\Delta_f H_m$ (Br^-, *ca.* 4000H_2O, 298.15 K) = – (121.20 ± 0.15) kJ·mol^{-1}, and of the same calculation procedure as for the dissolution of the tetrachloride, leads to $\Delta_f H^\circ_m$ ($ThBr_4$, cr, 298.15 K) = −(932.6 ± 4.7) kJ·mol^{-1}, without consideration for the uncertainty in the experimental value reported by Chauvenet. This value is very distinctly less negative than that resulting from better documented results and is given for information only. Consequently, this review selects:

$$\Delta_f H^\circ_m (ThBr_4, \beta, 298.15\ K) = -(963.8 \pm 2.0)\ kJ\cdot mol^{-1}.$$

VIII.3.1.3.2 Entropy

There are no experimental data for the heat capacity and therefore entropy of β-$ThBr_4$ and we have selected the estimated value of the entropy of Konings *et al.* [2006KON/MOR], based on the trends in the entropies of the actinide tetrahalides:

$$S^\circ_m (ThBr_4, \beta, 298.15K) = (227.0 \pm 5.0)\ J\cdot K^{-1}\cdot mol^{-1}.$$

This value is similar to that (228.0 ± 6.3) J·K^{-1}·mol^{-1} estimated by [1975RAN], which was accepted by [1977WAG/SCH] and [1983FUG/PAR]. With it, the selected Gibbs energy of formation is:

$$\Delta_f G^\circ_m (ThBr_4, \beta, 298.15\ K) = -(925.0 \pm 2.5)\ kJ\cdot mol^{-1}$$

The selected high temperature heat capacities are those estimated by Rand [1975RAN]:

$$[C^\circ_{p,m}]^{970K}_{298.15K} (ThBr_4, \beta, T) = 127.600 + 1.50624 \times 10^{-2}\,T - 6.1505 \times 10^5\,T^{-2}\ J\cdot K^{-1}\ mol^{-1}$$

$$C^\circ_{p,m} (ThBr_4, \beta, 298.15\ K) = (125.2 \pm 6.0)\ J\cdot K^{-1}\ mol^{-1}$$

$$[C^\circ_{p,m}]^{1300K}_{970K} (ThBr_4, l) = (171.5 \pm 10.0)\ J\cdot K^{-1}\cdot mol^{-1},$$

where the uncertainties are estimated by this review.

Scaife [1966SCA] reported a transition in $ThBr_4$(cr) at (693 ± 2) K with an enthalpy change of (4.1 ± 1.0) $kJ \cdot mol^{-1}$ (uncertainty limits estimated by this review); [1939FIS/GEW2] and [1980SIN/PRA] inferred melting points of (953 ± 3) K and (970 ± 2) K respectively from the intersection of their vapour curves, while [1974MAS/JHA2] estimated a value of (951 ± 5) K from their DTA curves. We have selected the higher value, with an uncertainty of ±10K, since there is some possibility that the $ThBr_4$ used by [1939FIS/GEW2] was less pure, see Section VIII.3.1.4, and DTA measurements are not always very precise. The enthalpy of fusion is obtained from the vapour pressure curves for the solid and liquid − see Section VIII.3.1.4.

The selected values are:

$$T_{\text{fus}}(\text{ThBr}_4, \beta) = (970 \pm 10)\ \text{K}$$

$$\Delta_{\text{trs}} H^{\circ}_{\text{m}}\ (\text{ThBr}_4, \text{cr}, 693\ \text{K}) = (5.0 \pm 1.5)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{fus}} H^{\circ}_{\text{m}}\ (\text{ThBr}_4, \text{cr}, 970\ \text{K}) = (54.39 \pm 5.00)\ \text{kJ}\cdot\text{mol}^{-1}.$$

VIII.3.1.4 $ThBr_4$(g)

VIII.3.1.4.1 Standard entropy and heat capacity

The $ThBr_4$(g) molecule is assumed to have T_d (tetrahedral) symmetry, as for ThF_4(g) and $ThCl_4$(g), with a Th–Br distance of 2.73 Å (see Konings and Hildenbrand [1998KON/HIL]). There is only one experimental measurement of the vibration frequencies, by [2001BEE/DYK] in an argon matrix, and we have accepted this, ν_3 = 230(3) cm^{-1}. The remaining frequencies are taken from a calculation using the B3LYP functional in the density functional model, as suggested by [2000GAG/SKY] (ν_1 = 207.8(1) cm^{-1}, ν_2 = 40.4(2) cm^{-1}, ν_4 = 44.6(3) cm^{-1}), where the numbers in parentheses are the degeneracy of the vibrations. These values for are preferred to the estimates selected by Konings and Hildenbrand [1998KON/HIL], which predate the density-functional calculations; in fact the calculated thermal functions for the two sets are quite similar.

The calculated values for the entropy and heat capacity of $ThBr_4$(g) at 298.15 K are:

$$S^{\circ}_{\text{m}}\ (\text{ThBr}_4, \text{g}, 298.15\ \text{K}) = (446.7 \pm 5.0)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C^{\circ}_{p,\text{m}}\ (\text{ThBr}_4, \text{g}, 298.15\ \text{K}) = (104.9 \pm 3.0)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and these are the selected values. The input data used are given in Table E-1.

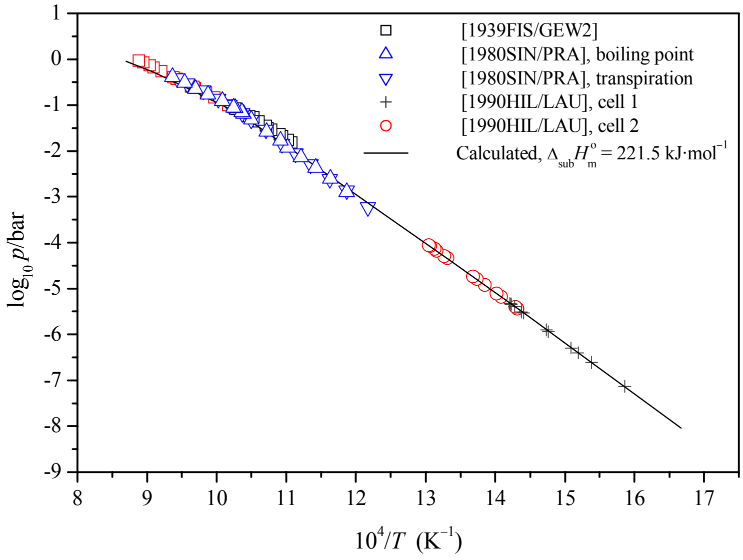
VIII.3.1.4.2 Enthalpy of formation

There are three measurements of the vapour pressures of $ThBr_4$(cr) and $ThBr_4$(l). The first measurements were by Fischer *et al.* [1939FIS/GEW2] using the boiling point method. Subsequently Singh *et al.* [1980SIN/PRA] studied the vaporisation of, again, both the solid and the liquid, using the transpiration and boiling point techniques, while Hildenbrand and Lau [1990HIL/LAU] used a torsion effusion technique to study the sublimation. The latter study is particularly valuable, since it shows that the molar mass of the vaporising species corresponds closely to that of $ThBr_4$ in the range of their experiments. These studies are summarised in Table VIII-26 and Figure VIII-11. For the measurements of [1980SIN/PRA], the data measured by the two techniques were consistent, and were thus combined.

Table VIII-26: Vapour pressure data for the vaporisation of $ThBr_4$(cr) and $ThBr_4$(l).

Method	Temperature range (K)	$\Delta_{sub}H^{o}_{m}$ (298.15 K) (kJ·mol^{-1})	Reference
Boiling point $ThBr_4$(cr)	903 – 950	219.0 ± 0.6	[1939FIS/GEW2]
Boiling point $ThBr_4$(l)	955 – 1126	218.6 ± 0.7	
Transpiration, $ThBr_4$(cr)	821 – 964	221.5 ± 1.8	[1980SIN/PRA]
Boiling point, $ThBr_4$(cr)	842 – 965		
Transpiration, $ThBr_4$(l)	974 – 1068	219.7 ± 0.6	[1980SIN/PRA]
Boiling point, $ThBr_4$(l)	982 – 1089		
Torsion effusion, $ThBr_4$(cr)	631 – 768	221.5 ± 0.3	[1990HIL/LAU]

Figure VIII-11: Vapour pressure of $ThBr_4$(cr) and $ThBr_4$(l).



The data of [1980SIN/PRA] and [1990HIL/LAU] for the solid agree excellently, while the pressures measured by Fischer *et al.* [1939FIS/GEW2] are somewhat higher. Moreover, the melting point given by [1980SIN/PRA], 970 K, is also noticeably higher than that deduced by [1939FIS/GEW2], 952 K. Thus it seems possible that the material used in the earlier study was less pure, and the enthalpy of vaporisation from the two later, very consistent studies of the solid is selected.

$$\Delta_{\text{sub}}H^{\circ}_{\text{m}}(\text{ThBr}_4, 298.15\text{ K}) = (221.5 \pm 5.0)\text{ kJ}\cdot\text{mol}^{-1}$$

where the uncertainty has been increased substantially from the statistical 2σ value to allow for uncertainties in the thermal functions.

The derived enthalpy of formation of $ThBr_4(g)$ is thus:

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{ThBr}_4, \text{g}, 298.15\text{ K}) = -(742.3 \pm 5.4)\text{ kJ}\cdot\text{mol}^{-1}$$

and the Gibbs energy of formation is:

$$\Delta_{\text{f}}G^{\circ}_{\text{m}}(\text{ThBr}_4, \text{g}, 298.15\text{ K}) = -(769.0 \pm 5.6)\text{ kJ}\cdot\text{mol}^{-1}$$

The vapour pressure for the crystal and liquid can be used to derive the enthalpy of fusion of $ThBr_4(cr)$. The best value to fit the vapour pressure of the liquid (see Figure VIII-11) gives:

$$\Delta_{\text{fus}}H^{\circ}_{\text{m}}(\text{ThBr}_4, 970\text{ K}) = (54.4 \pm 5.0)\text{ kJ}\cdot\text{mol}^{-1}.$$

VIII.3.1.5 Thorium tetrabromide hydrates

Chauvenet [1911CHA] measured the enthalpy of solution of the hepta-, deca- and dodecahydrate of thorium tetrabromide in *ca.* 16000 H_2O, as −94.35, −41.17 and − 9.62 $\text{kJ}\cdot\text{mol}^{-1}$. As discussed in Appendix A, comparison of these values with the enthalpy of solution of the anhydrous salt reported by the same author, −293.67 $\text{kJ}\cdot\text{mol}^{-1}$, leads to:

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{ThBr}_4\cdot 7\text{H}_2\text{O}, \text{cr}, 298.15\text{ K}) = -(3163.9 \pm 12.0)\text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{ThBr}_4\cdot 10\text{H}_2\text{O}, \text{cr}, 298.15\text{ K}) = -(4074.6 \pm 12.0)\text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}(\text{ThBr}_4\cdot 12\text{H}_2\text{O}, \text{cr}, 298.15\text{ K}) = -(4677.8 \pm 12.0)\text{ kJ}\cdot\text{mol}^{-1}$$

which are the selected values. The large uncertainty limits suggested by this review are to allow for the lack of experimental details in the values reported by Chauvenet and by the assumptions made in the calculations.

VIII.3.1.6 $ThOBr_2(cr)$

In their study of the properties of the quadrivalent actinide oxydihalides, Bagnall *et al.* [1968BAG/BRO] indicate that the oxydibromides possess a low symmetry structure and that their X-ray diffraction patterns could not be indexed. This review has not found any more recent information on the structure of $ThOBr_2(cr)$.

Chauvenet [1911CHA] measured the enthalpy of solution of $ThOBr_2$(cr) in *ca.* 16000 H_2O to be −116.98 $kJ\cdot mol^{-1}$. As discussed in Appendix A, use of the adopted constants for the hydrolysis of the thorium ion (Table VII-15) indicates that, in the resulting solution, the largest part of the thorium is found as polymeric hydroxide species, with appearance of a very small amount of precipitate of $Th(OH)_4$(am). Under these circumstances, these results will not be considered further.

The enthalpy of formation of the $ThOBr_2$(cr) can, however, be estimated, as done by Scaife *et al.* [1965SCA/TUR], Rand [1975RAN], and Fuger *et al.* [1983FUG/PAR] from the variation of the enthalpy of the reaction:

$$\tfrac{1}{2}ThO_2(cr) + \tfrac{1}{2}ThX_4(cr) \rightarrow ThOX_2(cr) \qquad \text{(VIII.16)}$$

as a function of the nature of the halogen X. From the values selected in this review, the enthalpy effect corresponding to Reaction (VIII.16) is $-(0.6 \pm 7.8)$, $-(25.15 \pm 2.10)$, and $-(48.6 \pm 2.9)$ $kJ\cdot mol^{-1}$ for the fluoride, chloride, and iodide cases, respectively. Use of the ionic radii [1976SHA] of the various halide ions (1.33, 1.81, 1.96, and 2.20 Å, respectively, for the fluoride, chloride, bromide, and iodide ions − for a co-ordination number of 6) leads to $-(34.7 \pm 5.0)$ $kJ\cdot mol^{-1}$ for reaction (VIII.16) above in the case of the bromide, and hence, to:

$$\Delta_f H^\circ_m(ThOBr_2, cr, 298.15\ K) = -(1129.8 \pm 5.4)\ kJ\cdot mol^{-1}$$

which is the selected value.

VIII.3.2 Aqueous thorium bromine compounds

VIII.3.2.1 Aqueous thorium bromide complexes

The chemical properties including the formation of bromide complexes are expected to be very similar for the chloride, bromide and iodide systems. There is only one experimental determination [1975RAG/RAM] of the equilibrium constants for the reactions

$$Th^{4+} + Br^- \rightleftharpoons ThBr^{3+}$$

$$Th^{4+} + 2Br^- \rightleftharpoons ThBr_2^{2+}\ .$$

These experiments have been made in a 1.0 M $(Na^+,H^+)(Br^-,ClO_4^-)$ ionic medium with constant hydrogen ion concentration $[H^+]$ = 0.60 M and result in the equilibrium constants $\log_{10}\beta_1 = -(0.092 \pm 0.03)$ and $\log_{10}\beta_2 = -(0.70 \pm 0.10)$. The first value is lower than the value for the corresponding chloride complex and selected by this review. The second complex is deduced from experimental data where a large part of the perchlorate ions in the ionic medium has been replaced by bromide; this will result in large changes in the activity coefficients and the existence of $ThBr_2^{2+}$ and the corresponding equilibrium constant is not accepted by this review. As in the corresponding chloride system, the experimental data can also be well described as a result of activity factor variations, without assuming the formation of complexes. By using the interaction coefficients given below this review finds and selects

$$\log_{10} \beta_1^{\circ} = (1.38 \pm 0.13)$$

and thus

$$\Delta_f G_m^{\circ}(\mathrm{ThBr^{3+}}, 298.15\ \mathrm{K}) = -(816.510 \pm 5.352)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

The following SIT coefficients should be used in calculations involving this complex:

$$\varepsilon(\mathrm{Th^{4+}, Br^-}) = \varepsilon(\mathrm{Th^{4+}, ClO_4^-}) = (0.70 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}},$$

$$\varepsilon(\mathrm{H^+, Br^-}) = \varepsilon(\mathrm{H^+, ClO_4^-}) = (0.14 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}\ \text{and}$$

$$\varepsilon(\mathrm{ThBr^{3+}, Br^-}) = \varepsilon(\mathrm{ThBr^{3+}, ClO_4^-}) = \varepsilon(\mathrm{ThCl^{3+}, ClO_4^-}) = (0.62 \pm 0.11)\ \mathrm{kg{\cdot}mol^{-1}}.$$

VIII.3.2.2 Aqueous thorium bromate complexes

The equilibrium constants for the reactions:

$$\mathrm{Th^{4+} + BrO_3^- \rightleftharpoons ThBrO_3^{3+}} \qquad \text{(VIII.17)}$$

$$\mathrm{Th^{4+} + 2BrO_3^- \rightleftharpoons Th(BrO_3)_2^{2+}} \qquad \text{(VIII.18)}$$

have been determined by Day and Stoughton [1950DAY/STO] in 0.5 M $\mathrm{HBrO_3}$-$\mathrm{HClO_4}$ but without uncertainty estimates. The reported values are $\log_{10} \beta_1 = (0.81 \pm 0.10)$ and $\log_{10} \beta_2 = (0.92 \pm 0.10)$, with the uncertainties estimated by this review based on the estimated accuracy of equilibrium constants determined using liquid-liquid extraction methods. These values have been used to estimate $\log_{10} \beta_1^{\circ} = (2.10 \pm 0.13)$ at zero ionic strength using the SIT with the ion interaction parameters reported in Table VIII-27 and $\log_{10} \beta_2^{\circ} = (3.10 \pm 0.13)$ using $\Delta\varepsilon(\text{VIII.18}) = -(0.55 \pm 0.15)\ \mathrm{kg{\cdot}mol^{-1}}$ estimated from the interaction coefficients in Table B-3. As shown in the following text, it is possible to describe the experimental data with only one complex using the NONLINT-SIT code and this review has therefore only accepted the equilibrium constant for the formation of $\mathrm{ThBrO_3^{3+}}$. Day and Stoughton [1950DAY/STO] have reported values of distribution coefficients (D) and the concentrations of various components in the experiments, and it is therefore possible to reinterpret these data. The NONLINT-SIT code was used for this purpose. A value of $\varepsilon(\mathrm{Th^{4+}, BrO_3^-}) = -(0.71 \pm 0.20)\ \mathrm{kg{\cdot}mol^{-1}}$ fitted from these data using the values of ion interaction parameters for $\varepsilon(\mathrm{H^+, ClO_4^-})$, $\varepsilon(\mathrm{H^+, BrO_3^-})$ and $\varepsilon(\mathrm{Th^{4+}, ClO_4^-})$ listed in Table VIII-27 reproduced the experimental data well without invoking ion pairs. Although the fitted value of $\varepsilon(\mathrm{Th^{4+}, BrO_3^-}) = -(0.71 \pm 0.20)\ \mathrm{kg{\cdot}mol^{-1}}$ explains the experimental data well, this value is too negative to be reasonable for this interaction. The negative value suggests strong interactions between $\mathrm{Th^{4+}}$ and $\mathrm{BrO_3^-}$ and shows that $\mathrm{Th(BrO_3)_n^{4-n}}$ complexes must be considered to explain these data. Using the ion interaction parameters listed in Table VIII-27, a value of $\Delta_f G_m^{\circ}/\mathrm{R}T(\mathrm{ThBrO_3^{3+}}) = -(280.981 \pm 0.066)$ is determined from these data. The fits to the experimental data are shown in Figure VIII-12. The close agreement between the experimental and predicted concentrations shows that the inclusion of only $\mathrm{Th^{4+}}$ and $\mathrm{ThBrO_3^{3+}}$ explains the entire data set very well when appropriate ion interaction parameters are included in the interpretations, without the inclusion of any additional species such as $\mathrm{Th(BrO_3)_2^{2+}}$ as proposed by [1950DAY/STO]. A value of $\Delta_f G_m^o / RT(\mathrm{ThBrO_3^{3+}}) = -(280.981 \pm 0.066)$, when combined with other appropriate auxiliary data reported in this review, provides $\log_{10} \beta_1^o = (1.897 \pm 0.028)$, a value similar to that calculated above. This review thus finds no evidence for the existence of complexes other than $\mathrm{ThBrO_3^{3+}}$. Since the NONLINT-SIT fitted value is based on a reinterpretation of [1950DAY/STO] data where the formation of $\mathrm{Th(BrO_3)_2^{2+}}$ is not considered and no simplifying assumptions about the composition of the aqueous system were made, this review considers values calculated from the NONLINT-SIT code to be reliable and selects:

$$\log_{10} \beta_1^o = (1.90 \pm 0.10)$$

and

$$\Delta_f G_m^o(\mathrm{ThBrO_3^{3+}}, 298.15\ \mathrm{K}) = -(696.56 \pm 5.37)\ \mathrm{kJ \cdot mol^{-1}}.$$

For the selected value, the present review has increased the estimated uncertainty from the NONLINT-SIT calculation to 0.10 (as for the experimental value).

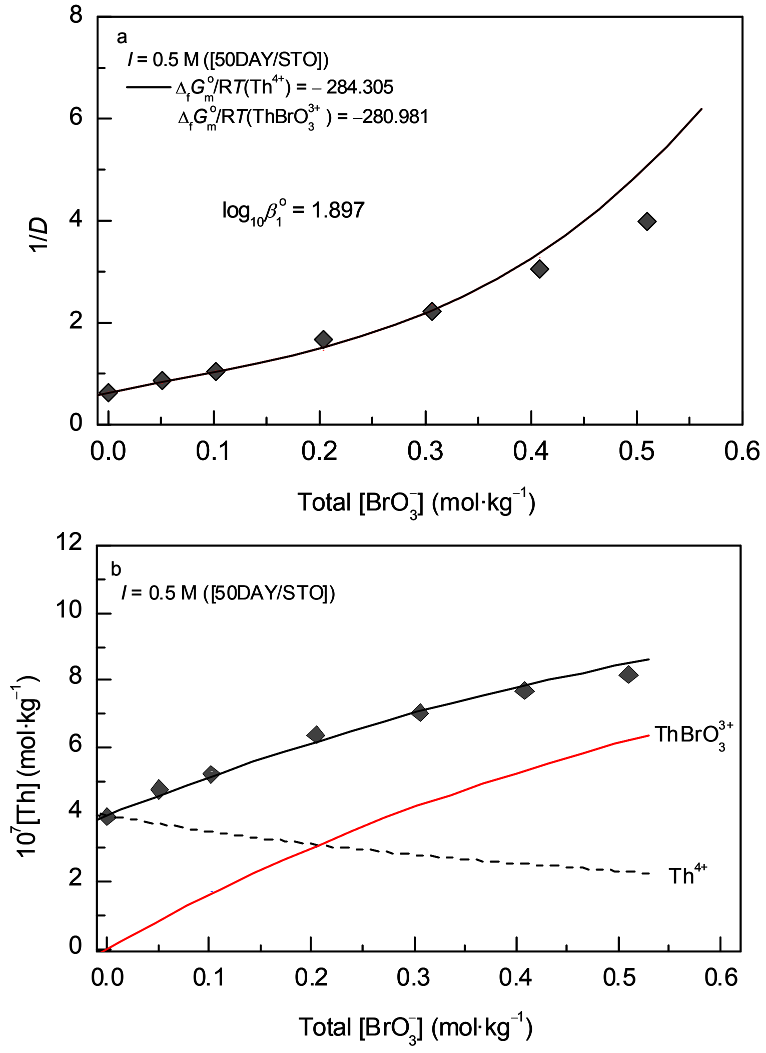
Table VIII-27: SIT ion interaction parameters used in NONLINT-SIT to determine the equilibrium constant for the formation of $\mathrm{ThBrO_3^{3+}}$ from the data of [1950DAY/STO] in 0.5 M $\mathrm{HBrO_3}$-$\mathrm{HClO_4}$ mixtures (for details see Figure VIII-12).

Species	ε ($\mathrm{kg \cdot mol^{-1}}$)	Reference
$\mathrm{H^+, ClO_4^-}$	0.14 ± 0.02	[2003GUI/FAN]
$\mathrm{H^+, BrO_3^-}$	0.14 ± 0.02	This review [a]
$\mathrm{Th^{4+}, ClO_4^-}$	0.70 ± 0.10	This review
$\mathrm{ThBrO_3^{3+}, ClO_4^-}$	0.62 ± 0.08	This review [b]

a: Assumed to be identical to that selected by NEA for ε($\mathrm{H^+, ClO_4^-}$).

b: Assumed to be identical to that for ε($\mathrm{UNO_3^{3+}, ClO_4^-}$) and similar to many other values for ε($\mathrm{AnX^{3+}, ClO_4^-}$) reported in [2003GUI/FAN].

Figure VIII-12: Experimental and predicted (NONLINT-SIT) values of 1/*D* *vs.* total $[\mathrm{BrO_3^-}]$ concentration or thorium concentrations *vs.* total $[\mathrm{BrO_3^-}]$ concentration at the ionic strength 0.51 m from [1950DAY/STO]. The predicted lines based on the ion-interaction parameters reported in Table VIII-27, and $\Delta_\mathrm{f}G^\circ_\mathrm{m}/\mathrm{R}T\,(\mathrm{Th^{4+}}) = -284.305$ (this review), $\Delta_\mathrm{f}G^\circ_\mathrm{m}/\mathrm{R}T(\mathrm{BrO_3^-}) = 7.693$ [2003GUI/FAN], and $\Delta_\mathrm{f}G^\circ_\mathrm{m}/\mathrm{R}T(\mathrm{ThBrO_3^{3+}}) = -280.981$ (fitted from this data). (a) Changes in 1/*D* as a function of bromate ion concentrations. (b) Changes in thorium concentrations as a function of bromate ion concentrations: the solid line depicts predicted total thorium concentration and the other lines depict predicted concentrations of different thorium species as marked.



VIII.4 Iodine compounds and complexes

VIII.4.1 Solid and gaseous thorium iodides

VIII.4.1.1 ThI_2(cr), ThI_3(cr)

The detailed Th-I phase diagram is still not known. Two solid lower iodides, ThI_3(cr) and ThI_2(cr), are well-established, and there are some indications that there is a stable phase with a composition close to ThI(cr), [1978KNA/MUN]. The liquid tetraiodide can also exist with I/Th < 4, [1964SCA/WYL].

ThI_3(cr) and ThI_2(cr) can be obtained by reaction of appropriate amounts of ThI_4 with thorium metal in sealed tantalum tubes [1949AND/EYE], [1949HAY/REH], [1951HAY/REH], [1963CLA/COR], [1964SCA/WYL], [1968GUG/JAC]. If hydrogen is used as the reducing agent, the compounds $ThI_2H_{0.7}$ and $ThI_2H_{1.8}$ are reported to be formed [1978STR/COR]. ThI_3(cr) and ThI_2(cr) display two crystal structures depending on the preparative conditions.

Beck and Strobel [1982BEC/STR] obtained single crystals of both phases of ThI_3(cr) by reacting thorium metal with ThI_4(cr) at 953 K. After short reaction times (2 − 3 days) crystals designated as α-ThI_3 were obtained and described, without details, as monoclinic (nearly orthorhombic), space group *B*2/*b* or *Bb*. After longer reaction times (4 − 6 weeks) crystals designated as β-ThI_3 were produced and fully indexed as orthorhombic, space group *Cccm*, with a = 8.735 Å, b = 20.297 Å and c = 14.661 Å [1982BEC/STR]. The relatively short Th−Th distances in this compound (3.46 to 3.80 Å) and the Th−I distances suggest that thorium is in the tetravalent state and that the compound has to be formulated as $Th^{4+}(I^-)_3(e^-)$, with the electrons delocalised or involved in Th-Th bonds.

Only one of the two reported structures of ThI_2(cr) has been completely solved: β-ThI_2, the high temperature phase, obtained at 973 to 1123 K, and unambiguously identified by [1963CLA/COR] and also reported by [1964SCA/WYL], is fully described by Guggenberger and Jacobson [1968GUG/JAC] as hexagonal, space group *P*6$_3$/*mmc*, with a = (3.97 ± 0.01) Å and c = (31.75 ± 0.04) Å. Again, from the Th-I distances, the compound should be formulated as $Th^{4+}(I^-)_2(e^-)_2$, which accounts for its electrical conductivity. The Th−Th distances, 3.97 Å [1968GUG/JAC], however, are much larger than those in ThI_3(cr). The α-ThI_2 phase, obtained by Scaife and Wylie [1964SCA/WYL] at lower preparative temperatures (*ca.* 873 K) than the β phase, was indexed by these authors on the basis of a hexagonal cell with a = 8.00 Å and c = 7.87 Å.

The DTA studies by Scaife and Wylie [1964SCA/WYL] show that ThI_3(cr) and ThI_2(cr) undergo peritectic transformations as follows: ThI_3(cr) into β-ThI_2 and liquid at 1019 K, and β-ThI_2 into thorium metal plus liquid at 1137 K; in each case the liquid has a I/Th ratio substantially less than 4. The solid-state transition of α- → β-ThI_2 occurs sluggishly at 873−973 K. Scaife and Wylie also discuss the evidence for another iodide of thorium with I/Th *ca.* 3.3−3.4 suggested by [1967GER/KRU] but indicate that its existence is doubtful. Knacke *et al.* [1978KNA/MUN] propose a somewhat different phase diagram, based on a mass-spectrometric study of the decomposition of ThI_4(cr). However, for a number of reasons discussed in Appendix A, these latter results are not accepted by this review.

Yosim [1960YOS] gives very preliminary details of a study of the pressures of ThI_4(g) above ThI_3(cr) and ThI_2(cr) (presumably, in practice, the {ThI_3(cr) + ThI_2(cr)} and {ThI_2(cr) + Th(cr)} diphasic fields), and suggests that the results indicate that the Gibbs energies of formation of ThI_4(cr), ThI_3(cr), ThI_2(cr) per iodine atom are very similar, which would be consistent with the phase diagram of [1964SCA/WYL]. There is insufficient detail in the paper to derive any more quantitative data from the study of [1960YOS].

VIII.4.1.2 ThI_4(cr)

As reported by Zalkin *et al.* [1964ZAL/FOR], thorium tetraiodide possesses monoclinic symmetry, space group $P2_1/n$, with a = (13.216 ± 0.007) Å, b = (8.068 ± 0.006) Å, c = (7.766 ± 0.006) Å, β = (98.68 ± 0.05)°. This structure is unusual, being different from that of both PaI_4(cr), of unknown structure [1976BRO/WHI] and that of UI_4(cr), monoclinic, but with space group $C2/c$ [1987LEV/TAY]. The structure of ThI_4(cr) is also different from that of other actinide tetrahalides and transition metal tetraiodides [1968BRO].

The enthalpy of formation is based on the measurement by [1973FUG/BRO] of its enthalpy of solution in 1 M and 6 M HCl, $-(322.0 \pm 0.6)$ kJ·mol^{-1} and $-(276.0 \pm 1.2)$ kJ·mol^{-1}, respectively. Values of −314 kJ·mol^{-1} and $-(330.1 \pm 2.1)$ kJ·mol^{-1} for the enthalpy of solution of ThI_4(cr) in 1 M HCl, were reported without details by Scaife *et al.* [1965SCA/TUR] and by Burgess and Kijowski [1981BUR/KIJ2], respectively. These latter values are noted for information only.

The data of [1973FUG/BRO] have been processed using the following auxiliary data: $\Delta_f H_m$ (Th^{4+}, 1.00 M HCl) = $-(769.877 \pm 1.600)$ kJ·mol^{-1} and $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl) = $-(758.957 \pm 1.600)$ kJ·mol^{-1} (see Section VI.1); the partial molar enthalpies of formation of hydroiodic acid, assumed to be the same in HCl solutions as in HI solutions of the same molality, $\Delta_f H_m$ (HI, partial, 1.00 M HCl) = $-(55.379 \pm 0.100)$ kJ·mol^{-1} [2000RAN/FUG]; and $\Delta_f H_m$ (HI, partial, 6.00 M HCl) = $-(46.747 \pm 0.200)$ kJ·mol^{-1}. These values lead to $-(669.393 \pm 1.800)$ kJ·mol^{-1} and $-(669.945 \pm 2.200)$ kJ·mol^{-1} for the enthalpy of formation of ThI_4(cr) from these two media. The weighted average of these two values:

$$\Delta_f H_m^\circ (ThI_4, \text{cr}, 298.15 \text{ K}) = -(669.6 \pm 2.2) \text{ kJ·mol}^{-1}$$

is selected, but the uncertainty limits have been kept at a level which reflects the fact that the two cycles used in the determination are not entirely independent.

Landis and Darnell [1960LAN/DAR] have attempted to measure the Gibbs energy of formation of ThI_4(cr) by measuring the TiI_4(g) pressure in the following 'equilibrium':

$$ThI_4(cr) + TiO_2(cr) \rightleftharpoons ThO_2(cr) + TiI_4(g)$$

from 637 to 745 K. However, as discussed in Appendix A, ThI_4(cr) and TiO_2(cr) can never be in true equilibrium, and the reaction studied by Landis and Darnell was therefore probably the following:

$$2ThOI_2(cr) + TiO_2(cr) \rightleftharpoons 2ThO_2(cr) + TiI_4(g)$$

and further discussion of the data of [1960LAN/DAR] is given in Section VIII.4.1.5.

VIII.4.1.2.1 Entropy

There are no experimental data for the heat capacity and therefore entropy of ThI_4(cr) and we have selected the estimated entropy value of Konings *et al.* [2006KON/MOR], based on consistent trends in the entropies of the actinide tetrahalides:

$$S^{\circ}_{m}(ThI_4, cr, 298.15\ K) = (251.0 \pm 5.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

This value is somewhat smaller than that (265.7 ± 12.5) $J{\cdot}K^{-1}{\cdot}mol^{-1}$ estimated by [1975RAN], but the values overlap within their combined uncertainties, and it is consistent with the vaporisation data (see Section VIII.4.1.4).

Flesch *et al.* [1986FLE/KNA] have measured the enthalpy increments in ThI_4(cr) and ThI_4(l) from 350 to 1030 K; as discussed in Appendix A, the results are rather scattered. [1986FLE/KNA] fitted the enthalpy increments for the solid to a linear equation, corresponding to a constant $C_{p,m}(ThI_4, cr)$ of 146 $J{\cdot}K^{-1}{\cdot}mol^{-1}$. However, very few solids have a constant heat capacity immediately above 298.15 K, and we have preferred to refit the data to the usual three-term equation.

$$[C^{\circ}_{p,m}]^{839K}_{298.15K}(ThI_4, cr, T) = 140.000 + 1.35\times10^{-2}\,T - 6.15\times10^{5}\,T^{-2}\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

giving the selected value:

$$C^{\circ}_{p,m}(ThI_4, cr, 298.15\ K) = (137.1 \pm 10.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

with a substantial uncertainty to cover the scatter in the data and the uncertainty in the fitting procedure.

The results from the measurements of the liquid were too scattered to allow any reliable value of its heat capacity to derived, but were consistent with the value of 176 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ estimated in [1975RAN] and this value has been selected:

$$[C^{\circ}_{p,m}]^{1100K}_{839K}(ThI_4, l) = (176.0 \pm 15.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

Flesch *et al.* [1986FLE/KNA] also determined the melting point to be (839 ± 2) K from eight different samples, confirming the early value of [1939FIS/GEW2]. The enthalpy of fusion resulting from their enthalpy curves is:

$$\Delta_{\text{fus}}H_{\text{m}}\,(\text{ThI}_4,\ 839\ \text{K}) = (48.0 \pm 10.0)\ \text{kJ·mol}^{-1}.$$

Both these values are consistent with the relevant vapour pressures studies discussed in Section VIII.4.1.4. The selected value for the Gibbs energy of formation is:

$$\Delta_{\text{f}}G^{\text{o}}_{\text{m}}\,(\text{ThI}_4,\ \text{cr},\ 298.15\ \text{K}) = -(659.5 \pm 2.7)\ \text{kJ·mol}^{-1}.$$

VIII.4.1.3 ThI(g), ThI$_2$(g), ThI$_3$(g)

There are no experimental data on these species, but we have calculated the thermal functions from estimated molecular parameters, so these species are considered together.

VIII.4.1.3.1 Standard entropy and heat capacity

The thermal functions of ThI(g), ThI$_2$(g) and ThI$_3$(g) were calculated assuming the molecular parameters shown in Table E-1. These are based on the parameters selected by [1977WAG/SCH], in turn derived principally from the estimates by [1973KRA/MOR]. No electronic contributions have been included, leading to considerable uncertainties in the thermal functions, especially for the monoiodide. The selected values, with uncertainties estimated by this review, are:

$$S^{\text{o}}_{\text{m}}\,(\text{ThI},\ \text{g},\ 298.15\ \text{K}) = (288.6 \pm 12.0)\ \text{J·K}^{-1}\text{·mol}^{-1}$$
$$C^{\text{o}}_{p,\text{m}}\,(\text{ThI},\ \text{g},\ 298.15\ \text{K}) = (37.5 \pm 6.0)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$S^{\text{o}}_{\text{m}}\,(\text{ThI}_2,\ \text{g},\ 298.15\ \text{K}) = (355.6 \pm 10.0)\ \text{J·K}^{-1}\text{·mol}^{-1}$$
$$C^{\text{o}}_{p,\text{m}}\,(\text{ThI}_2,\ \text{g},\ 298.15\ \text{K}) = (57.4 \pm 5.0)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$S^{\text{o}}_{\text{m}}\,(\text{ThI}_3,\ \text{g},\ 298.15\ \text{K}) = (430.0 \pm 10.0)\ \text{J·K}^{-1}\text{·mol}^{-1}$$
$$C^{\text{o}}_{p,\text{m}}\,(\text{ThI}_3,\ \text{g},\ 298.15\ \text{K}) = (81.8 \pm 5.0)\ \text{J·K}^{-1}\text{·mol}^{-1}.$$

These are the selected values.

VIII.4.1.3.2 Enthalpies of formation

There are no experimental data on the stabilities of the lower iodides. Hildenbrand *et al.* [1985HIL/GUR] have estimated enthalpies of formation, but these are based on estimated enthalpies of formation of the lower bromides, which are much different from the values selected by the review, and have not been accepted.

VIII.4.1.4 ThI$_4$(g)

VIII.4.1.4.1 Standard entropy and heat capacity

The ThI$_4$(g) molecule is assumed to have T_d (tetrahedral) symmetry, as for ThF$_4$(g) and ThCl$_4$(g) with an Th–I distance of 2.91 Å (see Konings and Hildenbrand [1998KON/HIL]). There are no experimental measurements if the vibration frequencies and we have accepted the values obtained from the B3LYP density functional in the density functional model, as suggested by [2000GAG/SKY] (ν_1 = 147.6(1) cm^{-1}, ν_2 = 29.0(2) cm^{-1}, ν_3 = 179.6(3) cm^{-1}, ν_4 = 33.9(3) cm^{-1}), where the numbers in parentheses are the degeneracy of the vibrations. These values are preferred to the estimates selected by Konings and Hildenbrand [1998KON/HIL], which predate the density-functional calculations.

The calculated values for the entropy and heat capacity of ThI_4(g) at 298.15 K are:

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThI_4, g, 298.15\ K}) = (478.5 \pm 6.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThI_4, g, 298.15\ K}) = (106.2 \pm 4.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

and these are the selected values. The input data used are given in Table E-1.

VIII.4.1.4.2 Enthalpy of formation

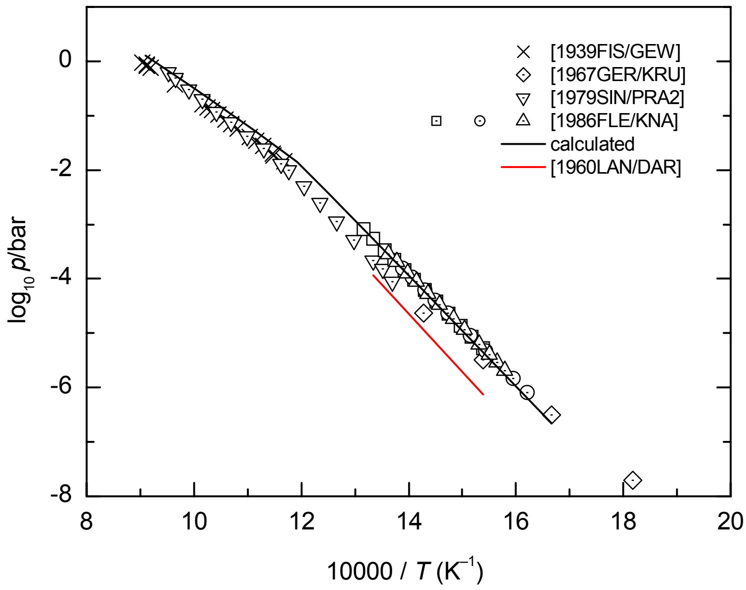
There are four measurements of the vapour pressures of ThI_4(cr) and ThI_4(l). The first measurements were by Fischer *et al.* [1939FIS/GEW2] using the boiling point method for ThI_4(l), whereas, Gerlach *et al.* [1967GER/KRU] deduced the vapour pressure of the solid from observations of the damping of a silica thread. Subsequently Singh *et al.* [1979SIN/PRA2] (data also reported in [1980PRA/NAG]) studied the vaporisation of, again, both the solid and the liquid, using the transpiration and boiling point techniques, while Flesch *et al.* [1986FLE/KNA] studied the sublimation by mass-loss effusion measurements. The latter study was supplemented by a separate mass-spectrometric study, which showed that there is a small decomposition pressure of I_2(g) (5 − 10%) in the vapour, even at 730 K. Thus the measurements at higher temperatures, especially over the liquid, which Scaife and Wylie [1964SCA/WYL] show can be hypostoichiometric, may be subject to error. In addition, Landis and Darnell [1960LAN/DAR] give just the vapour pressure equation from their unpublished study of the sublimation pressures, probably by Knudsen effusion. The study by [1978KNA/MUN], which suggests substantial decomposition in the vapour, has been discounted, as discussed in detail in Appendix A. The published studies are summarised in Table VIII-28 and Figure VIII-13. The table includes the enthalpies of sublimation at 298.15 K, calculated by the third law.

It will be seen that the data for the liquid are, perhaps surprisingly, very consistent, but the vapour pressures for the solid range over of a factor of *ca.* three, with the unpublished study referred to by [1960LAN/DAR] a further factor of two lower. The data are however quite consistent with the selected values of the entropy of the solid and gas, and the enthalpy of fusion.

Table VIII-28: Vapour pressure data for the vaporisation of ThI_4(cr) and ThI_4(l).

Method	Temperature range (K)	$\Delta_{sub}H^{o}_{m}$ (298.15 K) (kJ·mol^{-1})	Reference
Boiling point ThI_4(l)	856 – 1107	212.2 ± 0.5	[1939FIS/GEW2]
Damping of a silica thread	553 – 693	208.9 ± 9.5	[1967GER/KRU]
Boiling point, Transpiration, ThI_4(cr)	730 – 849	213.9 ± 3.0	[1979SIN/PRA2],
Boiling point, Transpiration, ThI_4(l)	853 – 1044	211.4 ± 2.5	[1980PRA/NAG]
Mass-loss effusion, ThI_4(cr)	617 – 760	208.5 ± 0.6	[1986FLE/KNA]

Figure VIII-13: Vapour pressure of ThI_4(cr) and ThI_4(l).



The weighted average of the three values of $\Delta_{sub}H^{o}_{m}$ (298.15 K) derived from the vaporisation of the solid is (208.7 ± 0.6) kJ·mol^{-1}, while that from the liquid is (212.2 ± 0.5) kJ·mol^{-1}. Since the decomposition to lower iodides and iodine will be less for the lower temperature measurements on the solid, the selected value is based on the former value, but with a substantially increased uncertainty to allow for this decomposition, possible reactions with container materials and uncertainties in the thermal functions of both the phases:

$$ThI_4(cr) \rightleftharpoons ThI_4(g) \qquad (VIII.19)$$

$$\Delta_{sub}H^{o}_{m}((VIII.19), 298.15\ K) = (209.0 \pm 5.0)\ kJ\cdot mol^{-1}.$$

The selected value for the enthalpy of formation is thus:

$$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}(\mathrm{ThI_4, g, 298.15\ K}) = -(460.6 \pm 5.5)\ \mathrm{kJ \cdot mol^{-1}}.$$

The calculated pressures are included in Figure VIII-13, together with the values from the equation given by [1960LAN/DAR] which have not been included in the average.

Allen and Yost [1954ALL/YOS] have measured the equilibrium constants of a reaction assumed to be Th(cr) + 4I(g) $\rightleftharpoons$ ThI_4(g) at four temperatures from 1447 to 1602 K, by optical density measurements of the iodine pressure − see Appendix A. The $\log_{10} K_p$ values are a reasonable linear function of $1/T$, albeit with some scatter, but with the Gibbs energy of I(g) from [1989COX/WAG], the results give for the above reaction, $\Delta_{\mathrm{r}} G_{\mathrm{m}}$ (1515 K) = −(334.1 ± 15.0) $\mathrm{kJ \cdot mol^{-1}}$, compared with the value calculated from the selected values, −(430.5 ± 10.6) $\mathrm{kJ \cdot mol^{-1}}$. Moreover, the calculated entropy change for the reaction at this temperature, −627.9 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ is a factor of two more negative than the calculated value, −306.4 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. These serious discrepancies indicate that the reaction involved was not that assumed, perhaps due to the presence of lower gaseous iodides under the experimental conditions.

Gerlach *et al.* [1968GER/PAW] have discussed the thermodynamic aspects of the use of the Th-I system for vapour-phase transport of thorium.

The selected value for the Gibbs energy of formation is:

$$\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{ThI_4, g, 298.15\ K}) = -(518.3 \pm 5.8)\ \mathrm{kJ \cdot mol^{-1}}.$$

VIII.4.1.5 Thorium oxyiodide $ThOI_2$(cr)

X-ray powder data of $ThOI_2$(cr) have been given by Scaife and Wylie [1965SCA/TUR] and by Corbett *et al.* [1969COR/GUI] but have not been indexed. The latter authors mention the existence of white and red forms of the compound. From the experimental conditions of its preparation, however, it is possible that the colour of the red form could be simply due to a slight reduction of the stoichiometric white form.

Chauvenet [1911CHA] measured the enthalpy of solution of $ThOI_2$(cr) in *ca.* 16000 H_2O as −90.08 $\mathrm{kJ \cdot mol^{-1}}$. As discussed in Appendix A, use of the adopted constants for the hydrolysis of the thorium ion (Table VII-15) indicates that, in the resulting solution, the largest part of the thorium is found as polymeric hydroxide species. Under these circumstances, these results will not be considered further. This was also the case for the other results of Chauvenet on the thorium oxychloride and oxybromide.

The enthalpy of solution of this compound in 1 M HCl according to the reaction:

$$\mathrm{ThOI_2(cr) + 2H^{+} \rightleftharpoons Th^{4+} + H_2O(l) + 2I^{-}} \qquad \text{(VIII.20)}$$

was reported by Scaife *et al.* [1965SCA/TUR] to be −(169.9 ± 1.7) $\mathrm{kJ \cdot mol^{-1}}$. Use of $\Delta_{\mathrm{f}} H_{\mathrm{m}}$ ($\mathrm{Th^{4+}}$, 1 M HCl) = −(769.877 ± 1.600) $\mathrm{kJ \cdot mol^{-1}}$ (based on the data given in

Chapter VI), the partial molar enthalpies of formation of hydriodic acid, assumed to be the same in HCl solutions as in HI solutions of the same molality, $\Delta_f H_m$ (HI, partial, 1.00 M HCl) = $-(55.379 \pm 0.100)$ kJ·mol^{-1}and the partial molar enthalpy of formation of water in the same medium, $\Delta_f H_m$ (H_2O, partial, 1.00 M HCl) = $-(285.848 \pm 0.041)$ kJ·mol^{-1} [2000RAN/FUG], leads to $\Delta_f H^\circ_m$ ($ThOI_2$, cr, 298.15 K) = $-(996.6 \pm 2.3)$ kJ·mol^{-1}.

In the determinations of [1965SCA/TUR], the final concentration of thorium in the solution was about 9×10^{-3} M, while the concentrations involved in the experiments leading to the enthalpy of formation of β-$ThCl_4$ and Th^{4+} were between 2 and 5×10^{-3} M [1949WES/ROB3], [1950EYR/WES], [1969SMI/THA], [1973FUG/BRO]. The uncertainty limits affecting the enthalpy of formation reported above are considered quite sufficient to cover the small differences in enthalpies of dilution.

The selected value is:

$$\Delta_f H^\circ_m (ThOI_2, \text{cr}, 298.15\ \text{K}) = -(996.6 \pm 2.3)\ \text{kJ·mol}^{-1}.$$

As noted in Appendix A, this value is consistent within the uncertainties with the study [1960LAN/DAR] if their data are assumed to involve $ThOI_2$(cr) rather than ThI_4(cr) – see also below.

The selected value corresponds to an enthalpy of formation of $-(48.6 \pm 2.9)$ kJ·mol^{-1} from ThO_2(cr) and ThI_4(cr), for one mole $ThOI_2$(cr), the most negative value for the thorium oxyhalide compounds.

Flesch *et al.* [1986FLE/KNA] have studied both the decomposition of $ThOI_2$(cr)

$$2ThOI_2(\text{cr}) \rightleftharpoons ThO_2(\text{cr}) + ThI_4(\text{g}) \qquad \text{(VIII.21)}$$

and the vapour pressure of ThI_4(cr)

$$ThI_4(\text{cr}) \rightleftharpoons ThI_4(\text{g}). \qquad \text{(VIII.22)}$$

Although the studies were made over somewhat different temperature ranges, (865 – 1020 K) for Reaction (VIII.21) and (617 – 760 K) for Reaction (VIII.22), the best way to combine these data is to subtract the equations representing the Gibbs energies of corresponding reactions to give for:

$$ThO_2(\text{cr}) + ThI_4(\text{cr}) \rightarrow 2ThOI_2(\text{cr}) \qquad \text{(VIII.23)}$$

$$\Delta_r G_m ((\text{VIII.23}), T) = -82131 + 19.91\,T \quad (\text{J·mol}^{-1}) \qquad \text{(VIII.24)}$$

around 800 K. This procedure conveniently eliminates many of the possible instrumental errors in the two sets of measurements.

The heat capacity of $ThOI_2$(cr) has not been measured, but has been assumed to be half the sum of those of ThO_2(cr) and ThI_4(cr):

$$[C^{\circ}_{p,\mathrm{m}}]^{1200\,\mathrm{K}}_{298.15\,\mathrm{K}}\,(\mathrm{ThOI_2, cr}, T) = 105.789 + 9.918\times10^{-3}\,T + 3.724\times10^{-7}\,T^{2} - 8.317\times10^{5}\,T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Hence the enthalpy and entropy values in Equation (VIII.24) will also be the values at 298.15 K. In fact the value of $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((VIII.22), 298.15 K) from the selected values, based on calorimetric work, is $-(97.2 \pm 5.8)$ kJ·mol^{-1}, reasonably close to the value derived from high temperature data $-(82.1 \pm 25.0)$ kJ·mol^{-1}.

If the value of $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((VIII.23), 800 K) = $-(97.2 \pm 5.8)$ kJ·mol^{-1} is imposed on the Gibbs energy expression for this reaction, the corresponding entropy of reaction becomes $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}$ ((VIII.23), 800 K) = $-(38.7 \pm 8.6)$ J·K^{-1}·mol^{-1}. If this, like the enthalpy, is assumed to be independent of temperature, the standard entropy of $\mathrm{ThOI_2}$(cr) becomes S°_{m} ($\mathrm{ThOI_2}$, cr, 298.15K) = (138.7 ± 5.2) J·K^{-1}·mol^{-1}.

A second, less reliable, estimate of S°_{m} ($\mathrm{ThOI_2}$, cr) can be derived from the study by Landis and Darnell [1960LAN/DAR]. It has been noted in Section VIII.4.1.2 and Appendix A that the reaction studied by these authors was probably:

$$2\mathrm{ThOI_2(cr)} + \mathrm{TiO_2(cr)} \rightleftharpoons 2\mathrm{ThO_2(cr)} + \mathrm{TiI_4(g)} \qquad \text{(VIII.25)}$$

since $\mathrm{ThOI_2}$(cr) will be formed very easily from $\mathrm{ThI_4}$(cr) and $\mathrm{TiO_2}$(cr). If this is so, this reaction can be used to calculate $\Delta_{\mathrm{r}}G_{\mathrm{m}}$ ((VIII.25), 700 K) = (47.2 ± 4.0) kJ·mol^{-1} and hence $\Delta_{\mathrm{f}}G_{\mathrm{m}}$ ($\mathrm{ThOI_2}$, cr, 700 K) = $-(1113.5 \pm 6.5)$ kJ·mol^{-1}. The auxiliary data for $\mathrm{TiO_2}$(cr) and $\mathrm{TiI_4}$(g) were taken from Table IV-1 and [1998CHA] respectively. Since the heat capacity of $\mathrm{ThOI_2}$(cr) is assumed to be the mean of those of $\mathrm{ThO_2}$(cr) and $\mathrm{ThI_4}$(cr), this would give S°_{m} ($\mathrm{ThOI_2}$, cr, 298.15K) = (137.6 ± 6.9) J·K^{-1}·mol^{-1}. This is in remarkable agreement with the value derived above from the decomposition data of [1986FLE/KNA]. However, no value for the entropy is selected, in view of the assumptions involved in both these derivations.

VIII.4.1.6 Thorium oxyiodide hydrates and related species

Our information on these species rests on the data furnished by [1911CHA], who reported -41.97 kJ·mol^{-1} and -35.31 kJ·mol^{-1}, respectively, for the enthalpies of solution in about 16000 $\mathrm{H_2O}$ of two compounds analysed as $\mathrm{ThOI_2{\cdot}3.5H_2O}$ {or $\mathrm{Th(OH)_2I_2{\cdot}2.5H_2O}$} and $\mathrm{Th(OH)I_3{\cdot}10H_2O}$. As these compounds were not unambiguously characterised and in view of the difficulty in ascertaining the dissolution process, these values are given here for information only.

VIII.4.2 Aqueous thorium iodine compounds

VIII.4.2.1 Aqueous thorium iodide complexes

There is no experimental information on the stoichiometry and equilibrium constants for the formation of thorium(IV) iodide complexes. The equilibrium constant for the formation of $\mathrm{UI^{3+}}$ can be used as guidance.

VIII.4.2.2 Aqueous thorium iodate complexes

The iodate complexes of Th(IV) have been studied by Day and Stoughton [1950DAY/STO] using liquid-liquid extraction. Their experimental data at I = 0.5 M were interpreted with a chemical model involving three complexes $\text{Th(IO}_3)_n^{4-n}$, n = 1−3, according to:

$$\text{Th}^{4+} + \text{IO}_3^- \rightleftharpoons \text{ThIO}_3^{3+} \qquad \log_{10}\beta_1 = (2.88 \pm 0.04),$$

$$\text{Th}^{4+} + 2\text{IO}_3^- \rightleftharpoons \text{Th(IO}_3)_2^{2+} \qquad \log_{10}\beta_2 = (4.79 \pm 0.05),$$

$$\text{Th}^{4+} + 3\text{IO}_3^- \rightleftharpoons \text{Th(IO}_3)_3^{+} \qquad \log_{10}\beta_3 = (7.15 \pm 0.05).$$

The high stability of the Th(IV) iodate complexes may seem surprising by comparison with the much lower values for the corresponding chlorate and bromate systems. However, $\text{HIO}_3\text{(aq)}$ is a significantly weaker acid ($\text{p}K_\text{a} \cong 0.80$) than $\text{HClO}_3\text{(aq)}$ and $\text{HBrO}_3\text{(aq)}$ (both with $\text{p}K_\text{a} \cong 0$) and can therefore be expected to form stronger complexes with metal ions. Nevertheless, it is important to have the equilibrium constants for the Th(IV) iodate complexes verified. However as the experimental data are of good quality this review has selected the equilibrium constants at I = 0.5 M from [1950DAY/STO] and extrapolated them to zero ionic strength using the SIT and following interaction coefficients (the values for the thorium iodate complexes are estimated by analogy with U(IV) and Th(IV) nitrate complexes):

$$\varepsilon(\text{Th}^{4+}, \text{IO}_3^-) = \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = (0.70 \pm 0.10)\ \text{kg·mol}^{-1},$$

$$\varepsilon(\text{H}^{+}, \text{IO}_3^-) = \varepsilon(\text{H}^{+}, \text{ClO}_4^-) = (0.14 \pm 0.02)\ \text{kg·mol}^{-1},$$

$$\varepsilon(\text{ThIO}_3^{3+}, \text{IO}_3^-) = \varepsilon(\text{ThIO}_3^{3+}, \text{ClO}_4^-) = \varepsilon(\text{ThNO}_3^{3+}, \text{ClO}_4^-) = (0.56 \pm 0.14)\ \text{kg·mol}^{-1},$$

$$\varepsilon(\text{Th(IO}_3)_2^{2+}, \text{IO}_3^-) = \varepsilon(\text{Th(IO}_3)_2^{2+}, \text{ClO}_4^-) = \varepsilon(\text{Th(NO}_3)_2^{2+}, \text{ClO}_4^-) = (0.43 \pm 0.18)\ \text{kg·mol}^{-1},$$

$$\varepsilon(\text{Th(IO}_3)_3^{+}, \text{IO}_3^-) = \varepsilon(\text{Th(IO}_3)_3^{+}, \text{ClO}_4^-) = \varepsilon(\text{Th(NO}_3)_3^{+}, \text{ClO}_4^-) = (0.25 \pm 0.15)\ \text{kg·mol}^{-1}.$$

The calculated equilibrium constants at I = 0 and the corresponding molar standard Gibbs energies of formation are:

$$\log_{10}\beta_1^\circ = (4.14 \pm 0.10) \qquad \Delta_\text{f}G_\text{m}^\circ(\text{ThIO}_3^{3+}, 298.15\ \text{K}) = -(854.75 \pm 5.38)\ \text{kJ·mol}^{-1}$$

$$\log_{10}\beta_2^\circ = (6.97 \pm 0.12) \qquad \Delta_\text{f}G_\text{m}^\circ(\text{Th(IO}_3)_2^{2+}, 298.15\ \text{K}) = -(997.24 \pm 5.56)\ \text{kJ·mol}^{-1}$$

$$\log_{10}\beta_3^\circ = (9.87 \pm 0.11) \qquad \Delta_\text{f}G_\text{m}^\circ(\text{Th(IO}_3)_3^{+}, 298.15\ \text{K}) = -(1140.13 \pm 5.82)\ \text{kJ·mol}^{-1}.$$

IX Thorium Group 16 compounds and complexes

IX.1 Sulphur compounds and complexes

IX.1.1 Solid and gaseous thorium sulphides

IX.1.1.1 Phase diagram and crystal structures

Zachariasen [1949ZAC], [1949ZAC3] unambiguously identified four phases in the range S/Th = 0.8 − 2.0 and elucidated their structures. From powder data, ThS(cr) is reported as cubic (NaCl type, $Fm\overline{3}m$), with a = (5.682 ± 0.002) Å and isomorphous with CeS and US, while ThS_2(cr) is orthorhombic ($PbCl_2$ type, $Pnmb\text{–}D_{2h}^{16}$), with a = (4.267 ± 0.002), b = (7.264 ± 0.003), and c = (8.617 ± 0.003) Å. Using single crystal data, Zachariasen also reported Th_2S_3(cr) as orthorhombic (Sb_2S_3 type, *Pbnm*) with a = (10.99 ± 0.05), b = (10.85 ± 0.05), and c = (3.96 ± 0.03) Å, isomorphous with U_2S_3, and Th_7S_{12}(cr) hexagonal ($P6_3/m$), with a = (11.063 ± 0.001) and c = (3.991 ± 0.001) Å. It was also noted, at the time, that the homogeneity range for that phase extends from S/Th = 1.71 to 1.76.

Graham and McTaggart [1960GRA/MCT] reported the compound Th_2S_5(cr) and suggested that the polysulphide described earlier by Strotzer and Zumbusch [1941STR/ZUM] as $ThS_{2.36}$ was, in fact, more correctly represented by $ThS_{2.5}$. Graham and McTaggart indicated, on the basis of powder data, that Th_2S_5(cr) was tetragonal ($P4_2/n$ or $P4_2/nmc$) with a = 5.43 Å and c = 10.15 Å. But, single crystal data by Noël and Potel [1982NOE/POT] yielded, in fact, an orthorhombic structure (*Pcnb*), nearly tetragonal, with a = (7.623 ± 0.004), b = (7.677 ± 0.004), and c = (10.141 ± 0.005) Å. Kohlmann and Beck [1999KOH/BEC] found no difference in the lattice parameters of samples of Th_2S_3(cr) prepared under different conditions or after partial decomposition, and therefore suggest that this phase does not have a significant range of homogeneity.

The details of the phase diagram are not well-known, but Grønvold *et al.* [1984GRO/DRO] have constructed a schematic diagram from the available melting and transformation data. The lattice parameters of samples of ThS(cr) equilibrated with Th(cr) or Th_2S_3(cr) (Eastman *et al.* [1950EAS/BRE] and Aronson [1967ARO]) differ slightly, suggesting that there may be a small range of homogeneity in ThS(cr), but the effect of possible oxygen contamination cannot be ruled out. As already noted, it seems likely that Th_7S_{12} also has a range of homogeneity.

IX.1.1.2 Thorium monosulphide, ThS(cr)

Heat capacity measurements on ThS have been reported over the range 1 to 350 K by Flotow *et al.* [1971FLO/OSB] and over the range 1.5 to 300 K by Danan [1973DAN] with good agreement, although there are small differences above 150 K. The reported values are $C_{p,\mathrm{m}}^{\circ}$(ThS, cr, 298.15 K) = (47.72 ± 0.48) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ [1971FLO/OSB], (48.3 ± 1.0) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ [1973DAN] and S_{m}°(ThS, cr, 298.15 K) = (69.81 ± 0.70)

$J \cdot K^{-1} \cdot mol^{-1}$ [1971FLO/OSB], (70.6 ± 1.4) $J \cdot K^{-1} \cdot mol^{-1}$ [1973DAN]. However, Danan [1973DAN] indicates that his measurements on ThS(cr) suffer from small uncertainties relating to the method of heating, and in his comparisons with the heat capacities of the mixed $Th_xU_{1-x}S$ sulphides, has preferred the data of [1971FLO/OSB].

The sample used by [1971FLO/OSB] was very well characterised. These authors reported a S/Th molar ratio of (1.043 ± 0.005) and a content of 950 ppm (by mass) of oxygen as the predominant impurity. The sulphur excess was attributed to the Th_2S_3(cr) phase and the appropriate correction applied, to give thermodynamic values for ThS(c); the correction amounted to −0.38% below 35 K, −0.06% at 50 K, −1.1% at 60 K changing more gradually to −2.0% at 150 K and above. This sample was also used for enthalpy of solution measurements by [1975OHA/ADE], who give fuller details of the major impurities (Th_2S_3 and ThOS) – see Appendix A for [1975OHA/ADE] for further details. Flotow *et al.* [1971FLO/OSB] also claim higher calorimetric precision than Danan [1973DAN].

We therefore select

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThS, cr, 298.15\ K}) = (47.72 \pm 0.50)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThS, cr, 298.15\ K}) = (69.81 \pm 0.70)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

which are the values of [1971FLO/OSB], with uncertainty limits, which, we believe, represent the 2σ interval. The low-temperature heat capacity data show a considerable contribution due to conduction, confirming the view that ThS(cr) contains Th^{4+} rather than Th^{2+} ions.

The heat capacity of ThS (cr) at higher temperatures has not been measured, but [1984GRO/DRO] have presented a detailed discussion of the estimates given by Voitovich and Shakhanova [1967VOI/SHA], Mills [1974MIL] and Rand [1975RAN], and their own additional estimates for the lattice, dilatational and electronic conduction contributions. Grønvold *et al.* [1984GRO/DRO] finally selected the values of [1975RAN], which lie in the middle of the band of the estimates, and we also do this:

$$[C^{\circ}_{p,\mathrm{m}}]^{2000\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThS, cr}, T) = 50.124 + 5.460 \times 10^{-3}\,T - 3.586 \times 10^{5}\,T^{-2} \quad \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

The melting temperature is not well-known. Samsonov and Popova [1957SAM/POP] and Shalek [1963SHA] have reported values of (2720 ± 50) and 2608 K respectively. No value can be selected at this time.

O'Hare *et al.* [1975OHA/ADE] studied the enthalpy of solution of a well-characterised sample of ThS by dissolution in 6.000 M HCl. The sample was the same as that used by Flotow *et al.* [1971FLO/OSB] for heat capacity measurements. More analytical details on the sample were given in [1975OHA/ADE] – see Appendix A. The S/Th ratio of the monosulphide phase in the sample was calculated by the authors to be (1.029 ± 0.019).

There is some ambiguity in the reported processing, since the paper reports what is described as a "measured enthalpy of reaction" for a reaction which both explicitly and implicitly involves $ThS_{1.029}$(cr). We therefore assume that it in fact refers to a measured value which has been adjusted for the presence of the impurities, although no mention is made in the paper as to the value assumed for $\Delta_f H^o_m$ (ThOS, cr, 298.15 K), which is not known experimentally.

Thus, for Reaction (IX.1):

$$ThS_{1.029}(cr) + 4H^+ \text{ (in 6.00 M HCl)} \rightarrow \{Th^{4+} + 1.029H_2S\} \text{ (in 6.00 M HCl)} + 0.971H_2(g) \quad \text{(IX.1)}$$

the authors obtained $\Delta_r H^o_m$ ((IX.1), 298.15 K) = −(394.05 ± 1.84) kJ·mol^{-1}. Combination of this value with $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl) = −(758.957 ± 1.600) kJ·mol^{-1} (see Section VI.1) – neglecting small dilution effects – and with $\Delta_f H_m$ (H_2S, 6.00 M HCl, 298.15 K) ≈ $\Delta_f H_m$ (H_2S, aq, 298.15 K) = −(38.6 ± 1.5) kJ·mol^{-1}, from the auxiliary values selected in this review, leads to $\Delta_f H_m$ ($ThS_{1.029}$, cr, 298.15 K) = −(404.63 ± 2.88) kJ·mol^{-1}. This result can be extrapolated to pure ThS by assuming that the enthalpy, as well as the Gibbs energy of the reaction $ThS_{1.029}(cr) \rightarrow 0.942ThS(cr) + 0.029Th_2S_3(cr)$ is slightly negative, as in [1975RAN]. This gives $\Delta_f H^o_m$ (ThS, cr, 298.15 K) < −(396.3 ± 3.1) kJ·mol^{-1}. Thus we select:

$$\Delta_f H^o_m \text{(ThS, cr, 298.15 K)} = -(396.3 \pm 6.2) \text{ kJ·mol}^{-1}$$

where the uncertainty has been doubled, in view of the assumptions made in its derivation. This selection yields:

$$\Delta_f G^o_m \text{(ThS, cr, 298.15 K)} = -(391.9 \pm 6.2) \text{ kJ·mol}^{-1}.$$

IX.1.1.3 Thorium monosulphide gas ThS(g)

In a mass-spectrometric study of the vapour effusing from a sample of US(cr) contained in tungsten, Cater *et al.* [1961CAT/RAU] tentatively attributed a weak peak at mass number 264 to ThS(g) from adventitious thorium impurity in the system. Grønvold *et al.* [1984GRO/DRO] have estimated the molecular parameters and tabulated the thermal functions of ThS(g), giving $C^o_{p,m}$ (ThS, g, 298.15 K) = (34.5 ± 2.0) J·K^{-1}·mol^{-1} and S^o_m (ThS, g, 298.15 K) = (252.4 ± 3.0) J·K^{-1}·mol^{-1} (uncertainties estimated by the review). Cater *et al.* [1964CAT/THO] attempted to measure the vaporisation of ThS by effusion from a tantalum cell from 1935 to 2464 K, but found that the measured 'pressures' were unreasonably high, due to 'flow' of ThS over the surface of the container, despite the temperatures being well below the melting point of ThS(cr) (> 2600 K), and give an estimated equation for the effective pressure, based on the measured slope of their (incorrect) measurements and an estimated entropy of vaporisation. Rand [1975RAN] also estimated a total vapour pressure over ThS(cr) by calculating the pressure from the congruent decomposition: ThS(cr) $\rightleftharpoons$ Th(g) + S(g), and adding a contribution of ThS(g) of 30% of $p_{Th(g)}$, based on the similar ratio in the vaporisation of US(cr). Grønvold *et al.* [1984GRO/DRO] accepted the latter estimate, after correcting a sign error in the calculation made in [1975RAN] for the faster effusion of S(g) compared to Th(g). They give the approximate equation for the effective pressure of ThS over ThS(cr) (*i.e.* the total pressure from the congruent vaporisation, but calculated assuming that ThS(g) is the only species):

$$\log_{10} p_e /\text{bar} \approx 7.5 - 33000/T. \qquad (1700-3000\ \text{K})$$

With the thermal functions estimated by [1984GRO/DRO], this corresponds to an enthalpy of formation $\Delta_f H^\circ_m$ (ThS, g, 298.15 K) = (300 ± 40) $\text{kJ}\cdot\text{mol}^{-1}$, where the uncertainty is again estimated by the review.

All these estimated data are given for information only, with no selected values.

IX.1.1.4 Thorium sesquisulphide, Th_2S_3(cr)

Eyring and Westrum [1953EYR/WES] determined the enthalpy of solution in 6.000M HCl media of well-characterised samples of Th_2S_3(cr) according to reaction:

$$Th_2S_3(cr) + 8H^+ \text{ (in 6.00 M HCl)} \rightarrow \{2Th^{4+} + 3H_2S\} \text{ (in 6.00 M HCl)} + H_2(g).$$

These results lead to the standard enthalpy of formation of this compound.

Three dissolution experiments were carried out in 6.000 M HCl and three others in the same medium containing 0.005 M Na_2SiF_6. No heat effect was detected due to the presence of Na_2SiF_6, which, however, appeared to increase the rate of dissolution. As the same authors [1950EYR/WES] had established as −(1.25 ± 0.42) $\text{kJ}\cdot\text{mol}^{-1}$ the effect of the presence of 0.005 M Na_2SiF_6 in the dissolution of Th(cr) in 6.000 M HCl, we have treated separately the two sets of data for the dissolution of Th_2S_3(cr). As outlined in Appendix A, the experimental results were recalculated using currently selected values for $\Delta_f H^\circ_m$ (H_2S, aq, 298.15 K) and $\Delta_f H^\circ_m$ (H_2S, g, 298.15 K). The use of $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl) = −(758.957 ± 1.600) $\text{kJ}\cdot\text{mol}^{-1}$ (see Section VI.1) and $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl - 0.005 M Na_2SiF_6) = −(760.207 ± 1.700) $\text{kJ}\cdot\text{mol}^{-1}$ (see above) leads, to $\Delta_f H^\circ_m$ (Th_2S_3, cr, 298.15 K) = −(1077.6 ± 5.5) and −(1080.4 ± 5.6) $\text{kJ}\cdot\text{mol}^{-1}$ from the 6.000 M HCl and (6.00 M HCl + 0.005 M Na_2SiF_6) media, respectively. As these two cycles are not entirely independent, we take their average as best representing the results of [1953EYR/WES], thus $\Delta_f H^\circ_m$ (Th_2S_3, cr, 298.15 K) = −(1079.0 ± 5.5) $\text{kJ}\cdot\text{mol}^{-1}$, keeping unchanged the uncertainty limits. This value is nearly 90 $\text{kJ}\cdot\text{mol}^{-1}$ more negative than that reported by Bear and McTaggart [1958BEA/MCT] by combustion calorimetry in oxygen. As briefly discussed in Appendix A, Bear and McTaggart gave no experimental details but acknowledged the difficulty in achieving complete and unambiguous reactions. For these reasons, their result is mentioned for information only.

Therefore this review selects the following standard enthalpy of formation, derived from the data in [1953EYR/WES]:

$$\Delta_f H_m^\circ (\mathrm{Th_2S_3,cr,\ 298.15\ K}) = -(1079.0 \pm 5.5)\ \mathrm{kJ\cdot mol^{-1}}.$$

Aronson [1967ARO] has used emf measurements on solid state cells, using CaF_2 as the electrolyte, at 1100 − 1200 K to provide thermodynamic information on the various diphasic fields in the Th-S system. Data were obtained for the phase fields ThS(cr) + Th_2S_3(cr), Th_2S_3(cr) + Th_7S_{12}(cr) and Th_7S_{12}(cr) + ThS_2(cr). As discussed in detail in Appendix A, there are some indications that equilibrium was not completely attained in this study, as is sometimes the case in emf studies of solid-state reactions involving other species as well as fluorides.

In the absence of any entropy or heat capacity data for the higher sulphides, no reliable data can be derived for Th_7S_{12}(cr) or ThS_2(cr). However, since we have reasonably precise enthalpies of formation for ThS(cr) and Th_2S_3(cr), the data for the reaction involving ThS(cr) + Th_2S_3(cr),

$$\mathrm{Th(cr)} + \mathrm{Th_2S_3(cr)} \rightarrow 3\mathrm{ThS(cr)} \qquad \text{(IX.2)}$$

can be used to derive an approximate value for the entropy of Th_2S_3(cr). With $\Delta_r G_m$ ((IX.2), 1173 K) = −(82.8 ± 8.2) kJ·mol^{-1}, and $\Delta_r C_{p,m}$ (IX.2) assumed to be zero, the derived value is S_m° (Th_2S_3, cr, 298.15 K) = (179.9 ± 18.0) J·K^{-1}·mol^{-1}, where the uncertainty excludes that from the assumed $\Delta_r C_{p,m}$. This is higher than, but overlaps with the estimate of Westrum and Grønvold [1963WES/GRO] based on modified Latimer additivity rules, (167 ± 17) J·K^{-1}·mol^{-1}. However, owing to the uncertainties in the evaluation, no value is selected for S_m° (Th_2S_3, cr, 298.15 K).

IX.1.1.5 Th_7S_{12}(cr)

As noted above, no unequivocal data for Th_7S_{12}(cr) can be derived from the emf study by Aronson [1967ARO] on the equilibria involving this phase, since there are incomplete thermodynamic data for Th_2S_3(cr) and ThS_2(cr), the two other phases involved in the relevant equilibria. Using estimated data, Rand [1975RAN] derived S_m° (Th_7S_{12}, cr, 298.15 K) = (644 ± 60) J·K^{-1}·mol^{-1} and $\Delta_f H_m^\circ$ (Th_7S_{12}, cr, 298.15 K) = − (4390 ± 300) kJ·mol^{-1}, but these values are given for information only.

IX.1.1.6 Thorium disulphide, ThS_2(cr)

The heat capacity of a sample of ThS_2(cr) was measured from 53 to 296 K by King and Weller [1959KIN/WEL]. Although Th and S analyses indicated a composition of $ThS_{1.974}$(cr) (see Appendix A), their values have been selected unchanged as applying to ThS_2(cr):

$$C_{p,m}^\circ (\mathrm{ThS_2,\ cr,\ 298.15\ K}) = (70.29 \pm 0.50)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S_m^\circ (\mathrm{ThS_2,\ cr,\ 298.15\ K}) = (96.23 \pm 1.70)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

Hartmann *et al.* [1961HAR/MOO] reported a mean heat capacity of (72.8 ± 2.2) J·K^{-1}·mol^{-1} from 298.15 to 773 K (see Appendix A), which however, would imply a rather abrupt flattening of $C_{p,\mathrm{m}}$ above 300 K, and this value is not used further.

Grønvold *et al.* [1984GRO/DRO] have discussed the experimental data and various estimates of the enthalpy of formation of ThS_2(cr). Their thorough analysis includes a discussion of the data for the reaction $ThO_2(cr) + 2H_2S(g) \rightleftharpoons ThS_2(cr) + 2H_2O(g)$ reported by Bloom [1947BLO] in a thesis which is not available to us. But we note that ThO_2(cr) and ThS_2(cr) may not coexist in true equilibrium, owing to the probable formation of ThOS(cr).

Grønvold *et al.* [1984GRO/DRO] also conclude that the enthalpy of formation derived from poorly documented combustion measurements by Hartmann *et al.* [1961HAR/MOO] ($\Delta_f H^\circ_m$(ThS_2, cr, 298.15 K) = $-(816 \pm 24)$ kJ·mol^{-1}, see Appendix A) is far too negative and base their selection on the calculations of [1975RAN] on the emf study by [1967ARO] of the reaction $Th(cr) + 6ThS_2(cr) \rightleftharpoons Th_7S_{12}(cr)$ (see Section IX.1.1.4 and Appendix A). The value suggested by [1984GRO/DRO] is $\Delta_f H^\circ_m$(ThS_2, cr, 298.15 K) = $-(628 \pm 42)$ kJ·mol^{-1}. Although these values are consistent with the early observations on the temperatures at which Th_7S_{12}(cr) and ThS_2(cr) begin to decompose, these calculations depend on a sequence of estimated data, and will not be adopted in this review.

IX.1.1.7 Thorium disulphide gas ThS_2(g)

Grønvold *et al.* [1984GRO/DRO] have given tentative estimates for the thermodynamic properties, based on comparison with ThO_2(g) and trends in sulphide dissociation energies: $C^\circ_{p,\mathrm{m}}$(ThS_2, g, 298.15 K) = (53.1 ± 3.0) J·K^{-1}·mol^{-1}, S°_m(ThS_2, g, 298.15 K) = (304.0 ± 10.0) J·K^{-1}·mol^{-1} and $\Delta_f H^\circ_m$(ThS_2, g, 298.15 K) = (75 ± 60) kJ·mol^{-1}, with the uncertainties estimated by this review. No data are selected in the present review.

IX.1.1.8 Thorium polysulphide Th_2S_5(cr)

Strotzer and Zumbusch [1941STR/ZUM] have measured the sulphur decomposition pressures over a sample of composition $ThS_{2.19}$ at four temperatures from 924 to 1027 K. Based on structural and analytical studies reported in the same paper (see Appendix A for a brief summary), they took this to be a mixture of ThS_2(cr) and Th_3S_7(cr). However, we have preferred the interpretation of Graham and McTaggart [1960GRA/MCT] and assumed the higher sulphide to be Th_2S_5(cr). After correcting the total pressure of sulphur vapour for the presence of 4−6% higher sulphur polymers (using the data of [1989GUR/VEY]), the Gibbs energy for decomposition:

$$4ThS_2(cr) + S_2(g) \rightleftharpoons 2Th_2S_5(cr) \qquad \text{(IX.3)}$$

is calculated to be $[\Delta_r G_m]^{1023\,\mathrm{K}}_{923\,\mathrm{K}}$ ((IX.3), T) = $-161600 + 151.2\,T$ (J·mol^{-1})

This indicates that the enthalpy of formation of Th_2S_5(cr) is *ca.* 8.3 kJ·mol^{-1} more negative than that of ThS_2(cr) in this temperature range. In the absence of any other thermodynamic data for ThS_2(cr) and $ThS_{2.5}$(cr), no further processing is possible and this equation is given for information only.

These data are consistent with the finding by [1999KOH/BEC] that $Th_2S_{2.5}$(cr) decomposes to the solid disulphide in a high vacuum at 873 K.

IX.1.1.9 Thorium oxysulphide ThOS(cr)

This compound is obtained by reacting thorium oxide with H_2S or sulphur vapour above 1273 K. It was reported by Zachariasen [1949ZAC] to be tetragonal (PbFCl structure, $D^7_{4h} - P4/nmm$) with $a = (3.962 \pm 0.002)$ and $c = (6.746 \pm 0.004)$ Å, isomorphous with heavier actinide oxysulphides. From single crystal data, Amoretti *et al.* [1979AMO/GIO] confirmed the space group attributed by [1949ZAC] and reported the lattice parameters as $a = (3.973 \pm 0.004)$ and $c = (6.773 \pm 0.008)$ Å.

The heat capacity of ThOS(cr) was measured by Amoretti *et al.* [1984AMO/BLA2] between 5 and 300 K. These authors reported:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThOS, cr, 298.15\ K}) = (67.25 \pm 1.35)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThOS, cr, 298.15\ K}) = (76.3 \pm 1.5)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

which are the selected data. Hartmann *et al.* [1961HAR/MOO] reported a mean heat capacity of $(76.6 \pm 2.3)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ from 298.15 to 773 K, which, although consistent with the low temperature data, has not been adopted owing to the inconsistencies in the mean heat capacities reported by [1961HAR/MOO] – see Appendix A.

As also briefly discussed in Appendix A, Hartmann *et al.* [1961HAR/MOO] reported, without any details, the value $\Delta_f H^{\circ}_{\mathrm{m}}(\mathrm{ThOS, cr, 298.15\ K}) = -(862 \pm 26)\ \mathrm{kJ\cdot mol^{-1}}$. This value is given for information only, since it would imply that ThOS(cr) was noticeably metastable with respect to ThO_2(cr) + ThS_2(cr).

IX.1.2 Solid and aqueous thorium sulphites

IX.1.2.1 Solid thorium sulphites

Golovnya *et al.* have prepared a number of thorium sulphite compounds [1967GOL/MOL2], and characterised them by IR and NMR spectroscopy and by thermographic and thermogravimetric methods [1967GOL/MOL3]. No thermodynamic data are reported for these compounds. The same authors have also reported the preparation of thorium sulphito compounds containing neutral organic molecules.

IX.1.2.2 Aqueous thorium sulphites

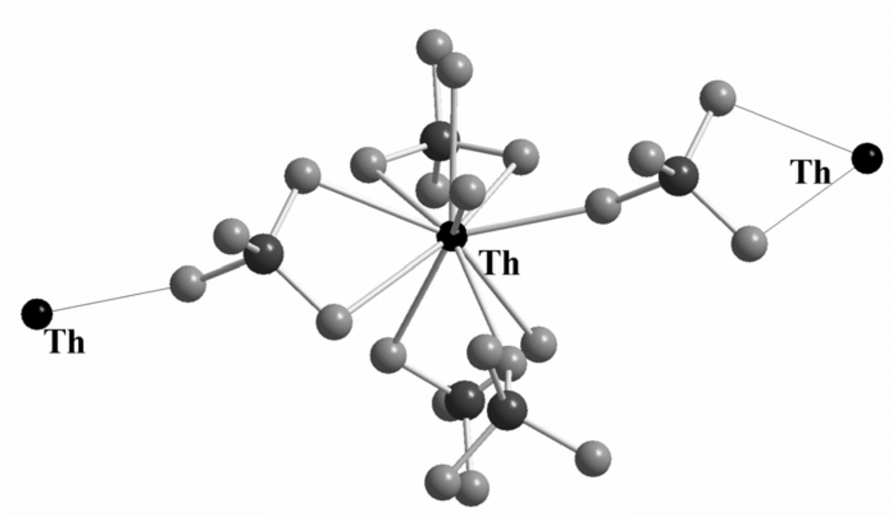
No experimental information is available on aqueous thorium sulphites.

IX.1.3 Solid and aqueous thorium sulphates

IX.1.3.1 Solid thorium sulphates, $Th(SO_4)_2(cr)$

The crystal structure of $Th(SO_4)_2(cr)$ has not been determined, but Habash and Smith [1992HAB/SMI] have determined that of $Cs_2Th(SO_4)_3(H_2O)_2(cr)$ from single crystal X-ray diffraction data [1992HAB/SMI]. The thorium atoms are coordinated by three sulphate ions that bind through two oxygen atoms, two sulphate ions that bind through a single oxygen atom and two water molecules, to give a ten-coordinated Th(IV) complex. Each sulphate acts as a bridge to adjacent Th atoms through a chelate bond to one and a single bond to the other, as shown in Figure IX-1. The Th(IV) has a coordination number of ten from the coordination of three bidentate and two monodentate coordinated sulphate. The remaining two coordination sites are taken by the two water ligands. The sulphate ions act as bridges to adjacent Th ions as indicated in the figure. This bonding indicates that the thorium sulphate complexes formed in solution may contain both unidentate and bidentate sulphate ions; this has been confirmed in a recent EXAFS study of Hennig *et al.* [2007HEN/SCH] as discussed in Appendix A.

Figure IX-1: The structure of $Cs_2Th(SO_4)_3(H_2O)_2(cr)$ from [1992HAB/SMI].



Mayer *et al.* [1960MAY/OWE] have reported enthalpy increment data for $Th(SO_4)_2(cr)$ from 623 to 897 K, from which they derived the following heat capacity equation:

$$[C^{\circ}_{p,\mathrm{m}}]^{900\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{Th(SO_4)_2, cr}, T) = 104.6 + 23.096\times10^{-2}\,T \quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

and thus

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Th(SO_4)_2, cr, 298.15\ K}) = (173.5 \pm 5.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

which is the selected value. The heat capacity equation has been assumed to be valid up to 1100 K in our assessment of the decomposition data discussed below. The uncertainty is estimated by the review. The extrapolated value at 323 K is 179.2 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, which is in tolerable agreement with the value of 172.3 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ from the very early work of Nilson and Pettersson [1880NIL/PET] for the mean $C^{\circ}_{p,\mathrm{m}}$ value from 273 to 373 K.

There are two manometric studies which have attempted to measure the decomposition pressures of $Th(SO_4)_2(cr)$:

$$\mathrm{Th(SO_4)_2 \rightleftharpoons ThO_2\,(cr) + 2SO_2(g) + O_2(g)} \qquad \text{(IX.4)}$$

by Wohler *et al.* [1908WOH/PLU] (848 to 1058 K) and by Mayer *et al.* [1960MAY/OWE] (908 to 1057 K). We note that this may not be the true equilibrium situation if $ThOSO_4(cr)$ is stable in this temperature range.

The pressures obtained by the former authors are nearly a factor of ten higher than those of Mayer *et al.* [1960MAY/OWE] as well as being more scattered. However, the equilibrium constant for the reaction is approximately proportional to p^3(total), so this difference gives very different Gibbs energies of reaction. A second law treatment of the data of [1908WOH/PLU], assuming the decomposition reaction above, leads to unreasonable values for the enthalpy of formation and entropy of $Th(SO_4)_2(cr)$ (see Appendix A). It seems clear that they were not studying the proposed equilibrium, or that water or another volatile component was present in their study and these data are not considered further.

Mayer *et al.* did not show that the $SO_2(g)/O_2(g)$ ratio in their experiments was 2:1, but they did analyse the samples after the experiments and could not detect any solid solution or oxysulphate. The equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ was established in the gas phase by the presence of a platinum coil in the gas stream. The equilibrium constants for Reaction (IX.4) calculated by the review agree closely with those given in the paper. Lacking any reliable entropy values for $Th(SO_4)_2(cr)$, we are forced to utilise a second-law treatment of the data, recognising that the derived values must have considerable uncertainty owing to the relatively small temperature interval. With the thermal data for $ThO_2(cr)$ from the present assessment and for $SO_2(g)$ and $O_2(g)$ from the Table IV-1, we finally derive the following values for $Th(SO_4)_2(cr)$ (see Appendix A): $S^{\circ}_{\mathrm{m}}(\mathrm{Th(SO_4)_2, cr, 298.15\,K}) = (146.3 \pm 4.9)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Th(SO_4)_2, cr, 298.15\ K}) = -(2543.2 \pm 4.9)\ \mathrm{kJ{\cdot}mol^{-1}}$ and $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{Th(SO_4)_2, cr, 298.15\ K}) = -(2307.4 \pm 5.1)\ \mathrm{kJ{\cdot}mol^{-1}}$.

However, $Th(SO_4)_2(cr)$ is probably less stable than the study by [1960MAY/OWE] indicates. As noted in Section IX.1.3.2, the solubility of

$Th(SO_4)_2 \cdot 9H_2O$ in water at low ionic strengths is close to 0.03 m. By far the most predominant aqueous species in these conditions is $Th(SO_4)_2(aq)$, so the equilibrium constant of the hypothetical metastable reaction:

$$Th(SO_4)_2(cr) \rightleftharpoons Th(SO_4)_2(aq),$$

must be greater than (0.03 ± 0.01). This implies that $\Delta_f G_m^o$ (Th(SO₄)₂, cr, 298.15 K) > $\{\Delta_f G_m^o(Th(SO_4)_2, aq, 298.15\ K) + RT \ln(0.03)\} = -(2256.8 \pm 3.6)\ kJ\cdot mol^{-1}$ and, using the difference between $\Delta_f G_m^o$ (298.15 K) and $\Delta_f H_m^o$ (298.15 K) from [1960MAY/OWE], $\Delta_f H_m^o(Th(SO_4)_2, cr, 298.15\ K) > -(2496.2 \pm 7.0)\ kJ\cdot mol^{-1}$.

Beck [1928BEC] has measured the enthalpy of reaction of $Th(SO_4)_2(cr)$ with an aqueous NaOH solution of unstated concentration at 20°C. As noted in Appendix A, it is impossible to derive unambiguous values for the enthalpy of formation of $Th(SO_4)_2(cr)$ from these data; but the more probable interpretation implies a value of $\Delta_f H_m^o(Th(SO_4)_2, cr, 298.15\ K) = -2502\ kJ\cdot mol^{-1}$, with an unknown, but large uncertainty.

In view of this considerable discrepancy between the values derived from [1960MAY/OWE], and the uncertainty of the data derived from [1928BEC], no thermodynamic data for $Th(SO_4)_2(cr)$ can be selected for this review.

IX.1.3.2 Aqueous thorium sulphates

The available thermodynamic data are of two types: stability constants, enthalpy and entropy of reaction for the formation of soluble complexes $Th(SO_4)_n^{4-2n}$ and solubility data for various solid phases. The two sources are linked because the solubility of the solid phases depends on the chemical speciation, *i.e.*, the sulphate complexes present in the aqueous phase. The analysis of the experimental stability constants has been made using the SIT model; however, this method cannot be used to describe the often very high solubility of the solid sulphate phases. In order to describe these data the present review has selected a set of equilibrium constants for the formation of $Th(SO_4)^{2+}$ and $Th(SO_4)_2(aq)$ at zero ionic strength based on the SIT model and then used these as constants in a Gibbs energy minimisation code (NONLINT-SIT) for modelling experimental data to determine equilibrium constants for the formation of $Th(SO_4)_3^{2-}$ and the solubility products of different thorium sulphate solids phases.

IX.1.3.2.1 Formation constants of thorium sulphate complexes

The experimental equilibrium constants have been obtained using liquid-liquid extraction methods with thenoyltrifluoroacetone (TTA) or dinonyl naphthalene sulphonic acid (DNNS) as extracting ligands, and by using ion-exchange. The experiments have in general been made at constant and high H^+ concentration, where the predominant sulphate species is HSO_4^-. The report of mixed HSO_4^- - SO_4^{2-} complexes by [1951ZEB/ALT] has not been considered reliable despite the fact that Nash and Cleveland [1983NAS/CLE] claim their formation in the Pu(IV)-sulphate system; these complexes were not accepted in [2001LEM/FUG] and [2003GUI/FAN]. Formation of ternary thorium-sulphate-nitrate complexes ($Th(NO_3)(SO_4)^+$ and $Th(NO_3)_2(SO_4)$) have been suggested [1958MAI/FOM], but for reasons given in Appendix A, this review has not accepted these complexes. All available data for the thorium-sulphate system have therefore been interpreted using a set of mononuclear complexes $Th(SO_4)_n^{4-2n}$ with $n = 1-4$ (Table IX-1). Most of the experimental data [1951ZEB/ALT], [1958MAI/FOM], [1959ZIE], [1972PAT/RAM] have been obtained at relatively high acidities (1.7 to 2 M) and nearly constant ionic strength (1.7 to 2.0 M); under these conditions $Th(SO_4)^{2+}$ and $Th(SO_4)_2(aq)$ are the predominant species. There is only one study [1963ALL/MCD] at relatively low acidity and high sulphate concentrations in which the formation of sulphate complexes higher than $Th(SO_4)_2(aq)$ has been discussed. Extrapolation of these data to zero ionic strength to calculate formation constants for the different thorium sulphate complexes is not straightforward; the "standard" SIT approach (linear extrapolations from concentration constants at different ionic strengths, and the use of concentration independent ion-interaction parameters) is not useful in the sulphate systems because the interaction parameters are concentration dependent and the information on this is not very accurate. From the available experimental concentration equilibrium constants it is not possible to calculate both equilibrium constants at zero ionic strength and the concentration-dependent SIT parameters. Hence this review has used a mixture of experimental and estimated interaction coefficients (Table IX-2) to calculate the equilibrium constants at zero ionic strength, based on a reinterpretation of experimental data using a NONLINT-SIT code modified from the one developed by Felmy and coworkers, [1995FEL], [1997STE/FEL] (see Appendix D). The results of these calculations along with the experimental values are given in Table IX-1.

The calculation of $\log_{10}{}^{*}\beta_1^{\circ}$ from the data given in Table IX-1 and Table IX-2 for the reaction:

$$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+ \tag{IX.5}$$

using $\log_{10}{}^{*}\beta_1$ at $I_m = 2.204$ m reported by [1959ZIE] and as detailed in Eq. (IX.6) and (IX.7) is given as an example.

$$\begin{aligned}\log_{10}{}^{*}\beta_1^{\circ} = {} & \log_{10}{}^{*}\beta_1 - \Delta z^2 D + \varepsilon(H^+, ClO_4^-)\, m_{ClO_4^-} + \varepsilon(H^+, HSO_4^-)\, m_{HSO_4^-} \\ & + \varepsilon(ThSO_4^{2+}, ClO_4^-)\, m_{ClO_4^-} + \varepsilon(ThSO_4^{2+}, HSO_4^-)\, m_{HSO_4^-} \\ & - \varepsilon(HSO_4^-, H^+)\, m_{H^+} - \varepsilon(HSO_4^-, ThSO_4^{2+})\, m_{ThSO_4^{2+}} - \varepsilon(HSO_4^-, Th^{4+})\, m_{Th^{4+}} \\ & - \varepsilon(Th^{4+}, ClO_4^-)\, m_{ClO_4^-} - \varepsilon(Th^{4+}, HSO_4^-)\, m_{HSO_4^-}\end{aligned} \tag{IX.6}$$

In Eq. (IX.6),

$$\varepsilon(H^+, ClO_4^-) m_{ClO_4^-} >> \varepsilon(H^+, HSO_4^-) m_{HSO_4^-}\ ;$$

$$\varepsilon(ThSO_4^{2+}, ClO_4^-) m_{ClO_4^-} >> (ThSO_4^{2+}, HSO_4^-) m_{HSO_4^-}\ ;$$

$$\varepsilon(HSO_4^-, H^+) m_{H^+} >> \varepsilon(HSO_4^-, ThSO_4^{2+}) m_{ThSO_4^{2+}} + \varepsilon(HSO_4^-, Th^{4+})\, m_{Th^{4+}}\ ;$$

$$\varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_4^-)m_{\mathrm{ClO}_4^-} >> \varepsilon(\mathrm{Th}^{4+},\mathrm{HSO}_4^-)m_{\mathrm{HSO}_4^-}.$$

Since $m_{\mathrm{ClO}_4^-} >> (m_{\mathrm{SO}_4^{2-}}$ and $m_{\mathrm{HSO}_4^-})$ and $m_{\mathrm{H}^+} >> (m_{\mathrm{ThSO}_4^{2+}}$ and $m_{\mathrm{Th}^{4+}})$, Eq. (IX.6) reduces to:

$$\begin{aligned}\log_{10} {}^*\beta_1^{\mathrm{o}} = \log_{10} {}^*\beta_1 - \Delta z^2 D + \{\varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-) + \varepsilon(\mathrm{ThSO}_4^{2+},\mathrm{ClO}_4^-)\}\, m_{\mathrm{ClO}_4^-} \\ - \varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_4^-)\, m_{\mathrm{ClO}_4^-} - \varepsilon(\mathrm{HSO}_4^-,\mathrm{H}^+)\, m_{\mathrm{H}^+} \qquad \text{(IX.7)}\end{aligned}$$

The value of $\log_{10} {}^*\beta_1$ reported by [1959ZIE] at I_c = 2.0 M and converted to the molal scale (I_m = 2.204 m) is 2.22. At I_m = 2.204 m and 25°C, D is equal to 0.234 and Δz^2 equals −12. The interaction parameters are $\varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_4^-) = (0.70 \pm 0.10)$ kg·mol^{-1}, $\varepsilon(\mathrm{HSO}_4^-,\mathrm{H}^+) \approx \varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1} and $\varepsilon(\mathrm{ThSO}_4^{2+},\mathrm{ClO}_4^-) = (0.3 \pm 0.1)$ kg·mol^{-1} (Table IX-2). The uncertainty in the calculated $\log_{10} \beta_1^{\mathrm{o}}$ is mainly determined by the uncertainty in $\Delta\varepsilon = -(0.40 \pm 0.14)$ kg·mol^{-1}, which in turn is dominated by the uncertainty in $\varepsilon(\mathrm{ThSO}_4^{2+},\mathrm{ClO}_4^-)$. The values of $\log_{10} {}^*\beta_1$ obtained from the data reported in the literature [1951ZEB/ALT], [1958MAI/FOM], [1959ZIE], [1972PAT/RAM] and the values recalculated to zero ionic strength, $\log_{10} {}^*\beta_1^{\mathrm{o}}$ (IX.5), are given in Table IX-1; the latter values agree well with one another, ranging between 4.13 to 4.29.

Table IX-1: Equilibrium constants of formation of aqueous thorium sulphate complexes at 25°C, unless otherwise noted, reported in the literature and those calculated by this review.

$\log_{10}\beta_1$	$\log_{10}\beta_2$	Medium	Molarity of metal ion (M), ligand (L), and H$^+$ (H)	Method	References
$\mathrm{Th}^{4+} + n\,\mathrm{HSO}_4^- \rightleftharpoons \mathrm{Th(SO_4)}_n^{4-2n} + n\mathrm{H}^+$					
2.3	3.4	1.7 M HClO$_4$	M = n.a., L = 0.05, H = 1.7	dis	[1958MAI/FOM]
4.29 ± 0.27	5.75 ± 0.21	I = 0		calc	This review^a
2.20	3.45	2.0 M NaClO$_4$	M = 5×10^{-4}, L = 0.04, H = 2	dis	[1951ZEB/ALT]
4.13 ± 0.32	5.65 ± 0.25	I = 0		calc	This review^a
2.34^b	3.59^b	2.0 M H(ClO$_4$, HSO$_4$)	M = n.a., L ≤ 0.096, H = 2	dis	[1972PAT/RAM]
	5.71 ± 0.25^b	I = 0		calc	This review^a
4.21 ± 0.32^b					
2.26	3.56	2.0 M H(ClO$_4$, HSO$_4$)	M = n.a., L ≤ 0.096, H = 2	dis	[1972PAT/RAM]
4.19 ± 0.32	5.76 ± 0.25	I = 0		calc	This review^a
2.24^c	3.5^c	2.0 M H(ClO$_4$, HSO$_4$)	M = n.a., L≤ 0.096, H = 2	dis	[1972PAT/RAM]
4.26 ± 0.32^c	5.82 ± 0.25^c	I = 0		calc	This review^a
2.22	3.56	2.0 M (H, Na)ClO$_4$	M = 10^{-5}, L ≤ 0.2, H = 1 or 2	cix	[1959ZIE]
4.15 ± 0.32	5.76 ± 0.25	I = 0		calc	This review^a
4.19 ± 0.32	5.73 ± 0.25	I = 0	n.a	ave	This review^d, selected

(Continued on next page)

Table IX-1: (continued)

$\log_{10} K$	Medium	Molarity of metal ion (M), ligand (L), and H^+ (H)	Method	References
$Th^{4+} + SO_4^{2-} \rightleftharpoons ThSO_4^{2+}$				
6.17 ± 0.32	$I = 0$	n.a	calc	This review[e], selected
5.440	$I = 0$	n.a	calc	[1982WAG/EVA]
$Th^{4+} + 2\,SO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq)$				
9.69 ± 0.27	$I = 0$	n.a	calc	This review[e], selected
11.592	$I = 0$	n.a	calc	[1992FEL/RAI]
$Th^{4+} + 3\,SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$				
10.748 ± 0.076	$I = 0$	n.a	calc	This review[f], selected
12.427	$I = 0$	n.a	calc	[1992FEL/RAI]
10.461	$I = 0$	n.a	calc	[1982WAG/EVA]
$Th^{4+} + 4\,SO_4^{2-} \rightleftharpoons Th(SO_4)_4^{4-}$				
8.441	$I = 0$	n.a	calc	[1982WAG/EVA]
-	$I = 0$	n.a	calc	This review[g]
$Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(HSO_4)(SO_4)^+ + H^+$				
– 2.9	2.0 M $NaClO_4$	$M = 5\times10^{-4}$, $L \leq 0.04$, $H = 0.09$	dis	[1951ZEB/ALT]
$Th(SO_4)_2 + SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$				
0.8	0–1.2 M $(Na_2, H_2)SO_4$	$M = 5\times10^{-4}$, $L \leq 1.2$, $H = 0.19$	dis	[1963ALL/MCD]
$Th(SO_4)_3^{2-} + SO_4^{2-} \rightleftharpoons Th(SO_4)_4^{4-}$				
– 2.0	0–1.2 M $(Na_2, H_2)SO_4$	$M = 5\times10^{-4}$, $L \leq 1.2$, $H = 0.19$	dis	[1963ALL/MCD]
$Th^{4+} + HSO_4^- + HNO_3 \rightleftharpoons Th(NO_3)(SO_4)^+ + 2\,H^+$				
3.3	1.7 M $HClO_4$	M = n.a., $L \leq 0.05$, $H = 1.7$	dis	[1958MAI/FOM]
$Th^{4+} + HSO_4^- + 2\,HNO_3 \rightleftharpoons Th(NO_3)_2(SO_4) + 3\,H^+$				
3.0	1.7 M $H(ClO_4, NO_3)$	$SO_4 \leq 0.05$, $NO_3 \leq 1.7$, $H = 1.7$	dis	[1958MAI/FOM]

a: Calculated value for the above reference, see text for details.

b: $t = 10°C$.

c: $t = 40°C$.

d: This average of all data at 25°C, recalculated to $I_m = 0$ with the SIT approach, is selected. There is very little variability in β_1 and β_2 values reported by different authors and the calculated standard deviation at zero ionic strength is based mainly on the errors in the SIT ion-interaction parameters used in these calculations.

e: The values of $\log_{10} \beta_1^{\circ}$ and $\log_{10} \beta_2^{\circ}$ determined in this review for the formation of $ThSO_4^{2+}$ and $Th(SO_4)_2(aq)$ were obtained by combining the average values of $\log_{10} {}^{*}\beta_1^{\circ}$ and $\log_{10} {}^{*}\beta_2^{\circ}$ with the $\log_{10} {}^{*}K_1^{\circ} = 1.98$ for the protonation of sulphate, $SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-$ (Table IV-2).

f: This $\log_{10} \beta_3^{\circ}$ value is based on reinterpretation of experimental data of [1963ALL/MCD] using the NONLINT-SIT code, for details see text and Appendix D.

g: No value recommended for this reaction, see text for details.

n.a.: not applicable.

Table IX-2: SIT ion interaction parameters used in developing the thorium-sulphate system model.

Species	Ion interaction coefficients (kg·mol^{-1})		References
	ε_1	ε_2	
H^+ - Cl^-	0.12 ± 0.01	0.00	Table B-4
H^+ - ClO_4^-	0.14 ± 0.02	0.00	Table B-4
H^+ - HSO_4^-	0.14 ± 0.02	0.00	This review[a]
H^+ - $Th(SO_4)_3^{2-}$	– 0.068 ± 0.003	0.093 ± 0.007	This review[b]
Li^+ - SO_4^{2-}	– 0.068 ± 0.003	0.093 ± 0.007	Table B-6
Li^+ - $Th(SO_4)_3^{2-}$	– 0.068 ± 0.003	0.093 ± 0.007	This review[b]
Na^+ - SO_4^{2-}	– 0.184 ± 0.002	0.139 ± 0.006	Table B-6
Na^+ - HSO_4^-	– 0.01 ± 0.02	0.00	Table B-5
Na^+ - $Th(SO_4)_3^{2-}$	– 0.091 ± 0.038	0.00	This review
K^+ - SO_4^{2-}	– 0.06 ± 0.02	0.00	Table B-5
K^+ - $Th(SO_4)_3^{2-}$	– 0.091 ± 0.038	0.00	This review[c]
NH_4^+ - SO_4^{2-}	– 0.184 ± 0.002	0.139 ± 0.006	This review[d]
NH_4^+ - $Th(SO_4)_3^{2-}$	– 0.091 ± 0.038	0.00	This review[c]
Th^{4+} - Cl^-	0.25 ± 0.03	0.00	Table B-4
Th^{4+} - ClO_4^-	0.70 ± 0.10	0.00	This review
Th^{4+} - HSO_4^-	0.70 ± 0.10	0.00	This review[a]
$ThSO_4^{2+}$ - Cl^-	0.14 ± 0.15	0.00	This review[e]
$ThSO_4^{2+}$ - ClO_4^-	0.3 ± 0.1	0.00	This review[f]

a: It is assumed that the values reported in Appendix B for Th^{4+} and H^+ with ClO_4^- apply to the corresponding HSO_4^- interaction.

b: It is assumed that values reported in Appendix B for (Li^+- SO_4^{2-}) are applicable to this interaction.

c: It is assumed that the values determined in this review for (Na^+- $Th(SO_4)_3^{2-}$) are applicable to this interaction as this is the only value available for any (M^+- SO_4^{2-}) interaction.

d: It is assumed that values reported in Appendix B for (Na^+- SO_4^{2-}) are applicable to this interaction. Although K^+ may be a better analogue for NH_4^+ than Na^+, the values for Na^+ were used because a consistent set of concentration independent and dependent epsilon values (ε_1 and ε_2) are available only for (Na^+- SO_4^{2-}) interactions. The ε_1 and ε_2 values for other K_2L and Na_2L interactions are very small in magnitude and do not differ greatly from each other.

e: Estimated from the correlation in Figure VI-4b which is assumed to hold also for cationic complex ions.

f: It is assumed that the value reported by [2003GUI/FAN] for (USO_4^{2+} - ClO_4^-) is applicable to this interaction.

The experimental data for the second equilibrium,

$$\mathrm{Th^{4+} + 2HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2H^+} \qquad \text{(IX.8)}$$

were described in the same way and recalculated to zero ionic strength. The variation in $\log_{10}{}^*\beta_2^\circ$ is small, from 5.65 to 5.82, between the different studies. The present review has selected the following average values for Reactions (IX.5) and (IX.8):

$$\log_{10}{}^*\beta_1^\circ\,\text{(IX.5)} = (4.19 \pm 0.32)$$

$$\log_{10}{}^*\beta_2^\circ\,\text{(IX.8)} = (5.73 \pm 0.25).$$

The uncertainty in these values is much larger than the estimated experimental errors in the individual experiments, but this is a result of the uncertainties in the ion interaction parameters and not in the calculated averages. By combining the selected values of $\log_{10}{}^*\beta_1^\circ$(IX.5) and $\log_{10}{}^*\beta_2^\circ$(IX.8) with $\log_{10}\beta_1^\circ = (1.98 \pm 0.05)$ from Table IV-2 for the protonation of sulphate, this review obtains and selects:

$$\log_{10}\beta_1^\circ\,\text{(IX.9)} = (6.17 \pm 0.32)$$

$$\log_{10}\beta_2^\circ\,\text{(IX.10)} = (9.69 \pm 0.27)$$

for the reactions:

$$\mathrm{Th^{4+} + SO_4^{2-} \rightleftharpoons ThSO_4^{2+}} \qquad \text{(IX.9)}$$

$$\mathrm{Th^{4+} + 2SO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq)} \qquad \text{(IX.10)}$$

The [1963ALL/MCD] study was conducted at relatively low acidity and as a function of the Na_2SO_4 concentration. They interpreted their data using estimated values for the formation of $ThSO_4^{2+}$ from the literature and by including $Th(SO_4)_2$(aq), $Th(SO_4)_3^{2-}$, and $Th(SO_4)_4^{4-}$ species. Felmy and Rai [1992FEL/RAI], in reinterpreting [1963ALL/MCD] data, showed that the species $Th(SO_4)_4^{4-}$ is not required because activity variations might also account for the observed experimental data; this review agrees with their conclusion. The experimental data of [1963ALL/MCD] were reinterpreted and used to calculate $\Delta_f G_m^\circ / RT$ ($Th(SO_4)_3^{2-}$). This was done using the NONLINT-SIT model with fixed values of $\Delta_f G_m^\circ / RT$ ($ThSO_4^{2+}$) = −(598.638 ± 0.737) and $\Delta_f G_m^\circ / RT$ ($Th(SO_4)_2$, aq) = −(906.869 ± 0.622); these values were calculated from the selected equilibrium constants $\log_{10}\beta_1^\circ$ (IX.9) = (6.17 ± 0.32) and $\log_{10}\beta_2^\circ$ (IX.10) = (9.69 ± 0.27) from this review, together with the selected auxiliary data. The "uncertainty" in the $\Delta_f G_m^\circ / RT$ values calculated above does not include the uncertainty in the selected Gibbs energy of formation of Th^{4+} and SO_4^{2-} as these quantities do not enter in the calculation of the equilibrium constant, *cf.* Appendix D. In this model the following ion interaction parameters (Table IX-2) were kept constant: $\varepsilon_1(Na^+, SO_4^{2-})$, $\varepsilon_2(Na^+, SO_4^{2-})$, $\varepsilon_1(Na^+, HSO_4^-)$ from [2003GUI/FAN] and the values of $\varepsilon_1(H^+, Th(SO_4)_3^{2-})$ and $\varepsilon_2(H^+, Th(SO_4)_3^{2-})$ which were set equal to those for $(Li^+, Th(SO_4)_3^{2-})$ and (Li^+, SO_4^{2-}) from [2003GUI/FAN]. The interaction parameter

$\varepsilon_1(\mathrm{Na}^+, \mathrm{Th(SO_4)_3^{2-}})$ was determined by fitting to the experimental data. All these interaction coefficients are listed in Table IX-2. The result of the least squares fit was $\Delta_f G_m^o / RT\,(\mathrm{Th(SO_4)_3^{2-}}) = -(1209.432 \pm 0.086)$ and $\varepsilon_1(\mathrm{Na}^+, \mathrm{Th(SO_4)_3^{2-}}) = -(0.091 \pm 0.038)$ kg·mol^{-1}. The estimated value of the ion interaction parameter for $\varepsilon_1(\mathrm{H}^+, \mathrm{Th(SO_4)_3^{2-}})$ does not significantly affect the fitted values because both this parameter and the H^+ molality are small. The fitted $\varepsilon_1(\mathrm{Na}^+, \mathrm{Th(SO_4)_3^{2-}})$ value is similar to the values for the interaction coefficients between Na^+ and other species having a double negative charge (cf. Appendix B). From the fitted value $\Delta_f G_m^o / RT(\mathrm{Th(SO_4)_3^{2-}}) = -(1209.432 \pm 0.086)$ (this uncertainty does not include that in the Gibbs energy of formation of Th^{4+} and $\mathrm{SO_4^{2-}}$, *cf.* Appendix D) and the interaction coefficients, this review calculates $\log_{10} \beta_3^o = (10.748 \pm 0.038)$ for the reaction:

$$\mathrm{Th}^{4+} + 3\mathrm{SO_4^{2-}} \rightleftharpoons \mathrm{Th(SO_4)_3^{2-}}. \qquad \text{(IX.11)}$$

However, the uncertainty in the NONLINT-SIT calculation does not account for the uncertainty in the estimated interaction coefficients. This review has therefore increased the uncertainty by a factor of two and selects

$$\log_{10} \beta_3^o\,(\text{IX.11}) = (10.748 \pm 0.076).$$

The close agreement between the experimental and predicted thorium concentrations at different $\mathrm{Na_2SO_4}$ concentrations for the data in [1963ALL/MCD] indicates that the aqueous phase model described above is reliable (Figure IX-2). The concentrations of different species as a function of $\mathrm{Na_2SO_4}$ concentrations are also depicted in Figure IX-2. The selected solution speciation model that includes $\mathrm{ThSO_4^{2+}}$, $\mathrm{Th(SO_4)_2(aq)}$, and $\mathrm{Th(SO_4)_3^{2-}}$ can now be tested against the experimental solvent extraction and ion exchange data [1959ZIE], [1972PAT/RAM] in Table IX-1. The close agreement between the experimental and predicted thorium concentrations in the aqueous phase shows that the selected model, which includes $\mathrm{Th(SO_4)_3^{2-}}$ in addition to the species $\mathrm{ThSO_4^{2+}}$ and $\mathrm{Th(SO_4)_2(aq)}$ proposed by [1959ZIE] and [1972PAT/RAM], is consistent with all of the experimental data (Figure IX-3 and Figure IX-4) and demonstrates that $\mathrm{Th(SO_4)_3^{2-}}$ never becomes dominant at the acidities and sulphate concentrations in these studies, as it does in [1963ALL/MCD]. However, the equilibrium constant for $\mathrm{Th(SO_4)_3^{2-}}$ is very important for the modelling of the solubility data as shown in Section IX.1.3.3).

Figure IX-2: Observed and predicted aqueous concentrations at 25°C for solvent extraction studies in Na_2SO_4 solutions [1963ALL/MCD]. The solid line depicts the predicted total aqueous thorium concentration and the other lines depict the predicted concentrations of the individual thorium species in the aqueous phase as indicated, based on thermodynamic data (Table IX-5) and ion interaction parameters (Table IX-2) selected in this review.

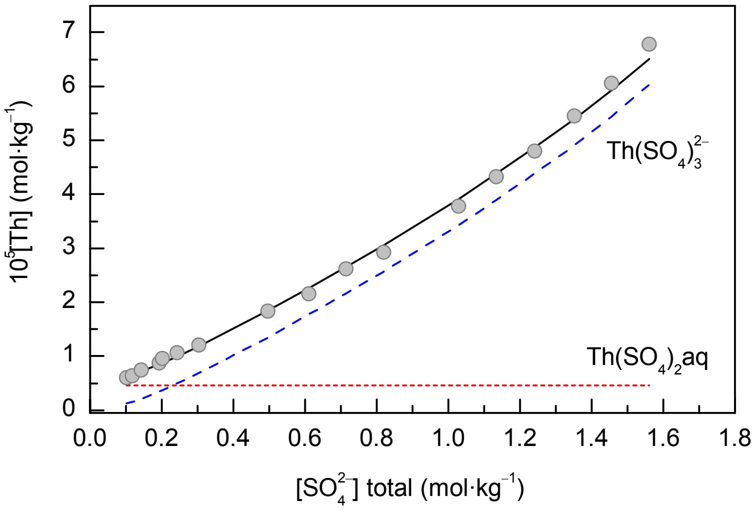


Figure IX-3: Observed and predicted concentrations at 25°C for ion-exchange studies in 2.2 m $HClO_4$ [1959ZIE]. The solid line depicts predicted total aqueous thorium concentration and the other lines depict predicted concentrations of different thorium species as marked, based on thermodynamic data (Table IX-5) and ion interaction parameters (Table IX-2) selected in this review.

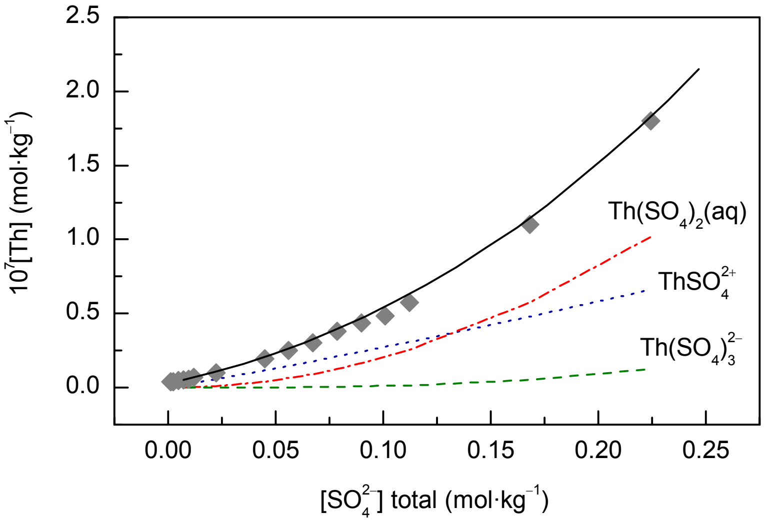
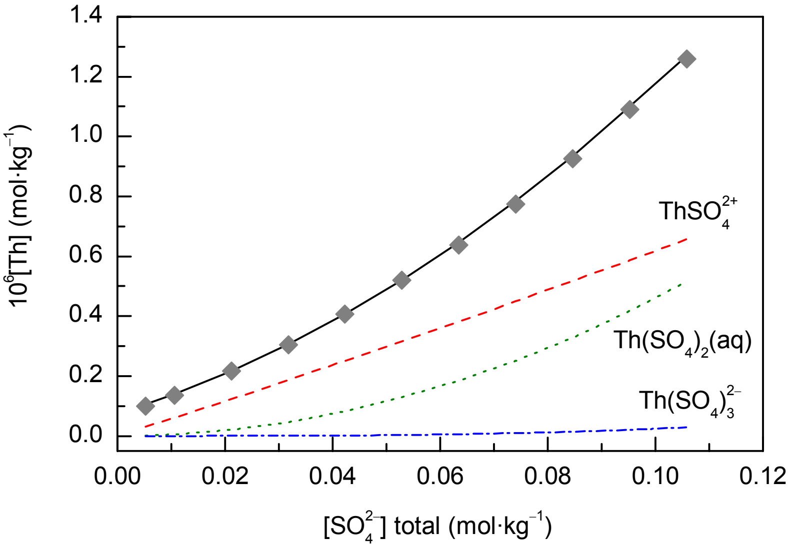


Figure IX-4: Observed and predicted aqueous concentrations at 25°C, ($[Th]_{org}$ = 10^{-6} M), for solvent extraction studies in 2.2 m $HClO_4$-H_2SO_4 media [1972PAT/RAM]. The solid line depicts predicted total aqueous thorium concentration and the other lines depict predicted concentrations of different thorium species as marked, based on thermodynamic data (Table IX-5) and ion interaction parameters (Table IX-2) selected in this review.



Although the selected experimental value of the equilibrium constant $\log_{10} \beta_3^{\circ}$ ((IX.11) is based on only the data of Allen and McDowell [1963ALL/MCD], there are several facts supporting its reliability. These include:

1) The value of $\varepsilon_1(Na^+, Th(SO_4)_3^{2-})$ = $-(0.091 \pm 0.038)$ kg·mol^{-1} fitted from [1963ALL/MCD] data is similar to the values for several other M_2X electrolytes; this is especially important since $Th(SO_4)_3^{2-}$ and Na^+ are the major species in this system and the uncertainty in $\log_{10} \beta_3^{\circ}$ due to uncertainty in $\varepsilon_1(Na^+, Th(SO_4)_3^{2-})$ is very small – for details see Appendix D.

2) The selected $\log_{10} \beta_3^{\circ}$ value is consistent with the solubility of several different thorium sulphate solids (*e.g.*, see Figures IX-5 to IX-7) as a function of sulphate concentrations, and

3) The selected value is in close agreement with that for the formation of $U(SO_4)_3^{2-}$.

IX.1.3.2.2 Enthalpy, entropy, and Gibbs energy of reaction for $ThSO_4^{2+}$, $Th(SO_4)_2(aq)$ and $Th(SO_4)_3^{2-}$

There are two experimental determinations of the enthalpy and entropy of reaction in the Th^{4+}-sulphate system. Patil and Ramakrishna [1972PAT/RAM] measured the temperature dependence of the equilibrium constants for the reactions:

$$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+ \qquad (IX.12)$$

$$ThSO_4^{2+} + HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + H^+ \qquad (IX.13)$$

and calculated the enthalpy of reaction assuming $\Delta_r C_{p,m} = 0$. Zielen measured the enthalpy of reaction for the equilibrium (IX.12) and (IX.14) using micro calorimetry, which is a more precise method.

$$Th^{4+} + 2HSO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq) + 2H^+ \qquad (IX.14)$$

Table IX-3 gives the experimental data and the derived enthalpy and entropy changes for Reactions (IX.15) and (IX.16), using the auxiliary data for HSO_4^- and SO_4^{2-} from Table IV-1.

$$Th^{4+} + SO_4^{2-} \rightleftharpoons ThSO_4^{2+} \qquad (IX.15)$$

$$Th^{4+} + 2SO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq) \qquad (IX.16)$$

Table IX-3: Enthalpy and entropy of reaction for the formation of Th(IV)-sulphate complexes. The data refer to 25°C and I = 2.0 M.

Reaction	Parameters at I = 2.0 M and 25°C		Reference
	$\Delta_r H_m$ (kJ·mol^{-1})	$\Delta_r S_m$ (J·K^{-1}·mol^{-1})	
$SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-$	23.18 ± 0.71	–	[1959ZIE]
$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+$	– 2.26 ± 0.21	34.8 ± 1.1	[1959ZIE]
	– 3.8	31.0	[1972PAT/RAM]
$Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2H^+$	– 5.98 ± 0.39	47.8 ± 1.3	[1959ZIE]
	– 3.8	55.7	[1972PAT/RAM]
$Th^{4+} + SO_4^{2-} \rightleftharpoons ThSO_4^{2+}$	20.92 ± 0.74	–	This review from data in [1959ZIE].
$Th^{4+} + 2\,SO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq)$	40.38 ± 1.08	–	

The enthalpies of reaction, $\Delta_r H_m^\circ$(IX.15) and $\Delta_r H_m^\circ$(IX.16), selected by the present review are based on the data of [1959ZIE] that have been obtained using calorimetry; these data are much more accurate than those from the temperature dependence of equilibrium constants in [1972PAT/RAM]. The experimental data refer to a 2.2 m $HClO_4$ ionic medium and this review has assumed that they are a good approximation of the values at zero ionic strength. The selected entropy of reaction at zero ionic strength has been obtained from the Gibbs energy of reaction at zero ionic strength and the selected enthalpy of reaction. The selected values are:

$$\Delta_r H_m^\circ((\text{IX.15}), 298.15\text{ K}) = (20.92 \pm 0.74)\text{ kJ·mol}^{-1}$$

$$\Delta_r S_m^\circ((\text{IX.15}), 298.15\text{ K}) = (188.291 \pm 6.610)\text{ J·K}^{-1}\text{·mol}^{-1}$$

$$\Delta_r H_m^\circ((\text{IX.16}), 298.15\text{ K}) = (40.38 \pm 1.08)\text{ kJ·mol}^{-1}$$

$$\Delta_r S_m^\circ((\text{IX.16}), 298.15\text{ K}) = (320.949 \pm 6.312)\text{ J·K}^{-1}\text{·mol}^{-1}.$$

The selected Gibbs energy and enthalpy of formation, and the entropy of $ThSO_4^{2+}$, $Th(SO_4)_2(aq)$ and $Th(SO_4)_3^{2-}$ are:

$$\Delta_f G_m^\circ(\text{ThSO}_4^{2+}, 298.15\text{ K}) = -(1484.0 \pm 5.6)\text{ kJ·mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{ThSO}_4^{2+}, 298.15\text{ K}) = -(1657.1 \pm 2.4)\text{ kJ·mol}^{-1}$$

$$S_m^\circ(\text{ThSO}_4^{2+}, 298.15\text{ K}) = -(216.3 \pm 17.3)\text{ J·K}^{-1}\text{ mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Th(SO}_4)_2\text{, aq}, 298.15\text{ K}) = -(2248.1 \pm 5.6)\text{ kJ·mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{Th(SO}_4)_2\text{, aq}, 298.15\text{ K}) = -(2547.0 \pm 2.7)\text{ kJ·mol}^{-1}$$

$$S_m^\circ(\text{Th(SO}_4)_2\text{, aq}, 298.15\text{ K}) = -(65.2 \pm 17.2)\text{ J·K}^{-1}\text{ mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Th(SO}_4)_3^{2-}, 298.15\text{ K}) = -(2998.15 \pm 5.46)\text{ kJ·mol}^{-1}$$

IX.1.3.3 Hydrated solid thorium sulphates

At least three hydrates, $Th(SO_4)_2·nH_2O(cr)$, (n = 4, 8 and 9) are stable; several other hydrates have been reported under various decomposition conditions, but are probably metastable. The phase in equilibrium with the saturated solution at 298.15 K is the tetrahydrate. Data on the Gibbs energies of formation of $Th(SO_4)_2·4H_2O$ and $Th(SO_4)_2·8H_2O$ derived from solubility measurements are discussed in Section IX.1.3.3.2. There is one further study on the stability of these hydrates by Kopp [1910KOP], who measured the enthalpies of solution of the two hydrates in *ca.* 1 M K_2CO_3 solution at around 288 K, and also the water vapour pressures of the solutions at which they coexist with the aqueous phase at 303.15 K (HCl, H_2SO_4 and HNO_3 solutions) and 315.15 K (water) – see Appendix A for details. If it is assumed that the (ill-defined) product formed by the reaction of the two hydrates is the same, and the small difference in temperature of the study from 298.15 K is neglected, the calorimetric data give $\Delta_r H_m^\circ$((IX.17), 298.15 K) = $-(58.0 \pm 5.0)$ kJ·mol^{-1} for the hydration reaction:

$$Th(SO_4)_2·4H_2O(cr) + 4H_2O(l) \rightleftharpoons Th(SO_4)_2·8H_2O(cr) \qquad (IX.17)$$

As discussed in Appendix A, the water vapour pressure data give a very different value of $\Delta_r H_m^\circ$((IX.17), 298.15 K) = $-(102.5 \pm 28.4)$ kJ·mol^{-1}, again ignoring the small temperature difference from 298.15 K. The large uncertainty is due to a combination of the tiny temperature range involved and the uncertainty in the activity of water in the carbonate solutions.

The value selected by this review is that from the calorimetric study:

$$\Delta_r H_m^o((\text{IX.17}), 298.15\text{ K}) = -(58.0 \pm 5.0)\text{ kJ}\cdot\text{mol}^{-1}$$

for Reaction (IX.17). No enthalpy values for the individual hydrates can be selected at this time.

A large number of hydrated thorium sulphates have been reported in the literature [1910KOP/HOL], [1910BAR], [1911BAR], [1912BAR], [1912WIR]. These compounds include $Th(SO_4)_2\cdot 9H_2O$, $Th(SO_4)_2\cdot 8H_2O$, $Th(SO_4)_2\cdot 4H_2O$, and a variety of hydrated double salts such as $Th(SO_4)_2\cdot Na_2SO_4\cdot 6H_2O$, $Th(SO_4)_2\cdot K_2SO_4\cdot 4H_2O$, $Th(SO_4)_2\cdot 2K_2SO_4\cdot 2H_2O$, $Th(SO_4)_2\cdot 3.5K_2SO_4$, $Th(SO_4)_2\cdot (NH_4)_2SO_4\cdot 4H_2O$, $Th(SO_4)_2\cdot 2(NH_4)_2SO_4\cdot 2H_2O$, and $Th(SO_4)_2\cdot 3(NH_4)_2SO_4\cdot 3H_2O$. $Th(SO_4)_2\cdot 9H_2O$ forms readily at room temperature and from relatively low acidities to near neutral conditions, while the other hydrated thorium sulphate compounds ($Th(SO_4)_2\cdot 8H_2O$, $Th(SO_4)_2\cdot 4H_2O$) are formed at relatively high acid concentrations (see Section IX.1.3.3.2); the double salts are only formed in concentrated sulphate solutions in the presence of Na^+, K^+ or NH_4^+. The structures of the following compounds have been determined using X-ray diffraction: $K_4Th(SO_4)_4(H_2O)_2$, [1966ARU/POR]; $Th(SO_4)_2(H_2O)_8$, [1983HAB/SMI]; $Na_2Th(SO_4)_3(H_2O)_6$, [1990HAB/SMI]; $Cs_2Th(SO_4)_3(H_2O)_2$, [1992HAB/SMI]; $Th(SO_4)_2((NH_2)_2CO)(H_2O)_3$, [1991HAB/BED]. Evstaf'eva *et al.* [1966EVS/MOL] studied the IR spectra of $Th(SO_4)_2$, $M_2Th(SO_4)_3\cdot xH_2O$ (where M = NH_4, $x = 5$; Cs, $x = 2$; $1/2Na(NH_2)_2CO$, $x = 6$), $M_4Th(SO_4)_4\cdot xH_2O$ (where M = K, $x = 2$ or 0; M = NH_4, $x = 2$; M = Rb, $x = 0$), $M_6Th(SO_4)_5\cdot 3H_2O$), (M = NH_4 or Cs), and $(NH_4)_8Th(SO_4)_6\cdot 2H_2O$. No thermodynamic data are given.

All the available data for thorium sulphate compounds are relatively old (prior to 1913) and primarily consist of solubility measurements as a function of the electrolyte concentrations at temperatures ranging from 16°C to 30°C. The solubility measurements have been made in systems that often contain an additional electrolyte, such as M_2SO_4, where M is an alkali metal ion or NH_4^+. Solubility data from a large number of these publications are compiled in [1965LIN2], in most cases as aqueous concentration of $Th(SO_4)_2$ in g per 100 g of H_2O, at different concentrations of the electrolytes in equilibrium with the different solids. In some cases the concentrations of the electrolyte are reported in molarity units, in other cases as weight percent of the solvent. No thermodynamic data are reported in the original publications, but [1992FEL/RAI], using a Pitzer ion-interaction model, have determined the chemical potentials and solubility products for most of these solids. This review has reinterpreted these data using the SIT model and the aqueous phase model described in Section IX.1.3.2. Comparisons of the solubility products for the various solid phases calculated in this review with those in [1992FEL/RAI] are reported in Table IX-4. Because of the inapplicability of the SIT model at the relatively high ionic strengths in some of the saturated solutions, this review has not selected the solubility products for the solid phases ($Th(SO_4)_2\cdot2(NH_4)_2SO_4\cdot2H_2O(cr)$, $Th(SO_4)_2\cdot3(NH_4)_2SO_4\cdot3H_2O(cr)$, $Th(SO_4)_2\cdot4H_2O(cr)$, $Th(SO_4)_2\cdot8H_2O(cr)$). The solubility product values determined in this review are on an average about 1.8 $\log_{10}$-units lower than those reported in [1992FEL/RAI], primarily as a result of differences in the aqueous phase models (*e.g.*, the $\log_{10}\beta_3^{\circ}$ value calculated in this review is 1.7 $\log_{10}$-units lower than the value used by [1992FEL/RAI]).

Table IX-4: Studies used in developing the thorium-sulphate data

	Experimental Parameters				$\log_{10} K^{\circ}$ [a]	
Solubility controlling solid	Sulphate conc. (m)	Medium	t (°C)	Data Points	[1992FEL/RAI]	This Review
$Th(SO_4)_2\cdot9H_2O$[b]	0.08−1.0	Li_2SO_4 (0-1.27 m Li)	25	4	−12.998	−11.250 ± 0.096
$Th(SO_4)_2\cdot9H_2O$[c]	0.06−1.9	$(NH_4)_2SO_4$ (0−2.5 m NH_4)	16	5	−13.031	−11.282 ± 0.142
$Th(SO_4)_2\cdot(NH_4)_2SO_4\cdot4H_2O$[c]	1.9−3.1	$(NH_4)_2SO_4$ (2.5−5.3 m NH_4)	16	3	−14.535	−12.542 ± 0.028
$Th(SO_4)_2\cdot2(NH_4)_2SO_4\cdot2H_2O$[c]	3.1−4.0	$(NH_4)_2SO_4$ (5.3−7.4 m NH_4)	16	3	−15.088	NV
$Th(SO_4)_2\cdot3(NH_4)_2SO_4\cdot3H_2O$[c]	4.2−5.4	$(NH_4)_2SO_4$ (8.0−10.7 m NH_4	16	2	−15.669	NV
$Th(SO_4)_2\cdot9H_2O$[c,d]	0.16−0.25	Na_2SO_4 (0.15−0.28 m Na)	16	2	−13.031	−11.282 ± 0.090
$Th(SO_4)_2\cdot Na_2SO_4\cdot6H_2O$[c,d]	0.40−1.13	Na_2SO_4 (0.47−2.15 m Na)	16	6	−15.788	−13.836 ± 0.174
$Th(SO_4)_2\cdot9H_2O$[c]	0.10−0.16	K_2SO_4 (0.05−0.12 m K)	16	2	−13.031	−11.282 ± 0.148
$Th(SO_4)_2\cdot K_2SO_4\cdot4H_2O$[c]	0.16−0.22	K_2SO_4 (0.13−0.16 m K)	16	4	−16.838	−15.007 ± 0.052
$Th(SO_4)_2\cdot2K_2SO_4\cdot2H_2O$[c]	0.16−0.18	K_2SO_4 (0.16−0.35 m K)	16	4	−20.612	−18.674 ± 0.218
$Th(SO_4)_2\cdot3.5K_2SO_4$[c]	0.23−0.28	K_2SO_4 (0.46−0.55 m K)	16	2	−24.660	−22.378 ± 0.392
$Th(SO_4)_2\cdot9H_2O$[b,e]	0.08−3.85	H_2SO_4 (0−7.7 m H)	25	11	−12.998	−11.251 ± 0.100
$Th(SO_4)_2\cdot8H_2O$[b,e]	6.1−7.07	H_2SO_4 (12.1−14.1 m H)	25	2	−12.896	NV
$Th(SO_4)_2\cdot8H_2O$[f]	0.10−0.12	HCl (0−6.15 m)	30	6	−12.896	−11.425 ± 0.496
$Th(SO_4)_2\cdot4H_2O$[f]	0.07−0.11	HCl (6.9−8.6 m)	30	3	−12.135	NV

a: Values for the reaction: $Th(SO_4)_2\cdot x[M_2SO_4]\cdot nH_2O \rightleftharpoons Th^{4+} + 2x\,M^{+} + (2+x)\,SO_4^{2-} + nH_2O\,(l)$.

b: From reference [1912BAR].

c: From reference [1911BAR].

d: From reference [1910BAR].

e: From reference [1912WIR].

f: From reference [1910KOP/HOL].

NV: No value, see text for details.

IX.1.3.3.1 $Th(SO_4)_2\cdot9H_2O(cr)$

The solubility of $Th(SO_4)_2\cdot9H_2O(cr)$ in Li_2SO_4 [1912BAR] and in H_2SO_4 [1912BAR] and [1912WIR] at 25°C and in Na_2SO_4 [1910BAR] and [1911BAR], K_2SO_4 [1911BAR], and $(NH_4)_2SO_4$ [1911BAR] at 16°C have been reported. Using the aqueous phase model described above in combination with $\varepsilon_1(Li^{+},SO_4^{2-}) = -(0.068 \pm 0.003)$

kg·mol^{-1} and $\varepsilon_2(\text{Li}^+, \text{SO}_4^{2-})$ = (0.093 ± 0.007) kg·mol^{-1} from [2003GUI/FAN] and assuming that the ε_1 and ε_2 values for $(\text{Li}^+, \text{Th(SO}_4)_3^{2-})$ are identical to those for $(\text{Li}^+, \text{SO}_4^{2-})$, the solubility data in Li_2SO_4 [1912BAR] were fitted to determine the solubility product of the solid phase. The computer code used (NONLINT-SIT) fits the Gibbs energy of formation of the solid resulting in $\log_{10} K_s^\circ$ (IX.18) = $-(11.250 \pm 0.096)$ and $\Delta_f G_m^\circ / RT$ ($\text{Th(SO}_4)_2{\cdot}9\text{H}_2\text{O}$) = $-(1771.408 \pm 0.222)$. Note that the uncertainty in the latter estimate does not include the uncertainty in the Gibbs energy of formation of Th^{4+} and SO_4^{2-} for reasons explained in Appendix D. The close agreement between the predicted and experimentally observed thorium concentrations (Figure IX-5) as a function of sulphate concentrations indicates that both the selected equilibrium constants and interaction parameters for thorium sulphate species are reliable. An essentially identical solubility product, $\log_{10} K_s^\circ$ (IX.18) = $-(11.251 \pm 0.100)$, and the corresponding value $\Delta_f G_m^\circ / RT = -(1771.410 \pm 0.232)$ was determined from the solubility of $\text{Th(SO}_4)_2{\cdot}9\text{H}_2\text{O(cr)}$ in < 0.6 *m* H_2SO_4 solutions at 25°C using ε_1 and ε_2 values for $(\text{H}^+, \text{Th(SO}_4)_3^{2-})$, $(\text{H}^+, \text{HSO}_4^-)$, and $(\text{Th}^{4+}, \text{HSO}_4^-)$ as listed in Table IX-2. A close agreement is also noted between the predicted and observed concentrations for the $\text{Th(SO}_4)_2{\cdot}9\text{H}_2\text{O(cr)}$ solubility in H_2SO_4 solutions (Figure IX-6). K_2SO_4, and $(\text{NH}_4)_2\text{SO}_4$); therefore this review considers the values to be reliable and selects the calculated solubility product of $\text{Th(SO}_4)_2{\cdot}9\text{H}_2\text{O(cr)}$ given above.

Figure IX-5: Observed and predicted concentrations at 25°C in equilibrium with $\text{Th(SO}_4)_2{\cdot}9\text{H}_2\text{O(cr)}$ in Li_2SO_4 solutions [1912BAR]. The solid line depicts predicted total thorium concentration and the other lines depict predicted concentrations of different thorium species as marked, based on ion interaction parameters (Table IX-2) and thermodynamic data (Table IX-5) selected in this review.

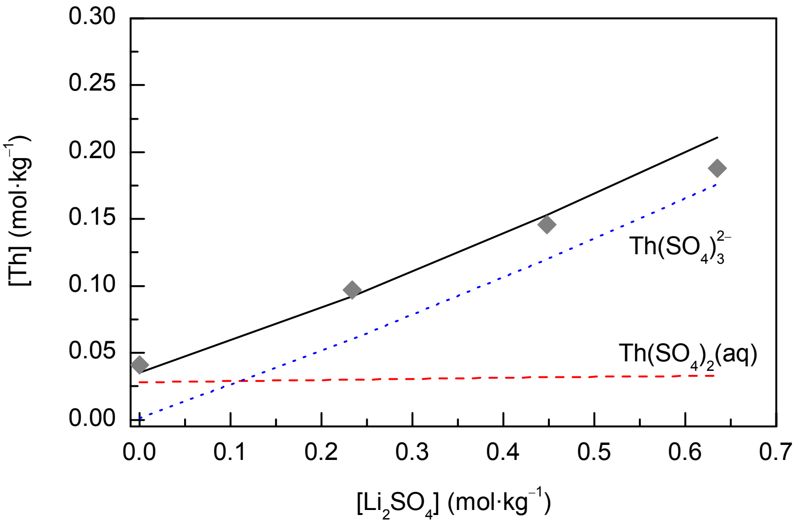
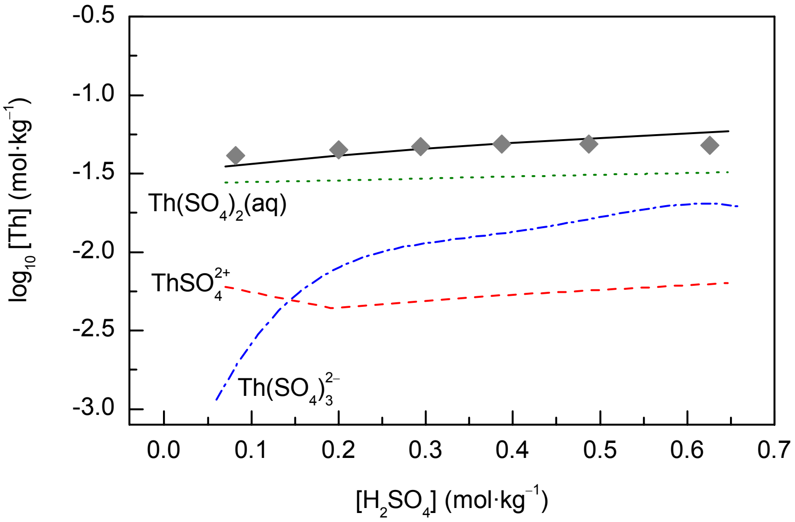


Figure IX-6: Observed and predicted concentrations at 25°C in equilibrium with $Th(SO_4)_2{\cdot}9H_2O(cr)$ in H_2SO_4 solutions [1912BAR]. The solid line depicts predicted total thorium concentration and the other lines depict predicted concentrations of different thorium species as marked, based on ion interaction parameters (Table IX-2) and thermodynamic data (Table IX-5)selected in this review.



Although the solubility products (and $\Delta_f G_m^o / RT$ $(Th(SO_4)_2{\cdot}9H_2O, cr)$ values) calculated above from the Li_2SO_4 and H_2SO_4 systems are essentially identical, this review selects the solubility product:

$$Th(SO_4)_2{\cdot}9H_2O(cr) \rightleftharpoons Th^{4+} + 2SO_4^{2-} + 9H_2O(l) \qquad (IX.18)$$

$$\log_{10} K_s^o\,(IX.18) = -(11.250 \pm 0.096)$$

and the corresponding value of

$$\Delta_f G_m^o / RT\ (Th(SO_4)_2{\cdot}9H_2O, cr) = -(1771.408 \pm 0.222)$$

based on Li_2SO_4 system at 25ºC because of the fewer number of assumptions made for the ion-interaction parameters used in interpretation of data. The value of $\Delta_f G_m^o / RT$ $(Th(SO_4)_2{\cdot}9H_2O, cr)$ was also obtained from solubility data in Na_2SO_4 [1910BAR] and [1911BAR], K_2SO_4 [1911BAR], and $(NH_4)_2SO_4$ [1911BAR] at 16°C, using the following auxiliary data: SIT ion-interaction coefficients as discussed below under the various chemical systems, and $\Delta_f G_m^o / RT$ values calculated from the selected aqueous thorium species in this review, of $H_2O(l)$ at 16ºC and of other species from selected auxiliary data as listed in Table IX-5. This review fitted a

$\Delta_f G_m^o / RT$ ($Th(SO_4)_2{\cdot}9H_2O$, cr) at 16°C as listed in Table IX-5. Figure IX-7 through Figure IX-9 show the agreement between the predicted and observed concentrations using the selected values. The NONLINT-SIT modelling parameters discussed above provide the solubility product for $Th(SO_4)_2{\cdot}9H_2O$(cr), $\log_{10} K_s^o$ (IX.18) equal to $-(11.250 \pm 0.096)$ and $-(11.282 \pm 0.090)$ at 25°C and 16°C, respectively, consistent with the small difference in temperatures between 25°C and 16°C. These solubility product values are based on several different chemical systems (Li_2SO_4, H_2SO_4, Na_2SO_4, K_2SO_4 and $(NH_4)_2SO_4$); therefore this review considers the values to be reliable and selects the calculated solubility product of $Th(SO_4)_2{\cdot}9H_2O$(cr) given above.

IX.1.3.3.2 $Th(SO_4)_2.8H_2O$(cr) and $Th(SO_4)_2.4H_2O$(cr)

Three different thorium solids, $Th(SO_4)_2{\cdot}9H_2O$(cr), $Th(SO_4)_2{\cdot}8H_2O$(cr) and $Th(SO_4)_2{\cdot}4H_2O$(cr), are reported to form in H_2SO_4 solutions, at different concentrations, ($Th(SO_4)_2{\cdot}9H_2O$(cr) from very low molalities to about 3.9 m H_2SO_4, $Th(SO_4)_2{\cdot}8H_2O$(cr) from 6.1 to 7.1 m, and $Th(SO_4)_2{\cdot}4H_2O$(cr) at 11.2 m) and at 25°C [1912BAR], [1912WIR]. The data at low H_2SO_4 molality (<~0.6 m) are discussed in Section IX.1.3.3.1 and in Figure IX-6. At higher H_2SO_4 molality ($0.6 < m < 3.9$) the agreement between the predicted and observed solubility is not satisfactory and this may be due either to the lack of reliable SIT ion-interaction parameters or the fact that the SIT model cannot be used at higher H_2SO_4 molalities. Because of this it is not possible to obtain thermodynamic data for $Th(SO_4)_2{\cdot}4H_2O$(cr) and $Th(SO_4)_2{\cdot}8H_2O$(cr) from the solubility data in [1912WIR] in H_2SO_4 solutions at concentrations greater than 6.1 m.

$Th(SO_4)_2{\cdot}8H_2O$(cr) and $Th(SO_4)_2{\cdot}4H_2O$(cr) are reported to be formed in about 0.05 m $Th(SO_4)_2$ solutions containing HCl at 30°C (see Appendix A entry [1910KOP]); $Th(SO_4)_2{\cdot}8H_2O$(cr) is formed from very low molalities to about 6.2 m HCl and $Th(SO_4)_2{\cdot}4H_2O$ at a HCl molality between 6.8 and 8.6 *m* [1910KOP/HOL]. In order to interpret these data, reliable values of appropriate SIT ion-interaction parameters are required; this review has used the experimental solubility data and a combination of experimentally determined and estimated ion interaction coefficients (ε_1 and ε_2) for (H^+,Cl^-), (H^+, HSO_4^-), (Th^{4+},Cl^-), (Th^{4+}, HSO_4^-) and ($ThSO_4^{2+}$, Cl^-) as reported in Table IX-2. This review found that the agreement between observed and calculated solubility was unacceptable when these parameters and experimental data was used to determine $\Delta_f G_m^o / RT$. A better agreement was found when $\Delta_f G_m^o / RT$ for the solids and ε_1 values of (Th^{4+},Cl^-) and ($ThSO_4^{2+}$, Cl^-) were simultaneously fitted from the entire data set; however, the fitted ε_1 values were considerably different from values for similar interactions. These attempts indicated that either the available (assumed) ε_1 values are not reliable or that the ionic strength is outside the range where the SIT model can be used. These experimental solubility data can be well described by the Pitzer ion-interaction model [1992FEL/RAI], which is applicable to these high ionic strength solutions, but it is not clear whether or not this is a result of the larger flexibility of a model with many adjustable parameters. If the SIT approach is confined to the data at

HCl concentrations $\leq 2\ m$, this review obtains the solubility product at 30°C, $\log_{10} K^{\circ}_{s}$ (IX.19) = $-(11.425 \pm 0.496)$, from the NONLINT-SIT fitted value of $\Delta_{f} G^{\circ}_{m} / RT$ ($Th(SO_4)_2 \cdot 8H_2O$, cr, 303.15 K) = $-(1673.241 \pm 1.140)$ and other thermodynamic modelling parameters listed in Table IX-2 and Table IX-5.

$$Th(SO_4)_2 \cdot 8H_2O(cr) \rightleftharpoons Th^{4+} + 2SO_4^{2-} + 8H_2O(l) \qquad (IX.19)$$

The value of $\log_{10} K^{\circ}_{s}$ (IX.19) at 30°C is not selected in this review, because of the relatively large uncertainty and the limited number of data points that have been interpreted using the SIT model on test solutions with high concentrations of HCl and H_2SO_4.

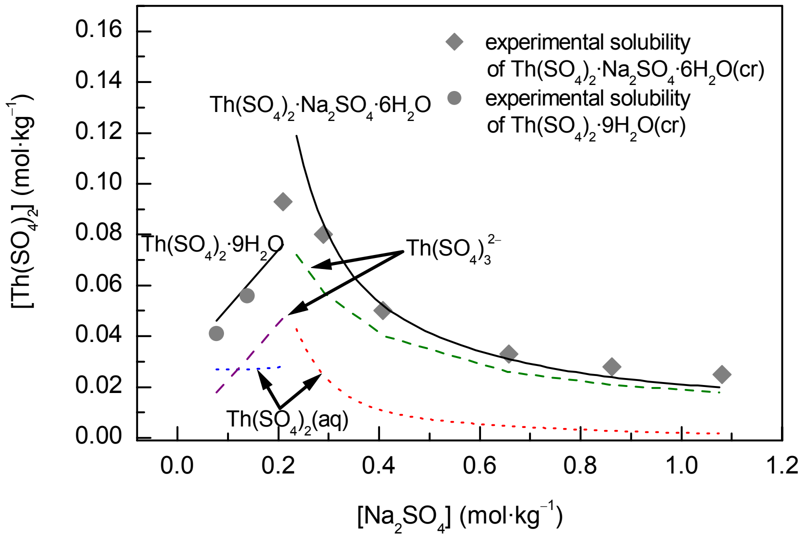
IX.1.3.3.3 $Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O(cr)$

The data on the solubility of $Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O(cr)$ in Na_2SO_4 solutions at 16°C as reported in [1910BAR] and [1911BAR] were used in conjunction with SIT ion interaction parameters ($\varepsilon_1(Na^+, SO_4^{2-}) = -(0.184 \pm 0.002)$ kg·mol^{-1} and $\varepsilon_2(Na^+, SO_4^{2-}) = (0.139 \pm 0.006)$ kg·mol^{-1} from [2003GUI/FAN], $\varepsilon_1(Na^+, Th(SO_4)_3^{2-}) = -(0.091 \pm 0.038)$ kg·mol^{-1} from this review) to determine the solubility products and the $\Delta_{f} G^{\circ}_{m} / RT$ values for the solid phases formed. Although Barre [1910BAR], [1911BAR] reports that the solubility data refer to $Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O(cr)$, the SIT modelling of these data shows that the first two samples are in fact in equilibrium with $Th(SO_4)_2 \cdot 9H_2O(cr)$. Using the fitted $\Delta_{f} G^{\circ}_{m} / RT$ ($Th(SO_4)_2 \cdot 9H_2O$, cr) at 16°C (Table IX-5) and other applicable thermodynamic parameters from Table IX-2 and Table IX-5, this review finds a close agreement between the experimental and predicted concentrations for these two points assuming $Th(SO_4)_2 \cdot 9H_2O(cr)$ to be the solubility determining solid phase (Figure IX-7).

The other solubility data were used by this review to fit $\Delta_{f} G^{\circ}_{m} / RT$ ($Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O$, cr, 298.15 K) = $-(2006.131 \pm 0.402)$ and to calculate the solubility product, $\log_{10} K^{\circ}_{s}$ (IX.20) = $-(13.836 \pm 0.174)$, for $Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O(cr)$ at 16°C by using the thermodynamic parameters listed in Table IX-2 and Table IX-5. This review has assumed that this value is close to that at 25°C and it has therefore been used as the selected value. Figure IX-7 shows that the selected equilibrium constants (Table IX-6) and ion-interaction parameters (Table IX-2) give a good description of the experimental data for Na and sulphate molalities ranging up to approximately 2.2 m and 1.1 m, respectively, for the solubility of $Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O(cr)$ in Na_2SO_4 solutions.

$$Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O(cr) \rightleftharpoons Th^{4+} + 3SO_4^{2-} + 2Na^{+} + 6H_2O(l) \qquad (IX.20)$$

Figure IX-7: Observed and predicted concentrations at 16°C in equilibrium with $Th(SO_4)_2{\cdot}9H_2O(cr)$ and $Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O(cr)$ in the presence of Na_2SO_4 ([1910BAR], [1911BAR]). The solid lines depict predicted total thorium concentrations in equilibrium with different solid phases and the other lines depict predicted concentrations of different thorium species as marked, based on thermodynamic data (Table IX-5) and ion interaction parameters (Table IX-2) selected in this review.



IX.1.3.3.4 $Th(SO_4)_2{\cdot}K_2SO_4{\cdot}4H_2O(cr)$, $Th(SO_4)_2{\cdot}2K_2SO_4{\cdot}2H_2O(cr)$, $Th(SO_4)_2{\cdot}3.5K_2SO_4(cr)$

The data on the solubility of $Th(SO_4)_2{\cdot}9H_2O(cr)$, $Th(SO_4)_2{\cdot}K_2SO_4{\cdot}4H_2O(cr)$, $Th(SO_4)_2{\cdot}2K_2SO_4{\cdot}2H_2O(cr)$, and $Th(SO_4)_2{\cdot}3.5K_2SO_4(cr)$ in K_2SO_4 solutions at 16°C as reported in [1911BAR] were used in conjunction with $\varepsilon_1(K^+, SO_4^{2-}) = -(0.06 \pm 0.02)$ kg·mol^{-1} (Appendix B) and assuming $\varepsilon_1(K^+, Th(SO_4)_3^{2-}) = -(0.091 \pm 0.038)$ kg·mol^{-1} to be identical to $\varepsilon_1(Na^+, Th(SO_4)_3^{2-})$ (Table IX-2), to determine the solubility products and values of $\Delta_f G_m^\circ / RT$ for all of the compounds with the exception of $Th(SO_4)_2{\cdot}9H_2O(cr)$. SIT modelling of the data reported by [1911BAR] shows that their first two samples are in fact in equilibrium with $Th(SO_4)_2{\cdot}9H_2O(cr)$. The value of $\Delta_f G_m^\circ / RT$ was therefore fixed at that at 16°C (Table IX-5) selected in this review, when calculating the solubility for these two samples. The close agreement between the experimental and predicted concentrations in equilibrium with $Th(SO_4)_2{\cdot}9H_2O(cr)$ confirms that the selected value of $\Delta_f G_m^\circ / RT$ ($Th(SO_4)_2{\cdot}9H_2O$, cr) or $\log_{10} K_s^\circ = -(11.282 \pm 0.090)$ for this compound is reliable. The values of $\Delta_f G_m^\circ / RT$ at 16°C for

$Th(SO_4)_2{\cdot}K_2SO_4{\cdot}4H_2O(cr)$, $Th(SO_4)_2{\cdot}2K_2SO_4{\cdot}2H_2O(cr)$, and $Th(SO_4)_2{\cdot}3.5K_2SO_4(cr)$ (Table IX-5) were determined from the solubility data [1911BAR]. Figure IX-8 shows the close agreement between observed and experimental solubility data. These selected Gibbs energy of formation data were used to calculate the solubility products at 16°C for the different solid phases and this review has selected the following values:

$$\log_{10} K_s^{\circ}\,(\text{IX.21}) = -(15.007 \pm 0.052),$$

$$\log_{10} K_s^{\circ}\,(\text{IX.22}) = -(18.674 \pm 0.218),$$

$$\log_{10} K_s^{\circ}\,(\text{IX.23}) = -(22.378 \pm 0.392),$$

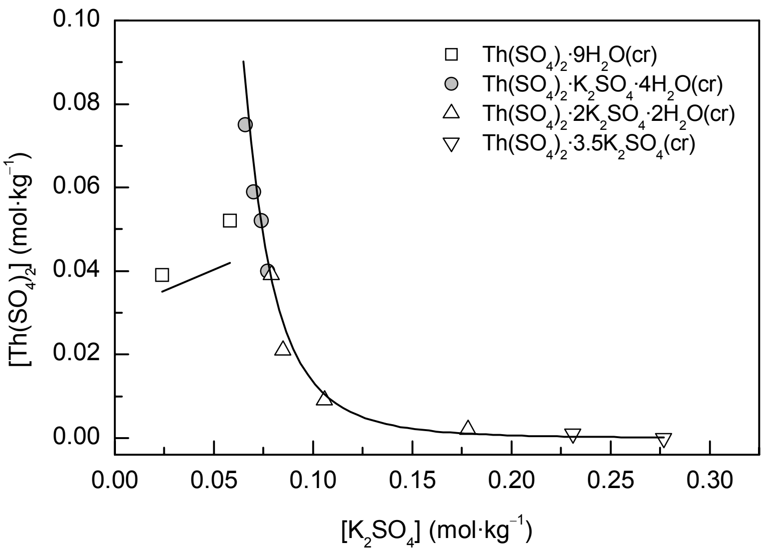
referring to the equilibria:

$$Th(SO_4)_2{\cdot}K_2SO_4{\cdot}4H_2O(cr) \rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2K^+ + 4H_2O(l) \qquad (\text{IX.21})$$

$$Th(SO_4)_2{\cdot}2K_2SO_4{\cdot}2H_2O(cr) \rightleftharpoons Th^{4+} + 4\,SO_4^{2-} + 4K^+ + 2H_2O(l) \qquad (\text{IX.22})$$

$$Th(SO_4)_2{\cdot}3.5K_2SO_4(cr) \rightleftharpoons Th^{4+} + 5.5\,SO_4^{2-} + 7K^+ \qquad (\text{IX.23})$$

Figure IX-8: Observed and predicted concentrations at 16°C in equilibrium with different thorium sulphate solids in the presence of K_2SO_4 [1911BAR]. The solid lines depict predicted total thorium concentrations in equilibrium with different solid phases, based on thermodynamic data (Table IX-5) and ion interaction parameters (Table IX-2) selected in this review.



IX.1.3.3.5 $Th(SO_4)_2\cdot(NH_4)_2SO_4\cdot4H_2O(cr)$, $Th(SO_4)_2\cdot2(NH_4)_2SO_4\cdot2H_2O(cr)$, and $Th(SO_4)_2\cdot3(NH_4)_2SO_4\cdot3H_2O(cr)$

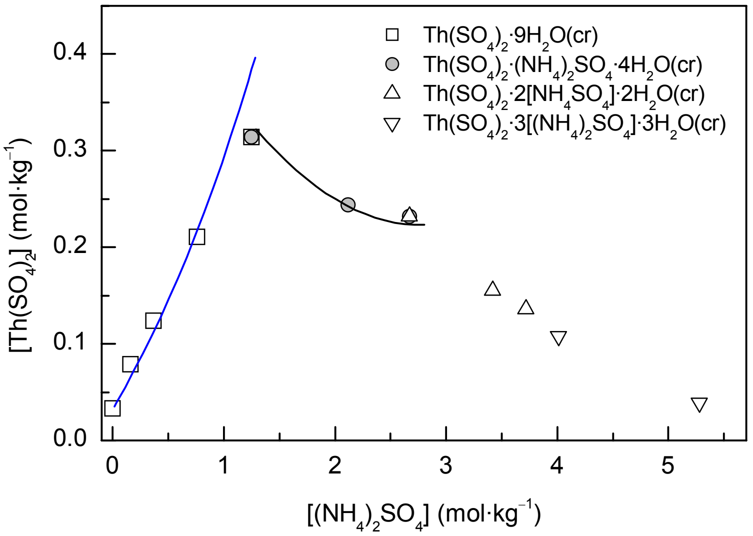
The data on the solubility of $Th(SO_4)_2\cdot9H_2O(cr)$, $Th(SO_4)_2\cdot(NH_4)_2SO_4\cdot4H_2O(cr)$, $Th(SO_4)_2\cdot2(NH_4)_2SO_4\cdot2H_2O(cr)$, and $Th(SO_4)_2\cdot3(NH_4)_2SO_4\cdot3H_2O(cr)$ in $(NH_4)_2SO_4$ solutions at 16°C are reported in [1911BAR]. Most of these solids form at very high $(NH_4)_2SO_4$ concentrations / ionic strengths (*e.g.*, $Th(SO_4)_2\cdot9H_2O(cr)$ at $I_m = 0$ to 3.75 m, $Th(SO_4)_2\cdot(NH_4)_2SO_4\cdot4H_2O(cr)$ at $I_m = 3.75$ to 7.95 m, $Th(SO_4)_2\cdot2(NH_4)_2SO_4\cdot2H_2O(cr)$ at $I_m = 7.95$ to 11.1 m, and $Th(SO_4)_2\cdot3(NH_4)_2SO_4\cdot3H_2O(cr)$ at $I_m = 12$ to 15.9 m); most of these ionic strengths are far outside the range of applicability of the SIT model and no attempt has therefore been made to determine the corresponding solubility product and Gibbs energy of formation of solids formed at > 3 m $(NH_4)_2SO_4$. The solubility products for $Th(SO_4)_2\cdot9H_2O(cr)$ and $Th(SO_4)_2\cdot(NH_4)_2SO_4\cdot4H_2O(cr)$ were determined by this review using experimental and estimated SIT ion-interaction parameters ($\varepsilon_1(NH_4^+,SO_4^{2-}) = -(0.184 \pm 0.002)$ kg·mol^{-1} and $\varepsilon_2(NH_4^+,SO_4^{2-}) = (0.139 \pm 0.006)$ kg·mol^{-1}, assumed to be identical to those for (Na^+,SO_4^{2-}); the value $\varepsilon_1(NH_4^+,Th(SO_4)_3^{2-}) = -(0.091 \pm 0.038)$ kg·mol^{-1} was assumed to be identical to that determined in this review for $(Na^+,Th(SO_4)_3^{2-})$ (Table IX-2). This review used the selected solubility product $\log_{10} K_s^\circ(Th(SO_4)_2\cdot9H_2O, cr)$ and the fitted value for $\log_{10} K_s^\circ(Th(SO_4)_2\cdot(NH_4)_2SO_4\cdot4H_2O, cr)$ at 16°C (Table IX-5) to compare experimental and calculated solubility data; the agreement (Figure IX-9) is good for ammonium and sulphate molality up to about 5.3 m and 3.1 m, respectively. These data were used to calculate a selected value of :

$$\log_{10} K_s^\circ(\text{IX.24}) = -(12.542 \pm 0.028),$$

for the reaction:

$$Th(SO_4)_2\cdot(NH_4)_2SO_4\cdot4H_2O(cr) \rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2\,NH_4^+ + 4H_2O(l) \qquad (\text{IX.24})$$

Figure IX-9**:** Observed and predicted concentrations at 16°C in equilibrium with different thorium sulphate solids in the presence of $(NH_4)_2SO_4$ [1911BAR]. Solid lines depict predicted total thorium concentrations in equilibrium with different solid phases.



IX.1.3.3.6 The consistency of the thermodynamic data for hydrated solid thorium sulphates

The solubility data shown in Figure IX-7 can be used to estimate the Na_2SO_4 concentration where $Th(SO_4)_2.9H_2O(cr)$ and $Th(SO_4)_2.Na_2SO_4.6H_2O(cr)$ are in equilibrium; in the same way Figure IX-9 provides information of the $(NH_4)_2SO_4$ concentration where $Th(SO_4)_2.9H_2O(cr)$ and $Th(SO_4)_2.(NH_4)_2SO_4.4H_2O(cr)$ are in equilibrium. When the two solid phases are in equilibrium with the solution we have for the following cases:

$$\frac{K_s^\circ\left(\mathrm{Th(SO_4)_2{\cdot}9H_2O}\right)}{\gamma_{\mathrm{SO_4^{2-}}}{}^2[\mathrm{SO_4^{2-}}]^2\,a_{\mathrm{H_2O}}{}^9}=\frac{K_s^\circ\left(\mathrm{Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O}\right)}{\gamma_{\mathrm{SO_4^{2-}}}{}^3[\mathrm{SO_4^{2-}}]^3\,\gamma_{\mathrm{Na^+}}{}^2[\mathrm{Na^+}]^2\,a_{\mathrm{H_2O}}{}^6}; \tag{IX.25}$$

and

$$\frac{K_s^\circ\left(\mathrm{Th(SO_4)_2{\cdot}9H_2O}\right)}{\gamma_{\mathrm{SO_4^{2-}}}{}^2[\mathrm{SO_4^{2-}}]^2\,a_{\mathrm{H_2O}}{}^9}=\frac{K_s^\circ\left(\mathrm{Th(SO_4)_2{\cdot}(NH_4)_2SO_4{\cdot}4H_2O}\right)}{\gamma_{\mathrm{SO_4^{2-}}}{}^3[\mathrm{SO_4^{2-}}]^3\,\gamma_{\mathrm{NH_4^+}}{}^2[\mathrm{NH_4^+}]^2\,a_{\mathrm{H_2O}}{}^4}; \tag{IX.26}$$

From equation (IX.25)[illegible]btain:

$$\log_{10}\frac{K_s^{\circ}\left(\mathrm{Th(SO_4)_2\cdot Na_2SO_4\cdot 6H_2O}\right)}{K_s^{\circ}\left(\mathrm{Th(SO_4)_2\cdot 9H_2O}\right)} = \log_{10}\frac{\left(\gamma_{\mathrm{Na^+}}[\mathrm{Na^+}]\right)^2\left(\gamma_{\mathrm{SO_4^{2-}}}[\mathrm{SO_4^{2-}}]\right)}{a_{\mathrm{H_2O}}{}^{3}} \qquad \text{(IX.27)}$$

The two solid phases are at equilibrium when $[\mathrm{Na_2SO_4}] = (0.28 \pm 0.03)$ m, where the term $\log_{10}((\gamma_{\mathrm{Na^+}}[\mathrm{Na^+}])^2(\gamma_{\mathrm{SO_4^{2-}}}[\mathrm{SO_4^{2-}}])/a_{\mathrm{H_2O}}{}^3) = -(2.35 \pm 0.15)$, whereas the value calculated from the experimental solubility products is $-(13.836 \pm 0.174) + (11.282 \pm 0.090) = -(2.554 \pm 0.196)$. The agreement is satisfactory, and consistent with the uncertainty estimate in the NONLINT-SIT solubility products.

In the same way for the phase equilibrium between $\mathrm{Th(SO_4)_2\cdot 9H_2O(cr)}$ and $\mathrm{Th(SO_4)_2\cdot (NH_4)_2SO_4\cdot 4H_2O(cr)}$ at $\mathrm{(NH_4)_2SO_4} = (1.15 \pm 0.10)$ m the term $\log_{10}((\gamma_{\mathrm{NH_4^+}}[\mathrm{NH_4^+}])^2(\gamma_{\mathrm{SO_4^{2-}}}[\mathrm{SO_4^{2-}}])/a_{\mathrm{H_2O}}{}^5)$ is $-(1.17 \pm 0.12)$; the value calculated from the experimental solubility products is $-(12.542 \pm 0.028) + (11.282 \pm 0.090) = -(1.260 \pm 0.094)$. These two values are also in good agreement indicating that the uncertainty estimates in the NONLINT-SIT solubility products are satisfactory. To conclude, the assessed solubility products and the corresponding Gibbs energies of formation for the phases $\mathrm{Th(SO_4)_2\cdot 9H_2O(cr)}$, $\mathrm{Th(SO_4)_2\cdot Na_2SO_4\cdot 6H_2O(cr)}$ and $\mathrm{Th(SO_4)_2\cdot (NH_4)_2SO_4\cdot 4H_2O(cr)}$ are consistent with each other and the experimental data.

IX.1.3.4 Summary of thorium sulphate systems analysed by the NONLINT-SIT model

The SIT ion-interaction parameters, $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}/\mathrm{R}T$ values, and the values of equilibrium constants for aqueous and solid phases determined in this review are listed in Table IX-2, Table IX-5, and Table IX-6, respectively. The model where ion interactions are described using the two-term equation proposed by [1980CIA], $\varepsilon = \varepsilon_1 + \varepsilon_2\log_{10} I_{\mathrm{m}}$ is not very satisfactory at very low ionic strengths, where ε can attain unrealistic values. However, activities calculated from this version of the model are correct even under those conditions, since in the expression for $\log_{10}\gamma_{\mathrm{M}}$, ε appears only in a term $\varepsilon\cdot m$, (see Equation (B.4)), which does not diverge when $m \rightarrow 0$. In any case, all the solubility studies discussed in Sections IX.1.3.3.3 and IX.1.3.3.5 involve ionic strengths where the ε values are still reasonable. The uncertainties may be somewhat larger than those listed as a result of the assumption for some species that the values of $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}/\mathrm{R}T$ at 16 and 30°C are the same as those at 25°C.

Table IX-5: Selected molar Gibbs energies at 298.15 K unless otherwise identified.

Species	$\Delta_f G_m^o / RT$	$\Delta_f G_m^o$ (kJ·mol^{-1})	Reference
$H_2O(l)$ (16°C)	− 96.375	− 231.699	[1992FEL/RAI]
$H_2O(l)$	− 95.661	− 237.140	Table IV-1
$H_2O(l)$ (30°C)	− 95.297	− 240.200	[1992FEL/RAI]
Na^+	− 105.670	− 261.953	Table IV-1
K^+	− 113.963	− 282.510	Table IV-1
Cl^-	− 52.932	− 131.217	Table IV-1
SO_4^{2-}	− 300.126	− 744.004	Table IV-1
HSO_4^-	− 304.689	− 755.315	Table IV-1
OH^-	− 63.421	− 157.219	Table IV-1
NH_4^+	− 32.029	− 79.398	Table IV-1
Li^+	− 118.161	− 292.918	Table IV-1
Th^{4+}	− 284.305	− 704.783 ± 5.298	This Review
$ThSO_4^{2+}$	− 598.638 ± 0.737	− 1484.006 ± 1.827	This Review
$Th(SO_4)_2(aq)$	− 906.869 ± 0.622	− 2248.102 ± 1.542	This Review
$Th(SO_4)_3^{2-}$	− 1209.432 ± 0.086	− 2998.147 ± 0.213	This Review
$Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O(cr)$ (16°C)	− 2006.131 ± 0.402	− 4823.021 ± 0.966	This Review[a]
$Th(SO_4)_2{\cdot}(NH_4)_2SO_4{\cdot}4H_2O(cr)$ (16°C)	− 1663.120 ± 0.064	− 3998.374 ± 0.154	This Review[a]
$Th(SO_4)_2{\cdot}K_2SO_4{\cdot}4H_2O(cr)$ (16°C)	− 1832.665 ± 0.118	− 4405.984 ± 0.284	This Review[a]
$Th(SO_4)_2{\cdot}2K_2SO_4{\cdot}2H_2O(cr)$ (16°C)	− 2176.409 ± 0.500	− 5232.394 ± 1.202	This Review[a]
$Th(SO_4)_2{\cdot}3.5K_2SO_4(cr)$ (16°C)	− 2784.266 ±0.902	− 6693.767 ± 2.169	This Review[a]
$Th(SO_4)_2{\cdot}9H_2O(cr)$	− 1771.408 ± 0.222	− 4391.269 ± 0.550	This Review
$Th(SO_4)_2{\cdot}9H_2O(cr)$ (16°C)	− 1777.909 ± 0.206	− 4274.343 ± 0.495	This Review[a]
$Th(SO_4)_2{\cdot}8H_2O(cr)$ (30°C)	− 1673.241 ± 1.140	− 4217.477 ± 2.873	This Review[a]

a: Temperature-dependent $\Delta_f G_m^o / RT$ values for some of the key species (*e.g.* $Th(SO_4)_3^{2-}$) dominant in these solubility studies are not available. However, the reported equilibrium constants for the formation of $ThSO_4^{2+}$ and $Th(SO_4)_2(aq)$ covering the range in the experimental temperatures (16° to 30°C) differ insignificantly from each other ([1972PAT/RAM], Table IX-1) and this review has therefore assumed that this is also the case for $Th(SO_4)_3^{2-}$. Also, significant changes in ion-interaction parameters are not expected with these slight changes in experimental temperatures. Therefore, two combinations of parameters were used to determine the solubility product of the solid phases: at the experimental temperatures, a A^{φ} term in the Debye-Hückel expression and $\Delta_f G_m^o / RT$ (H_2O) from temperature-dependent expression of [1989GRE/MOL] as noted in [1992FEL/RAI], and at 25°C, $\Delta_f G_m^o / RT$ of all of the other species as noted in this table and the ion-interaction parameters. The Gibbs energies reported for these compounds at temperatures other than 25°C are fitted parameters from NONLINT-SIT and are relative to the thermodynamic data reported in this table. Because ln K^o (defined as $[-\ln K^o = \Sigma(\Delta_f G_m^o / RT)_{\text{products}} - \Sigma(\Delta_f G_m^o / RT)_{\text{reactants}}]$) is constant based on the observed experimental solubilities and the selected aqueous phase model, changes in the input $\Delta_f G_m^o / RT$ value of the aqueous species by x would change the fitted $\Delta_f G_m^o / RT$ of the solid phase by the same amount. However, the calculated solubility product from these different sets of $\Delta_f G_m^o / RT$ will remain constant. These NONLINT-SIT calculations thus help us fulfil our primary objectives of fitting these data to obtain accurate values of the solubility products (Table IX-6) and testing the reliability of the aqueous phase model selected in this study (Figures IX-7 to IX-9).

Table IX-6: Selected equilibrium constants of different thorium-sulphate reactions based on SIT model at 25ºC unless otherwise identified. The uncertainties may be somewhat larger than those listed as a result of the assumption for some species that the values of $\Delta_f G_m^o / RT$ at 16 and 30ºC are the same as those at 25ºC.

Reaction	$\log_{10} K^o$
$Th^{4+} + SO_4^{2-} \rightleftharpoons ThSO_4^{2+}$	6.170 ± 0.320
$Th^{4+} + 2\,SO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq)$	9.690 ± 0.270
$Th^{4+} + 3\,SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$	10.748 ± 0.076
$Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O(cr)$ (16°C) $\rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2Na^+ + 6H_2O(l)$	-13.836 ± 0.174[a]
$Th(SO_4)_2{\cdot}(NH_4)_2SO_4{\cdot}4H_2O(cr)$ (16°C) $\rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2\,NH_4^+ + 4H_2O(l)$	-12.542 ± 0.028[a]
$Th(SO_4)_2{\cdot}K_2SO_4{\cdot}4H_2O(cr)$ (16°C) $\rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2K^+ + 4H_2O(l)$	-15.007 ± 0.052[a]
$Th(SO_4)_2{\cdot}2K_2SO_4{\cdot}2H_2O(cr)$ (16°C) $\rightleftharpoons Th^{4+} + 4\,SO_4^{2-} + 4K^+ + 2H_2O(l)$	-18.674 ± 0.218[a]
$Th(SO_4)_2{\cdot}3.5K_2SO_4(cr)$ (16°C) $\rightleftharpoons Th^{4+} + 5.5\,SO_4^{2-} + 7K^+$	-22.378 ± 0.392[a]
$Th(SO_4)_2{\cdot}9H_2O(cr) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 9H_2O(l)$	-11.250 ± 0.096
$Th(SO_4)_2{\cdot}9H_2O(cr)$ (16°C) $\rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 9H_2O(l)$	-11.282 ± 0.090[a]
$Th(SO_4)_2{\cdot}8H_2O(cr)$ (30°C) $\rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 8H_2O(l)$	-11.425 ± 0.496[a]

a: It is reasonable to assume that the solubility product values for these solid phases determined at 16ºC and 30ºC apply to 25ºC because 1) the experimental temperatures (ranging from 16 to 30ºC) differ only slightly from 25ºC, 2) the equilibrium constants for the formation of $ThSO_4^{2+}$ and $Th(SO_4)_2(aq)$ reported at 10ºC, 25ºC, and 30ºC differ insignificantly from each other, and 3) the solubility products calculated for $Th(SO_4)_2{\cdot}9H_2O(cr)$ at 16ºC and 25ºC are essentially identical as listed in this table.

IX.1.4 Thorium thiosulphates

IX.1.4.1 Aqueous thorium thiosulphates

No experimental information is available on aqueous thiosulphate complexes of thorium.

IX.2 Selenium compounds and complexes

IX.2.1 Solid and gaseous thorium selenides

IX.2.1.1 Phase diagram and crystal structures

The phase diagram of the Th-Se system is not well-known, and precise thermodynamic data cannot be given for any of the phases. The compounds identified in this system are reminiscent of the Th-S system.

D'Eye *et al.* [1952EYE/SEL] determined the crystal structure of the ThSe phase to be cubic (NaCl type, $Fm\bar{3}m$) with a = (5.875 ± 0.002) Å. The homogeneity range was found to extend from about $ThSe_{0.95}$ to $ThSe_{1.1}$ at 1473 K (a = 5.879 Å, Th-rich, to 5.855 Å, Se-rich, for quenched samples with vacant Se sites or Th sites, respectively). The melting point of the stoichiometric compound was measured [1952EYE/SEL] as 2153 K.

The same authors indexed the sesquiselenide in terms of an orthorhombic structure (Sb_2S_3 type, *Pbnm)* with a = (11.57 ± 0.05), b = (11.34 ± 0.05), and c = (4.27 ± 0.01) Å. Graham and McTaggart [1960GRA/MCT] disagree as to the existence of Th_2Se_3 as a discrete phase (although an earlier paper from the same laboratory [1958BEA/MCT] report an enthalpy of formation for this compound).

D'Eye *et al.* [1952EYE/SEL] reported a narrow solid solution range for the Th_2Se_3 phase extending between $ThSe_{1.4}$ and $ThSe_{1.5}$ at 1473 K. They also indicated that this phase decomposes peritectically at (1753 ± 10) K.

The complex X-ray pattern of the Th_7Se_{12} phase was indexed by D'Eye *et al.* [1952EYE/SEL] in terms of a hexagonal cell and D'Eye [1953EYE] later confirmed that it was isostructural with Th_7Se_{12} (space group $P6_3/m$), with a = (11.569 ± 0.006) and c = (4.23 ± 0.01) Å. Graham and McTaggart [1960GRA/MCT] could not obtain this phase. D’Eye *et al.* [1952EYE/SEL] also give the melting point of Th_7Se_{12} as 1733 K.

The compound $ThSe_2$(cr) was identified by D'Eye *et al.* [1952EYE/SEL] and found to have an orthorhombic structure ($PbCl_2$ type, $Pmnb–D_{2h}^{16}$), although X-ray powder patterns were rather poor. A subsequent determination by D'Eye [1953EYE] gave a = (4.420 ± 0.002), b = (7.610 ± 0.002), c = (9.064 ± 0.002) Å. The formation of this phase was confirmed by [1960GRA/MCT] but they gave larger lattice parameters: a = 4.435, b = 7.629, c = 9.085 Å.

D’Eye and coworkers [1952EYE/SEL], [1954EYE/SEL] observed that $ThSe_2$(cr) loses selenium when heated *in vacuo* at 1273 K and decomposes before melting.

Some controversy still exists concerning selenides with higher selenium content than the diselenide. Although some evidence for a polyselenide of composition Th_3Se_7 was presented by D’Eye *et al.* [1952EYE/SEL], Graham and McTaggart [1960GRA/MCT] found that, at 623 K, selenium was rapidly removed from selenium-rich samples to leave a compound with formula Th_2Se_5(cr). This composition was maintained at that temperature for over one week. They report a tetragonal unit cell ($P4_2/n$ or $P4_2/nmc$) with a = 5.629 and c = 10.764 Å. According to single crystal studies by Noël [1980NOE] the structure of Th_2Se_5(cr) is orthorhombic, nearly tetragonal (space group *Pcnb*), with a = (7.94 ± 0.01), b = (7.94 ± 0.01), and c = (10.728 ± 0.005) Å. Kohlmann and Beck [1999KOH/BEC] more recently confirmed the results of [1980NOE], but gave more precise lattice parameters: a = (7.9223 ± 0.0004),

b = (7.9375 ± 0.0004), and c = (10.7155 ± 0.0003) Å at an unspecified room temperature. Kohlmann and Beck [1999KOH/BEC] indicate that Th_2Se_5(cr) has no homogeneity range, but one of the samples prepared by [1980NOE] showed lattice parameters significantly different from the others, which could lead to the opposite conclusion. Bear and McTaggart indicate that Th_2Se_5(cr) loses selenium when heated *in vacuo* to 1223 K and decomposes before melting.

From powder diffraction data, Noël [1980NOE] reports the lattice parameters of monoclinic ($P2_1/m$) $ThSe_3$(cr) as a = (5.72 ± 0.01), b = (4.21 ± 0.01), c = (9.64 ± 0.01) Å, β = (97.05 ± 0.05)°, confirming earlier unpublished results by Grønvold, as cited in [1984GRO/DRO]. The phase is apparently isostructural with $ThTe_3$, US_3, USe_3 and UTe_3.

IX.2.1.2 Thorium monoselenide ThSe(cr)

Mills [1974MIL] estimated $\Delta_f H^\circ_m$(ThSe, cr, 298.15 K) = – (356 ± 40) kJ·mol^{-1}. Westrum and Grønvold [1963WES/GRO] estimated S°_m(ThSe, cr, 298.15 K) = (92 ± 8) J·K^{-1}·mol^{-1} while [1974MIL] suggested (84 ± 28) J·K^{-1}·mol^{-1} from comparison with the value for ThS(cr).

These estimated values are given for information only and no values are selected.

IX.2.1.3 Thorium monoselenide gas ThSe(g)

Grønvold *et al.* [1984GRO/DRO] have estimated the thermodynamic properties, based on a comparison with ThO(g) and ThS(g) and trends in chalcogenide spectroscopic data. The rounded values are: $C^\circ_{p,m}$(ThSe, g, 298.15 K) = (36.1 ± 3.0) J·K^{-1}·mol^{-1}, S°_m(ThSe, g, 298.15 K) = (264.4 ± 5.0) J·K^{-1}·mol^{-1} and $\Delta_f H^\circ_m$(ThSe, g, 298.15 K) = (351 ± 50) kJ·mol^{-1}, with the uncertainties estimated by this review.

No data are selected.

IX.2.1.4 Thorium sesquiselenide Th_2Se_3(cr)

D'Eye *et al.* [1952EYE/SEL] reported a narrow solid solution range for the Th_2Se_3(cr) phase extending between $ThSe_{1.4}$ and $ThSe_{1.5}$ at 1473 K. Bear and McTaggart [1958BEA/MCT] reported without details the value $\Delta_f H^\circ_m$(Th_2Se_3, cr, 298.15 K) = – 937 kJ·mol^{-1} from combustion calorimetry in oxygen. As briefly discussed in Appendix A, these authors acknowledged difficulties in achieving complete and unambiguous reactions. As in the case of the corresponding sulphide and telluride, their results are mentioned for information only.

Westrum and Grønvold [1963WES/GRO] estimated S°_m(Th_2Se_3, cr, 298.15 K) = (213 ± 8) J·K^{-1}·mol^{-1} by a modified Latimer additivity scheme, while Mills [1974MIL] estimated (205 ± 21) J·K^{-1}·mol^{-1} from the estimated value for Th_2S_3(cr).

No values are selected.

IX.2.1.5 Heptathorium dodecaselenide Th_7Se_{12}(cr)

As mentioned above, there is some question as to the identity of this phase. The estimates $\Delta_f H_m^\circ$ (Th_7Se_{12}, cr, 298.15 K) = −(3515 ± 290) $kJ \cdot mol^{-1}$ by Mills [1974MIL] and S_m° (Th_7Se_{12}, cr, 298.15 K) = (791 ± 88) $J \cdot K^{-1} \cdot mol^{-1}$ by Westrum and Grønvold [1963WES/GRO] are given for information only.

IX.2.1.6 Thorium diselenide $ThSe_2$(cr)

Mills [1974MIL] estimated $\Delta_f H_m^\circ$ ($ThSe_2$, cr, 298.15 K) = −(544 ± 84) $kJ \cdot mol^{-1}$ by analogy with the enthalpies of formation of related compounds, while Westrum and Grønvold [1963WES/GRO] estimated S_m° ($ThSe_2$, cr, 298.15 K) = (126 ± 13) $J \cdot K^{-1} \cdot mol^{-1}$ on the basis of a Latimer additivity scheme.

No values are selected.

IX.2.1.7 Thorium diselenide gas $ThSe_2$(g)

Grønvold *et al.* [1984GRO/DRO] have given tentative estimates for the thermodynamic properties, based, as for the disulphide, on comparison with ThO_2(g) and trends in chalcogenide dissociation energies. Their rounded values are: $C_{p,m}^\circ$ ($ThSe_2$, g, 298.15 K) = (55.4 ± 4.0) $J \cdot K^{-1} \cdot mol^{-1}$, S_m° ($ThSe_2$, g, 298.15K) = (326.7 ± 12.0) $J \cdot K^{-1} \cdot mol^{-1}$ and $\Delta_f H_m^\circ$ ($ThSe_2$, g, 298.15K) = (192 ± 50) $kJ \cdot mol^{-1}$, with the uncertainties are estimated by this review.

No values are selected.

IX.2.1.8 Thorium triselenide $ThSe_3$(cr)

Mills [1974MIL] estimated $\Delta_f H_m^\circ$ ($ThSe_3$, cr, 298.15 K) = −(565 ± 84) $kJ \cdot mol^{-1}$, based on his own evaluation for $\Delta_f H_m^\circ$ ($ThSe_2$, cr, 298.15 K), assuming little increase in stability from the diselenide to the triselenide. Westrum and Grønvold [1963WES/GRO] estimated S_m° ($ThSe_3$, cr, 298.15 K) = (167 ± 17) $J \cdot K^{-1} \cdot mol^{-1}$.

No values are selected.

IX.2.1.9 Dithorium pentaselenide Th_2Se_5(cr)

Mills [1974MIL] estimated $\Delta_f H_m^\circ$ (Th_2Se_5, cr, 298.15 K) = −(1105 ± 167) $kJ \cdot mol^{-1}$ by analogy with the enthalpies of formation of related compounds, while Westrum and Grønvold [1963WES/GRO] estimated S_m° (Th_2Se_5, cr, 298.15 K) = (293 ± 25) $J \cdot K^{-1} \cdot mol^{-1}$ on the basis of a Latimer additivity scheme.

No values are selected.

IX.2.1.10 Thorium oxyselenide ThOSe(cr)

ThOSe(cr) was found by [1952EYE/SEL] as a contaminant in preparations of ThSe to $ThSe_2$ phases and was also obtained in a single phase by the same authors by heating ThO_2 and $ThSe_2$ in equimolar proportions *in vacuo* at 1223 K. It was reported to be tetragonal (PbFCl structure, $D_{4h}^{7} - P4/nmm$) with a = (4.038 ± 0.005) and c = (7.019 ± 0.005) Å. It is thus isomorphous with the corresponding oxysulphide and oxytelluride.

According to [1952EYE/SEL], ThOSe melts without degradation at 2473 K.

The heat capacity of ThOSe(cr) was measured by Amoretti *et al.* [1984AMO/BLA2] between 5 and 300 K. These authors reported:

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{ThOSe, cr, 298.15\ K}) = (72.65 \pm 1.50)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{ThOSe, cr, 298.15\ K}) = (93.5 \pm 1.9)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

and these are the selected values.

IX.2.2 Solid and aqueous thorium selenites

IX.2.2.1 Solid thorium selenites

The available thermodynamic data ([1956CHU], [1999NES/GLY]) on thorium selenites has recently been reviewed by [2005OLI/NOL]. The value of $\log_{10} K^{\circ}_{s,0}$ ((IX.28), 298.15) = −(22.0 ± 2.0) was estimated by [2005OLI/NOL] from the data of [1956CHU], but was not selected. The estimated values $\log_{10} K^{\circ}$ ((IX.29), 298.15) = − (6.499 ± 0.560), $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}$ ((IX.29), 298.15 K) = (37.094 ± 3.195) kJ·mol^{-1}, $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((IX.29), 298.15 K) = (94.1 ± 2.9) kJ·mol^{-1}, and $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}$ ((IX.29), 298.15 K) = (191.2 ± 4.5) J·K^{-1}·mol^{-1} were selected by [2005OLI/NOL] based on the [1999NES/GLY] data and these values are accepted in this review.

$$\mathrm{Th(SeO_3)_2(s)} \rightleftharpoons \mathrm{Th^{4+}} + 2\ \mathrm{SeO_3^{2-}} \qquad \text{(IX.28)}$$

$$\mathrm{Th(SeO_3)_2 \cdot H_2O(cr)} \rightleftharpoons \mathrm{Th(SeO_3)_2(cr)} + \mathrm{H_2O(g)} \qquad \text{(IX.29)}$$

IX.2.2.2 Aqueous thorium selenites

No experimental information is available on aqueous selenite complexes of thorium.

IX.2.3 Solid thorium selenates

There is no information on the structures or thermodynamic data of solid thorium selenates.

IX.3 Tellurium compounds and complexes

IX.3.1 Solid and gaseous thorium tellurides

IX.3.1.1 Phase diagram

There is little information on the details of Th-Te system, but the phases ThTe(cr), $\mathrm{Th_7Te_{12}}$(cr) and $\mathrm{ThTe_2}$(cr) and a higher telluride have been identified, as discussed under these compounds.

IX.3.1.2 Thorium monotelluride ThTe(cr)

D'Eye and Sellman [1954EYE/SEL] found a ThTe phase with a cubic structure with $a = (3.827 \pm 0.002)$ Å with no observable range of homogeneity. Decomposition into the elements was reported to start at about 773 K when the compound was heated *in vacuo.* Although [1954EYE/SEL] described the structure as the CsCl type (bcc), they reported the space group to be O_h^1, $Pm\bar{3}m$. However, Ferro [1955FER2] and Haessler *et al.* [1976HAE/NOV] report a bcc CsCl type, with similar lattice parameters (3.828, 3.824 Å respectively) for this phase, which is therefore taken to belong to the space group $Im\bar{3}m$. D'Eye and Sellman [1954EYE/SEL] indicated that ThTe(cr) decomposes below 1273 K *in vacuo* but by contrast, a melting point of 1953 K without apparent decomposition was observed by Handwerk and Kruger [1971HAN/KRU] when the compound was heated in flowing inert gas at 1-3 bar.

Mills [1974MIL] estimated $\Delta_f H_m^\circ$(ThTe, cr, 298.15 K) = $-(243 \pm 40)$ kJ·mol^{-1} which may be somewhat too negative, since with estimated thermal functions, this implies that decomposition into the elements is completely negligible at both 773 and 1273 K (*cf.* [1954EYE/SEL]), unless the phase becomes non-stoichiometric, or adventitious oxidation was occurring. Westrum and Grønvold [1963WES/GRO] and Mills [1974MIL] estimated values of S_m°(ThTe, cr, 298.15 K) = (100 ± 13) and (92 ± 13) J·K^{-1}·mol^{-1} respectively. These estimated values are given for information only and no values can be selected.

IX.3.1.3 Thorium monotelluride gas ThTe(g)

Grønvold *et al.* [1984GRO/DRO] have estimated the thermodynamic properties, based on a comparison with ThO(g) and ThS(g) and trends in chalcogenide spectroscopic data. The rounded values are: $C_{p,m}^\circ$(ThTe, g, 298.15 K) = (36.7 ± 5.0) J·K^{-1}·mol^{-1}, S_m°(ThTe, g, 298.15 K) = (272.4 ± 10.0) J·K^{-1}·mol^{-1} and $\Delta_f H_m^\circ$(ThTe, g, 298.15 K) = (406 ± 50) kJ·mol^{-1}, with the uncertainties estimated by this review.

No data are selected.

IX.3.1.4 Th_7Te_{12}(cr) /Th_2Te_3(cr)

Graham and McTaggart [1960GRA/MCT] reported a hexagonal structure (a = 12.49, c = 4.354 Å, space group $P6_3/m$) for a phase, reported to be Th_2Te_3(cr), prepared from the elements by heating at 873 K, but no analysis is given. They suggest that their compound is isostructural with Th_7S_{12}(cr) and Th_7Se_{12}(cr). However, they also observed that the measured density was appreciably lower than that calculated for Th_7Te_{12}(cr) and considered this composition to be unlikely. More recently, Tougait *et al.* [1998TOU/POT] have clarified the structure (but not unambiguously the composition) of this phase, which, incidentally, was not observed by [1954EYE/SEL]. Tougait *et al.* [1998TOU/POT] prepared long needle-shaped single crystals of a phase, described as Th_7Te_{12}(cr), by chemical vapour transport of iodine on to a sample with the composition Th_2Te_3. However, no chemical analysis of the crystals is presented, and the composition is based solely on the crystallographic results. The phase is hexagonal, space group $P\bar{6}$, a = (12.300 ± 0.002), c = (4.566 ± 0.001) Å, with a density of 8.75 g·cm^{-3}, (and thus isostructural with U_7Te_{12}(cr)). Small quantities of a second phase, thought to be ThOTe(cr) (see Section IX.3.1.8), were also found indicating, not surprisingly, some oxygen contamination.

Bear and McTaggart [1958BEA/MCT] reported $\Delta_f H^\circ_m$(298.15 K) = −314 kJ·mol^{-1} for a phase described as $ThTe_{1.5}$(cr). No experimental details whatever are given of either the sample or the determination, and this value is not considered further by the review. Westrum and Grønvold [1963WES/GRO] estimated S°_m($ThTe_{1.71}$, cr, 298.15 K) to be (100 ± 13) J·K^{-1}·mol^{-1}.

These values are given for information only and no values can be selected.

IX.3.1.5 Solid thorium ditelluride, $ThTe_2$(cr)

D'Eye and Sellman [1954EYE/SEL] found a ditelluride, but were unable to determine its structure, stating only that it had low symmetry. Graham and McTaggart [1960GRA/MCT], however, suggested that it has a hexagonal structure with a = 8.49, c = 9.01 Å, (and thus not isostructural with the corresponding sulphide and selenide), but indicated that this may only be a pseudo-cell. The compound was obtained by these authors in the degradation of higher tellurides at 873 K *in vacuo* by slow sublimation of tellurium. When $ThTe_{2.0}$(cr) was heated [1960GRA/MCT] to 1073 K *in vacuo* for a few weeks in an attempt to grow larger crystals, a new phase with a composition close to $ThTe_{1.9}$(cr) was found, contaminated with a small amount of ThOTe(cr). Many of the observed X-ray diffraction lines for this phase corresponded to a hexagonal cell with a = 12.33 Å, but a c-axis of the required magnitude for a phase of the Th_7X_{12} type could not be found. Most lines were accounted for with c = 13.8 Å, but this cell was not considered altogether satisfactory.

There are no measured thermochemical data for the ditelluride, but Mills [1974MIL] has estimated the values $\Delta_f H^\circ_m$($ThTe_2$, cr, 298.15 K) = −(364 ± 50) kJ·mol^{-1} by analogy with values for related compounds and S°_m($ThTe_2$, cr, 298.15 K) = (134 ± 13) J·K^{-1}·mol^{-1}. The latter is somewhat smaller than the estimate by [1963WES/GRO], (142 ± 13) J·K^{-1}·mol^{-1}.

No values are selected.

IX.3.1.6 Thorium ditelluride gas $ThTe_2$(g)

Grønvold *et al.* [1984GRO/DRO] have given tentative estimates for the thermodynamic properties based, as for the disulphide, on comparison with ThO_2(g) and trends in chalcogenide dissociation energies. The rounded values are: $C^\circ_{p,m}$($ThTe_2$, g, 298.15 K) = (56.4 ± 5.0) J·K^{-1}·mol^{-1} S°_m($ThTe_2$, g, 298.15 K) = (341.4 ± 15.0) J·K^{-1}·mol^{-1} and $\Delta_f H^\circ_m$($ThTe_2$, g, 298.15 K) = (290 ± 60) kJ·mol^{-1}, with the uncertainties estimated by this review.

No data are selected.

IX.3.1.7 $ThTe_3$(cr)

Graham and McTaggart [1960GRA/MCT] reported finding a monoclinic phase of composition $ThTe_{3.5}$(cr), with $a = 6.14$, $b = 4.31$, $c = 10.44$ Å, $\beta = 98.4°$) isostructural with $ZrSe_3$(cr), but suggested that this was in fact $ThTe_3$(cr) admixed with Te(cr). D'Eye and Sellman [1954EYE/SEL], however, gave the composition of the most tellurium-rich phase as $ThTe_{2.66}$(cr) and stated that it degrades easily to $ThTe_2$(cr) when heated *in vacuo.* The composition of this higher telluride remains unclear.

As for the other tellurides, there are only estimates for the thermochemical properties. [1984GRO/DRO] suggested $\Delta_f H_m^\circ$ ($ThTe_3$, cr, 298.15 K) = −(377 ± 60) kJ·mol^{-1} and [1963WES/GRO] S_m° ($ThTe_2$, cr, 298.15 K) = (182 ± 17) J·K^{-1}·mol^{-1}.

No values are selected.

IX.3.1.8 Thorium oxytelluride ThOTe(cr)

As described by D’Eye and Sellman [1954EYE/SEL], this compound is obtained by heating a stoichiometric mixture of thorium metal, thorium dioxide, and tellurium overnight at 1373 K. Ferro [1955FER2] indicates that the compound can also be prepared by careful oxidation of ThTe. The formation of some single crystals identified as ThOTe(cr) was reported without details by Tougait *et al.* [1998TOU/POT] in the preparation of Th_7Te_{12} by chemical vapour transport (see Section IX.3.1.4).

In contrast to ThOSe(cr), which melts without degradation, ThOTe(cr) is reported to decompose to ThO_2, Th, and Te when heated *in vacuo* to an unspecified temperature [1954EYE/SEL]. It was reported to be tetragonal (PbFCl structure, $D_{4h}^7 - P4/nmm$) with $a = (4.120 \pm 0.005)$ and $c = (7.559 \pm 0.005)$ Å, isomorphous with the corresponding oxysulphide and oxyselenide [1954EYE/SEL]. Note that in the original paper the value for the c axis was erroneously given as (9.544 ± 0.005) kX units instead of (7.544 ± 0.005) kX units.

X Thorium Group 15 compounds and complexes

X.1 Nitrogen compounds and complexes

X.1.1 Solid and gaseous thorium nitrides

There are two solid nitrides, the semimetal compound ThN(cr), and the Th(IV) compound Th_3N_4(cr), both of which have a small range of homogeneity at high temperatures. Benz and Zachariasen [1966BEN/ZAC] showed that the phase previously thought to be Th_2N_3(cr) is in fact the oxynitride Th_2N_2O(cr) (see Section X.1.1.4).

X.1.1.1 Thorium mononitride ThN(cr)

Thorium mononitride has a face centred cubic NaCl structure, $Fm\bar{3}m$, with a = (5.159 ± 0.001) Å [1966ARO/AUS], [1972DAN/NOV] and is isostructural with all the lower actinide mononitrides [1967BEN/HOF], [1967AUS/ARO].

The low-temperature heat capacity of ThN(cr) was measured by Danan *et al.* [1972DAN/NOV] between 7 and 300 K and by de Novion and Costa between 3 and 9 K [1970NOV/COS]. The results of [1972DAN/NOV] lead to S°_{m}(ThN, cr, 298.15 K) = (56.0 ± 1.0) $J{\cdot}K^{-1}{\cdot}mol^{-1}$. Dell [1973DEL] cites a further value of S°_{m} (ThN, cr, 298.15 K) = (57.3 ± 0.4) $J{\cdot}K^{-1}{\cdot}mol^{-1}$ from unpublished heat capacity measurements of Dell and Martin, in marginal agreement with the value of [1972DAN/NOV]. The latter is selected here with larger uncertainty limits, thus:

$$S^{\circ}_{m}(\text{ThN, cr, 298.15 K}) = (56.0 \pm 1.5)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

The heat capacity values given by the two authors agree excellently and provide the selected value:

$$C^{\circ}_{p,m}(\text{ThN, cr, 298.15 K}) = (45.0 \pm 1.1)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

Ono *et al.* [1973ONO/KAN] have measured the heat capacity of ThN(cr) from *ca.* 450 to 850 K. They fitted their results to an equation which gives a rather lower $C^{\circ}_{p,m}$ at 298.15 K than the selected value, so their data have been refitted with a constraint of $C^{\circ}_{p,m}$(ThN, cr, 298.15 K) = 45.0 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, see Appendix A, to give the following equation, which is extrapolated to 2000 K:

$$[C^{\circ}_{p,m}]^{2000\,K}_{298.15\,K}(\text{ThN, cr}, T) = 47.836 + 1.3775 \times 10^{-2}\ T - 6.172 \times 10^{5}\ T^{-2} \quad J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

Adachi *et al.* [2005ADA/KUR] have made a molecular dynamics calculation for thorium mononitride in the temperature range from 300 to 2800 K to evaluate the thermophysical properties including heat capacity ($C^{\circ}_{v,m}$). An electronic contribution, based on the very low temperature results of de Novion and Costa [1970NOV/COS] was added to calculate $C^{\circ}_{p,m}$. However, as noted in Appendix A, these calculated $C^{\circ}_{p,m}$ values are *ca.* 10 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ smaller than the experimental values of [1973ONO/KAN] discussed above, and have been discounted.

There have been no calorimetric studies of the enthalpy of formation of ThN(cr) and the enthalpy of formation is derived from the nitrogen pressures of the decomposition of Th_3N_4(cr). These have been measured by Aronson and Auskern [1966ARO/AUS] (1723 to 2073 K) and by Kusakabe and Imoto [1971KUS/IMO], [1972KUS/IMO] (1723 to 2170 K) with reasonable agreement. The compositions of the solid-phase compositions were not established in either of these studies but, from the investigation of the Th-N system by Benz *et al.* [1967BEN/HOF], it seems clear that there will be significant non-stoichiometry in both ThN(cr) and Th_3N_4(cr) above *ca.* 1723 K. Thus only the lowest temperature points of the two studies [1966ARO/AUS] and [1971KUS/IMO] have been utilised. For the reaction:

$$2\mathrm{Th_3N_4(cr)} \rightleftharpoons 6\mathrm{ThN(cr)} + \mathrm{N_2(g)} \qquad \text{(X.1)}$$

the mean value of $\Delta_r G_m$ ((X.1), 1723 K) of (65.5 ± 5.4) $\mathrm{kJ\cdot mol^{-1}}$ has been combined with the thermal data to give:

$$\Delta_r H_m^\circ\text{((X.1), 298.15 K)} = (326.2 \pm 52.0)\ \mathrm{kJ\cdot mol^{-1}}$$

and thus

$$\Delta_f H_m^\circ\text{(ThN, cr, 298.15 K)} = -(381.2 \pm 10.0)\ \mathrm{kJ\cdot mol^{-1}},$$

which is the selected value, where the uncertainties include those attributable to possible errors in the heat capacity data.

Sedmidubský *et al.* [2005SED/KON] have made *ab initio* calculations of the enthalpies of formation of the actinide mononitrides, using density functional theory. They find good agreement with the experimental data for UN(cr) and NpN(cr), but larger differences for both ThN(cr) and PuN(cr). For ThN(cr) they calculate $\Delta_f H_m^\circ$ (ThN, cr, 298.15 K) = −347.9 $\mathrm{kJ\cdot mol^{-1}}$. The uncertainty was not given by the authors, but is estimated by the review to be at least 15.0 $\mathrm{kJ\cdot mol^{-1}}$. Their value of $\Delta_f H_m^\circ$ (ThN, cr, 298.15 K) is indeed, notably more positive than that derived above. However, if the enthalpy of formation of ThN(cr) were as large as −347.9 $\mathrm{kJ\cdot mol^{-1}}$, the decomposition pressure of N_2(g) in Reaction (X.1) at 1723 K would be as low as 10^{-8} bar, compared to the experimental values of *ca.* 10^{-2} bar from the consistent data of [1966ARO/AUS] and [1971KUS/IMO], assuming the two consistent measurements of the enthalpy of formation of Th_3N_4(cr) (see Section X.1.1.3) are correct. The selected value is therefore the value derived above, $\Delta_f H_m^\circ$ (ThN, cr, 298.15 K) = −(381.2 ± 10.0) $\mathrm{kJ\cdot mol^{-1}}$.

Olson and Mulford [1965OLS/MUL] and Benz *et al.* [1967BEN/HOF] have measured nitrogen pressures from the decomposition of ThN(cr) at very high temperatures (2689 to 3096 K), with good agreement. However under these conditions ThN(cr) is, according to the phase diagram given by [1967BEN/HOF], substantially hypostoichiometric and Th(l) dissolves appreciable amounts of nitrogen, so no reliable information on stoichiometric ThN(cr) can be derived from these measurements.

It may be noted that Rand [1975RAN] combined all these investigations [1966ARO/AUS], [1965OLS/MUL], [1967BEN/HOF], [1971KUS/IMO] of the nitrogen decomposition pressures of ThN(cr) and Th_3N_4(cr) with the extensive phase diagram data reported by Benz *et al.* [1967BEN/HOF], [1972BEN], and gives an approximate Gibbs-energy diagram, showing the values of the nitrogen potential ΔG_{N_2} as a function of temperature for the Th + ThN_{1-x}, $ThN_{1\pm x}$ single-phase and ThN_{1+x}-Th_3N_4 regions. Such details of the non-stoichiometric regions are not of immediate concern to this review and are mentioned for information only.

Benz *et al.* [1967BEN/HOF] have studied the evaporation of $ThN_{1\pm x}$(cr), which occurs mainly by decomposition to Th(g) and N_2(g), with a small amount of ThN(g) see Section X.1.1.2). They observed that at 2200 K the congruently evaporating composition is $ThN_{0.88}$, which as shown by Rand [1975RAN], is consistent with the phase diagram observations of Benz *et al.* [1967BEN/HOF].

The data of [1965OLS/MUL] and [1967BEN/HOF] show that ThN melts effectively congruently under 1 − 2 bar pressure of nitrogen at (3080 ± 30) K. The above selections yield:

$$\Delta_f G_m^\circ(\text{ThN, cr, 298.15 K}) = -(353.6 \pm 10.0)\ \text{kJ}\cdot\text{mol}^{-1}.$$

X.1.1.2 Gaseous thorium mononitride ThN(g)

In a mass-spectrometric study, Gingerich [1968GIN] has detected very small amounts of ThN(g) in the vapour over a mixture ThP(cr) + BN(cr) and gives values for the partial pressures of the species in the gaseous equilibrium:

$$\text{Th(g)} + 0.5\text{N}_2\text{(g)} \rightleftharpoons \text{ThN(g)}$$

at 2702 and 2745 K, using a silver calibration to convert from ion intensities to partial pressures. Both Gingerich [1968GIN] and Rand [1975RAN] have estimated molecular parameters for ThN(g) by a comparison of the values for MN(g) and MO(g) species of other tetravalent metals. As Gingerich does not quote his values, our calculations are based on the parameters given by Rand [1975RAN]. However those values of r = 1.93 Å and B = 0.3 cm^{-1} are not consistent, so we have changed B to the value consistent with r = 1.93 Å, *viz.* B = 0.3426 cm^{-1}. The remaining parameters are ω = 775 cm^{-1}, ωx = 3 cm^{-1}, ground-state degeneracy = 2. Our value of the Gibbs energy function at 2700 K is *ca.* 5 $J\cdot K^{-1}\cdot mol^{-1}$ greater than that quoted by [1975RAN]. The thermal functions from the selected parameters give S_m°(ThN, g, 298.15 K) = (245.8 ± 10.0) $J\cdot K^{-1}\cdot mol^{-1}$ and lead finally to $\Delta_f H_m^\circ$(ThN, g, 298.15 K) = (502 ± 25) $kJ\cdot mol^{-1}$ by a third-law calculation.

This value indicates that the gaseous nitride is always a very minor species (1 to 100 ppm) compared with Th(g) and N_2(g) at the very high temperatures where vaporisation of ThN is at all appreciable. In view of this and the numerous uncertainties in both the experimentation (paucity of data, ionisation cross-sections *etc.)* and the thermal functions for ThN(g), the above values are given for information only.

X.1.1.3 Th_3N_4(cr)

Th_3N_4(cr) has a rhombohedral structure, space group $R\bar{3}m$; the lattice parameters for the corresponding hexagonal cell are a = (3.875 ± 0.002) Å and c = (27.39 ± 0.04) Å [1971BOW/ARN]. Juza and Gerke [1968JUZ/GER] have reported, in addition, the preparation of a β-modification of Th_3N_4(cr), with a monoclinic distortion of the La_2O_3 lattice with a = 6.952, b = 3.830, c = 6.206 Å, β = 90.71°. It transforms monotropically to α-Th_3N_4(cr).

The selected heat capacities and entropy at 298.15 K are those from the unpublished measurements of Dell and Martin cited by Dell [1973DEL] but with substantially increased uncertainties in view of the total lack of details of this study [1973DEL].

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Th_3N_4, cr, 298.15\ K}) = (147.7 \pm 8.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{Th_3N_4, cr, 298.15\ K}) = (183.1 \pm 15.0)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

Ono *et al.* [1973ONO/KAN] have measured the heat capacity of Th_3N_4(cr) from *ca*. 450 to 850 K. They fitted their results to an equation which gives a rather lower $C^{\circ}_{p,\mathrm{m}}$ at 298.15 K than the selected value, so their data have been refitted with a constraint of $C^{\circ}_{p,\mathrm{m}}$(Th_3N_4, cr, 298.15 K) = 147.7 J·K^{-1}·mol^{-1}, see Appendix A, to give the following equation, which is extrapolated to 2000 K:

$$[C^{\circ}_{p,\mathrm{m}}]^{2000\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{Th_3N_4, cr}, T) = 181.517 + 26.181\times10^{-3}\,T - 37.000\times10^{5}\,T^{-2}\quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

Sato [1939SAT] has measured the mean heat capacity of a sample whose composition was essentially equivalent to a mixture of Th_3N_4(cr) and ThO_2(cr) over three temperature ranges from 273.2 to 776.2 K. However as noted in Appendix A, it is not clear whether this was simply a mixture or a solid solution of these phases (and thus close to the composition of the oxynitride Th_2N_2O(cr)), and these data have not been considered further in the review.

Neumann *et al.* [1932NEU/KRO], [1934NEU/KRO] have reported two separate measurements of the enthalpy of formation of Th_3N_4(cr) – see Appendix A. The first, by combustion of thorium in nitrogen, gives $\Delta_f H^{\circ}_{\mathrm{m}}$($Th_3N_4$, cr, 298.15 K) = – (1306.3 ± 16.3) kJ·mol^{-1} (average of three experiments), while the second, by combustion of Th_3N_4(cr) in oxygen (one experiment only) gives $\Delta_f H^{\circ}_{\mathrm{m}}$($Th_3N_4$, cr, 298.15 K) = – (1308.1 ± 11.5) kJ·mol^{-1}. The selected value results from giving equal weight to each of the four individual measurements:

$$\Delta_f H^{\circ}_{\mathrm{m}}(\mathrm{Th_3N_4, cr, 298.15\ K}) = -(1306.8 \pm 15.0)\ \mathrm{kJ\cdot mol^{-1}}.$$

The measurements of the nitrogen dissociation pressure of Th_3N_4(cr) have been discussed in Section X.1.1.2, where they are used to calculate the enthalpy of formation of ThN(cr). The selected value for the Gibbs energy of formation is:

$$\Delta_f G_m^\circ(\text{Th}_3\text{N}_4, \text{cr}, 298.15\ \text{K}) = -(1200.1 \pm 15.7)\ \text{kJ·mol}^{-1}.$$

X.1.1.4 $Th_2N_2O(cr)$

The oxynitride Th_2N_2O(cr) is now well characterised [1966BEN/ZAC]; it is hexagonal, space group $R\bar{3}m$, with a = (3.8833 ± 0.0003) Å, c = (6.1870 ± 0.0003) Å. Juza and Gerke [1968JUZ/GER] give a = 3.880 Å, c = 6.180, in general agreement with the more precise results of [1966BEN/ZAC], although such a precision should require an explicit indication of the temperature.

Kusakabe and Imoto [1971KUS/IMO], [1972KUS/IMO] have measured nitrogen pressures in the 'Th_2N_2O', 'ThO_2', 'ThN' three-phase region from 1723 to 2258 K. However, mutual solubility among all these phases is appreciable at the higher temperatures. Benz [1967BEN] has suggested that there might be very considerable solubility between Th_2N_2O and Th_3N_4, although, subsequently [1972BEN], he showed that the mononitride phase in equilibrium with ThO_2 and Th_2N_2O contains rather little (< 0.02%) oxygen, even at 2000 K.

Moreover, combination of the nitrogen pressure measure by [1971KUS/IMO] for the reaction:

$$4\text{Th}_2\text{N}_2\text{O(cr)} \rightleftharpoons 6\text{ThN(cr)} + 2\text{ThO}_2\text{(cr)} + \text{N}_2\text{(g)} \qquad \text{(X.2)}$$

with the corresponding value for the Th_3N_4-ThN system, Reaction (X.1) gives for the all-solid reaction:

$$\text{Th}_3\text{N}_4\text{(cr)} + \text{ThO}_2\text{(cr)} \rightarrow 2\text{Th}_2\text{N}_2\text{O(cr)} \qquad \text{(X.3)}$$

$$[\Delta_r G_m]_{1723\,\text{K}}^{2258\,\text{K}}\ (\text{X.3}) = -162348 + 70.156\ T$$

This therefore corresponds to a highly negative entropy change for an all-solid reaction, and this in conjunction with the uncertainties in the formation of solid solutions in the solid phases, suggests that the reaction studied may not have been that given in (X.2), or there were other experimental errors in the study of this reaction. These data of [1971KUS/IMO] are therefore not considered further in this review.

Thus, no thermodynamic data for Th_2N_2O(cr) are selected.

X.1.2 Aqueous thorium azides

The only experimental study of chemical equilibria in the aqueous Th(IV)-azide system is a potentiometric investigation by Maggio *et al.* [1974MAG/ROM]. This investigation was made at 25°C in a 3.00 M $NaClO_4$ ionic medium, using potentiometric determination of the free hydrogen ion concentration. The equilibrium constants $\log_{10}\beta_1$ (X.4) = (3.09 ± 0.11) and $\log_{10}\beta_2$ (X.5) = (6.37 ± 0.08) refer to the following reactions:

$$\text{Th}^{4+} + \text{N}_3^- \rightleftharpoons \text{ThN}_3^{3+} \qquad \text{(X.4)}$$

$$\text{Th}^{4+} + 2\,\text{N}_3^- \rightleftharpoons \text{Th(N}_3)_2^{2+} \qquad \text{(X.5)}$$

These equilibrium constants were determined by a least-squares method and the uncertainty estimate is given at the 3σ level. All experimental details are given in the publication and these values have been selected by the present review. In a previous publication Maggio *et al.* [1967MAG/ROM] have determined the equilibrium constant for the protonation of $\mathrm{N_3^-}$ under the same conditions as in [1974MAG/ROM] and report $\log_{10} K$ (X.6) = 4.78 for the reaction:

$$\mathrm{H^+ + N_3^- \rightleftharpoons HN_3(aq)} \qquad \text{(X.6)}$$

There is no error estimate in [1967MAG/ROM] and the uncertainty has therefore been estimated by this review to be ±0.03. There are a large number of determinations of $\log_{10} K$ (X.6) at different ionic strength, which have been used to calculate $\log_{10} K^{\circ}$ (X.6) = (4.65 ± 0.03) and the ionic interaction parameter $\varepsilon(\mathrm{N_3^-},\mathrm{Na^+})$ = (0.015 ± 0.02) kg·mol^{-1}; the latter is the same as that estimated and selected in [2003GUI/FAN] but the uncertainty is five times smaller. The value of $\log_{10} K^{\circ}$ is within the estimated uncertainty the same as that selected in [2003GUI/FAN], $\log_{10} K^{\circ}$ (X.6) = (4.70 ± 0.08). This review has therefore not changed the previously selected value in [2003GUI/FAN]. Using the ion-interaction parameters selected in Appendix B and assuming $\varepsilon(\mathrm{ThN_3^{3+}},\mathrm{ClO_4^-})$ = (0.55 ± 0.15) kg·mol^{-1} and $\varepsilon(\mathrm{Th(N_3)_2^{2+}},\mathrm{ClO_4^-})$ = (0.40 ± 0.15) kg·mol^{-1}, this review has calculated the equilibrium constants at zero ionic strength:

$$\log_{10} \beta_1^{\circ}\ (\text{X.4}) = (4.44 \pm 0.64)$$

$$\log_{10} \beta_2^{\circ}\ (\text{X.5}) = (8.59 \pm 0.64)$$

where the uncertainty estimates also include the uncertainties in the interaction coefficients.

The selected Gibbs energy of formation calculated from the selected equilibrium constants and auxiliary data are:

$$\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{ThN_3^{3+}}, 298.15\ \mathrm{K}) = -(381.93 \pm 6.74)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{Th(N_3)_2^{2+}}, 298.15\ \mathrm{K}) = -(57.41 \pm 7.58)\ \mathrm{kJ\cdot mol^{-1}}.$$

There is no experimental information on the enthalpy and entropy of reaction for the species formed in the Th(IV)-azide system.

X.1.3 Thorium nitrates

X.1.3.1 Solid thorium tetranitrates, $\mathrm{Th(NO_3)_4(cr)}$

Pure anhydrous thorium nitrate is difficult to prepare. It is obtained by thermal decomposition of an adduct resulting from the interaction of the tetrahydrate with dinitrogen pentoxide in anhydrous nitric acid [1955FER/KAT]. Other preparative routes involving dinitrogen tetroxide have also been explored [1965SCH/KOE], [1984KUM/TUC].

The properties of this compound have not been extensively studied. Its enthalpy of solution (H_2O/Th molar ratio = 2500) was reported without details by Ferraro *et al.* [1956FER/KAT] to be −(145.2 ± 2.0) kJ·mol^{-1}, the uncertainty being estimated by this review.

As discussed in Appendix A, the dissolution reaction can be written as:

$$\begin{aligned}\mathrm{Th(NO_3)_4(cr)} + 2500\,\mathrm{H_2O(l)} \rightleftharpoons\ & 0.2387\,\mathrm{Th^{4+}} + 0.3370\,\mathrm{Th(NO_3)^{3+}}\\ & + 0.2384\,\mathrm{Th(NO_3)_2^{2+}} + 0.1730\,\mathrm{Th(OH)^{3+}}\\ & + 0.0079\,\mathrm{Th(OH)_2^{2+}} + 0.0024\,\mathrm{Th_2(OH)_3^{5+}}\\ & + 3.1861\,\mathrm{NO_3^-} + 0.1962\,\mathrm{H^+} \quad \text{in } 2499.8040\,\mathrm{H_2O(l)}\end{aligned}$$

As can be seen, the nitrate complexes are, in the main, the dominant thorium species in solution. As there are no experimental values for the enthalpy of formation of these complexes (neither for thorium nor for uranium), we will not attempt to use further the experimental results of [1956FER/KAT] which are given here for information only.

X.1.3.2 Thorium tetranitrate hydrates

Although various hydrates have been described in the literature, Ferraro *et al.* [1954FER/KAT] showed that only the penta- and tetrahydrate could be obtained from the $Th(NO_3)_4$-HNO_3-H_2O system. Brown, in the most recent Gmelin supplement [1987BRO], gives a ternary phase diagram for this system. $Th(NO_3)_4\cdot 5H_2O(cr)$ is the phase in equilibrium with the saturated solution at 298.15 K.

Both these hydrates have been studied crystallographically. The tetrahydrate is reported by Charpin *et al.* [1987CHA/CHE] to be monoclinic, space group $P2_1/n$, with a = (7.438 ± 0.001) Å, b = (17.530 ± 0.008) Å, c = (9.183 ± 0.001) Å, and β = (99.72 ± 0.01)° based on X-ray diffraction studies on single crystals. The pentahydrate is orthorhombic, space group *Fdd*2, and two groups of authors give lattice parameters in agreement: a = (11.182 ± 0.003) Å, b = (22.873 ± 0.005) Å, and c = (10.573 ± 0.003) Å, according to Ueki *et al.* [1966UEK/ZAL], from X-ray diffraction studies, and: a = (11.191 ± 0.007) Å, b = (22.889 ± 0.015) Å, and c = (10.579 ± 0.007) Å, according to Taylor *et al.* [1966TAY/MUE] from neutron diffraction data.

The enthalpy of solution of the tetrahydrate in 350H_2O was reported without details by Ferraro *et al.* [1956FER/KAT] as −(32.01 ± 1.70) kJ·mol^{-1}, the uncertainty being that estimated by this review.

The dissolution reaction can be written as:

$$\begin{aligned}\mathrm{Th(NO_3)_4\cdot 4H_2O(cr)} + 350\,\mathrm{H_2O(l)} \rightleftharpoons\ & 0.0284\,\mathrm{Th^{4+}} + 0.2050\,\mathrm{Th(NO_3)^{3+}}\\ & + 0.7426\,\mathrm{Th(NO_3)_2^{2+}} + 0.0223\,\mathrm{Th(OH)^{3+}}\\ & + 0.0011\,\mathrm{Th(OH)_2^{2+}} + 0.0003\,\mathrm{Th_2(OH)_3^{5+}}\\ & + 2.3098\,\mathrm{NO_3^-} + 0.0254\,\mathrm{H^+}\\ & \text{in } 353.9746\,\mathrm{H_2O(l)} \qquad (X.7)\end{aligned}$$

As in the case of the dissolution of the anhydrous thorium nitrate in water by the same authors, these results cannot be used as such for the determination of the enthalpy of formation of the compound, due to the lack of experimental data on the enthalpies of formation of the thorium nitrate complexes. This is also the case for the enthalpy of solution of the pentahydrate in water to reach the same final concentration, also given by the same authors as $\Delta_{\text{sol}}H^{\circ}_{\text{m}}$ ($Th(NO_3)_4{\cdot}5H_2O$, cr, 298.15 K) = $-(14.85 \pm 1.70)$ kJ·mol^{-1}. However, as discussed below, the difference between the enthalpies of solution of the pentahydrate and the tetrahydrate in the same medium, $-(17.16 \pm 2.40)$ kJ·mol^{-1}, reported by these authors has been used to obtain $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ ($Th(NO_3)_4{\cdot}4H_2O$, cr, 298.15 K).

Morss and McCue [1976MOR/MCC] measured the enthalpy of solution of high purity $Th(NO_3)_4{\cdot}5H_2O$(cr) in 0.01 M $HClO_4$ at 293.15, 298.15, and 308.15 K. At infinite dilution, and after a small correction for hydrolysis, the value $\Delta_{\text{sol}}H^{\circ}_{\text{m}}$ ($Th(NO_3)_4{\cdot}5H_2O$, cr , 298.15 K) = $-(19.807 \pm 0.250)$ kJ·mol^{-1}, was reported. The uncertainty in this value is estimated by the present review.

Use of $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (Th^{4+}, 298.15 K) = $-(768.7 \pm 2.3)$ kJ·mol^{-1}, $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (H_2O, l, 298.15 K) = $-(285.83 \pm 0.04)$ kJ·mol^{-1} and $\Delta_{\text{f}}H^{\circ}_{\text{m}}$($NO_3^-$, aq, 298.15 K) = $-(206.85 \pm 0.40)$ kJ·mol^{-1} leads to

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}\,(\text{Th(NO}_3)_4{\cdot}5\text{H}_2\text{O, cr, 298.15 K}) = -\,(3005.4 \pm 2.8)\ \text{kJ·mol}^{-1}$$

which is the selected value.

The enthalpy of formation of the tetrahydrate can be calculated from this value, together with the difference between the enthalpies of solution of the pentahydrate and the tetrahydrate in 350 mol H_2O by [1956FER/KAT], $-(17.16 \pm 0.40)$ kJ·mol^{-1}, and the partial molar enthalpy of formation of water in the resulting solution. There are insufficient data to calculate the latter precisely, but in such a dilute solution (*ca.* 0.15 m) it will differ very little from $\Delta_{\text{f}}H^{\circ}_{\text{m}}$ (H_2O, l, 298.15 K), so we have taken $\Delta_{\text{f}}H_{\text{m}}$($H_2O$, partial, 298.15 K) = $-(285.83 \pm 1.0)$ kJ·mol^{-1} with increased uncertainty limits. This gives

$$\Delta_{\text{f}}H^{\circ}_{\text{m}}\,(\text{Th(NO}_3)_4{\cdot}4\text{H}_2\text{O, cr, 298.15 K}) = -\,(2702.4 \pm 3.8)\ \text{kJ·mol}^{-1}$$

which is the selected value.

The heat capacity of the pentahydrate has been measured by Cheda *et al.* [1976CHE/WES]. Their results,

$$C^{\circ}_{p,\text{m}}\,(\text{Th(NO}_3)_4{\cdot}5\text{H}_2\text{O, cr, 298.15 K}) = (480.7 \pm 0.8)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

$$S^{\circ}_{\text{m}}\,(\text{Th(NO}_3)_4{\cdot}5\text{H}_2\text{O, cr, 298.15 K}) = (543.1 \pm 0.8)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

are selected in this review, but with increased uncertainty limits. The entropy of this compound has been used in this review for the evaluation of:

$$S^{\circ}_{m}(\mathrm{Th}^{4+}, 298.15\ \mathrm{K}) = -(423.1 \pm 16.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

– see Section VI.1.

The Gibbs energy of formation is calculated to be:

$$\Delta_{f}G^{\circ}_{m}(\mathrm{Th(NO_3)_4{\cdot}5H_2O, cr}, 298.15\ \mathrm{K}) = -(2322.7 \pm 2.8)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

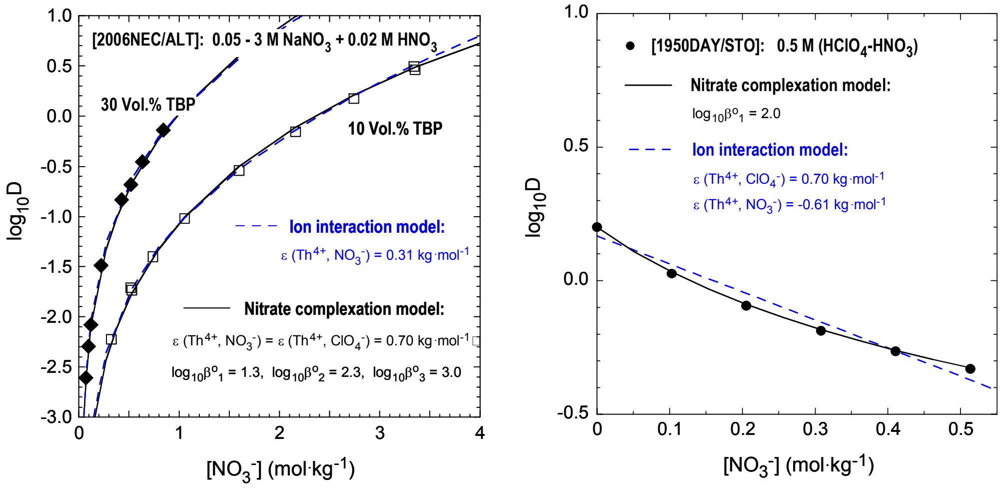
As mentioned in the discussion of the results of [1976MOR/MCC] in Section VI.1 and in Appendix A, the solubility of the pentahydrate in water at 298.15 K has been measured by Appelblatt *et al.* [1973APE/AZO] as 3.74 $\mathrm{mol{\cdot}kg^{-1}}$ and by [1976MOR/MCC] as 3.66 $\mathrm{mol{\cdot}kg^{-1}}$. As noted, the selected value is (3.7 ± 0.1) $\mathrm{mol{\cdot}kg^{-1}}$.

Vapour pressure measurements of thorium nitrate solutions have been reported by Robinson and Levien [1947ROB/LEV] and by Appelblatt *et al.* [1973APE/AZO2]. Enthalpies of dilution and vapour pressure data on thorium nitrate solutions have been correlated by Fricke [1929FRI2]. Lange and Miederer [1957LAN/MIE] have also reported enthalpies of dilution.

X.1.3.3 Aqueous thorium nitrates

The available information on chemical equilibria in the Th(IV)-nitrate system, [1950DAY/STO], [1951ZEB/ALT], [1956FOM/MAI], [1960DAN], [1968TED/RUM], [1976SOU/SHA] and [2006NEC/ALT] indicates that the complexes formed are weak and we have then the general problem already mentioned to decide if the systems should be treated using a complex formation or an ion-interaction model. For reasons given in the following text and in Appendix A for [2006NEC/ALT], only the equilibrium constants in that paper have been accepted by this review. As in the case of the chloride complexes, this review has re-evaluated the experimental TBP extraction study of [2006NEC/ALT] in aqueous nitrate media (0.05 – 3 M $\mathrm{NaNO_3}$ + 0.02 M $\mathrm{HNO_3}$) and the TTA extraction study of [1950DAY/STO] in 0.5 M $\mathrm{HClO_4}$-$\mathrm{HNO_3}$ and found that both approaches describe the experimental observations with about the same accuracy (Figure X-1). However, the value of $\varepsilon(\mathrm{Th}^{4+},\mathrm{NO}_3^-)$ calculated from the data of [1950DAY/STO] in 0.5 M $\mathrm{HClO_4}$-$\mathrm{HNO_3}$ is –0.61 $\mathrm{kg{\cdot}mol^{-1}}$. This review finds this value unlikely; such a large negative value would indicate the presence of strong ion-ion interactions, *cf.* the discussion on $\varepsilon(\mathrm{Th}^{4+},\mathrm{BrO}_3^-)$, and suggests that the data in [1950DAY/STO] are affected by unidentified systematic errors; these data have therefore not been accepted by the review. The value $\varepsilon(\mathrm{Th}^{4+},\mathrm{NO}_3^-) = -0.61\ \mathrm{kg{\cdot}mol^{-1}}$ is very different from $\varepsilon(\mathrm{Th}^{4+},\mathrm{NO}_3^-) = (0.31 \pm 0.12)\ \mathrm{kg{\cdot}mol^{-1}}$ determined by [2006NEC/ALT] in a study accepted by this review.

Figure X-1: Experimental distribution coefficients of Th(IV) in the TBP extraction study of [2006NEC/ALT] (aqueous phase: 0.05 − 3 M $NaNO_3$ + 0.02 M HNO_3, 22°C) and the TTA extraction study of [1950DAY/STO] (aqueous phase: 0.5 M $H(ClO_4\text{-}NO_3)$, 25°C) and data evaluation using both the ion interaction model (dashed lines) and the nitrate complexation model (solid lines).



To remain consistent with previous volumes in the series of "Chemical Thermodynamics", the present review continues to use the complex formation model. This choice has support from the results of large-angle X-ray diffraction studies of aqueous solution that clearly demonstrate chemical bonding of NO_3^- to Th(IV) in hydroxide complexes [1968JOH2] and [1991JOH/MAG]. Figure VII-4 shows the coordination around Th from a single crystal X-ray diffraction study of a basic thorium nitrate compound [1968JOH].

In the corresponding U(IV)-nitrate system one observes a change in the UV/Vis absorption spectrum of the U^{4+} ion on addition of nitrate, an observation that is difficult to reconcile with the ion-interaction model. As the chemistry of Th(IV) and U(IV) is very similar we have additional support for the complex formation model:

$$\mathrm{Th}^{4+} + n\,\mathrm{NO}_3^- \rightleftharpoons \mathrm{Th(NO_3)}_n^{4-n} \tag{X.8}$$

When using this model the interaction coefficient of Th^{4+} in nitrate solution is set equal to the value in non-complexing perchlorate solution $\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = \varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4^-) = (0.70 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$. The $\Delta\varepsilon_n$(X.8) values from the analogous reactions of U(IV), $\Delta\varepsilon(n = 1) = -(0.21 \pm 0.05)\ \mathrm{kg{\cdot}mol^{-1}}$ and $\Delta\varepsilon(n = 2) = -(0.41 \pm 0.13)\ \mathrm{kg{\cdot}mol^{-1}}$ in HNO_3 media and $\Delta\varepsilon(n = 1) = -(0.10 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$ and $\Delta\varepsilon(n = 2) = -(0.19 \pm 0.16)\ \mathrm{kg{\cdot}mol^{-1}}$ in $NaNO_3$ media [1992GRE/FUG], are used for ionic strength corrections. The experimental data in [1960DAN] have been obtained by measuring the distribution of trace amounts of Th(IV) between a nitrate loaded anion exchanger and test solutions with nitrate concentrations varying between 1.56 and 8.44 M. These data indicate the formation of an uncharged complex $\text{Th(NO}_3)_4\text{(aq)}$ and of anionic species $\text{Th(NO}_3)_5^-$ and $\text{Th(NO}_3)_6^-$ but the reported equilibrium constants are not accepted by this review for reasons given in Appendix A. The experimental data from [1968TED/RUM] have been obtained using cation exchange in a 2.00 M $\text{H}^+(\text{NO}_3^-, \text{ClO}_4^-)$ ionic medium; they report the formation of three nitrate complexes $\text{Th(NO}_3)_n^{4-n}$, $n = 1-3$. The experimental method and the analysis of the data seem satisfactory, but the reported values for the equilibrium constants seem too large, *cf.* Appendix A and have therefore not been accepted by this review. The data from [1976SOU/SHA] have also been obtained using cation exchange, but in test solutions where the ionic strength varies and are therefore not used by this review. Recalculation of the equilibrium constant from [1950DAY/STO], $\log_{10} \beta_1$ (X.8) = 0.67 at 25°C and an ionic strength of 0.50 M $\text{H(ClO}_4, \text{NO}_3)$, gives $\log_{10} \beta_1^\circ = 1.97$, significantly larger than the corresponding value for the formation of $\text{U(NO}_3)^{3+}$, $\log_{10} \beta_1^\circ = (1.47 \pm 0.13)$ that is based on several different experimental determinations. The stability of actinide complexes in a given oxidation state is in general smaller for thorium complexes than for other actinides; the value from [1950DAY/STO] is larger than that for U(IV), another reason why it is not accepted. The values recalculated from the study of [2006NEC/ALT], $\log_{10} \beta_1^\circ = (1.3 \pm 0.2)$ and $\log_{10} \beta_2^\circ = (2.3 \pm 0.4)$, in combination with $\log_{10} \beta_3^\circ = (3.0 \pm 0.5)$ derived with an estimated SIT coefficient of $\varepsilon(\text{Th(NO}_3)_3^+, \text{ClO}_4^-) = (0.25 \pm 0.15)\ \text{kg·mol}^{-1}$, are close to the corresponding values for the analogous U(IV) nitrate complexes (*cf.* Table X-1). In particular $\log_{10} \beta_1^\circ(\text{Th(NO}_3)^{3+})$ fits well into the series of the formation constants selected in previous NEA-TDB reviews for the nitrate complexes of tetravalent actinides; $\log_{10} \beta^\circ$ values of analogous complexes usually increase from Th(IV) to Pu(IV).

Table X-1: Formation constants of An(IV) nitrate complexes at $I = 0$ and 25°C.

An(IV)	$\log_{10} \beta_1^\circ$	$\log_{10} \beta_2^\circ$	$\log_{10} \beta_3^\circ$	Reference
Th(IV)	1.97 (a)			Recalculated from [1950DAY/STO]
	1.67 ± 0.84	2.25 ± 1.34		Recalculated from [1951ZEB/ALT]
	2.19 ± 0.38 (a)	3.41 ± 0.46 (a)	3.64 ± 0.41 (a)	Recalculated from [1956FOM/MAI]
	2.59 ± 0.37 (a)	3.83 ± 0.49 (a)	3.74 ± 0.50 (a)	Recalculated from [1968TED/RUM]
	1.3 ± 0.2	2.3 ± 0.4	3.0 ± 0.5	Recalculated from [2006NEC/ALT]
U(IV)	1.47 ± 0.13	2.30 ± 0.35	(b)	[1992GRE/FUG]
Np(IV)	1.90 ± 0.15			[2001LEM/FUG]
Pu(IV)	1.95 ± 0.15			[2001LEM/FUG]

a: Not accepted by this review.

b: The evidence for the formation of $\text{U(NO}_3)_3^+$ at higher nitrate concentration was discussed in [1992GRE/FUG] but the reported literature values of $\log_{10} \beta_3$ in 2.0−3.5 M $\text{H(ClO}_4\text{-NO}_3)$ were not accepted.

Using liquid-liquid extraction with TTA as extractant, Zebroski *et al.* [1951ZEB/ALT] derived formation constants of β_1 = 2.83 M^{-1} and β_2 = 1.91 M^{-2} in a 5.97 M $Na(NO_3,ClO_4)$ ionic medium with nitrate concentrations up to 4.93 M. Because of the high ionic strength (I_m = 8.4 $mol\cdot kg^{-1}$) the values extrapolated to I = 0 with the SIT have very large uncertainties (*cf.* Table X-1). Fomin and Maiorova [1956FOM/MAI] suggest the formation of the complexes $Th(NO_3)_n^{4-n}$, n = $1-4$, in 2.00 M $H(NO_3,ClO_4)$, with a chemical model based on only five different nitrate concentrations. However, the liquid-liquid two-phase system used by [1956FOM/MAI] (Th extraction with TBP from aqueous $HClO_4$-HNO_3 mixtures) is not appropriate for studying the thorium nitrate complexation because the composition of the thorium complexes extracted into the organic phase varies with the ClO_4^- / NO_3^- ratio in the aqueous phase. The calculated formation constants are considerably overestimated. Using the value of $\log_{10} \beta_1$ = (0.78 ± 0.04) calculated in [1956FOM/MAI] and the SIT with $\Delta\varepsilon(n = 1) = -0.21$ $kg\cdot mol^{-1}$ this review obtains $\log_{10} \beta_1^{\circ} = 2.19$, which differs considerably from the corresponding values for other actinides, *cf.* Table X-1. This review has therefore not accepted the equilibrium constants proposed by Fomin and Maiorova. Peppard *et al.* [1962PEP/NAM] have made a detailed study of extraction equilibria in the toluene-Th(IV)-Cl^-- NO_3^- system. However, there is no quantitative information on complex formation equilibria with nitrate.

Despite the few experimental data for the Th(IV)-nitrate system, this review has selected the equilibrium constants:

$$\log_{10} \beta_1^{\circ} = (1.3 \pm 0.2)$$

$$\log_{10} \beta_2^{\circ} = (2.3 \pm 0.4)$$

based on the data from [2006NEC/ALT] as described in Appendix A. This choice is supported by the good agreement with the corresponding data for the U(IV)-nitrate system.

It has to be emphasised that these equilibrium constants must not be combined with $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)$ $kg\cdot mol^{-1}$ used in the Sections VII.3 and VIII.1.2 on aqueous thorium hydroxide and fluoride complexes; this value refers to a strict ion interaction approach where the effect of nitrate complexation is included in the interaction coefficient. The equilibrium constants for the formation of nitrate complexes must be combined with $\varepsilon(Th^{4+}, NO_3^-) = \varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)$ $kg\cdot mol^{-1}$, $\varepsilon(Th(NO_3)^{3+}, NO_3^-) = \varepsilon(Th(NO_3)^{3+}, ClO_4^-) = (0.56 \pm 0.14)$ $kg\cdot mol^{-1}$, $\varepsilon(Th(NO_3)_2^{2+}, NO_3^-) = \varepsilon(Th(NO_3)_2^{2+}, ClO_4^-) = (0.43 \pm 0.18)$ $kg\cdot mol^{-1}$, and $\varepsilon(Th(NO_3)_3^{+}, NO_3^-) = \varepsilon(Th(NO_3)_3^{+}, ClO_4^-) = (0.25 \pm 0.15)$ $kg\cdot mol^{-1}$. The selected equilibrium constants yield:

$$\Delta_f G_m^{\circ}(Th(NO_3)^{3+}, 298.15\ K) = -(823.0 \pm 5.4)\ kJ\cdot mol^{-1}$$

$$\Delta_f G_m^{\circ}(Th(NO_3)_2^{2+}, 298.15\ K) = -(939.5 \pm 5.8)\ kJ\cdot mol^{-1}.$$

X.1.4 Thorium nitrite complexes

There are no experimental studies reported of Th(IV) nitrite complexes in aqueous solution, only an investigation in methanol [1968GOL/KAL] that reports the formation of the ternary complexes $Th(OMe)_2NO_2^+$, $Th(OMe)_2(NO_2)_2$ and $Th(OMe)_2(NO_2)_3^-$ and their equilibrium constants. However, this information cannot be used to make estimates of the composition and equilibrium constants of nitrite complexes in aqueous solution. As the nitrite ion is a much stronger base than nitrate ion, one may however expect the Th(IV) nitrite complexes to be stronger than the corresponding nitrate complexes.

X.2 Phosphorus compounds and complexes

X.2.1 Solid and gaseous thorium phosphides

There are only two solid thorium phosphides, ThP(cr) and Th_3P_4(cr), and little thermodynamic information is available on either of these.

X.2.1.1 Thorium monophosphide ThP(cr)

ThP(cr) has the fcc NaCl structure, isomorphous with most of the lower actinide MX(cr) compounds, (X = N, S, P). It was initially thought to have a considerable range of homogeneity [1965GIN/WIL], but in a detailed study of the Th-ThP subsystem, Javorsky and Benz [1967JAV/BEN] showed that the lower phase boundary is at *ca.* $ThP_{0.98}$ over most of its range of stability. The upper phase boundary has still not been established.

The lattice parameter of the stoichiometric phase was found to be (5.833 ± 0.001) Å after long anneals at 1523 and 1073 K [1967JAV/BEN]. These authors also determined the (congruent) melting point of (3263 ± 60) K, slightly higher than the ‘apparent’ melting point in helium gas given by Baskin [1969BAS], 3173 K, but the latter author was unable to determine whether this was the true melting point, or the temperature of a eutectic with the tungsten container. The higher value is preferred.

Maurice *et al.* [1979MAU/BOU] have measured the heat capacity of ThP(cr) from 2 to 15 K, but there are no other heat capacity data above this temperature. Rand [1975RAN] estimated the entropy of ThP(cr) by a comparison of the entropies of thorium and uranium compounds of nitrogen, sulphur and phosphorus, as S°_m (ThP, cr, 298.15 K) = (70.3 ± 4.2) $J\cdot K^{-1}\cdot mol^{-1}$. The corresponding enthalpy of formation was calculated by the same author from the combined measurements of the emf study by [1966GIN/ARO] and the mass spectrometric study by [1963GIN/EFI] as $\Delta_f H^\circ_m$ (ThP, cr, 298.15 K) = (347 ± 42) $kJ\cdot mol^{-1}$. As noted below and in Appendix A, there are some doubts about the validity of the data obtained in the latter study, and these values are given for information only.

X.2.1.2 Gaseous thorium phosphide ThP(g)

Gingerich [1968GIN], [1969GIN2] has made two mass-spectrometric determinations of the pressures of ThP(g) existing over Th-B-P alloys at four temperatures between 2702 and 2804 K and gave partial pressures of the species in the three equilibria:

$$\mathrm{ThP(g)} \rightleftharpoons \mathrm{Th(g)} + \mathrm{P(g)}$$

$$\mathrm{ThP(g)} \rightleftharpoons \mathrm{Th(g)} + 0.5\mathrm{P_2(g)}$$

$$\mathrm{ThP(g)} + \mathrm{P(g)} \rightleftharpoons \mathrm{Th(g)} + \mathrm{P_2(g)}$$

Gingerich [1969GIN] further estimated molecular parameters for ThP(g) by established spectroscopic approximations. We have repeated these calculations, using these estimates, and used third-law calculations to derive average values of $\Delta_f H_m^\circ$ (ThP, g, 298.15 K) = (537 ± 8), (551 ± 8), and (547 ± 6) kJ·mol^{-1} from the three reactions, with S_m° (ThP, g, 298.15 K) = (276.6 ± 10.0) J·K^{-1}·mol^{-1}. The auxiliary data for P(g) and P_2(g) were taken from Table IV-1 and [1989COX/WAG]. This indicates a value of $\Delta_f H_m^\circ$ (ThP, g, 298.15 K) = (545 ± 30) kJ·mol^{-1}, where the increased uncertainty includes those in the experimentation and the estimates of the thermal functions for ThP(g). This value shows that ThP(g) is always a quite minor species in the vaporisation of ThP, and in view of this and the paucity of the experimental data, the above values are given for information only, as for ThN(g).

X.2.1.3 Th_3P_4(cr)

Th_3P_4(cr) has a bcc structure, space group $I\bar{4}3d$, isomorphous with many of the actinide compounds with the same stoichiometry, except the nitrides. Indeed, it was the first of the group of compounds with this structure to be characterised. The lattice parameter of Th_3P_4 determined by various authors from samples obtained by various procedures involving direct reaction of the elements or of their hydrides varies over a range of 0.05 Å [1983WED]. We will only cite here the most precise result of Price and Warren [1965PRI/WAR] who report a = (8.6530 ± 0.0005) Å, for samples obtained from high purity analysed thorium metal.

Rand [1975RAN] estimated the entropy and enthalpy of formation of Th_3P_4(cr) with that of the monophosphide (see Section X.2.1.1) as S_m° (Th_3P_4, cr, 298.15 K) = (246.8 ± 12.6) J·K^{-1}·mol^{-1} and $\Delta_f H_m^\circ$ (Th_3P_4, cr, 298.15 K) = (1146 ± 126) kJ·mol^{-1}. As noted immediately below and in Appendix A, there are some doubts about the validity of some of the data employed and these values are given for information only.

There are two complementary measurements of the thorium and phosphorus potentials in this system. Gingerich and Efimenko [1963GIN/EFI] have measured mass-spectrometrically the pressures of the phosphorus species over thorium phosphides from $ThP_{0.63}$(cr) to $ThP_{1.27}$(cr) in the range 1131 to 2243 K, while Gingerich and Aronson [1966GIN/ARO] have measured the thorium activities in the {Th(cr) (saturated with P) + ThP_{1-x}(cr) and {ThP_{1+x}(cr) + Th_3P_4(cr)} diphasic regions from 1073 to 1223 K using solid-state electrochemical cells with a CaF_2(cr) electrolyte. However, as noted in Appendix A, there are several indications that equilibrium was not attained in the mass-spectrometric study [1963GIN/EFI], even at the highest temperatures, and these data are not used in this review.

Gingerich and Aronson [1966GIN/ARO] employed two cells:

(I) Th, $ThF_4|CaF_2|ThF_4$, Th, $ThP_{0.55}$ and

(II) Th, $ThF_4|CaF_2|ThF_4$, ThP, Th_3P_4.

The emf of the first cell relates to the activity of thorium in the P-saturated metal, and is of no immediate interest to the review. The ThP samples contained up to 2 mol% oxygen, so these results presumably refer to oxygen-saturated ThP(cr). More details are given in Appendix A.

The standard deviation of the emf cell (II) at the mid-temperature was estimated to be as much as 11.4 mV, since there were noticeable differences in the emf for mixtures with P/Th ratios of 1.21, 1.15 and 1.01, particularly the last. This may be due to non-stoichiometry in ‘ThP’, or the greater effect of oxygen contamination near the stoichiometric composition of the monophosphide, or to slow attainment of equilibrium.

The detailed results are not reported, but for cell (II), the authors calculated the Gibbs energy of the cell reaction:

$$4\text{ThP(cr)} \rightleftharpoons \text{Th}_3\text{P}_4\text{(cr)} + \text{Th(cr)} \qquad \text{(X.9)}$$

to be

$$[\Delta_r G_m]_{1073\,\text{K}}^{1223\,\text{K}}((\text{X.9}), T) = -(224700 \pm 23400) + (38.9 \pm 31.0)\, T \quad \text{J}\cdot\text{mol}^{-1}$$

where the uncertainties are twice those quoted by the authors.

In the absence of any other selected thermodynamic data for the thorium phosphides, no further processing of these results can be attempted.

X.2.2 Solid thorium hypophosphites and phosphites

Many thorium hypophosphites, phosphites, their hydrates and related compounds with monovalent cations (usually K^+) have been mentioned in the literature (see the Gmelin review by Bickel [1993BIC]), but the information available is essentially limited to preparation procedures, analysis, vibrational spectra and some DTA studies. X-ray structures have not been reported and, in fact, many of these compounds are amorphous to X-rays. Since no thermodynamic data relevant to this review have been reported, these compounds are not considered further.

X.2.3 Thorium phosphate compounds and complexes

X.2.3.1 Solid thorium phosphates

On the basis of X-ray diffraction and thermogravimetric data, Burdese and Borlera [1963BUR/BOR] presented a phase diagram for the system P_2O_5-ThO_2, in which they identified five compounds: $Th(PO_3)_4$, ThP_2O_7, $Th_3(PO_4)_4$, $(ThO)_2P_2O_7$, and $(ThO)_3(PO_4)_2$. Structural information (see Table X-2) are given for the first three compounds but not for the oxysalts $(ThO)_2P_2O_7$, and $(ThO)_3(PO_4)_2$ which are reported to form above 1423 K.

Table X-2: Structural data for thorium phosphates.

Phase	Symmetry	Space Group	Lattice parameters (Å)	Reference
α-$Th(PO_3)_4$ (< 1023 K)	orthorhombic		$a = 14.35$ $b = 15.11$ $c = 9.05$	[1963BUR/BOR]
			$a = 6.947 \pm 0.004$ $b = 15.120 \pm 0.020$ $c = 9.069 \pm 0.007$	[1972MAS/GRE][a]
$Th(PO_3)_4$	tetragonal		$a = 11.440 \pm 0.010$ $c = 14.978 \pm 0.020$	[1972MAS/GRE]
$Th(PO_3)_4$	triclinic		$a = 15.51 \pm 0.015$ $b = 8.251 \pm 0.007$ $c = 8.796 \pm 0.008$ $\alpha = 117.80 \pm 0.70°$ $\beta = 112.32 \pm 0.50°$ $\gamma = 89.14 \pm 0.05°$	[1972MAS/GRE][b]
$Th_3(PO_4)_4$	monoclinic		$a = 10.55$ $b = 10.66$ $c = 8.80$ $\beta = 106.68°$	[1963BUR/BOR]
α-ThP_2O_7 (< 1083 K)	cubic		$a = 8.721 \pm 0.006$	[1963BUR/BOR2]
β-ThP_2O_7 (> 1083 K)	orthorhombic		$a = 11.620 \pm 0.007$ $b = 12.80 \pm 0.01$ $c = 7.121 \pm 0.004$	[1963BUR/BOR2][c]
$Th_4(PO_4)_4P_2O_7$	orthorhombic	*Pcam*	$a = 12.8646 \pm 0.0009$ $b = 10.4374 \pm 0.0008$ $c = 7.0676 \pm 0.0005$	[1996BEN/BRA]

a: Apparent cell, based on extended exposures; the authors propose also a real cell with doubled *a* and *b* parameters.

b: Primitive cell with 4 $Th(PO_3)_4$ units deduced for an A-face-centred cell with 8 formula units.

c: Values in agreement with the less precise values reported by the same authors in [1963BUR/BOR].

For the metaphosphate $Th(PO_3)_4$, Burdese and Borlera [1963BUR/BOR] indicate an orthorhombic structure stable up to 1023 K. However, for the same compound, Masse and Grenier [1972MAS/GRE] (see Table X-2) found three structures (orthorhombic, tetragonal and monoclinic), in three different crystals selected from the same preparation, but with no indication of the temperature range in which they are stable. The lattice parameters reported by [1972MAS/GRE] for the orthorhombic structure do not correspond to those given by [1963BUR/BOR]. Masse and Grenier [1972MAS/GRE] also indicate an alternative method of preparation of the monoclinic form. The structure of thorium orthophosphate, $Th_3(PO_4)_4$ was characterised as monoclinic by [1963BUR/BOR].

More recently, in the framework of broad studies on the potentialities of phosphate matrices for radioactive waste storage, different compounds ($Th_2(PO_4)_2{\cdot}HPO_4{\cdot}H_2O$; $ThOHPO_4$; and Th-phosphates containing F, SO_4, Cs, or Ba) have been synthesised from aqueous solutions ([2000THO/DAC], [2001BRA/DAC2], [2002BRA/DAC]). Since no thermodynamic data relevant to the review have been reported, these compounds are not considered further. Also, in this context of radioactive waste disposal, Bénard *et al.* [1996BEN/BRA] characterised $Th_4(PO_4)_4P_2O_7$, thorium phosphate diphosphate (TPD), the synthesis of which has been summarised in [2001BRA/DAC]. The TPD structure was determined by [1996BEN/BRA] as orthorhombic, space group *Pcam*, from powder and single crystal X-ray diffraction (see Table X-2). Infra-red spectroscopy measurements confirmed the presence of P_2O_7 entities in the compound. This result and further studies by the same group, in particular in [1998BRA/DAC], led the authors to cast doubt about the conditions of preparation and identification of various phosphates and related compounds (including $Th_3(PO_4)_4$) described in the earlier literature. The thermal diffusivity, thermal conductivity and specific heat of TPD were reported by Dacheux *et al.* [2002DAC/CHA] between room temperature and 1273 K.

The equation for the fit to C_p in the text of [2002DAC/CHA] seems to be in error, and we have refitted their results for the specific heat to the relation:

$$C_p = 0.46262 + 6.94205\times10^{-5}\,T - 1.2367\times10^{-10}\,T^2 - 9402.0\,T^{-2}\ (\mathrm{J{\cdot}K^{-1}{\cdot}g^{-1}})$$

which for a molecular weight of 1505.981 corresponds to the molar heat capacity equation:

$$[C^{\circ}_{p,\mathrm{m}}]^{1273\mathrm{K}}_{298.15\mathrm{K}} = 696.70 + 0.10455\,T - 1.8625\times10^{-7}\,T^2 - 1.4159\times10^{7}\,T^{-2}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

The calculated value of the heat capacity at 298.15 K is thus

$$C^{\circ}_{p,\mathrm{m}}\,(\mathrm{Th_4(PO_4)_4P_2O_7, cr, 298.15\ K}) = (569 \pm 15)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

which is the selected value, with an uncertainty estimated by the review.

The only thermochemical values on the phosphate compounds reported above have been deduced from solubility measurements and are discussed in the Section X.2.3.2.

X.2.3.1.1 Solid thorium phosphate hydrates

The preparation and a number of properties of numerous hydrates of thorium phosphate and of acid and basic phosphates, as well as some of their properties, have been described in the literature – see the review in the Gmelin Handbook [1993BIC], which also includes a survey of ternary phosphates (and their hydrates) with a number of cations. Some of these compounds have been studied in relation with the determination of phosphate complexes in solution and are discussed in the relevant Section X.2.3.2.

X.2.3.1.2 Solid thorium hypophosphate

The compound $ThP_2O_6 \cdot 11H_2O$ was reported more than a century ago [1899KAU]. It has subsequently attracted attention for its low solubility in moderately concentrated hydrochloric acid and was recommended for removing thorium from its admixtures with the rare earth elements ([1948MOE/SCH] and references therein). The water content appears quite dependent of the mode of preparation; for instance, [1953MOE/QUI] report a mode of preparation leading to the dihydrate which, although not gelatinous like the more hydrated species, still appears non-crystalline by X-ray diffraction. Moeller and Quinty [1952MOE/QUI] describe the synthesis of $ThP_2O_6(s)$ with an unspecified water content and determined its solubility in 1 – 6 M hydrochloric acid ($[Th] = 2.5 \times 10^{-5}$ M in 1 M HCl), demonstrating that this solid phase is sparingly soluble. There are no other thermodynamic data reported for this compound.

X.2.3.2 Aqueous complexes with phosphate ions

The chemical reactions in the aqueous Th(IV)-phosphate system have been investigated experimentally using liquid-liquid distribution and solubility measurements; in addition there are a number of qualitative studies that do not provide thermodynamic data. The most precise studies have been made using liquid-liquid distribution; Zebrovski *et al.* [1951ZEB/ALT] using thenoyltrifluoroacetone (TTA) and Elyaoui *et al.* [1990ELY/BRI] using di(2-ethylhexyl)phosphoric acid (HDEHP) as extracting ligands. The first study [1951ZEB/ALT] was made at a constant ionic strength of 2.00 M $(Na,H)ClO_4$ in test solutions at four different and constant hydrogen ion concentrations, 0.25, 0.50, 1.00 and 2.00 M that allowed a proper determination of the stoichiometry of the ternary complexes $ThH_p(PO_4)_q^{(4+p-3q)}$. The latter study [1990ELY/BRI] was made at an ionic strength of 0.200 M in the pH range 0.7 – 3.5 and at phosphoric acid concentrations up to 1.0 M. Elyaoui *et al.* used “electrostatic considerations” to suggest the stoichiometry listed in Table X-3. The proposed stoichiometry of the complexes is very different from those proposed in [1951ZEB/ALT] and the constants of [1990ELY/BRI] have not been accepted by this review.

Table X-3: Equilibrium constants for complexes formed in the Th(IV)-phosphate system at 25°C and an ionic strength of 0.20 M from [1990ELY/BRI]. The first column contains the stoichiometry as deduced from the experimental liquid-liquid distribution data and the last column the stoichiometry proposed using electrostatic considerations. H_{-n} denotes the number of protons formed in the reaction, but not their origin.

Experimental stoichiometry of the complexes in [1990ELY/BRI]	Equilibrium constant, $\log_{10} K$	Proposed stoichiometry of the complexes in [1990ELY/BRI]
$ThH_{-2}(H_3PO_4)^{2+}$	5.22 ± 0.04	$Th(OH)(H_2PO_4)^{2+}$
$ThH_{-3}(H_3PO_4)^{+}$	3.62 ± 0.04	$Th(OH)_2(H_2PO_4)^{+}$
$ThH_{-1}(H_3PO_4)^{3+}$	5.65 ± 0.05	$Th(H_2PO_4)^{3+}$
$ThH_{-3}(H_3PO_4)_2^{+}$	4.70 ± 0.04	$Th(OH)(H_2PO_4)_2^{+}$
$ThH_{-4}(H_3PO_4)_3(aq)$	2.90 ± 0.04	$Th(OH)(H_2PO_4)_3(aq)$
$ThH_{-3}(H_3PO_4)_4(aq)$	3.86 ± 0.04	$Th(H_2PO_4)_4(aq)$
$ThH_{-7}(H_3PO_4)_5^{3-}$	-3.65 ± 0.13	$Th(OH)_2(H_2PO_4)_5^{3-}$ or $Th(H_2PO_4)_3(HPO_4)_2^{3-}$

Quantitative solubility experiments have been described in [1956CHU/STE], [1967MOS/ESS], [1994BAG/FOU], [1995OST], [1999FOU/LAG] and [2001THO/DAC]. Moeller *et al.* [1948MOE/SCH] describe the use of phosphate precipitation as an analytical method for the determination of thorium and Matijević and Milić [1963MAT/MIL] describe the use of phosphate to obtain information on colloid precipitation.

Chukhlantsev and Stepanov [1956CHU/STE], measured the solubility of what they claimed were the solid phases $Th_3(PO_4)_4(s)$ and $Th(HPO_4)_2(s)$; the composition of the first phase has been questioned [1996BEN/BRA], [1998BRA/DAC], see Section X.2.3.1. The solubilities were measured as a function of pH in nitric and sulphuric acid solutions in the pH range 1.80−2.45; Chukhlantsev and Stepanov noticed a difference in solubility between the two media but made no attempt to analyse the data in terms of a chemical model. They report a solubility product $\log_{10} K_{s,0} = -(79.2 \pm 0.8)$ in nitric acid and $\log_{10} K_{s,0} = -(78 \pm 1)$ in sulphuric acid for the reaction:

$$Th_3(PO_4)_4(s) \rightleftharpoons 3Th^{4+} + 4PO_4^{3-}.$$

Chukhlantsev and Stepanov found $\log_{10} K_{s,0} = -57.6$ for ^{234}Th-doped $Th_3(PO_4)_4(s)$ and suggest that the difference between this value and the other two determinations is due to the formation of $Th_3(OH)_3(PO_4)_3(s)$ but no evidence for this is presented. For reasons given in Appendix A these values have not been accepted by the present review. It can be noted that these values differ significantly from that proposed in [1994BAG/FOU], $\log_{10} K^{\circ}_{s,0} = -(112 \pm 2.1)$.

The equilibrium constant reported by [1956CHU/STE] for the reaction:

$$\mathrm{Th(HPO_4)_2(s, hyd)} \rightleftharpoons \mathrm{Th^{4+}} + 2\mathrm{HPO_4^{2-}}$$

was $\log_{10} K_{s,0} = -(26.6 \pm 0.2)$ in nitric acid and $\log_{10} K_{s,0} = -(20.9 \pm 0.4)$ in sulphuric acid. When the experiments were repeated using a Th-tracer marked solid, a solubility product of $\log_{10} K_{s,0} = -19.9$, with an unknown uncertainty, was obtained; it is not clear from the paper if these experiments have been made in nitric or sulphuric acid. These values are not accepted by this review. Moskvin *et al.* [1967MOS/ESS] have also determined the solubility product for $Th(HPO_4)_2{\cdot}4H_2O(s)$, but have taken the formation of phosphate complexes into account; their reported solubility product is $\log_{10} K_{s,0} = -26.89$.

Moskvin *et al.* [1967MOS/ESS] have reported equilibrium constants, $\log_{10} \beta_n$, for the reactions:

$$\mathrm{Th^{4+}} + n\,\mathrm{HPO_4^{2-}} \rightleftharpoons \mathrm{Th(HPO_4)_n^{4-2n}} \qquad n = 1-3$$

from solubility measurements using $Th(HPO_4)_2{\cdot}4H_2O(s)$. The experiments were made in 0.35 M $HClO_4$ by varying the phosphoric acid concentration from 0.1 mM to 1.5 M, but under these conditions it is not possible to determine the proton content of the complexes formed. The equilibrium constants $\log_{10} \beta_1 = 10.6$, $\log_{10} \beta_2 = 22.6$ and $\log_{10} \beta_3 = 31.3$, reported by Moskvin *et al.*, are conditional constants for species that contain 1, 2 and 3 coordinated phosphate groups, but where the proton stoichiometry is unknown. At the high acidity used in [1967MOS/ESS], one expects the formation of complexes containing H_3PO_4 and $H_2PO_4^-$ as ligands as shown in [1951ZEB/ALT]. As these species have not been considered by Moskvin *et al.*, their chemical model is not correct, and the proposed equilibrium constants have not been accepted by this review. The solubility product for $Th(HPO_4)_2{\cdot}4H_2O(s)$, $\log_{10} K_{s,0} = -26.89$, is considerably smaller than the value $\log_{10} K_{s,0} = -21$ (-19.9 for the experiments using a ^{234}Th tracer) proposed in [1956CHU/STE]. In view of the shortcomings indicated above this review has not selected any of the equilibrium constants proposed by Moskvin *et al.*

Baglan *et al.* [1994BAG/FOU] determined the solubility of $Th_3(PO_4)_4(s)$ in 0.01 − 1 M perchloric acid (the ionic strength was not constant) at room temperature. They calculated $[Th^{4+}]$ from the measured total concentration by using the known hydrolysis constants; the concentration of phosphate is so low that phosphate complexes can be neglected. The solubility product at zero ionic strength was calculated using estimates of the activity coefficients of the participating ions, but the procedure is not detailed in the paper. Baglan *et al.* report:

$$\log_{10} K^{\circ}_{s,0} = -(112.0 \pm 2.1)$$

for the reaction: $\mathrm{Th_3(PO_4)_4(s)} \rightleftharpoons 3\mathrm{Th^{4+}} + 4\mathrm{PO_4^{3-}}$

This value, assumed to apply to 298.15 K, has therefore not been selected by this review, but may be used for scoping calculations.

Fourest *et al.* [1999FOU/LAG] have prepared and carefully characterised the solid $Th_4(PO_4)_4P_2O_7(s)$ and subsequently measured its solubility in the pH range 0 to 10.5; the temperature was 25°C and the ionic medium 0.1 M $NaClO_4$. The analysis of the experimental data is in the view of this review ambiguous (Appendix A) and the information provided does not allow selection of equilibrium constants.

In two more recent studies [2006DAC/CLA] and [2006CLA/FOU], the Orsay group has studied the rate of dissolution of β-$Th_{4-x}U_x(PO_4)_4(P_2O_7)$ but there are no thermodynamic data in these studies.

Östhols [1995OST] studied the solubility of microcrystalline $ThO_2(cr)$ in the pH range 5 − 13 in the presence of 0.01 and 0.1 M phosphate. He noticed that the solubility $s = 10^{-6.4}$ M, in the pH range 5 − 10, was close to that predicted using published hydrolysis constants and solubility products. A small increase in solubility was noticed in the presence of 0.1 M phosphate in the pH range 10.5 − 13. There is no information on equilibrium constants for phosphate complexes in this study, but it may be noted that the phosphate complexes are so weak that the hydroxide complexes are dominant under the experimental conditions used. He also suggests that the influence of phosphate on the solubility of Th(IV) in most natural water systems will not be significant; the present review accepts these conclusions.

Thomas *et al.* [2001THO/DAC] studied the rate of dissolution of solid solutions of U(IV) and Th(IV) phosphate phases. The paper proposes a reaction mechanism and also gives extensive information on phase characterisation. Of particular interest is the solid $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ for which the authors report a solubility product at zero ionic strength, $\log_{10} K^{\circ}_{s,0} = -(66.6 \pm 1.2)$ with a reference to a forthcoming publication; as this is not available to the present review, this solubility product is not accepted.

Zebroski *et al.* [1951ZEB/ALT] have made the most extensive study of the complex formation in the Th(IV)-phosphate system and the only one that can be used to determine the stoichiometry of the complexes formed. The experiments have been made at trace levels of Th(IV) using liquid-liquid extraction at 25°C and an ionic strength of 2.00 M $(Na,H)ClO_4$. The authors report equilibrium constants for the reactions:

$$Th^{4+} + H_3PO_4 \rightleftharpoons Th(H_3PO_4)^{4+} \qquad (X.10)$$

$$\log_{10} \beta\,(X.10) = 1.89$$

$$Th^{4+} + H_3PO_4 \rightleftharpoons Th(H_2PO_4)^{3+} + H^+ \qquad (X.11)$$

$$\log_{10} {}^*\beta\,(X.11) = 2.18$$

$$Th^{4+} + 2H_3PO_4 \rightleftharpoons Th(H_2PO_4)(H_3PO_4)^{3+} + H^+ \qquad (X.12)$$

$$\log_{10} {}^*\beta\,(X.12) = 4.15$$

$$Th^{4+} + 2H_3PO_4 \rightleftharpoons Th(H_2PO_4)_2^{2+} + 2H^+ \qquad (X.13)$$

$$\log_{10} {}^*\beta\,(X.13) = 3.90.$$

There are no uncertainty estimates in [1951ZEB/ALT]. This review has no access to the primary experimental data, but finds no reason to question the quality of this study and has accordingly selected the equilibrium constants proposed by Zebroski *et al.* The stabilities of other actinide(IV) phosphates of similar composition are not known, except for the formation of the corresponding $Pu(H_3PO_4)^{4+}$ complex, $\log_{10} \beta^\circ$ (X.10) has a similar value of (2.4 ± 0.3) [2003GUI/FAN]. We note also that the stoichiometries of the selected complexes are the same as those for the uranyl(VI)-phosphate system and there is a reasonable linear correlation between the $\log_{10} \beta^\circ$ values (the equilibrium constants for the reactions $M + (n)L \rightleftharpoons ML(n)$, not the reported $\log_{10} {}^*\beta^\circ$ values) for $M = UO_2^{2+}$ and $M = Th^{4+}$.

The experimental data of Elyahyaoui *et al.* [1990ELY/BRI] are precise, *cf.* Table X-3, but for reasons given above and in Appendix A the proposed equilibrium constants have not been selected by this review.

From the data of Zebroski *et al.* [1951ZEB/ALT] and assuming the following ion interaction coefficients $\varepsilon(Th^{4+}, ClO_4^-) = \varepsilon(Th(H_3PO_4)^{4+}, ClO_4^-) = (0.70 \pm 0.10)$ kg·mol^{-1}; $\varepsilon(Th(H_2PO_4)^{3+}, ClO_4^-) = \varepsilon(Th(H_2PO_4)(H_3PO_4)^{3+}, ClO_4^-) = \varepsilon(M^{3+}, ClO_4^-) \cong (0.5 \pm 0.1)$ kg·mol^{-1}; $\varepsilon(Th(H_2PO_4)_2^{2+}, ClO_4^-) = \varepsilon(M^{2+}, ClO_4^-) \cong (0.4 \pm 0.1)$ kg·mol^{-1}, and $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1}, we find the following equilibrium constants and Gibbs energies of reaction at 25°C and zero ionic strength:

$$\log_{10} \beta^\circ (X.10) = (1.89 \pm 0.31) \qquad \Delta_r G_m^\circ = -(10.79 \pm 1.77)\ \text{kJ·mol}^{-1}$$

$$\log_{10} {}^*\beta^\circ (X.11) = (3.45 \pm 0.32) \qquad \Delta_r G_m^\circ = -(19.69 \pm 1.83)\ \text{kJ·mol}^{-1}$$

$$\log_{10} {}^*\beta^\circ (X.12) = (5.42 \pm 0.32) \qquad \Delta_r G_m^\circ = -(30.94 \pm 1.83)\ \text{kJ·mol}^{-1}$$

$$\log_{10} {}^*\beta^\circ (X.13) = (6.20 \pm 0.32) \qquad \Delta_r G_m^\circ = -(35.39 \pm 1.83)\ \text{kJ·mol}^{-1}$$

The corresponding standard molar Gibbs energies of formation, calculated using these constants and $\Delta_f G_m^\circ (Th^{4+}, 298.15\ K) = -(704.8 \pm 5.3)$ kJ·mol^{-1} selected by this review are:

$$\Delta_f G_m^\circ (Th(H_3PO_4)^{4+}, 298.15\ K) = -(1864.9 \pm 5.8)\ \text{kJ·mol}^{-1}$$

$$\Delta_f G_m^\circ (Th(H_2PO_4)^{3+}, 298.15\ K) = -(1873.8 \pm 5.8)\ \text{kJ·mol}^{-1}$$

$$\Delta_f G_m^\circ (Th(H_2PO_4)(H_3PO_4)^{3+}, 298.15\ K) = -(3034.5 \pm 6.4)\ \text{kJ·mol}^{-1}$$

$$\Delta_f G_m^\circ (Th(H_2PO_4)_2^{2+}, 298.15\ K) = -(3038.9 \pm 6.4)\ \text{kJ·mol}^{-1}$$

There is no information on the enthalpy and entropy of reaction in the Th(IV)-phosphate system.

X.2.3.3 Other aqueous thorium phosphate species

Filinov *et al.* [1960FIL/TEK] studied the solubility of $ThP_2O_7(s)$ in 0.0237−0.204 M $Na_4P_2O_7$ solutions and found that the solubility decreased from 0.0205 to 0.0077 M. The paper contains no information of the pH and no thermodynamic data can therefore be deduced. In solutions of sulphuric, nitric and hydrochloric acid the solubility of $ThP_2O_7(s)$ increased linearly with $[H^+]$ but the experimental data are only given in figures and can therefore not be analysed by the present review. The authors suggest an equilibrium constant of $\log_{10} K$ (X.14) = (5.25 ± 0.17) for the stepwise reaction:

$$ThP_2O_7(aq) + P_2O_7^{4-} \rightleftharpoons Th(P_2O_7)_2^{4-} \qquad (X.14)$$

There is no justification in [1960FIL/TEK] for the stoichiometry and the equilibrium constant is therefore not accepted by this review. The only conclusion to be drawn from this study is qualitative, that complexes are formed in the Th(IV)-pyrophosphate system.

Merkusheva *et al.* [1967MER/SKO] determined the solubility of $ThP_2O_7(s)$ at 25°C in a 0.1 M (Na, H)ClO_4 ionic medium by varying the concentration of H^+ in the various test solutions between 100 and 5 mM and measuring the corresponding concentrations. They report the following equilibrium constants: $\log_{10} K_{s,0}$ (X.15) = − (24.25 ± 0.02) and $\log_{10} \beta_1$ (X.16) = (18.0 ± 0.2) for the reactions

$$ThP_2O_7(s) \rightleftharpoons Th^{4+} + P_2O_7^{4-} \qquad (X.15)$$

and

$$Th^{4+} + P_2O_7^{4-} \rightleftharpoons ThP_2O_7(aq) \qquad (X.16)$$

where the uncertainties are those given by the authors; however, the details of the procedure used to deduce them is not clear. The equilibrium constants depend on the auxiliary data used and the dissociation constants of pyrophosphoric acid used differ substantially from those selected in the present review. In addition the authors have not tested other equilibrium models than the one proposed; in particular they have not considered the possible formation of ternary complexes $ThH_p(P_2O_7)_q$ (charge omitted for simplicity). The stepwise equilibrium constant for Reaction (X.14), $\log_{10} K$ = 5.25, seems unexpectedly small compared to the equilibrium constant for Reaction (X.16), $\log_{10} K$ = 18.0; for these reasons this review has not accepted the proposed equilibrium constants.

Dissolution of $Th_2(PO_4)(P_2O_7)$ and solid solutions of $(Th,Pu)_2(PO_4)(P_2O_7)$ have been studied by [2002ROB/DAC], but no information on thermodynamic data is given. The dissolution of monazite in carbonate media is discussed in [2002ABD], but here also there is no thermodynamic information.

X.3 Solid thorium arsenides

The phase diagram of the Th-As system is still quite poorly defined, except for the Th-rich region, which was studied in detail by Benz [1968BEN]. There are three compounds, whose compositions and structures are given in Table X-4. The diarsenide has two forms, with a transformation temperature of *ca.* 1373 K [1966HUL2].

The only studies of thermodynamic data for thorium arsenides are the measurements of the heat capacities of ThAs(cr) and $Th_3As_4(cr)$ from 5 to 300 K by

[1980BLA/TRO] and [1980BLA/LAG], see Appendix A. The derived values of the entropy and heat capacity are the selected values:

$$S^{\circ}_{\mathrm{m}}\,(\mathrm{ThAs, cr, 298.15\ K}) = (79.8 \pm 0.5)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$C^{\circ}_{p,\mathrm{m}}\,(\mathrm{ThAs, cr, 298.15\ K}) = (50.5 \pm 0.5)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$S^{\circ}_{\mathrm{m}}\,(\mathrm{Th_3As_4, cr, 298.15\ K}) = (274.6 \pm 1.5)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$
$$C^{\circ}_{p,\mathrm{m}}\,(\mathrm{Th_3As_4, cr, 298.15\ K}) = (183.3 \pm 1.5)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

where the uncertainties are estimated by the review.

Table X-4: Structural data for thorium arsenides.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)	Reference
ThAs	fcc, $Fm\bar{3}m$	NaCl	$a = 5.972$	[1955FER]
			$a = 5.976 \pm 0.001$	[1968BEN]
			$a = 5.976 \pm 0.001$	[1980BLA/TRO]
Th_3As_4	bcc, $I\bar{4}3d$	Th_3P_4	$a = 8.843$	[1955FER]
			$a = 8.945 \pm 0.005^*$	[1980BLA/LAG]
α-$ThAs_2$	orthorhombic	$PbCl_2$	$a = 7.287 \pm 0.003$	
< *ca.* 1473 K	*Pnma*		$b = 4.002 \pm 0.002$	[1966HUL2]
			$c = 9.784 \pm 0.004$	
β-$ThAs_2$	tetragonal	Cu_2Sb	$a = 4.086$	[1955FER]
> *ca.* 1473 K	*P4/nmm*		$c = 8.575$	

* No clear explanation can be given for the large difference between this value and that from [1955FER], unless there is a printing error. A value of (8.845 ± 0.005) Å would bring the lattice parameter from [1980BLA/LAG] in more reasonable agreement with the value given by [1955FER] and with their own value for the lattice parameter of U_3As_4(cr), (8.528 ± 0.005) Å.

X.4 Solid thorium antimonides

The phase diagram of the Th-Sb system has not been studied systematically. According to Ferro [1956FER], who carried out an X-ray investigation of phases prepared by from the elements at *ca.* 1273 K, there are three compounds, whose compositions and structures are given in Table X-5.

Table X-5: Structural data for thorium antimonides.

Phase	Symmetry, space group	Structural type	Lattice parameters (Å)	Reference
ThSb	fcc, $Fm\bar{3}m$	NaCl	$a = 6.318$	[1956FER]
Th_3Sb_4	bcc, $I\bar{4}3d$	Th_3P_4	$a = 9.372$	[1956FER]
$ThSb_2$	Tetragonal, *P4/nmm*	Cu_2Sb	$a = 4.353$	[1956FER]
			$c = 9.172$	

The only thermodynamic data for this system are those reported by Kadochnikov *et al.* [1974KAD/POY], who measured the emf of the cell:

$$\text{Th} \mid \text{KCl-NaCl-3 wt\%ThCl}_x \mid \mid \text{KCl-NaCl-3 wt\%ThCl}_4 \mid \text{Sb-Th(l)} + \text{ThSb}_2\text{(cr)}$$

from 939 to 1093 K. From these data, the thorium potential in the diphasic region {Sb(l) + $ThSb_2$(cr)} is given by

$$\Delta_{\mathrm{f}} G_{\mathrm{m}}\,(\mathrm{Th}) = -319173 + 77.574\,T \;\;(\mathrm{J{\cdot}mol^{-1}}).$$

These data cannot be processed further without an assumption regarding the activity of antimony in the saturated Th-Sb liquid. With the very small solubilities of Th in Sb(l), also measured by [1974KAD/POY], $\log_{10} x_{\mathrm{Th}} = -6820/T + 4.07$, (giving x_{Th} = 0.0074 at 1100 K) the activity of Sb will be very little different from the ideal value, and hence the Gibbs energy of formation of $ThSb_2$(cr) can be calculated to be:

$$[\Delta_{\mathrm{f}} G^{\mathrm{o}}_{\mathrm{m}}]^{1093\mathrm{K}}_{939\mathrm{K}}\,(\mathrm{ThSb_2, cr}, T) = -3183400 + 76.76\,T \;\;(\mathrm{J{\cdot}mol^{-1}}),$$

where the standard state for Sb is Sb(l), and these values are selected.

X.5 Solid thorium bismuthides

X.5.1 Phase diagram and structures

The phase diagram of the Th-Bi system is still rather ill-defined. The most recent study by [1982BOR/BOR2] (who give a tentative phase diagram) indicates the existence of four compounds, whose compositions and structures are given in Table X-6. However, these authors note that the ThBi(cr) may be metastable, and that the Th_5Bi_3(cr) phase may be stabilised by minor impurities, like some other phases with this structure. Dahlke *et al.* [1969DAH/GAN] reported the possible existence of a phase more thorium-rich than Th_5Bi_3(cr), but this has not been confirmed by subsequent workers – see also Appendix A for further comments on the study by [1969DAH/GAN]. The solubility of thorium in Bi(l) was assessed by [1981CHI/AKH] from six separate studies up to 1974 to be given by the expression:

$$\log_{10} x_{\mathrm{Th}} = -3618/T + 1.513 \qquad (688-1373\ \mathrm{K})$$

where x_{Th} is the mole fraction of thorium in the melt.

Table X-6: Structural data for thorium bismuthides.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)	Reference
Th_5Bi_3	hexagonal, $P6_3/mcm$	Mn_5Si_3	$a = 9.590$ $c = 6.623$	[1982BOR/BOR2]
ThBi	bcc, $Pm\bar{3}m$	CsCl	$a = 3.909$	[1982BOR/BOR2]
Th_3Bi_4	bcc, $I\bar{4}3d$	Th_3P_4	$a = 9.559$ $a = 9.562$	[1975FER], [1982BOR/BOR2]
$ThBi_2$	Tetragonal, $P4/nmm$	Cu_2Sb	$a = 4.492$ $c = 9.298$	[1975FER]
			$a = 4.495$ $c = 9.308$	[1982BOR/BOR2]

X.5.2 Thermodynamic data

X.5.2.1 Enthalpy of formation

Borzone *et al.* [1982BOR/BOR2] have reported measurements of the enthalpy of formation at *ca.* 300 K of 13 Th-Bi alloys ranging from $Th_{0.2}Bi_{0.8}$ to $Th_{0.75}Bi_{0.25}$. An isoperibol aneroid calorimeter was used to measure the reaction enthalpy by direct combination of the elements. Reaction was incomplete in the measurements of five further alloys. The resulting enthalpies of formation were consistent with the formation of the four compounds given in Table X-7 and the following values for their enthalpies of formation were derived:

$$\Delta_f H_m^\circ(\mathrm{Th_5Bi_3, cr, 298.15\ K}) = -(532.2 \pm 16.7)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{ThBi, cr, 298.15\ K}) = -(162.3 \pm 4.2)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{Th_3Bi_4, cr, 298.15\ K}) = -(597.5 \pm 14.6)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{ThBi_2, cr, 298.15\ K}) = -(207.1 \pm 6.3)\ \mathrm{kJ \cdot mol^{-1}}$$

and these are the selected values. The small difference in the temperature of measurement and 298.15 K has been ignored.

The general trend of the enthalpies of formation of these compounds appears similar to that observed for compounds of uranium [1968KUB] and a number of lanthanides [1980BOR/BOR] with arsenic, antimony, and bismuth; more generally, these trends are also in satisfactory agreement with those deduced from the model of Miedema *et al.* [1977MIE/BOE].

X.5.2.2 Gibbs energies

There are three sets of measurements of the thorium–bismuth system: two relatively consistent emf studies around 1000 K, and a Knudsen study which is more difficult to interpret. Wiswall and Egan [1963WIS/EGA] have reported thorium activities in unsaturated solutions in bismuth, measured in an emf cell involving $ThCl_4$ dissolved in

LiCl-KCl eutectic. They found that at 1073 K the excess Gibbs energy of solution of thorium was constant from x_{Th} = 0.00135 to 0.0080, and hence for the dissolution α-Th = $[\mathrm{Th}]_{\mathrm{Bi}}$, $\Delta_{\mathrm{sln}}G_{\mathrm{m}}$ (Th, 1073 K) = −118000 + 20542·$\log_{10}x_{\mathrm{Th}}$ (J·mol^{-1}), with an uncertainty estimated by this review to be ± 3000 J·mol^{-1}. Poyarkov *et al.* [1974POY/LEB] made similar measurements (but using NaCl-KCl(l) as the solvent) in the two-phase region {liquid bismuth + compound} from 953 to 1093 K. They suggested that the phase in equilibrium with Bi(l) was Th_3Bi_4(cr), but the more recent work by [1982BOR/BOR2] indicates that $ThBi_2$(cr) is stable up to *ca.* 1500 K and the data of [1974POY/LEB] have been assumed to refer to the partial Gibbs energy of thorium in the {Bi(l) + $ThBi_2$(cr)} phase field: $\Delta_{\mathrm{sln}}G_{\mathrm{m}}$ (Th) = −224220 + 67.78 T (J·mol^{-1}), with an uncertainty estimated by the review to be ± 3500 J·mol^{-1}. If it is assumed that the constant excess Gibbs energy of solution of thorium measured by [1963WIS/EGA] at 1073 K can be extrapolated to the phase boundary, calculated to be at x_{Th} = (0.0138 ± 0.0050) from the solubility equation assessed by [1981CHI/AKH] noted above, then $\Delta_{\mathrm{sln}}G_{\mathrm{m}}$ (Th, 1073 K) = −(156.2 ± 4.1) kJ·mol^{-1}. This is in reasonable agreement with the value of − (151.5 ± 3.0) kJ·mol^{-1} given by the study of [1974POY/LEB]. All the uncertainties in these calculations are estimated by the review. The data of [1974POY/LEB] can be used to calculate the Gibbs energy of formation of $ThBi_2$(cr) around 1000 K. With the low solubility of thorium, the chemical potential of bismuth in the melt will be close to the ideal value and $\Delta_{\mathrm{f}}G_{\mathrm{m}}$ ($ThBi_2$, cr) (from Bi(l)) in the temperature range of the study by [1974POY/LEB] is calculated to be:

$$[\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}]^{1100\mathrm{K}}_{950\mathrm{K}}(\mathrm{ThBi_2, cr}, T) = -222900 + 66.3\,T \quad \mathrm{J\cdot mol^{-1}}.$$

After allowing for the enthalpy of fusion of Bi(cr) (11.3 ± 0.4) kJ·mol^{-1} [1994LAN] the derived enthalpy of formation in this temperature range is thus consistent with that measured at *ca.* 300 K by [1982BOR/BOR2], − (207.1 ± 6.3) kJ·mol^{-1}, discussed above, although the entropy change is numerically quite large (*ca.* −(25.5 J·K–1·mol–1 from Bi(cr)).

The thermodynamic properties of the Th-Bi system have also been studied by Dahlke *et al.* [1969DAH/GAN]. These authors measured the total effusion pressures of (essentially) Bi(g) + Bi_2(g) over a number of phase fields in this system (from 884 to 1759 K, depending on the phase field). The pressures, and the composition of the effusing sample, were inferred from weight losses; X-ray diffraction studies were made on a number of quenched samples. As noted in detail in Appendix A, their pressure measurements are not in accord with other published phase diagrams; in particular, no discontinuity in the pressures was observed at the composition Th_5Bi_3. Moreover, Dahlke *et al.* [1969DAH/GAN] found evidence for the formation of a thorium-rich phase with a composition around Th_3Bi(cr), but this phase has not been observed in any other studies. They also indicated that the monobismuthide phase has a considerable range of homogeneity, from $ThBi_{0.8}$ to $ThBi_{1.08}$, for which there is no independent evidence. There is also a more severe problem in their calculation of the individual Bi(g) and Bi_2(g) from the effusion rate, since the equation they used for the dimerisation reaction was not appropriate at higher temperatures. Their results have thus been completely recalculated from the published raw data, as described in Appendix A. The revised Gibbs energies of solution of bismuth in the various diphasic fields are given in Table X-7.

The melt in equilibrium with the most thorium-rich phase contains an unknown amount of bismuth at the temperatures involved (1690 − 1760 K), so even with corrected bismuth pressures, it is impossible to use these vaporisation data alone to calculate Gibbs energies of formation of the intermediate compounds. However, combination of the bismuth potential in the diphasic field {Th_3Bi_4(cr) + $ThBi_2$(cr)} with the Gibbs energy of formation of $ThBi_2$(cr) in a similar temperature range measured by Poyarkov *at al.* [1974POY/LEB], provides an estimate of $\Delta_f G_m$ (Th_3Bi_4, cr) in the temperature range 950 – 1150 K:

$$[\Delta_f G^o_m]^{1100\text{K}}_{950\text{K}} (\text{Th}_3\text{Bi}_4, \text{cr}, T) = -605440 + 176.43\ T \quad \text{J·mol}^{-1}$$

In principle, this could be extended to the remaining phase fields, but owing to uncertain phase boundaries of ThBi(cr), and discrepancies with the phase diagram, this is not thought to be a meaningful proposition.

Table X-7: Bismuth potentials in the diphasic field in the Th-Bi system.

Phase field	$\Delta_{sln}G_m$ (Bi) (J·K^{-1}·mol^{-1})	Temperature range (K)
(Th,Bi)(l) + Th_3Bi(cr)	−237850 + 29.30 T	1691 − 1759
Th_3Bi(cr) + $ThBi_{1-x}$(cr)	− 147218 + 15.60 T	1474 − 1723
$ThBi_{1+x}$(cr) + Th_3Bi_4(cr)	− 144119 + 54.35 T	1126 − 1433
Th_3Bi_4(cr) + $ThBi_2$(cr)	− 31631 + 11.233 T	951 − 1165
$ThBi_2$(cr) + (Bi,Th)(l)	− 188 + 0.636 T	916 − 1073

XI Thorium Group 14 compounds and complexes

XI.1 Carbon compounds and complexes

XI.1.1 Solid thorium carbides

There have been two extensive reviews of the thermodynamics of the Th-C system by [1975RAN], [1984HOL/RAN], since which there has been little work on these compounds. Our treatment therefore lends fairly heavily on the latter review, with a few updates and corrections as appropriate.

There is a large corpus of data on the phase relationships and stability of the thorium carbides. Unfortunately, much of this information is conflicting, and it is still not possible to give many precise values for the thermodynamic properties of the carbides. These discrepancies may be due in part to the great difficulty encountered in preventing oxygen contamination of these materials.

XI.1.1.1 Phase diagram

There is little new information to add to the review of the somewhat conflicting information on the phase relationships given by [1984HOL/RAN], which gives the preferred phase diagram, the essential points of which are summarised below.

There are only two carbides stable at 1 bar pressure, the “monocarbide”, which has a wide range of homogeneity, even at low temperatures, and a “dicarbide” whose range of homogeneity is less certain. For neither carbide does the range of homogeneity include the stoichiometric ratio. A somewhat unusual feature of the system is that the miscibility gaps between the face-centred cubic of Th(cr) and “ThC”(cr) and between the “ThC(cr)” and “ThC_2(cr)” both close at high temperatures to form a single face-centred cubic phase, so that, by changing the temperature, it is possible to pass continuously from Th(cr, fcc) to ThC_2(cr, fcc).

In addition to these two carbides, Krupka [1970KRU] showed that the sesquicarbide is easily formed from a mixture of “ThC” and “ThC_2” heated to 1473 K at the relatively low pressure of 30 kbar. It has a body-centred cubic structure space group *I4/3d,* Pu_2C_3-type, isomorphous with the sesquicarbides of uranium, neptunium and plutonium with $a = (8.556 \pm 0.005)$ Å. The relative ease of formation of this phase suggests that the Gibbs energy of the decomposition reaction $Th_2C_3(cr) \rightleftharpoons ThC(cr) + ThC_2(cr)$ is only just positive at 1 bar pressure.

XI.1.1.2 Thorium monocarbide ThC_{1-x}(cr)

Thorium monocarbide has the NaCl face-centred cubic structure, space group $Fm\bar{3}m$, isomorphous with most of the actinide MX compounds. The limits of composition are still not well-defined, but up to *ca.* 1300 K probably extend from $ThC_{0.67}$(cr) to $ThC_{0.97}$(cr), the lattice parameter at room temperature varying from (5.303 ± 0.002) to (5.346 ± 0.002) Å, see [1984HOL/RAN]. As noted earlier, at higher temperatures the phase forms a continuous solid solution with both Th(cr) and "ThC_2"(cr). A more detailed literature account of the crystal structures of the thorium carbides is given by Kleykamp in his review of the general properties of thorium carbides for the Gmelin Handbook [1992KLE].

Low-temperature heat capacities have been measured by Harness *et al.* [1964HAR/MAT] from 1.8 to 4.2 K (uncharacterised sample), by Maurice *et al.* [1979MAU/BOU] from 2 to 15 K ($ThC_{0.75}$) and by Danan [1975DAN] from 2 to 300 K. The first two studies are mentioned for information only. Danan used two samples: one of overall composition $ThC_{0.965}N_{0.015}O_{0.020}$, which was used over the whole temperature range, and a second sample containing more oxygen (unspecified in [1975DAN], but *ca.* 2% ThO_2 according to [1984HOL/RAN]). The latter sample was certainly studied from 2 to 10 K, to confirm the low temperature data; it is not clear if any measurements at higher temperatures were made with this sample. Danan makes no mention of correction for the impurities in either sample, but merely attributes his given heat capacity and derived thermal functions to ThC(cr). For the moment we shall take these results to apply to the most carbon-rich composition of the monocarbide, giving (S°_{m} ($ThC_{0.97}$, cr, 298.15 K) − S_{m} ($ThC_{0.97}$, cr, 0 K)) = (58.0 ± 0.8) $J{\cdot}K^{-1}{\cdot}mol^{-1}$.

A randomisation entropy corresponding to $-R\,(0.97\ln 0.97 + 0.03\ln 0.03)$ gives S_{m} ($ThC_{0.97}$, cr, 0 K) = (1.1 ± 0.5) $J{\cdot}K^{-1}{\cdot}mol^{-1}$ and thus

$$S^{\circ}_{m}\,(\mathrm{ThC_{0.97}, cr, 298.15\ K}) = (59.1 \pm 0.9)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

which with

$$C^{\circ}_{p,m}\,(\mathrm{ThC_{0.97}, cr, 298.15\ K}) = (45.2 \pm 0.4)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

are the selected values. The uncertainty in the randomisation entropy takes account of the possibility that near the upper phase boundary, the ThC_{1-x} phase may contain some C_2 groups as well as carbon vacancies, and the uncertainty in the composition.

The high-temperature heat capacity of the monocarbide has not been measured, but following [1984HOL/RAN], has been estimated from that of UC and the low-temperature heat capacities:

$$[C^{\circ}_{p,m}]^{2270\mathrm{K}}_{298.15\mathrm{K}}\,(\mathrm{ThC_{0.97}, cr}, T) = 46.02 + 25.52\times10^{-3}\,T - 18.83\times10^{-6}\,T^{2} + 5.44\times10^{-9}\,T^{3} - 6.28\times10^{5}\,T^{-2}\ \ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

This has been refitted to three equations consistent with the NEA formalism, the lowest range of which is

$$[C^{\circ}_{p,m}]^{1000\mathrm{K}}_{298.15\mathrm{K}}\,(\mathrm{ThC_{0.97}, cr}, T) = 50.067 + 1.27868\times10^{-2}\,T - 4.40301\times10^{-6}\,T^{2} - 7.3671\times10^{5}\,T^{-2}\ \ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

These data are mentioned for information only.

There have been two studies of the enthalpies of combustion of thorium monocarbides, by Huber *et al.* [1968HUB/HOL2] and Lorenzelli *et al.* [1971LOR/DIE], in both cases with a number of samples of different compositions. As it is apparent from the discussion of the papers in Appendix A, there is excellent agreement on the enthalpy of formation near the $ThC_{1.00}$ composition since [1968HUB/HOL2] give $\Delta_f H^\circ_m$ ($ThC_{1.00}$, cr, 298.15 K) = $-(123.8 \pm 4.6)$ kJ·mol^{-1} and [1971LOR/DIE] $\Delta_f H^\circ_m$ ($ThC_{1.01}$, cr, 298.15 K) = $-(126.4 \pm 10.5)$ kJ·mol^{-1}. However, at other compositions the values of [1968HUB/HOL2] are consistently more negative than those of Lorenzelli *et al.*, even allowing for an uncertainty of 0.02 in the C/Th ratios.

Since the upper phase boundary of 'ThC' at 298.15 K is taken to be $ThC_{0.97}$, very small (for [1968HUB/HOL2], negligible) corrections have been made for the presence of the small amount of $ThC_{1.94}$(cr) presumably present in these samples, to give $\Delta_f H^\circ_m$ ($ThC_{0.97}$, cr, 298.15 K) = $-(123.8 \pm 4.6)$ kJ·mol^{-1} [1968HUB/HOL2] and $-(126.5 \pm 10.5)$ kJ·mol^{-1} [1971LOR/DIE]. The selected value is the weighted mean, with an increased uncertainty:

$$\Delta_f H^\circ_m (ThC_{0.97}, cr, 298.15\ K) = -(124.2 \pm 6.3)\ kJ\cdot mol^{-1}.$$

Both investigations show that the enthalpy of formation decreases very sharply in magnitude across the homogeneity range to *ca.* $-(40$ to $70)$ kJ·mol^{-1} at the thorium-rich phase boundary. For further details see the entries in Appendix A.

Holley *et al.* [1984HOL/RAN] give a detailed discussion of the two emf studies of the thorium potential in the single-phase ThC_{1-x}(cr), by Aronson and Sadofsky [1965ARO/SAD] (1073 to 1223 K) and by Satow [1967SAT2], (from 1000 to 1223 K), using the cell $ThC_{1-x} + ThF_4|CaF_2\ |ThF_4 + Th$, which are outside the scope of the present review, as are the higher temperature measurements by [1989YAM/KOY] from 2060 to 2330 K, using mass-spectrometric Knudsen effusion.

Aronson and Sadofsky [1965ARO/SAD] and Satow [1967SAT2] also measured the thorium potentials on the $ThC_{0.97}$ (cr)–$ThC_{1.94}$(cr) diphasic region, from the emf of the cell $ThC_{0.97} + ThC_{1.94} + ThF_4|CaF_2\ |ThF_4 + Th$, but in view of the uncertainties in the thermal functions of $ThC_{0.97}$(cr), these data have not been used by this review.

The selected value for Gibbs energy of formation is:

$$\Delta_f G^\circ_m (ThC_{0.97}, cr, 298.15\ K) = -(124.5 \pm 6.3)\ kJ\cdot mol^{-1}.$$

XI.1.1.3 Thorium dicarbide

XI.1.1.3.1 Standard entropy, heat capacity and enthalpy of formation

Thorium dicarbide has three polymorphs. Because of their range of homogeneity, unique transformation temperatures cannot be given; those quoted below are for the phase in equilibrium with carbon. The low temperature form, stable below (1690 ± 40) K, is monoclinic, space group *C2/c* (CuO type) with $a = (6.692 \pm 0.003)$, $b = (4.223 \pm 0.003)$, $c = (6.744 \pm 0.003)$ Å, $\beta = (103.12 \pm 0.11)°$ [1968BOW/KRI] at room temperature, as determined by neutron diffraction. These results confirmed the lattice parameters and space group established earlier by Hunt and Rundle

[1951HUN/RUN] by X-ray and neutron diffraction The second form, stable over the short temperature range from (1690 ± 40) to (1763 ± 45) K is tetragonal, space group *I4/mmm* (CaC_2 type). The parameters (at 1723 K) vary from a = (4.221 ± 0.003), c = (5.394 ± 0.003) Å for the carbon-poor boundary to a = (4.165 ± 0.003), c = (5.420 ± 0.003) Å at the carbon-rich boundary [1976PIA/ZAU]. The form stable at higher temperatures has the cubic fluorite structure, space group $Fm\bar{3}m$, with the a parameter varying from (5.70 ± 0.01) to (5.806 ± 0.005) Å at 1823 K [1968BOW/KRI]. More detailed structural data on the three dicarbide polymorphs can be found in [1992KLE].

The limits of composition of these phases are still not well-defined; the significant variation in parameters observed by [1968BOW/KRI] and [1976PIA/ZAU] and others in the tetragonal β and cubic γ high temperature phases, suggests an appreciable range of composition in these polymorphs (as does the difference in the β–γ transition temperature for carbon-poor and carbon-rich samples). However there are a number of studies [1969SEA/KEG] [1971BEN/BAL] which suggest that the monoclinic α-phase has a negligible range of homogeneity below *ca.* 1573 K with the composition $ThC_{1.94}$ [1969BEN/STO].

Takahashi *et al.* [1965TAK/WES2] and Westrum *et al.* [1965WES/TAK2] have measured the low-temperature heat capacities of two samples of the dicarbide, with compositions of $ThC_{1.98}$(cr) and $ThC_{1.93}$(cr) respectively. The former sample probably contained some free carbon, but the consistent values of (S°_{m} (298.15 K) − S_{m} (0 K)) of (68.6 ± 0.3) $J\cdot K^{-1}\cdot mol^{-1}$ from the two studies has been taken to refer to the $ThC_{1.94}$(cr) composition. The assumption that this phase contains randomly mixed C and C_2 groups then gives a randomisation entropy of S_{m} ($ThC_{1.94}$, cr, 0 K) = (1.9 ± 0.3) $J\cdot K^{-1}\cdot mol^{-1}$, to give:

$$S^{\circ}_{m}(\mathrm{ThC_{1.94}, cr, 298.15\ K}) = (70.5 \pm 0.4)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

which with

$$C^{\circ}_{p,m}(\mathrm{ThC_{1.94}, cr, 298.15\ K}) = (56.8 \pm 0.2)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

are the selected values, where the uncertainties have been increased to allow for uncertainties in the compositions.

No high-temperature heat capacities have been measured, but Westrum *et al.* [1965WES/TAK2] estimated $C_{p,m}$ of the dicarbide by the procedure suggested by Krikorian [1962KRI] for estimating the heat capacity of carbides, to provide the following equation:

$$[C_{p,m}]^{1700\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThC_{1.94}, cr}, T) = 63.5 + 12.09 \times 10^{-3}\ T - 9.25 \times 10^{5}\ T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

Holley *et al.* [1984HOL/RAN] give another (five-parameter) estimate by comparison specifically with uranium dicarbide (which has a pronounced upward curvature in the heat capacity at high temperatures). For convenience, their equation has been refitted to two extended Kelley equations to conform to NEA usage

$$[C_{p,\mathrm{m}}]^{900\mathrm{K}}_{298.15\mathrm{K}}(\mathrm{ThC}_{1.94}, \mathrm{cr}, T) = 61.00 + 2.62460 \times 10^{-2}\, T \\ - 7.978 \times 10^{-6}\, T^2 - 1.0031 \times 10^{6}\, T^{-2}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$[C_{p,\mathrm{m}}]^{1700\mathrm{K}}_{900\mathrm{K}}(\mathrm{ThC}_{1.94}, \mathrm{cr}, T) = 194.418 - 1.5869 \times 10^{-1}\, T + 6.5061 \times 10^{-6}\, T^2 \\ - 2.2169 \times 10^{7}\, T^{-2}\quad \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

These equations have been used in the analysis of the Gibbs energy data, but are not selected.

Following [1984HOL/RAN], the enthalpies of the monoclinic to tetragonal and tetragonal to cubic transitions are estimated to be 2.1 and 10.4 $\mathrm{kJ{\cdot}mol^{-1}}$, at the respective temperatures of 1690 and 1763 K.

$$\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}(\mathrm{ThC_2}, \mathrm{cr}, 1690\ \mathrm{K}) = (2.1 \pm 0.5)\ \mathrm{kJ{\cdot}mol^{-1}}$$

$$\Delta_{\mathrm{trs}}H^{\circ}_{\mathrm{m}}(\mathrm{ThC_2}, \mathrm{cr}, 1763\ \mathrm{K}) = (10.4 \pm 2.0)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

The α–β transition involves only small crystallographic movements and is thus likely to be associated with only a small enthalpy change; the value for the β–γ transition is estimated from that for the similar transition in $\mathrm{UC_2}$(cr). The heat capacities of the high temperature phases are estimated to have the same constant value:

$$[C^{\circ}_{p,\mathrm{m}}]^{1763\mathrm{K}}_{1690\mathrm{K}}(\mathrm{ThC_2}, \beta) = (83.7 \pm 10.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$[C^{\circ}_{p,\mathrm{m}}]^{2500\mathrm{K}}_{1763\mathrm{K}}(\mathrm{ThC_2}, \gamma) = (83.7 \pm 10.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

There have been two studies of the enthalpies of combustion of thorium dicarbides, by Huber *et al.* [1968HUB/HOL2] and Lorenzelli *et al.* [1971LOR/DIE]. [1968HUB/HOL2] studied two separate samples of $\mathrm{ThC_{1.91}}$(cr), containing 0.07 and 0.02 wt% oxygen, which was assumed to be present as $\mathrm{ThO_2}$(cr) or $\mathrm{SiO_2}$(cr). This introduces an additional uncertainty into the results, since some of the oxygen, at least, was probably dissolved in the dicarbide phase, especially in the first sample – see Appendix A. The values obtained were $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{ThC_{1.91}}, \mathrm{cr}, 298.15\ \mathrm{K}) = -(124.3 \pm 7.5)$ and $-(125.1 \pm 5.4)\ \mathrm{kJ{\cdot}mol^{-1}}$.

These values are much less negative than those obtained by [1971LOR/DIE], given as $-(159.0 \pm 16.7)\ \mathrm{kJ{\cdot}mol^{-1}}$. Their sample was said to contain traces of monocarbide, but no other details are given of the oxygen content, or any corrections applied to the measured value – see Appendix A. The data from Huber *et al.* [1968HUB/HOL2] have been preferred, and their mean value is the selected enthalpy of formation. This is also taken to refer to the $\mathrm{ThC_{1.94}}$(cr) composition, with an increased uncertainty:

$$\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{ThC_{1.94}}, \mathrm{cr}, 298.15\ \mathrm{K}) = -(124.7 \pm 7.5)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

These selected data give $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{ThC_{1.94}}, \mathrm{cr}, 298.15\ \mathrm{K}) = -(126.7 \pm 7.5)$ $\mathrm{kJ{\cdot}mol^{-1}}$.

XI.1.1.3.2 Gibbs energy

There are a considerable number of studies to measure the Gibbs energy of the dicarbide. Three methods have been employed:

- the decomposition pressures from the vaporisation reaction, taken to be

$$ThC_{1.94}(cr) \rightleftharpoons Th(g) + 1.94C(cr) \qquad (XI.1)$$

- measurement of the CO(g) pressures in the reaction of thoria and graphite:

$$ThO_2(cr) + 3.94C(cr) \rightleftharpoons ThC_{1.94}(cr) + 2CO(g). \qquad (XI.2)$$

- emf studies using a CaF_2 solid electrolyte, which give Gibbs energies of the reactions:

$$Th(cr) + 1.94C(cr) \rightleftharpoons ThC_{1.94}(cr) \qquad (XI.3)$$

or

$$\frac{(1-x)}{(2-y)} ThC_{2-y}(cr) + \frac{(1+x-y)}{(2-y)} Th(cr) \rightleftharpoons ThC_{1-x}(cr) \qquad (XI.4)$$

However, the interpretation of most of these measurements is fraught with uncertainties, not only because the uncertainties in the phase boundaries of all the solid phases involved. The vapour over the dicarbide contains appreciable amounts of $ThC_2(g)$ and $ThC_4(g)$ as well as minor amounts of other gaseous carbides (see Section XI.1.2) while there is almost certainly some dissolution of oxygen into the dicarbide in Reaction (XI.2).

The experimental studies are summarised in Table XI-1. Since the thermal functions of the dicarbide are estimated we have, at this stage, just converted the relevant Gibbs energy measurements to derive the Gibbs energy of formation as a function of *T*, given in Table XI-1 in order to establish the consistency of the data. The results are shown in Figure XI-1. The data of [1981BES/LIN] have not been processed, since there seem to be differences, sometimes of a factor of *ca.* 100, between their tabulated and plotted pressures of CO(g) in Reaction (XI.3).

Aronson and Sadofsky [1965ARO/SAD] and Satow [1967SAT2] also measured the thorium potentials in the $ThC_{0.97}$ (cr)-$ThC_{1.94}$(cr) diphasic region, from the emf of the cell $ThC_{1-x} + ThC_{2-y} + ThF_4|CaF_2\ |ThF_4$+Th, but in view of the uncertainties in the thermal functions of $ThC_{0.97}$(cr), these data have not been utilised by this review. The two studies [1964LOF/KRI], [1967WEE/MOR], which attempted to use absorption spectroscopy to determine the pressure of Th(g) in the carbon-saturated dicarbide system are subject to considerable uncertainty; the pressures of Th(g) over Th(l), which were used to calibrate the pressures, gave results for which the enthalpy of vaporisation was widely different from the accepted values. No individual pressures are given, so their results cannot be plotted in the figure. Short summaries of each paper are given in Appendix A.

Table XI-1: Gibbs energy studies to measure $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ (ThC_{2-x}).

Reference	Method	Reaction	Temperature range (K)	Derived $\Delta_{\mathrm{r}}G_{\mathrm{m}}$ ((XI.3),T) ($J\cdot mol^{-1}$)
[1963LON/GRA]	Target effusion	(XI.1)	2278 – 2897	– 96452 – 1.74 T
[1964ARO]	emf	(XI.3)	1073 – 1223	– 151613 + 30.88 T
[1964EGA]	emf	(XI.3)	973 – 1243	– 156244 + 30.88 T
[1964JAC/BAR]	Mass– spectrometric effusion	(XI.1)	2371 – 2642	– 160101 + 11.44 T
[1964LOF/KRI]	Absorption spectroscopy	(XI.1)	2440 – 2772	see text
[1965ARO/SAD]	Emf	(XI.4)	1073 – 1223	see text
[1967SAT2]	Emf	(XI.3)	993 – 1223	– 146858 + 24.06 T
[1967SAT2]	Emf	(XI.4)	993 – 1223	see text
[1967WEE/MOR]	Absorption spectroscopy	(XI.1)	2585 – 2689	
	From ThO_2 (cr) + C(cr) reaction			
[1927PRE/HIN]	Manometric	(XI.2)	2057 – 2494	– 242657 + 36.71 T
[1964HOL/GRE]	Torsion effusion	(XI.2)	*ca.* 1560 – 1680	– 146130 + 22.52 T
[1971HEI/DJE]	Manometric	(XI.2)	2156 – 2410	– 87826 – 20.21 T
[1974DJE/DOD]	Thermogravimetry		2219 – 2319	– 94267 – 17.99 T
[1976PIA/ZAU]	Manometric	(XI.2)	1738 – 2283	– 71026 + 35.65 T
[1981BES/LIN]	Manometric (diaphragm deflection)	(XI.2)	1328 – 1976	Inconsistencies in paper – see text

Figure XI-1: Gibbs energy of formation of $ThC_{1.94}$(cr).

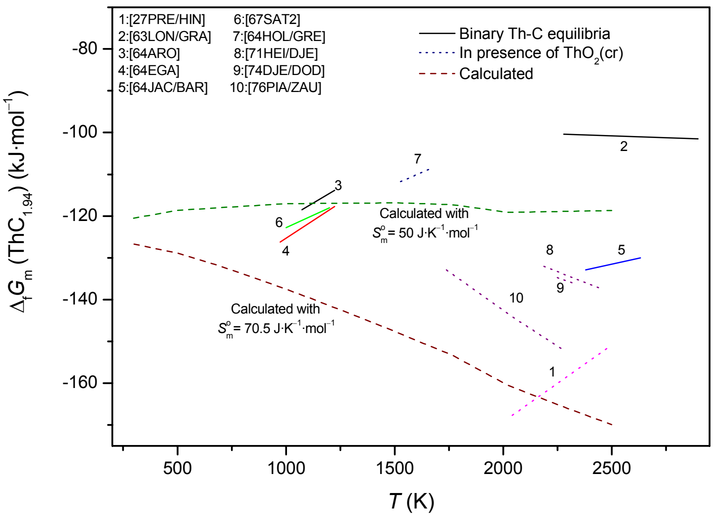


Figure XI-1 illustrates that $\Delta_f G^o_m$ (ThC_{2-x}) calculated from various experimental studies are extremely scattered and that the Gibbs energy of formation calculated from the enthalpy of formation and entropy at 298.15 K and the estimated thermal functions, shows a marked discrepancy between the calorimetric values and most of the high temperature Gibbs energy measurements. Any plausible differences in the thermal functions would not resolve this discrepancy. As noted by [1984HOL/RAN], the main cause of this difference is the positive entropy of formation of $ThC_{1.94}$(cr). However, the measured entropies of $ThC_{0.91}$(cr) and $ThC_{1.94}$(cr) are very similar to those for UC(cr) and 'UC_2(cr)' [2003GUI/FAN], as would be expected, and it is very unlikely that S^o_m ($ThC_{1.94}$, cr, 298.15 K) is as small as the value (*ca.* 50 $J\cdot K^{-1}\cdot mol^{-1}$) required to give even approximate agreement with some of the Gibbs energy data. The causes of these large discrepancies in the data for the thorium carbides are far from clear. This review therefore selects only the data at 298.15 K, which are relatively consistent, and much less exposed to the problems of uncertain phase boundary composition and oxygen contamination that plague the high temperature measurements. Even so, any data for the carbides must clearly be used with due discretion.

XI.1.2 Gaseous thorium carbides

All the gaseous carbide species ThC_n(g) with $n = 1$ to 6 have been identified mass-spectrometrically by Gupta and Gingerich [1980GUP/GIN], but all except ThC_2(g) and ThC_4(g) are very minor species, and only these latter will be considered in this review.

XI.1.2.1 Thorium dicarbide gas ThC_2(g)

The vapour species in the 'ThC_2(cr)' + C(cr) region have been investigated mass-spectrometrically by Jackson *et al.* [1964JAC/BAR] (2371 − 2642 K), Kohl and Stearns [1974KOH/STE] (2686 − 2906 K), Gingerich [1978GIN] (2542 − 2710 K) and Gupta and Gingerich [1980GUP/GIN] (2417 − 2693 K), all using Knudsen effusion, and by Sasaki *et al.* [1971SAS/KUB] (2545 − 2780 K) using the Langmuir method.

The mass-spectrometric measurements show similar amounts of Th(g) and ThC_2(g) in the vapour around 2500 K, with ThC_4(g) also being present in smaller, but still appreciable amounts at the higher temperatures.

The agreement between all these investigations is quite good, in contrast to many other measurements on the condensed phases in the Th-C system. From the data of Jackson *et al.* [1964JAC/BAR], we obtain the following equation:

$$\mathrm{Th(g)} + 2\mathrm{C(cr)} \rightleftharpoons \mathrm{ThC_2(g)} \qquad \text{(XI.5)}$$

$$[\Delta_r G_m]^{2650\,\mathrm{K}}_{2350\,\mathrm{K}}\ ((\text{XI.5}), T) = (67632 - 29.325\ T)$$

while the study of Kohl and Stearns [1974KOH/STE] gives for the Gibbs energy of reaction:

$$[\Delta_r G_m]^{2906\,\mathrm{K}}_{2628\,\mathrm{K}}\ ((\text{XI.5}), T) = (81046 - 31.430 \times T).$$

These data are appreciably more scattered than those of [1964JAC/BAR].

At 2640 K, where they overlap, these values differ by *ca.* 8.5 kJ·mol^{-1}, well within the uncertainty of the measurements. The paper by [1978GIN] deals mainly with the pressures of ThC_3(g); although data for Reaction (XI.5) were also obtained, there is insufficient detail in the paper for them to be included in the current analysis.

Gupta and Gingerich [1980GUP/GIN] also studied the gaseous thorium carbides mass-spectrometrically, using a mixture of ThC_2, UC_2, Rh and excess graphite heated to 2300−2700 K in a graphite-lined Ta effusion cell. They identified all the gaseous carbide species ThC_n(g) with $n = 1$ to 6. As noted in Appendix A, they do not report their results in sufficient detail for them to be analysed, but they do imply that their results for Reaction (XI.5) are close to those of Kohl and Stearns [1974KOH/STE].

It is difficult to derive any reliable thermodynamic data from the Langmuir measurements by Sasaki *et al.* [1971SAS/KUB] from 2545 to 2780 K. The authors derive the enthalpy of Reaction (XI.5) to be $\Delta_r H_m$ ((XI.5), 2662 K) = (108.0 ± 19.7) kJ·mol^{-1} from the variation of the ratio of the fluxes of ThC_2(g) to Th(g), the uncertainty not including those relating to the detector efficiency and ionisation cross-sections of Th(g) and ThC_2(g). This is noticeably larger than the corresponding values from the reasonably consistent effusion measurements of [1964JAC/BAR] and [1974KOH/STE] and is not considered further.

Molecular parameters for ThC_2(g) have been estimated by [1964JAC/BAR], [1974KOH/STE] and [1980GUP/GIN] who regarded Th−C_2 as being similar to Th−O, with a linear Th−C=C structure. However, there is now considerable evidence from *ab initio* calculations [1995ROS/BAL], [1996ROS/BAL] that the corresponding lanthanide dicarbides have a symmetrical fan-shaped C_{2v} structure. Very recently, Kovács and Konings [2008KOV/KON] have made similar calculations for ThC_2(g) and ThC_4(g). For ThC_2, they find that the most stable structure is a less symmetrical essentially L-shaped molecule (C_s symmetry), with Th−C bond lengths of 2.155 and 2.473 Å, and a C−C bond length of 1.287 Å. The corresponding Th−C−C angles are 88.1° and 60.6° (see Appendix A). As noted there, the effective charge on the Th atom is calculated to be 1.60, so the electronic contributions to the partition function for ThC_2(g) are assumed to be the same as those for ThO(g) (see Section VII.1.2 and Table E-1). [2008KOV/KON] also give the three calculated harmonic vibration frequencies (see Table E-1). The molecular parameters for ThC_2(g) lead to the calculated values $C^{\circ}_{p,m}$ (ThC_2, g, 298.15 K) = (45.1 ± 2.0) J·K^{-1}·mol^{-1} and S°_{m} (ThC_2, g, 298.15 K) = (285.3 ± 4.0) J·K^{-1}·mol^{-1}

With these thermal functions, a third-law treatment of the data from [1964JAC/BAR] and [1974KOH/STE] gives $\Delta_f H_m$ (ThC_2, g, 298.15 K) = (784.7 ± 9.2) kJ·mol^{-1} and (801.5 ± 8.1) kJ·mol^{-1} respectively, where the uncertainties do not include those from the experimental difficulties (conversion from ion intensities to pressures, *etc.*) and those in the estimated electronic levels for ThC_2(g). However, the consistent values of the entropy of the reaction Th(g) + 2C(cr) $\rightleftharpoons$ ThC_2(g) derived from the vaporisation data are much smaller than those calculated from the thermal functions, (29.3 *vs.* 61.6 J·K^{-1} mol^{-1} at 2500 K [1964JAC/BAR], 31.8 *vs.* 59.2 J·K^{-1} mol^{-1} at 2796 K [1974KOH/STE]).

In view of this considerable discrepancy in the entropy values this review does not feel confident in selecting any thermodynamic data for ThC_2(g).

XI.1.2.2 Thorium tetracarbide gas ThC_4(g)

Kohl and Stearns [1974KOH/STE] have also measured the pressures of ThC_4(g) in the vapour over 'ThC_2'(cr) + C(cr). At 2700 K, the ThC_4(g) pressure is 15% of the thorium pressure, so this species cannot be neglected. Jackson *et al.* [1964JAC/BAR] do not report observing it in their measurements at lower temperatures and this is consistent with the data derived below.

From their recent *ab initio* calculations, Kovács and Konings [2008KOV/KON] found that ThC_4(g) has a symmetrical C_{2v} structure with two co-planar C−Th−C groups, one with Th−C = 2.365 Å, and a C−Th−C angle of 91.6°, and the second (inside the first) with Th−C = 2.532 Å, and a C−Th−C angle of 31.2° − see Appendix A for more details. Kovács and Konings [2008KOV/KON] also give the nine calculated harmonic vibration frequencies (see Table E-1). Since the effective charge on the Th atom in ThC_4(g) was calculated to be 1.66, the electronic contributions to the partition function for ThC_4(g) were assumed to be the same as those for ThO(g) (see Section VII.1.2 and Table E-1). This structure is, of course entirely different from the linear C_2−Th−C_2 assumed by Kohl and Stearns [1974KOH/STE], but is similar to that indicated for LaC_4(g) by [1997ROS/BAL]. The molecular parameters for fan-shaped ThC_4(g) molecule lead to the calculated values: $C^{\circ}_{p,\mathrm{m}}$ (ThC_4, g, 298.15 K) = (69.3 ± 2.0) J·K^{-1}·mol^{-1} and S°_{m} (ThC_4, g, 298.15 K) = (307.4 ± 6.0) J·K^{-1}·mol^{-1}.

With these parameters, a third-law treatment of the data by [1974KOH/STE] gives $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (ThC_4, g, 298.15 K) = (884.0 ± 7.7) kJ·mol^{-1}, where the uncertainty does not include those from the experimental difficulties (conversion from ion intensities to pressures, *etc.*) and those in the estimated electronic levels for ThC_4(g). The measurements of Gupta and Gingerich [1980GUP/GIN] suggest a somewhat lower proportion of ThC_4(g) in the gas phase, but agree with values calculated from the above enthalpy within the combined uncertainties. However, the entropy of the reaction Th(g) + 4C(cr) $\rightleftharpoons$ ThC_4(g) at 2796 K derived from the vaporisation data of [1974KOH/STE], 89.9 J·K^{-1}·mol^{-1}, is appreciably greater than that calculated from the thermal functions, 73.1 J·K^{-1}·mol^{-1}.

In view of this considerable discrepancy in the entropy values this review does not feel confident in selecting any values for ThC_4(g).

XI.1.3 Thorium carbonates

Experimental studies of thorium carbonates date back to the time of Berzelius [1829BER], who identified the formation of sparingly soluble basic thorium carbonates. Cleve [1874CLE] made an early identification of the compound $Na_6[Th(CO_3)_5]\cdot12H_2O$, but formulated this as a double salt $Th(CO_3)_2\cdot3Na_2CO_3\cdot12H_2O$. The strong complex formation between Th(IV) and the carbonate ion is apparent in the formation of a number of solid phases, some of which have been characterised by single-crystal X-ray diffraction [1975VOL/RIM2], [1975VOL/RIM3]. The formation of soluble carbonate complexes was indicated by the solubility of sparingly soluble thorium compounds such as monazite in carbonate media, a fact that was used in hydrometallurgical schemes for the recovery of thorium [2002ABD].

XI.1.3.1 Solid thorium carbonate compounds

In the earlier literature dealing with tetravalent actinides in carbonate solution, the formation of An(IV) carbonate solids like $An(OH)_2CO_3\cdot xH_2O(s)$ or $AnOCO_3\cdot xH_2O(s)$ was postulated while solubility studies performed in the last decade have shown that the An(IV) hydrous oxides are the solubility limiting solid phases and do not transform into An(IV) carbonate or hydroxo-carbonate solids. An attempt of Ryabchikov *et al.* [1963RYA/VOL] to prepare the postulated solids $Th(OH)_2CO_3\cdot6H_2O(s)$ [1911CHA2] or $ThOCO_3\cdot8H_2O(s)$ [1959RYA/GOL] in sodium and potassium carbonate solution led to the formation of $Na_6[Th(CO_3)_5]\cdot12H_2O(cr)$ and $K_6[Th(CO_3)_5]\cdot8H_2O(cr)$, respectively. Dash *et al.* [2001DAS/KRI], [2002DAS/SIN] report the formation of $ThOCO_3(s)$ and $Th(CO_3)_2(s)$ by thermal decomposition of thorium oxalate hexahydrate, finally leading to $ThO_2(cr)$. The authors report the characterisation by XRD, XPS, DTA/TGA and other methods. However, this review has doubts on the existence of these thorium compounds. The broad XRD bands ascribed to the intermediate $ThOCO_3(s)$ and $Th(CO_3)_2(s)$ compounds are at the same position as the peaks of the final product $ThO_2(cr)$. The XRD patterns look very similar to those reported by [2000RAI/MOO] and [2003NEC/ALT] for microcrystalline $ThO_2(s)$ with particle/crystallite sizes in the range 4 − 20 nm.

The following thorium carbonate solid phases have been synthesised in corresponding bicarbonate or carbonate solutions and characterised by chemical analysis, thermogravimetry and X-ray diffraction:

- $Na_6[Th(CO_3)_5]\cdot12H_2O(cr)$ [1963RYA/VOL], [1973DER/FAU], [1975VOL/RIM3],
- $K_6[Th(CO_3)_5]\cdot xH_2O(cr)$, with $x = 8$ or 12 [1963RYA/VOL],
- $(NH_4)_6[Th(CO_3)_5]\cdot3H_2O(cr)$ [1961CHE/GOL],
- $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot4H_2O(cr)$ [1973DER/FAU], [1975VOL/RIM2].

Thermodynamic data are not reported for these solids. However, the solubility data determined with $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ [1961LUZ/KOV2], [1973DER/FAU3] allow the determination of the solubility constant at zero ionic strength (*cf.* Section XI.1.3.3) and the molar standard Gibbs energy of formation:

$$\Delta_f G^\circ_m(Na_6[Th(CO_3)_5]\cdot 12H_2O, \text{cr}, 298.15\ \text{K}) = -(8002.6 \pm 7.3)\ \text{kJ}\cdot\text{mol}^{-1}.$$

XI.1.3.2 Aqueous thorium complexes with carbonate

Both qualitative and quantitative data are available. Only the quantitative data can be used to obtain thermodynamic parameters, but the qualitative information can in some cases be used to corroborate the quantitative conclusions, *e.g.* concerning the stoichiometry of complexes and the mode of coordination of the carbonate ligand. Quantitative determinations of the stoichiometry and equilibrium constants are described in the following section. These studies are complicated by the formation of sparingly soluble solid phases and the formation of ternary Th(IV)-hydroxide-carbonate species. This review will therefore begin with a short summary of the advantages and disadvantages of the various methods used to deduce the stoichiometry and equilibrium constants in the ternary Th(IV)-carbonate-water system.

The analysis of experimental data is facilitated if the ternary system is reduced to a "formal" three-component system by keeping the concentration of one component, A, constant and varying the other two, B and C. These data provide information on the stoichiometry of the complexes with respect to the two components that are varied and their conditional equilibrium constants. By repeating the investigation in new series of experiments where the concentration of A is still constant but with the values (A_1, A_2, A_3 *etc.*) in the different series, one can determine the stoichiometry with respect to A and the equilibrium constants for the ternary complexes. The choice of components in the thorium carbonate system depends on the pH region investigated; at low pH where the partial pressure of CO_2 can be measured it is practical to use $CO_2(g)$ as one of the components, the other two being the concentrations of Th^{4+} and H^+. The chemical equilibria are then formulated as:

$$m\text{Th}^{4+} + n\text{CO}_2(\text{g}) + q\text{H}_2\text{O} \rightleftharpoons \text{Th}_m(\text{OH})_q(\text{CO}_2)_n^{4m-q} + q\text{H}^+ \qquad (\text{XI.6})$$

The conditional equilibrium constants (for a given partial pressure p_{CO_2} of carbon dioxide) for these reactions are:

$$^{*}K_{p,m,q} = \frac{\sum_{n}^{N}[\text{Th}_m(\text{OH})_q(\text{CO}_2)_n^{4m-q}][\text{H}^+]^q}{[\text{Th}^{4+}]^m} \qquad (\text{XI.7})$$

where

$$^{*}K_{p,m,q} = \frac{[\mathrm{Th}_m(\mathrm{OH})_q^{4m-q}][\mathrm{H}^+]^q}{[\mathrm{Th}^{4+}]^m} + \frac{[\mathrm{Th}_m(\mathrm{OH})_q(\mathrm{CO}_2)^{4m-q}][\mathrm{H}^+]^q}{[\mathrm{Th}^{4+}]^m}$$

$$+ \frac{[\mathrm{Th}_m(\mathrm{OH})_q(\mathrm{CO}_2)_2^{4m-q}][\mathrm{H}^+]^q}{[\mathrm{Th}^{4+}]^m} + \ldots$$

$$^{*}K_{p,m,q} = {}^{*}\beta_{m,q,0} + {}^{*}\beta_{m,q,1}p_{\mathrm{CO}_2} + {}^{*}\beta_{m,q,2}p^2_{\mathrm{CO}_2} + \ldots. \tag{XI.8}$$

The equilibrium constants $^{*}\beta_{m,q,n}$ for the species $\mathrm{Th}_m(\mathrm{OH})_q(\mathrm{CO}_2)_n^{4m-q}$ refer to Reaction (XI.6). Details in the analysis of such data are given in [1961ROS/ROS]. The stoichiometry of the complexes in terms of the components is unique, but CO_2 is not bonded as such in the complexes but as HCO_3^- and/or CO_3^{2-}, for which $(OH)(CO_2) \equiv HCO_3^-$ and $(OH)_2(CO_2) \equiv CO_3^{2-}$. The so-called proton ambiguity makes it impossible to decide on the origin of the proton released in the complex formation reactions using potentiometric data. This means that one cannot distinguish *e.g.* between complexes such as $Th(OH)(HCO_3)^{2+}$ and $Th(CO_3)^{2+}$. However, there are other experimental methods that allow such distinctions to be made, *e.g.* using the different vibration modes in HCO_3^- and CO_3^{2-} determined by Raman spectroscopy. Moreover, HCO_3^- is a very weak ligand compared to OH^- and CO_3^{2-}. For instance in the case of trivalent actinides and lanthanides, the formation constant of $M(HCO_3)^{2+}$ is 4−5 orders of magnitude lower than those of $M(OH)^{2+}$ and $M(CO_3)^+$ [1981CIA/FER], [1985SPA], [2003GUI/FAN]. For tetravalent metal ions the difference is expected to be even larger, so the formation of Th(IV) bicarbonate complexes need not be taken into account.

Most investigations of carbonate complexation in the Th(IV) system have been made at such high pH that one cannot use measurements of the partial pressure of CO_2. Many of these studies have been made using solubility measurements where the total concentration of Th(IV) is low. In order to facilitate the analysis of the experimental data it is practical to work with buffers of HCO_3^- / CO_3^{2-} or CO_3^{2-}/OH^- where the concentration of one of the buffer components is kept constant. However, this procedure has in general not been used, a fact that complicates the interpretation of the experimental data. A particular problem arises in the interpretation of solubility data. In these cases a unique chemical model cannot be obtained unless an assumption is made about the nuclearity of the complexes formed. Solubility data only give information on the charge of the species formed and there is no *a priori* reason to assume that there is only a single species with a particular charge; when interpreting the solubility data one in general assumes that only mononuclear species are formed, *cf.* Section VII.3.1.3. For bicarbonate and carbonate solutions and HCO_3^- / CO_3^{2-} buffers at C_{tot} above 0.1 M, where the solubility is rather high, this assumption is supported by EXAFS measurements [1997FEL/RAI], [2006ALT/NEC]. The EXAFS spectra of about 1 mM Th solutions do not provide any evidence for the formation of polynuclear thorium carbonate complexes under these conditions.

XI.1.3.2.1 Solubility of ThO_2(am, hyd) in carbonate solution and formation constants of ternary Th(IV)-hydroxide-carbonate complexes

Östhols *et al.* [1994OST/BRU], Rai *et al.* [1995RAI/FEL], Felmy *et al.* [1997FEL/RAI], [1999FEL/RAI] and Altmaier *et al.* [2005ALT/NEC], [2006ALT/NEC], have performed solubility studies with hydrous thorium oxide as the solid phase, in order to determine the stoichiometry and equilibrium constants of the thorium complexes with carbonate. The possible variation of the solid phase, dried or aged ThO_2(am, hyd) or $Th(OH)_4$(am) precipitates, does not seem to have complicated the experiments as indicated by the good agreement between the solubility measured by different authors under comparable conditions, *cf.* the discussion in [2005ALT/NEC] Appendix A. The experimental solubility data in [1994OST/BRU] and [2005ALT/NEC] have been measured at constant ionic strength (I = 0.5 M), either in the presence of CO_2(g) at partial pressures of 0.1 and 1.0 bar, or in carbonate/bicarbonate buffer solutions, partly with additions of NaOH. In a very recent study Altmaier *et al.* [2006ALT/NEC] extended their measurements with carbonate/bicarbonate buffers to a wide range of ionic strength, I = 0.1 − 4.0 M ($NaHCO_3$-Na_2CO_3-NaCl). Rai *et al.* [1995RAI/FEL] measured the solubility of ThO_2(am, hyd) in $NaHCO_3$ and Na_2CO_3-NaOH solutions (up to high carbonate concentrations) of variable ionic strength. Based on this study, Felmy *et al.* [1997FEL/RAI] derived a model with Pitzer parameters for the complex $Th(CO_3)_5^{6-}$ which was later extended to Na_2CO_3 solutions containing 0.1 M NaOH and 2.33 m or 4.67 m NaCl [1999FEL/RAI]. The experimental conditions of the solubility studies in [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI], [2005ALT/NEC], [2006ALT/NEC], are summarised in Table XI-2. They cover widely varying conditions, a $-\log_{10}[H^+]$ range of 4 − 13, carbonate concentrations up to 2 M and ionic strength varying from I = 0.1 M to more than 6 M in Na_2CO_3 solutions and Na_2CO_3-NaCl mixtures.

This review has made extensive use of the discussion in [2005ALT/NEC] that is the most comprehensive of the experimental studies so far; this paper also contains an analysis of some previous studies. The simultaneous evaluation of the different sets of experimental data at I = 0.5 M in [2005ALT/NEC] indicates that $ThOH(CO_3)_4^{5-}$ and $Th(OH)_2(CO_3)_2^{2-}$ are the most important ternary complexes while $Th(OH)_2(CO_3)$(aq), $Th(OH)_3(CO_3)^-$ and $Th(OH)_4(CO_3)^{2-}$ are of minor significance. According to the comprehensive test calculations in [2005ALT/NEC], binary carbonate complexes and other ternary complexes give no significant contributions to the solubility under the experimental conditions of [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI] and [2005ALT/NEC]; only upper limits could be derived for their formation constants. Altmaier *et al.* [2005ALT/NEC] demonstrated that the solubility data determined by different authors under different experimental conditions could be consistently described with a unique set of complexes and equilibrium constants. However this speciation model is not consistent with those of Östhols *et al.* [1994OST/BRU] and Felmy *et al.* [1997FEL/RAI], [1999FEL/RAI] who proposed $Th(CO_3)_5^{6-}$ as the dominant complex at carbonate concentrations of $0.1 - 2.0$ M and $\mathrm{Th(OH)_3(CO_3)^-}$ in near-neutral solutions of lower (bicarbonate) concentration.

Table XI-2: Experimental conditions of the available sets of solubility data with ThO_2(am, hyd) in carbonate solution (22 − 25°C).

Reference	Medium	I (mol·L^{-1})	Carbonate	pH range
[1994OST/BRU]	$NaClO_4$, CO_2(g)	0.5	p_{CO_2} = 0.1 bar	$-\log_{10}[H^+] = 4.6 - 7.4$
		0.5	p_{CO_2} = 1.0 bar	$-\log_{10}[H^+] = 4.1 - 6.3$
	Na(HCO_3-CO_3-ClO_4)	0.5	C_{tot} = 0.10 M	$-\log_{10}[H^+] = 8.2 - 10.5$
[2005ALT/NEC]	NaCl, CO_2(g)	0.5	p_{CO_2} = 0.1 bar	$-\log_{10}[H^+] = 5.0 - 7.6$
		0.5	p_{CO_2} = 1.0 bar	$-\log_{10}[H^+] = 4.4 - 6.6$
	Na(HCO_3-CO_3-OH-Cl)	0.5	C_{tot} = 0.10 M	$-\log_{10}[H^+] = 8.7 - 13.0$
		0.5	C_{tot} = 0.04 M	$-\log_{10}[H^+] = 8.7 - 12.5$
		0.5	C_{tot} = 0.015 M	$-\log_{10}[H^+] = 8.7 - 13.0$
	Na_2CO_3-NaOH	var.	C_{tot} = 0.25 − 2.0 M	$[OH^-]$ = 0.1 M
[2006ALT/NEC]	$NaHCO_3$-Na_2CO_3	0.1 − 0.3	C_{tot} = 0.1 M	$-\log_{10}[H^+] = 8.7 - 10.8$
	Na(HCO_3-CO_3-Cl)	0.1	C_{tot} = 0.02 M	$-\log_{10}[H^+] = 8.9 - 10.2$
		0.5	C_{tot} = 0.02 M	$-\log_{10}[H^+] = 8.7 - 10.6$
		2.0	C_{tot} = 0.02 M	$-\log_{10}[H^+] = 8.5 - 10.5$
		4.0	C_{tot} = 0.02 M	$-\log_{10}[H^+] = 8.6 - 10.0$
[1995RAI/FEL]	Na_2CO_3-NaOH	3.0 − 3.5	C_{tot} = 1.0 M	$[OH^-]$ = 0.01 − 0.5 M
and [1997FEL/RAI]	Na_2CO_3-NaOH	var.	C_{tot} = 0.001 − 2.0 M	$[OH^-]$ = 0.1 M
	$NaHCO_3$	var.	C_{tot} = 0.01 − 0.25 M	$-\log_{10}[H^+] = 8.6 - 9.5$
[1999FEL/RAI]	Na_2CO_3 + 2.3 m NaCl + 0.1 M NaOH	var.	C_{tot} = 0.1 − 2.3 M	$[OH^-]$ = 0.1 M
	Na_2CO_3 + 4.7 m NaCl + 0.1 M NaOH	var.	C_{tot} = 0.1 − 2.3 M	$[OH^-]$ = 0.1 M

The equilibrium constants $\log_{10} K^{\circ}_{s,1yz} = (\log_{10} K^{\circ}_{s,0} + \log_{10} \beta^{\circ}_{1yz})$ derived by the different authors from their solubility studies with ThO_2(am, hyd) are given in Table XI-3[1]. The notation 1*yz* refers to the stoichiometric coefficients in Eqs (XI.9) and (XI.10):

$$\mathrm{Th(OH)_4(am)} + z\,\mathrm{CO_3^{2-}} \rightleftharpoons \mathrm{Th(OH)}_y(\mathrm{CO_3})_z^{4-y-2z} + (4-y)\,\mathrm{OH^-} \qquad \text{(XI.9)}$$

The solubility constants, $\log_{10} K^{\circ}_{s,0}$, selected in this review for dried or aged ThO_2(am, hyd) were combined with $\log_{10} K^{\circ}_{s,1yz}$ to calculate the formation constants of different species, $\log_{10} \beta^{\circ}_{1yz}$, according to the generalised reactions:

$$\mathrm{Th^{4+}} + y\,\mathrm{OH^-} + z\,\mathrm{CO_3^{2-}} \rightleftharpoons \mathrm{Th(OH)}_y(\mathrm{CO_3})_z^{4-y-2z} \qquad \text{(XI.10)}$$

Table XI-3: Equilibrium constants for thorium complexes with carbonate relevant in solubility studies with dried or aged ThO_2(am, hyd) at 22−25°C. (Uncertainties are given as 2σ).

Complex (1yz)	$\log_{10} K_{s,1yz}$ ($I = 0.5$ M)	$\log_{10} K^{\circ}_{s,1yz}$	$\log_{10} \beta^{\circ}_{1yz}$ [a]	Reference
(105) = $Th(CO_3)_5^{6-}$	< -13.2	< -16.6	< 31.0	[2005ALT/NEC]
	-12.9 ± 0.4	-16.4 ± 0.4	31.6 ± 0.6	[1994OST/BRU]
		-18.4	29.1 ± 0.9	[1997FEL/RAI]
			31.0 ± 0.7	This review [b]
(114) = $Th(OH)(CO_3)_4^{5-}$	-10.0 ± 0.1	-12.0 ± 0.2	35.6 ± 0.5	[2005ALT/NEC]
(121) = $Th(OH)_2CO_3$(aq)	-17.5 ± 0.2	-17.1 ± 0.3	30.5 ± 0.6	[2005ALT/NEC]
(122) = $Th(OH)_2(CO_3)_2^{2-}$	-11.2 ± 0.1	-10.8 ± 0.2	36.8 ± 0.5	[2005ALT/NEC]
(131) = $Th(OH)_3(CO_3)^-$	-9.7 ± 0.5	-9.3 ± 0.5	38.3 ± 0.7	[2005ALT/NEC]
	-7.6 ± 0.3[c]	-7.2 ± 0.3[c]	40.8 ± 0.6[c]	[1994OST/BRU]
(141) = $Th(OH)_4(CO_3)^{2-}$	-7.2 ± 0.3	-7.2 ± 0.3	40.4 ± 0.6	[2005ALT/NEC]

a: The formation constants $\log_{10} \beta^{\circ}_{1yz}$ for the reactions $\mathrm{Th^{4+}} + y\mathrm{OH^-} + z\mathrm{CO_3^{2-}} \rightleftharpoons \mathrm{Th(OH)}_y(\mathrm{CO_3})_z^{4-y-2z}$ are calculated according to: $\log_{10} \beta^{\circ}_{1yz} = \log_{10} K^{\circ}_{s,1yz} - \log_{10} K^{\circ}_{s,0}$ with the $\log_{10} K^{\circ}_{s,0}$ values calculated by this review: $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$ [2005ALT/NEC], $-(48.0 \pm 0.5)$ [1994OST/BRU], or $-(47.5 \pm 0.9)$ selected by for aged ThO_2(am, hyd).

b: Evaluated in Section XI.1.3.2.2.

c: Based on high Th concentrations caused by colloidal / polymeric species (*cf.* discussion below and in Appendix A).

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[1] As hydrous thorium oxide (ThO_2(am, hyd) = $ThO_2 \cdot xH_2O$(am) with x = 2.4−2.5 [1994OST/BRU], [2002NEC/MUL]) has a stoichiometry close to $Th(OH)_4$(am), it is more convenient to write the reactions with $Th(OH)_4$(am) as component rather than as: $\mathrm{Th(OH)_4(am, hyd)} + 2\mathrm{H_2O(l)} + z\mathrm{CO_3^{2-}} \rightleftharpoons \mathrm{Th(OH)}_y(\mathrm{CO_3})_z^{4-y-2z} + (4-y)\mathrm{OH^-}$, because particularly at high ionic strength, the term $2 \log_{10} a_w$ would have a significant effect on ionic strength corrections.

Östhols *et al.* [1994OST/BRU], and Altmaier *et al.* [2005ALT/NEC], [2006ALT/NEC] used the SIT approach for ionic strength corrections. The ion interaction coefficient for the complex $\mathrm{Th(CO_3)_5^{6-}}$ is set equal to the known value of the analogous U(IV) complex, $\varepsilon(\mathrm{Th(CO_3)_5^{6-}}, \mathrm{Na^+}) = \varepsilon(\mathrm{U(CO_3)_5^{6-}}, \mathrm{Na^+}) = -(0.30 \pm 0.15)$ kg·mol^{-1} [2003GUI/FAN] and the value of $\varepsilon(\mathrm{ThOH(CO_3)_4^{5-}}, \mathrm{Na^+}) = -(0.22 \pm 0.13)$ kg·mol^{-1} has been derived from $\log_{10} K_{s,114}$ values in 0.1 − 0.4 M NaCl ($\Delta\varepsilon$ = (0.22 ± 0.05) kg·mol^{-1}) [2006ALT/NEC]. For the other complexes it is not possible to evaluate simultaneously the equilibrium constants and SIT coefficients from the available data. Therefore the unknown ion interaction coefficients $\varepsilon(\mathrm{Na^+}, \mathrm{Th(OH)_y(CO_3)_z^{4-y-2z}})$ have been estimated from known values for actinide complexes of analogous charge and similar size [2005ALT/NEC] (Table XI-4). Because the uncertainties of estimated SIT coefficients should not exceed ±0.2 kg·mol^{-1}, the extrapolation of equilibrium constants at I = 0.5 M to zero ionic strength should have a relatively small error.

Table XI-4: SIT coefficients for Th(IV) carbonate and hydroxide-carbonate complexes estimated from charge type analogues [2005ALT/NEC] except otherwise stated.

i	j	$\varepsilon(i, j)$ (kg·mol^{-1})
$\mathrm{Th(CO_3)_5^{6-}}$	$\mathrm{Na^+}$	− 0.30 ± 0.15 [a]
$\mathrm{Th(OH)(CO_3)_4^{5-}}$	$\mathrm{Na^+}$	− 0.25 ± 0.20
		− 0.22 ± 0.13 [b]
$\mathrm{Th(OH)_2(CO_3)(aq)}$	$\mathrm{Na^+}$, $\mathrm{Cl^-}$, $\mathrm{ClO_4^-}$	0
$\mathrm{Th(OH)_2(CO_3)_2^{2-}}$	$\mathrm{Na^+}$	− 0.1 ± 0.2
$\mathrm{Th(OH)_3(CO_3)^-}$	$\mathrm{Na^+}$	− 0.05 ± 0.20
$\mathrm{Th(OH)_4(CO_3)^{2-}}$	$\mathrm{Na^+}$	− 0.1 ± 0.2

a: $\varepsilon(\mathrm{U(CO_3)_5^{6-}}, \mathrm{Na^+})$ from [2003GUI/FAN].

b: Experimental value from [2006ALT/NEC].

The thermodynamic model of Felmy *et al.* [1997FEL/RAI], [1999FEL/RAI] is based on Pitzer's ion interaction approach including binary and ternary parameters for the complex $\mathrm{Th(CO_3)_5^{6-}}$ (*cf.*, Appendix A review of [1997FEL/RAI]). Accordingly, the value of $\log_{10} K^{\circ}_{s,105}$ is not directly comparable to that of [1994OST/BRU].

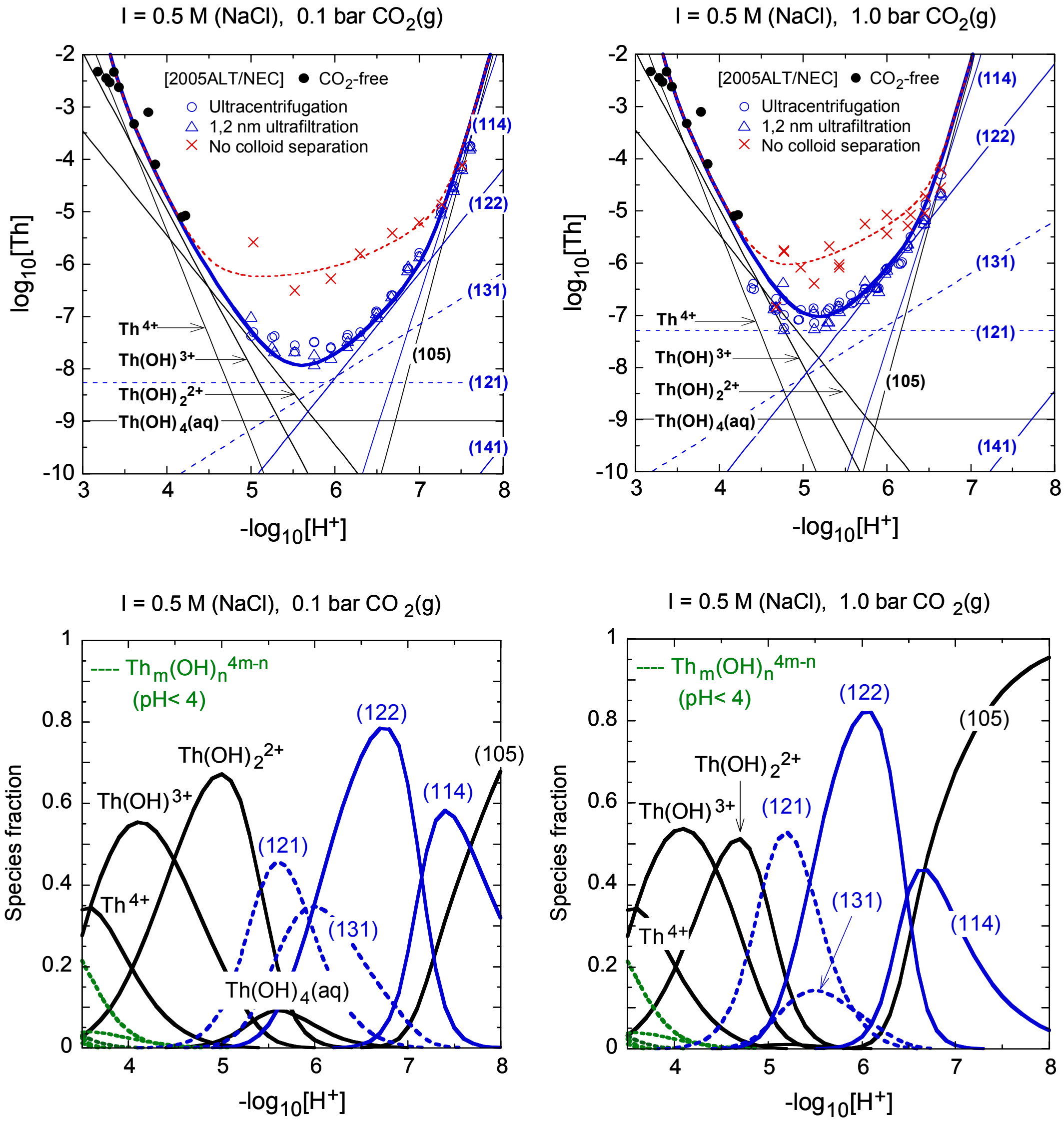
The binary and ternary complexes (Table XI-3) give reliable predictions of the solubility of $\mathrm{ThO_2}$(am, hyd) in carbonate solutions as is demonstrated in the examples that follow. The equilibrium constant values for the ternary complexes in Table XI-3 are those proposed by [2005ALT/NEC] and the value for $\mathrm{Th(CO_3)_5^{6-}}$ is that selected by this review. They are used together with the SIT coefficients in Table XI-4 to compare the calculated and experimental solubility data for all studies. For a better survey of the aqueous speciation, the corresponding speciation diagrams are also calculated, *cf.* Figure XI-2 and Figure XI-3.

The analysis of the experimental data in the thorium-carbonate system requires information on the equilibrium constants in the binary Th(IV)-hydroxide system. Therefore calculation of ThO_2(am, hyd) solubility in carbonate solution included hydrolysis constants selected in the present review and the solubility constants $\log_{10} K^{\circ}_{s,0}$ recalculated in the present review for dried or aged ThO_2(am, hyd) from the solubility data determined in the same study in carbonate-free solutions $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$ [2005ALT/NEC] and $-(48.0 \pm 0.5)$ [1994OST/BRU]. For the evaluation of studies where only solubility data in carbonate solution are reported [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI], [2006ALT/NEC] the value selected by this review for aged ThO_2(am, hyd), $\log_{10} K^{\circ}_{s,0} = -(47.5 \pm 0.9)$, is used.

XI.1.3.2.1.1 Solubility studies under CO_2(g)

The close agreement between the calculations based on the estimated SIT coefficients in Table XI-4 and data of [2005ALT/NEC] is not surprising since Altmaier *et al.* used these data in their evaluation. The solubility study of Östhols *et al*. [1994OST/BRU] under CO_2(g) partial pressures of 0.1 and 1.0 bar shows evidence for the formation of polynuclear ternary complexes or colloids. The thorium concentrations measured in the range pH = 4.6 − 6.5 after 220 nm filtration are comparable to those measured by Altmaier *et al*. [2005ALT/NEC] under the same conditions without removing colloidal or polynuclear species (crosses in Figure XI-2). However, considerably lower Th concentrations were obtained after 1.2 nm ultrafiltration and ultracentrifugation [2005ALT/NEC], indicating that the concentrations in [1994OST/BRU] for the pH region 4.6 to 6.5 do not refer to $Th(OH)_4$(aq) and $Th(OH)_3(CO_3)^-$ but to large polymers or colloids (*cf*. discussion of [1994OST/BRU] in Appendix A).

Figure XI-2: Solubility of ThO_2(am, hyd) and speciation under 0.1 and 1.0 bar CO_2(g) in 0.5 M NaCl [2005ALT/NEC]. The calculations are based on the equilibrium constant and SIT coefficients selected in the present review and the solubility constants calculated from the data in carbonate-free solutions, $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$. The dotted curves are calculated with the equilibrium constants proposed by Östhols *et. al.* [1994OST/BRU] for $Th(OH)_4$(aq) and $Th(OH)_3(CO_3)^-$ (see text for notation of Th(IV) hydroxide-carbonate complexes).



XI.1.3.2.1.2 Solubility studies in carbonate/bicarbonate buffers

Östhols *et al.* [1994OST/BRU] and Altmaier *et al.* [2005ALT/NEC], [2006ALT/NEC] also measured the solubility of ThO_2(am, hyd) in carbonate/bicarbonate buffers of constant ionic strength and given total carbonate concentration ($C_{tot} = [HCO_3^-] + [CO_3^{2-}]$). In [2005ALT/NEC] the pH range was extended up to pH 13 by adding NaOH. The solubility data at I = 0.5 M ($NaHCO_3$-Na_2CO_3-$NaClO_4$ solutions with C_{tot} = 0.1 M [1994OST/BRU] and $NaHCO_3$-Na_2CO_3-NaOH-NaCl solutions with C_{tot} = 0.1, 0.04 and 0.015 M [2005ALT/NEC]) were also included in the data evaluation of [2005ALT/NEC]. As shown in Figure XI-3 for the highest and lowest values of C_{tot} = 0.1 and 0.015 M at I = 0.5 M, the complex (114) = $Th(OH)(CO_3)_4^{5-}$ is the dominant species at pH 8 − 10.5 and responsible for the relatively high solubility in this pH range. The complex (141) = $Th(OH)_4(CO_3)^{2-}$, dominant at pH > 11, causes only a slight increase of the solubility compared to carbonate-free solutions.

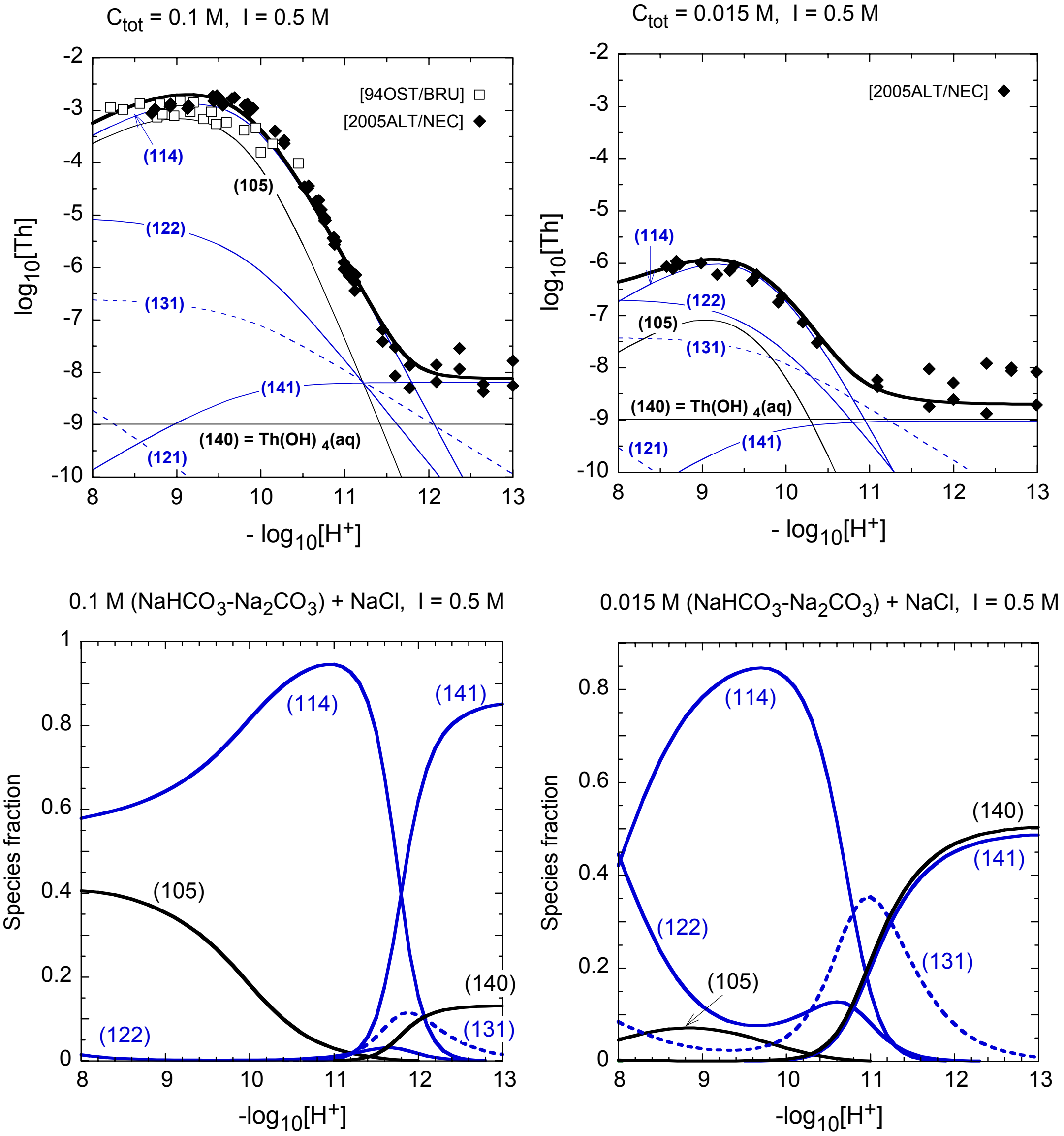
In their most recent study, Altmaier *et al.* [2006ALT/NEC] extended their solubility study with ThO_2(am, hyd) to cover a wider range of ionic strength. As shown in Appendix A, the experimental solubility data at a total carbonate concentration of C_{tot} = 0.02 M and constant ionic strengths of I = 0.1, 0.5, 2.0 and 4.0 M ($NaHCO_3$-Na_2CO_3-NaCl) are well predicted with the equilibrium constants and SIT coefficients selected by this review. The large increase of the solubility in the range of the maximum at $-\log_{10}[H^+]$ around 9.5, from $\log_{10}[Th] = -6.2$ at I = 0.1 M to −3.4 at I = 4.0 M, is consistent with the ionic strength dependence expected for the reaction:

$$Th(OH)_4(am) + 4CO_3^{2-} \rightleftharpoons Th(OH)(CO_3)_4^{5-} + 3OH^- \qquad (XI.11)$$

The same holds for the solubility increase of about an order of magnitude at C_{tot} = 0.1 M, when the ionic strength is kept constant at I = 0.5 M by adding NaCl or $NaClO_4$ compared to that in 0.1 M ($NaHCO_3$-Na_2CO_3) without addition of background electrolyte, *i.e.*, at the same carbonate concentration but at somewhat lower (variable) ionic strength of $I = [HCO_3^-] + 3[CO_3^{2-}]$ = 0.1 M at $-\log_{10}[H^+] < 9$ and 0.3 M at −(log10([H+] > 10.

The (105) complex $Th(CO_3)_5^{6-}$ was not included in the model calculations of Altmaier *et al.* [2005ALT/NEC], [2006ALT/NEC] but the equilibrium constant selected by this review for the pentacarbonate complex (Section XI.1.3.2.2) does not lead to a significant change of the calculated solubility under the conditions of the test solutions (carbonate/bicarbonate buffers at $-\log_{10}[H^+]$ = 8 − 13 and $C_{tot} \leq 0.1$ M, $-\log_{10}[H^+]$ = 5.0 − 7.6 under 0.1 bar CO_2(g) and $-\log_{10}[H^+]$ = 4.4 − 6.6 under 1.0 bar CO_2(g)) if used in addition to their data for the ternary complexes (*cf.* Figure XI-2 and Figure XI-3). The pentacarbonate complex is not dominant under these conditions; however, as shown in Figure XI-2, it is calculated to be the dominant species at $-\log_{10}[H^+] > 7.6$ under 0.1 bar CO_2(g) and at $-\log_{10}[H^+] > 6.6$ under 1.0 bar CO_2(g).

Figure XI-3: Solubility of ThO_2(am, hyd) and speciation at I = 0.5 M ($NaHCO_3$-Na_2CO_3-NaOH-NaCl) and a total carbonate concentration of C_{tot} = 0.1 and 0.015 M [2005ALT/NEC]. The corresponding data of [1994OST/BRU] at C_{tot} = 0.1 and I = 0.5 M ($NaClO_4$ media) are shown for comparison. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review and $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$ calculated from the data in carbonate-free solutions.



C_{tot} = 0.1 M, I = 0.5 M

C_{tot} = 0.015 M, I = 0.5 M

0.1 M ($NaHCO_3$-Na_2CO_3) + NaCl, I = 0.5 M

0.015 M ($NaHCO_3$-Na_2CO_3) + NaCl, I = 0.5 M

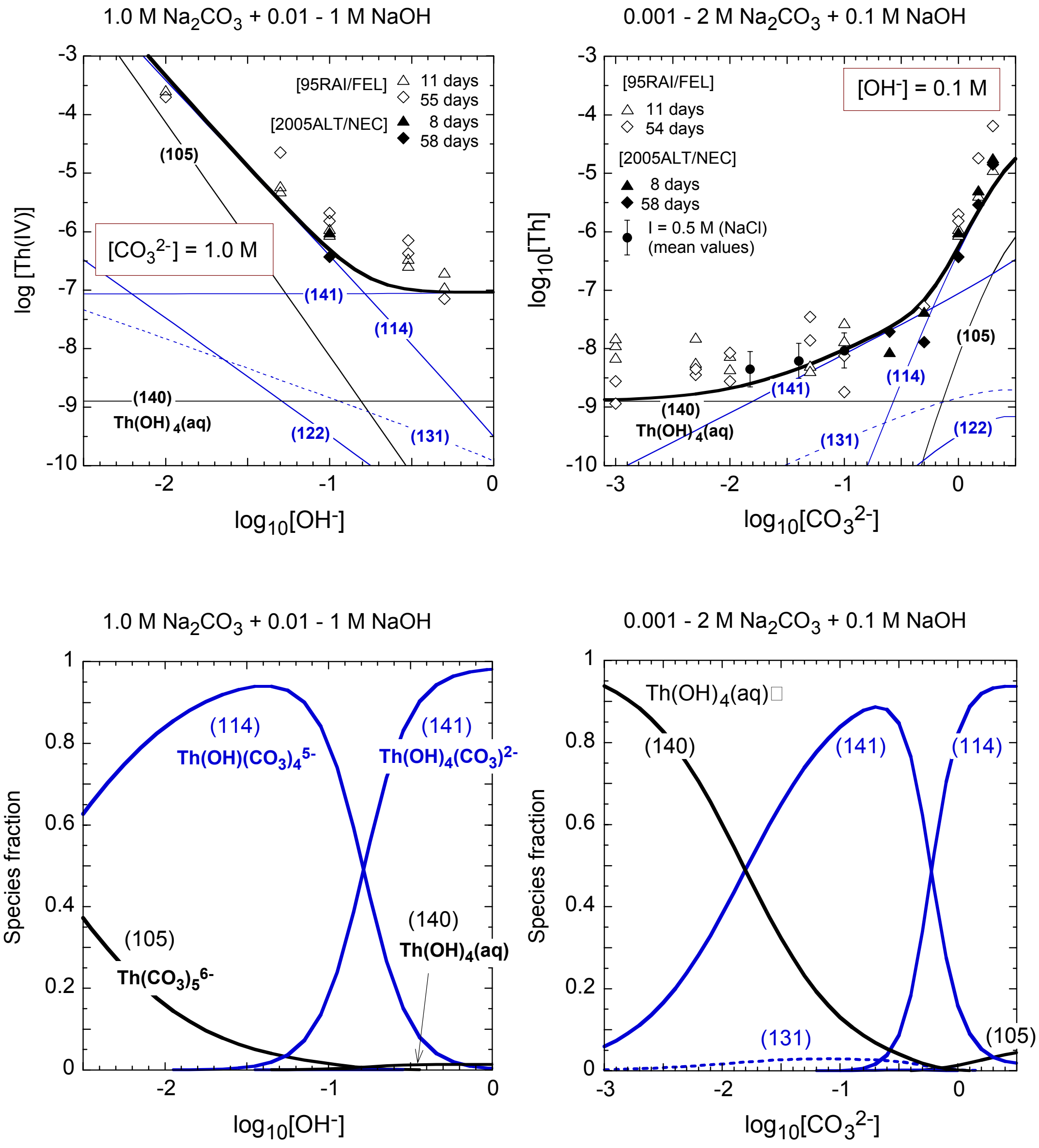
The solubility determined by Rai *et al.* [1995RAI/FEL], [1997FEL/RAI] with ThO_2(am, hyd) in 0.01 − 0.25 M $NaHCO_3$ solutions of varying ionic strength is also well described with the equilibrium constants and SIT coefficients selected by this review (*cf.* Appendix A). The complex (122) = $Th(OH)_2(CO_3)_2^{2-}$ is calculated to be dominant in 0.01 − 0.05 M $NaHCO_3$. This is consistent with the models proposed by Rai *et al.* for U(IV) [1998RAI/FEL], Np(IV) [1999RAI/HES] and Pu(IV) [1999RAI/HES2]. The complex (114) = $Th(OH)(CO_3)_4^{5-}$ is dominant in 0.05 − 0.4 M $NaHCO_3$ and, as confirmed by EXAFS measurements [1997FEL/RAI], the pentacarbonate complex (105) = $Th(CO_3)_5^{6-}$ is dominant in bicarbonate solutions above 0.4 M.

XI.1.3.2.1.3 Solubility studies at high pH and carbonate concentration

Solubility data determined by Rai *et al.* [1995RAI/FEL], [1997FEL/RAI] with ThO_2(am, hyd) in 1.0 M Na_2CO_3 containing 0.01 − 1.0 M NaOH and in 0.001 − 2.0 M Na_2CO_3 containing 0.1 M NaOH were confirmed by some additional experimental data of [2005ALT/NEC]. Although these conditions partly exceed the validity range of the SIT, the solubilities predicted with the equilibrium constants and SIT coefficients selected in the present review are in good agreement with the experimental data (Figure XI-4). The dependence of the solubility on $\log_{10}[OH^-]$ and $\log_{10}[CO_3^{2-}]$ is reasonably consistent with the dominance of the complexes (141) = $Th(OH)_4(CO_3)^{2-}$ and (114) = $Th(OH)(CO_3)_4^{5-}$, but not with the limiting carbonate complex (105) = $Th(CO_3)_5^{6-}$.

Altmaier *et al.* [2005ALT/NEC] noticed that a somewhat better fit is obtained by including (in addition to the species given in Table XI-3) the complex $Th(OH)_2(CO_3)_4^{6-}$ with $\log_{10}\beta^{\circ}_{124} \leq (34.3 \pm 0.6)$ and an estimated interaction coefficient of $\varepsilon(Th(OH)_2(CO_3)_4^{6-}, Na^+) = -(0.3 \pm 0.2)$ kg·mol^{-1}. This holds as well for two further sets of experimental data from [1999FEL/RAI] in 2.33 and 4.67 m NaCl containing 0.1 − 2.3 M Na_2CO_3 and 0.1 M NaOH, in particular for the higher carbonate concentrations in 4.67 m NaCl (*cf.* Appendix A review of [1999FEL/RAI]). However, these conditions are beyond the validity range of the SIT and changing $\varepsilon(Th(OH)(CO_3)_4^{5-}, Na^+)$ or $\varepsilon(Th(CO_3)_5^{6-}, Na^+)$ within their uncertainty ranges also yields good fits. Felmy *et al.* [1999FEL/RAI] described their results with Pitzer's ion interaction approach including binary and ternary parameters for the complex $Th(CO_3)_5^{6-}$ given in Appendix A.

Figure XI-4: Solubility of ThO_2(am, hyd) and speciation at high pH and carbonate concentration: Experimental data from [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC] in 1.0 M Na_2CO_3 containing 0.01 − 1.0 M NaOH (left side) and in 0.001 − 2.0 M Na_2CO_3 containing 0.1 M NaOH (right side). The calculations are based on the equilibrium constants, SIT coefficients and $\log_{10} K^{o}_{s,0}$ (aged ThO_2(am, hyd)) = − 47.5 selected in the present review, taking into account the variation of the solution composition and ionic strength.



XI.1.3.2.1.4 Summary

The available solubility data for ThO_2(am, hyd) in carbonate solution (19 sets of experimental data from different groups of authors) under widely varying conditions: pH 4.5 − 13, carbonate concentrations up to 2 M and ionic strength varying from I = 0.1 M to 4.0 M (even up more than 6 M) are well described with only a few ternary complexes, the most important ones being $Th(OH)(CO_3)_4^{5-}$, $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)_4(CO_3)^{2-}$.

The (114) complex ($Th(OH)(CO_3)_4^{5-}$) is responsible for the high Th concentrations in the solubility studies with ThO_2(am, hyd) at pH 7 − 8 under 0.1 − 1.0 bar CO_2(g) (Figure XI-2) and at pH 8 − 10 at C_{tot} = 0.02 − 0.1 M (Figure XI-3), in particular at high ionic strength, but also at high pH (pH 11 − 13) and carbonate concentrations of 0.3 − 2.0 M (Figure XI-4).

The (122) complex ($Th(OH)(CO_3)_4^{5-}$) is dominant both at pH 5.5 − 7 under 0.1 − 1.0 bar CO_2(g) (Figure XI-2) and at C_{tot} = 0.01 − 0.1 and pH 8 − 9, particularly at low ionic strength (*e.g.*, in bicarbonate solutions as also shown in analogous solubility studies with U(IV), Np(IV) and Pu(IV) hydrous oxides [1998RAI/FEL], [1999RAI/HES], [1999RAI/HES2]). The contribution of this complex to the thorium concentration in solubility studies with ThO_2(am, hyd) is in the range $10^{-7} - 10^{-4}$ M.

The (141) complex ($Th(OH)(CO_3)_4^{5-}$) is the dominant species at pH > 11 and carbonate concentrations in the range of 0.02 − 0.5 M (Figure XI-3 and Figure XI-4). The concentration of this complex is rather low and does not exceed 2×10^{-7} M. However, its concentration is significantly greater than that of $Th(OH)_4$(aq).

Hence, the following formation constants and SIT coefficients are selected:

$$\log_{10} \beta^{\circ}_{114}(\mathrm{Th(OH)(CO_3)_4^{5-}}, 298.15\ \mathrm{K}) = (35.6 \pm 0.5)$$
$$\varepsilon(\mathrm{Th(OH)(CO_3)_4^{5-}}, \mathrm{Na^+}) = -(0.22 \pm 0.13)\ \mathrm{kg{\cdot}mol^{-1}}.$$

$$\log_{10} \beta^{\circ}_{112}(\mathrm{Th(OH)_2(CO_3)_2^{2-}}, 298.15\ \mathrm{K}) = (36.8 \pm 0.5)$$
$$\varepsilon(\mathrm{Th(OH)_2(CO_3)_2^{2-}}, \mathrm{Na^+}) = -(0.1 \pm 0.2)\ \mathrm{kg{\cdot}mol^{-1}}.$$

$$\log_{10} \beta^{\circ}_{141}(\mathrm{Th(OH)_4(CO_3)^{2-}}, 298.15\ \mathrm{K}) = (40.4 \pm 0.6)$$
$$\varepsilon(\mathrm{Th(OH)_4(CO_3)^{2-}}, \mathrm{Na^+}) = -(0.1 \pm 0.2)\ \mathrm{kg{\cdot}mol^{-1}}.$$

The complexes $Th(OH)_2(CO_3)$(aq) and $Th(OH)_3(CO_3)^-$ are found to be relevant only at low carbonate concentrations in the near neutral pH range, *e.g.*, in the studies under 0.1 and 1.0 bar CO_2(g) they have maximum contributions of 30 − 50 % in the solubility minimum range at pH 5 − 6 (Figure XI-2). The speciation schemes indicate that the predominance regions of $Th(OH)_2(CO_3)$(aq) and $Th(OH)_3(CO_3)^-$ are between those of $Th(OH)_2^{2+}$, $Th(OH)_2(CO_3)_2^{2-}$ and $Th(OH)_4$(aq). However, the maximum effect on the calculated solubility is less than 0.3 $\log_{10}$-units (at thorium concentrations of $10^{-8} - 10^{-6}$ M). Under nearly all other conditions these two species are negligible. The formation constants and SIT coefficients

$$\log_{10} \beta^{\circ}_{121}(\mathrm{Th(OH)_2(CO_3)(aq)}, 298.15\ \mathrm{K}) = (30.5 \pm 0.6)$$

(SIT coefficients equal to zero)

$$\log_{10} \beta^{\circ}_{131}(\mathrm{Th(OH)_3(CO_3)^-}, 298.15\ \mathrm{K}) = (38.3 \pm 0.7)$$

$$\varepsilon(\mathrm{Th(OH)_3(CO_3)^-}, \mathrm{Na^+}) = -(0.05 \pm 0.2)\ \mathrm{kg{\cdot}mol^{-1}}.$$

are not selected but recommended as guidance. The speciation lines of these complexes are shown as dashed lines in the model calculations.

The solubility data at high carbonate concentrations (> 0.5 M) and pH > 12 [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI], in particular with additions of NaCl, can be better described by assuming the formation of an additional (124) complex = $\mathrm{Th(OH)_2(CO_3)_4^{6-}}$, with:

$$\log_{10} \beta^{\circ}_{124}(\mathrm{Th(OH)_2(CO_3)_4^{6-}}, 298.15\ \mathrm{K}) \le (34.3 \pm 0.6)$$

$$\varepsilon(\mathrm{Th(OH)_2(CO_3)_4^{6-}}, \mathrm{Na^+}) = -(0.3 \pm 0.2)\ \mathrm{kg{\cdot}mol^{-1}}.$$

(A similar situation occurred in the evaluation of the U(IV) solubility data in 3.0 and 3.3 m K_2CO_3 containing 0.01 − 0.8 m NaOH or KOH, respectively, *cf.*, Appendix A review of [1998RAI/FEL] in [2003GUI/FAN]). However, these conditions are beyond the validity range of the SIT. Moreover, the model is not unique; changing $\varepsilon(\mathrm{Th(OH)(CO_3)_4^{5-}}, \mathrm{Na^+})$ or $\varepsilon(\mathrm{Th(CO_3)_5^{6-}}, \mathrm{Na^+})$ within their uncertainty ranges also yields good fits. Under all other conditions discussed in this review this complex is a minor species (less than 10%). Therefore an equilibrium constant for this complex was not selected.

XI.1.3.2.2 Formation constant of $\mathrm{Th(CO_3)_5^{6-}}$

The pentacarbonate complex (105) is not dominant in the studies discussed above, but is in carbonate and bicarbonate solutions at C_{tot} > 0.2 M and pH = 8 − 11 (*e.g.*, in 0.2 − 2 M $NaHCO_3$ or Na_2CO_3, see below) where the solubility of ThO_2(am, hyd) is very high. Additional studies based on solubility experiments of Östhols *et al.* [1994OST/BRU], Altmaier *et al.* [2006ALT/NEC] and Felmy *et al.* [1997FEL/RAI], liquid-liquid extraction by João *et al.* [1987JOA/BIG2], [1995JOA/BUR] and EXAFS data [1997FEL/RAI], [2006ALT/NEC] will be discussed in this section.

The limiting carbonate complex is an important species in the Th(IV)-carbonate system. However, as discussed above, the formation constant of $\mathrm{Th(CO_3)_5^{6-}}$ is not available directly from the solubility measurements in [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC], [2006ALT/NEC]. All solubility measurements with ThO_2(am, hyd) were performed either at carbonate concentrations $C_{\mathrm{tot}} \le 0.1$ M, which is not high enough to form $\mathrm{Th(CO_3)_5^{6-}}$ as the dominant complex, or at pH > 12 where, due to the competition between $\mathrm{OH^-}$ and $\mathrm{CO_3^{2-}}$ ligands, ternary complexes $\mathrm{Th(OH)(CO_3)_4^{5-}}$ and possibly $\mathrm{Th(OH)_2(CO_3)_4^{6-}}$ become dominant, even at high carbonate concentrations.

In the intermediate range, 0.2 M < C_{tot} < 2 M and pH = 8 − 11 (*e.g.*, in 0.2 − 2 M $NaHCO_3$ or Na_2CO_3 solutions), where EXAFS studies have identified the limiting carbonate complex $Th(CO_3)_5^{6-}$ as the dominant species, the solubility of ThO_2(am, hyd) is very high. Under these conditions the solubility of thorium is limited by $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ with thorium concentrations in the range 0.02 − 0.05 M [1961LUZ/KOV2], [1973DER/FAU3]. There is no other independent thermodynamic information for this solid phase; therefore only the equilibrium constant for the reaction:

$$Na_6[Th(CO_3)_5]\cdot 12H_2O(s) \rightleftharpoons 6Na^+ + Th(CO_3)_5^{6-} + 12H_2O(l) \qquad \text{(XI.12)}$$

can be derived (*cf.*, Section XI.1.3.3), but not the formation constant $\log_{10} \beta^o_{105}$. It may seem surprising that the limiting carbonate complex $Th(CO_3)_5^{6-}$ is also dominant in $NaHCO_3$ solutions above 0.2 M where the concentration of CO_3^{2-} is orders of magnitude lower than in the corresponding Na_2CO_3 solutions. However, the same holds true for the competing OH^- ligand and the ratio between the two most important complexes $[Th(CO_3)_5^{6-}]:[Th(OH)(CO_3)_4^{5-}]$ under these conditions does not depend on the absolute concentration of carbonate but on the ratio $[CO_3^{2-}]/[OH^-]$ according to:

$$Th(CO_3)_5^{6-} + OH^- \rightleftharpoons Th(OH)(CO_3)_4^{5-} + CO_3^{2-} \qquad \text{(XI.13)}$$

with

$$\log_{10} \frac{[Th(CO_3)_5^{6-}]}{[Th(OH)(CO_3)_4^{5-}]} = \log_{10} \beta_{105} - \log_{10} \beta_{114} + \log_{10} \frac{[CO_3^{2-}]}{[OH^-]} \qquad \text{(XI.14)}$$

The equilibrium constants derived from the solvent extraction studies of Joao *et al.* [1987JOA/BIG2], [1995JOA/BUR] are not reliable. For instance with $\log_{10} \beta_{105}$ = (28.3 ± 0.2) derived from the study of [1987JOA/BIG2] at I = 1.0 M (guanidinium carbonate / bicarbonate solution) and assuming the same value for I = 1.0 M (Na_2CO_3-$NaHCO_3$), the concentration of $Th(CO_3)_5^{6-}$ is always significantly below that of $Th(OH)(CO_3)_4^{5-}$ ($\log_{10} \beta_{114}$ = (34.2 ± 0.5) at I = 1.0 M). The ratio between the two complexes is given by:

$$\log_{10} \frac{[Th(CO_3)_5^{6-}]}{[Th(OH)(CO_3)_4^{5-}]} = -(5.9 \pm 0.5) + \log_{10} \frac{[CO_3^{2-}]}{[OH^-]} \qquad \text{(XI.15)}$$

where $\log_{10} \frac{[CO_3^{2-}]}{[OH^-]}$ is generally smaller than 5.

The solubility data determined with a dried Th(IV) oxyhydroxide phase at I = 0.5 M, both at C_{tot} = 0.1 M and under CO_2 partial pressures of 1.0 and 0.1 bar [1994OST/BRU], [2005ALT/NEC], set an upper limit for the formation constant of $Th(CO_3)_5^{6-}$. Altmaier *et al.* [2005ALT/NEC] indicate that $\log_{10} K^o_{s,105}$ is more negative than − 16.6, which is consistent, within the uncertainties, with the value of − (16.4 ± 0.3) from [1994OST/BRU]. If this value is combined with $\log_{10} K^o_{s,0}$ = − (47.6 ± 0.5) or

– (48.0 ± 0.5), respectively (calculated by this review from the solubility data determined in these studies with the same solid phase in carbonate-free solutions), an upper limit of $\log_{10} \beta^{\circ}_{105} <$ (31.3 ± 0.6) is obtained.

EXAFS measurements in various carbonate and bicarbonate solutions [1997FEL/RAI], [1997HES/FEL], [2006ALT/NEC] give only qualitative information on the speciation because the spectra could not be deconvoluted into single component contributions. However, in combination with the known formation constant of $\text{Th(OH)(CO}_3)_4^{5-}$ ($\log_{10} \beta^{\circ}_{114}$ = (35.6 ± 0.5), *cf.* Section XI.1.3.2.1), the most important competing species in these solutions, the information from the EXAFS studies allows the estimation of the equilibrium constant $\log_{10} \beta^{\circ}_{105}$ within a certain range.

Felmy *et al.* [1997FEL/RAI], [1997HES/FEL] recorded EXAFS spectra of Th(IV) in 1.0 or 2.0 M Na_2CO_3 [1] and in 1.0, 0.5, 0.25, 0.17, and 0.10 M $NaHCO_3$. In the Na_2CO_3 solution and in 1.0 and 0.5 M $NaHCO_3$ the limiting carbonate complex is undoubtedly the dominant species. In the 0.25 and 0.17 M $NaHCO_3$ solutions the average number of CO_3^{2-} ligands (derived from the Th-C and Th-O_{distal} scattering paths) decreases slightly. The distance r(Th-O) and the total coordination number (N_O = (10 ± 1)) remain approximately constant, whereas in 0.10 M $NaHCO_3$ both r(Th-O) and N_O and also the number of CO_3^{2-} ligands is significantly lower. As particularly the coordination numbers have large uncertainties, a quantitative speciation or a clear-cut identification of the complexes is not possible. However, applying Equation (XI.14) a minimum value for the formation constant of $\text{Th(CO}_3)_5^{6-}$ can be derived from the observation that $\text{Th(CO}_3)_5^{6-}$ is the major complex at $NaHCO_3$ concentrations above 0.3 M. The pH of these solutions is not given in [1997FEL/RAI], but in comparable samples of U(IV) [1998RAI/FEL] and Pu(IV) [1999RAI/HES2] in 0.2 – 0.5 M bicarbonate solution the H^+ concentration is in the range $-\log_{10}[H^+] = 8 - 9$. Using NEA-TDB auxiliary data to calculate the dissociation constant of water and the protonation constant of carbonate in 0.3 M $NaHCO_3$ at $-\log_{10}[H^+] = 8 - 9$, we obtain an approximately constant value of $\log_{10}([CO_3^{2-}]/[OH^-])$ = 3.5. Combining this value with $\log_{10} \beta_{114}$ = (34.4 ± 0.5) ($\log_{10} \beta^{\circ}_{114}$ = (35.6 ± 0.5)), the relation [105]/[114] > 1 (more than 50% of the thorium present as $\text{Th(CO}_3)_5^{6-}$) requires a minimum value of $\log_{10} \beta_{105} >$ (30.9 ± 0.5). Extrapolation to zero ionic strength with the SIT yields the following lower limit: $\log_{10} \beta^{\circ}_{105} >$ (30.8 ± 0.5).

Altmaier *et al.* [2006ALT/NEC] reported an EXAFS spectrum of a thorium solution in 1.0 M Na_2CO_3/0.1 M $NaHCO_3$ which is consistent with those measured in [1997FEL/RAI] for thorium solutions at high carbonate or bicarbonate concentrations. However, the EXAFS spectrum of a saturated solution taken from the solubility study at I = 0.5 M ($NaHCO_3$-Na_2CO_3-NaCl), C_{tot} = 0.1 M, and $-\log_{10}[H^+]$ = 9.16 ($\log_{10}([CO_3^{2-}]/[OH^-])$ = 3.0) is clearly different and indicates that the limiting carbonate complex is not dominant (less than 50%) under these conditions

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[1] The exact composition of this solution is not known, *cf.* Appendix A review of [1997FEL/RAI].

ate complex is not dominant (less than 50%) under these conditions [2006ALT/NEC]. As $Th(OH)(CO_3)_4^{5-}$ (with $\log_{10}\beta_{114} = (34.3 \pm 0.5)$, $\log_{10}\beta^{\circ}_{114} = (35.6 \pm 0.5)$) is the only other relevant species in this solution, the relation [105]/[114] < 1 yields an upper limit of $\log_{10}\beta_{105} < (31.3 \pm 0.5)$ (corresponding to $\log_{10}\beta^{\circ}_{105} < (31.2 \pm 0.5)$). This observation is consistent with the interpretation of the solubility data under these conditions [2005ALT/NEC], [2006ALT/NEC] (*cf.* Figure XI-3 in Section XI.1.3.2.1).

Table XI-5: Equilibrium constants for $Th(CO_3)_5^{6-}$ at 22−25°C (uncertainties are given as 2σ).

Method	$\log_{10} K^{\circ}_{s,105}$	$\log_{10}\beta^{\circ}_{105}$	Reference
extr		28.3 ± 0.2 [a]	[1987JOA/BIG2]
extr		21.5 ± 0.5 [b]	[1995JOA/BUR]
sol	< -16.6	$< 31.0 \pm 0.5$ [c]	[2005ALT/NEC]
sol	-16.4 ± 0.4	31.6 ± 0.6 [c]	[1994OST/BRU]
sol	-18.4 [d]	29.1 ± 0.9 [c]	[1997FEL/RAI]
		31.0 ± 0.7	This review

a: $\log_{10}\beta_{105}$ at I = 1.0 M (guanidinium carbonate/bicarbonate solution), recalculated by this review, *cf.* Appendix A.

b: This value is the average from experimental data at three different ionic strengths, 0.025, 0.050 and 0.70 M extrapolated to $I = 0$ by this review using $\Delta\varepsilon = -0.6$ kg·mol^{-1}, based on the interaction coefficients in Appendix B and assuming $\varepsilon(Th(CO_3)_5^{6-}, NH_4^+/C(NH_2)_3^+) = \varepsilon(U(CO_3)_5^{6-}, Na^+)$ in the ammonium/guanidium nitrate medium used. For reasons given in Appendix A, these values have not been accepted by this review.

c: Calculated according to: $\log_{10}\beta^{\circ}_{105} = \log_{10} K^{\circ}_{s,105} - \log_{10} K^{\circ}_{s,0}$ with the $\log_{10} K^{\circ}_{s,0}$ values calculated by this review: $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$ [2005ALT/NEC], $-(48.0 \pm 0.5)$ [1994OST/BRU], or $-(47.5 \pm 0.9)$ selected for aged ThO_2(am, hyd).

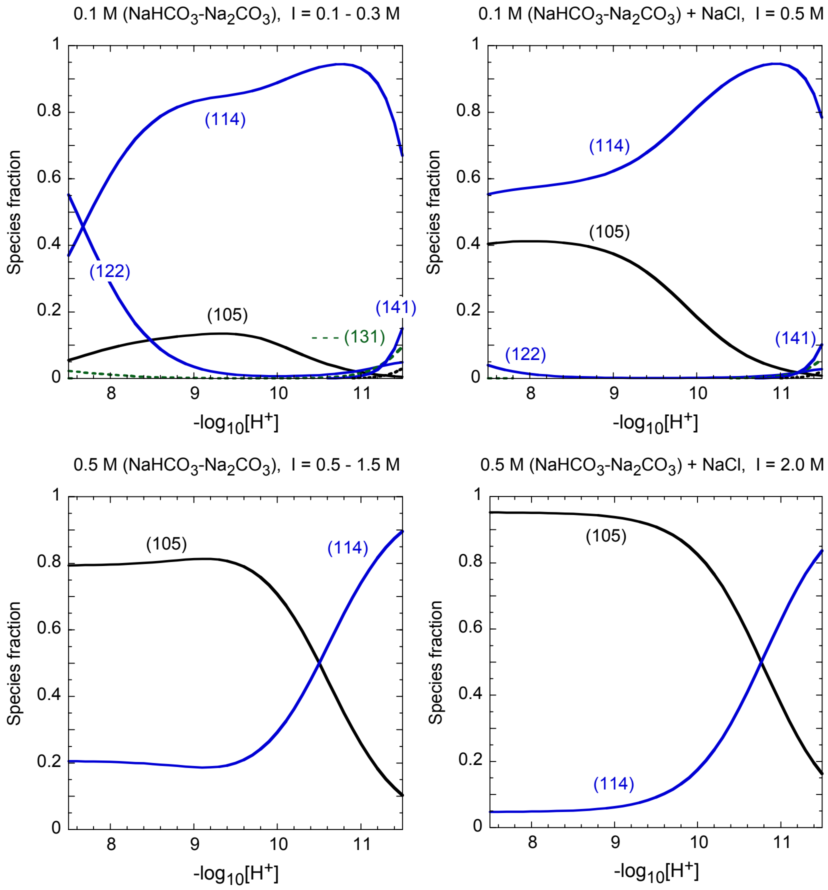
d: Based on Pitzer's ion interaction approach (*cf.* Appendix A review of [1997FEL/RAI]) and hence not directly comparable to the $\log_{10} K^{\circ}_{s,105}$ values from [1994OST/BRU] and [2005ALT/NEC] which are calculated with the SIT.

Combining the information from the solubility of ThO_2(am, hyd) at I = 0.5 M [1994OST/BRU], [2005ALT/NEC] and from the EXAFS studies in carbonate and bicarbonate solutions [1997FEL/RAI], [2006ALT/NEC], the formation constant of $Th(CO_3)_5^{6-}$ must be in the range: $(30.8 \pm 0.5) < \log_{10}\beta^{\circ}_{105} < (31.2 \pm 0.5)$. Based on the ion interaction coefficient $\varepsilon(Th(CO_3)_5^{6-}, Na^+) = \varepsilon(U(CO_3)_5^{6-}, Na^+) = -(0.30 \pm 0.15)$ kg·mol^{-1}, this review selects a value of:

$$\log_{10}\beta^{\circ}_{105}\,(Th(CO_3)_5^{6-}, 298.15\ K) = (31.0 \pm 0.7)$$

where the uncertainty covers the whole range of values deduced from the previous discussions. In order to illustrate the discussion above, Figure XI-5 shows speciation schemes calculated with the selected formation constants for $Th(CO_3)_5^{6-}$ and the ternary Th(IV)-hydroxide-carbonate complexes.

Figure XI-5: Speciation schemes calculated with the selected formation constants for $Th(CO_3)_5^{6-}$ and the ternary Th(IV)-hydroxide-carbonate complexes. Left side: 0.1 and 0.5 M $NaHCO_3$-Na_2CO_3 solutions of varying ionic strength (I = [$NaHCO_3$] + 3[Na_2CO_3])[1]. Right side: $NaHCO_3$-Na_2CO_3-NaCl (or $NaClO_4$) solutions of the same carbonate concentration (C_{tot} = 0.1 and 0.5 M), but at constant ionic strength (I = 0.5 and 2.0 M, respectively.)



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[1] The calculations are accounting for the continuous variation of $\log_{10} K_w$, $\log_{10} K_2$ (protonation constant of CO_3^{2-}) and the formation constants of the thorium complexes when ionic strength varies from $I = m_{NaHCO_3}$ at pH < 9 to I = 3 $m_{Na_2CO_3}$ at pH > 10.

The speciation depends not only on the H^+ and carbonate concentration; it is also significantly affected by the ionic strength. Higher ionic strength favours the formation of the higher charged complex $Th(CO_3)_5^{6-}$ (z^2 = 36) compared to $Th(OH)(CO_3)_4^{5-}$ (z^2 = 25) and particularly compared to $Th(OH)_2(CO_3)_2^{2-}$ (z^2 = 4) (*cf.* the speciation at C_{tot} = 0.1 M in pure $NaHCO_3$-Na_2CO_3 solution (I = 0.1 − 0.3 M, left side) and in $NaHCO_3$-Na_2CO_3-(NaCl or $NaClO_4$) with ionic strength kept constant at I = 0.5 M by additions of NaCl or $NaClO_4$ (right side).

XI.1.3.3 Solubility of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ and $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot 4H_2O(s)$

There are two experimental studies of the solubility of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ in sodium carbonate and bicarbonate solutions, from Luzhnaya and Kovaleva [1961LUZ/KOV2] and Dervin and Faucherre [1973DER/FAU3]. These studies are discussed in Appendix A. This review has reinterpreted the experimental data and calculated the solubility product $\log_{10} K^{\circ}_{s,5}$ for the reaction:

$$Na_6[Th(CO_3)_5]\cdot 12H_2O(s) \rightleftharpoons 6Na^+ + Th(CO_3)_5^{6-} + 12H_2O(l) \qquad (XI.16)$$

The values of $\log_{10} K^{\circ}_{s,5} = -(11.3 \pm 0.3)$, $-(11.2 \pm 0.4)$, and $-(11.0 \pm 0.5)$ derived by this review from the solubility of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ in 0.79 − 2.8 m Na_2CO_3 [1961LUZ/KOV2], in Na_2CO_3-$NaNO_3$ solution (at $[Na^+]$ = 2.0 M and $[CO_3^{2-}]$ = 0.15 − 1.0 M) [1973DER/FAU3], and in 2.0 M $NaHCO_3$-$NaNO_3$ (at $[Na^+]$ = 2.0 M and $[HCO_3^-]$ = 0.2 − 1.0 M) [1973DER/FAU3], respectively, are in good agreement, in particular taking into account the relatively large uncertainties arising from the SIT coefficients used for the extrapolation to zero ionic strength. However it should be noted that the values at zero ionic strength are only based on the experimental data at $I < 5\ \text{mol}\cdot\text{kg}^{-1}$. The following mean value is selected:

$$\log_{10} K^{\circ}_{s,5}\,(Na_6[Th(CO_3)_5]\cdot 12H_2O(s)) = -(11.2 \pm 0.4).$$

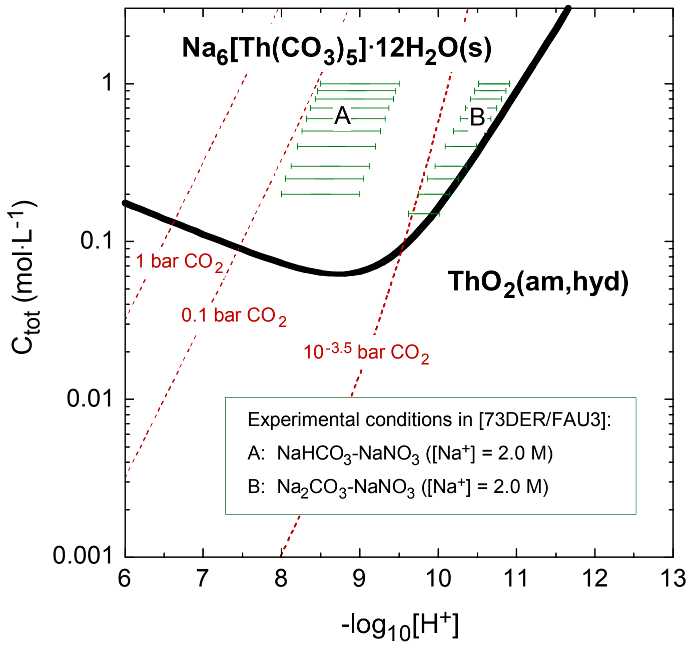
It is not possible to calculate the formation constant of $Th(CO_3)_5^{6-}$ from these data; however, they provide information of the stoichiometry of the dominant complex.

Figure XI-6 shows the stability field of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ compared to ThO_2(am, hyd), which is found to be the stable solubility limiting phase in many other solubility studies [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC], [2006ALT/NEC]. These solubility measurements with ThO_2(am, hyd) were performed either at carbonate concentrations $C_{tot} \le 0.1$ M or at pH > 12. The borderline for the solid transformation:

$$Na_6[Th(CO_3)_5]\cdot 12H_2O(s) + 4OH^- \rightleftharpoons ThO_2(\text{am, hyd}) + 6Na^+ + 5CO_3^{2-} + 14H_2O(l) \quad (XI.17)$$

is calculated for the conditions in [1973DER/FAU3] ($NaHCO_3$-Na_2CO_3-$NaNO_3$ solutions at a constant sodium ion concentration of $[Na^+]$ = 2.0 M). $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ is stable only at high Na^+ and carbonate concentrations but Figure XI-6 shows that it is not stable at high pH, where ThO_2(am, hyd) is the stable phase. The stability region of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ coincides with the range where the solubility of ThO_2(am, hyd) is rather high ($[Th]_{tot} > 0.01$ M) and with the range where $Th(CO_3)_5^{6-}$ is the dominant complex in solution.

Figure XI-6: Stability region of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ compared to aged ThO_2(am, hyd) ($\log_{10} K^{\circ}_{s,0} = -47.5$) at $[Na^+] = 2.0$ M ($NaHCO_3$-Na_2CO_3-$NaNO_3$) and 25°C. The regions A and B indicate the experimental conditions in [1973DER/FAU3]; the dotted lines show the corresponding values of the total carbonate concentration C_{tot} and $-\log_{10}[H^+]$ for equilibrium CO_2 partial pressures of 1.0, 0.1, and $10^{-3.5}$ bar (air).



The approximately constant solubility of 0.021 to 0.029 mol·L^{-1} observed by [1973DER/FAU3] for all bicarbonate and most of the carbonate solutions (up to 0.5 M Na_2CO_3) indicates that ternary Th(IV)-hydroxide-carbonate complexes are not dominant under these conditions. The formation of additional complexes would increase the solubility significantly. A test as to whether the thermodynamic data selected in this review, in particular for the complex $Th(OH)(CO_3)_4^{5-}$, are compatible with the experimental data of [1973DER/FAU3] requires the values of pH or H^+ concentration which were not determined by [1973DER/FAU3]. The following section describes an alternative method of testing the compatibility.

The pH values in the bicarbonate solutions are estimated ([1998RAI/FEL], [1999RAI/HES2]) to be in the range of 8 − 9.5 for 0.2 − 1.0 M bicarbonate solutions and they clearly fall in the stability region of $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ (*cf.* region A in Figure XI-6). For the Na_2CO_3-$NaNO_3$ solutions in [1973DER/FAU3] the situation is more complicated. Assuming a closed system, the H^+ concentrations of the $NaNO_3$ solutions containing 0.2 − 1.0 M Na_2CO_3 are calculated to be in the range $-\log_{10}[H^+] = 11.0 - 11.5$ which is outside the stability range of $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$. However, the precipitation of ThO_2(am, hyd) with a much lower solubility under these conditions (*cf.* Figure XI-7 and Figure XI-8 below) was not observed by [1973DER/FAU3]. Moreover, $Th(OH)(CO_3)_4^{5-}$ is calculated to be the dominant complex at these pH values and hence the solubility of $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ would be considerably increased by the formation of this additional complex, but this was not observed by [1973DER/FAU3] (maximum solubility in 1.0 M Na_2CO_3: $[Th]_{tot} = 0.046\ mol\cdot L^{-1}$). On the other hand, the formation of $Th(OH)(CO_3)_4^{5-}$ according to:

$$Th(CO_3)_5^{6-} + H_2O(l) \rightleftharpoons Th(OH)(CO_3)_4^{5-} + CO_3^{2-} + H^+ \qquad (XI.18)$$

results in a decrease of pH. For instance in 1.0 M Na_2CO_3, an equilibrium state would be reached at $-\log_{10}[H^+] = 10.9$ for a solution containing 0.025 M $Th(CO_3)_5^{6-}$ and 0.021 M $Th(OH)(CO_3)_4^{5-}$. A further decrease of pH, particularly for the lower carbonate concentrations, is expected due to the absorption of $CO_2(g)$ from the atmosphere. Therefore we may estimate that the pH values are a) in the stability field of $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ and b) shifted to the values in equilibrium with the CO_2 partial pressure of air (*cf.* region B in Figure XI-6).

Figure XI-7 and Figure XI-8 show the solubility data of Dervin and Faucherre [1973DER/FAU3] at the highest and the lowest total carbonate concentration of C_{tot} = 1.0 and 0.2 M, respectively, in comparison with the solubility of ThO_2(am, hyd) under these conditions. The results of [1973DER/FAU3] are consistent with the solubility and speciation calculated with the equilibrium constants selected in this review. The limiting carbonate complex is the dominant species under the experimental conditions of [1973DER/FAU3], while at higher pH the ternary complex $Th(OH)(CO_3)_4^{5-}$ becomes the dominant aqueous species and ThO_2(am, hyd) the solubility limiting solid phase. Figure XI-7 shows that the somewhat higher solubility of $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ in 1 M Na_2CO_3 compared to that in 1 M $NaHCO_3$ + 1 M $NaNO_3$ is not caused by the formation of $Th(CO_3)_6^{8-}$ as assumed by Dervin and Faucherre, but by the variation of the medium composition and increasing ionic strength (*cf.* slight increase of the (105) concentration line in Figure XI-7 with increasing pH), and by the contributions from the complex $Th(OH)(CO_3)_4^{5-}$, also increasing with pH (*cf.* the concentration line of (114) and speciation diagrams in Figure XI-7 and Figure XI-8).

Figure XI-7: Solubility and speciation of thorium at a total carbonate concentration of C_{tot} = 1.0 M. Experimental data for $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ in 1.0 M $NaHCO_3$ + 1.0 M $NaNO_3$ and in 1.0 M Na_2CO_3 [1973DER/FAU3], [1961LUZ/KOV2] and for ThO_2(am, hyd) in 1.0 M Na_2CO_3 containing 0.01 − 1.0 M NaOH [1995RAI/FEL], [2005ALT/NEC]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review taking into account the variation of the solution composition and ionic strength.

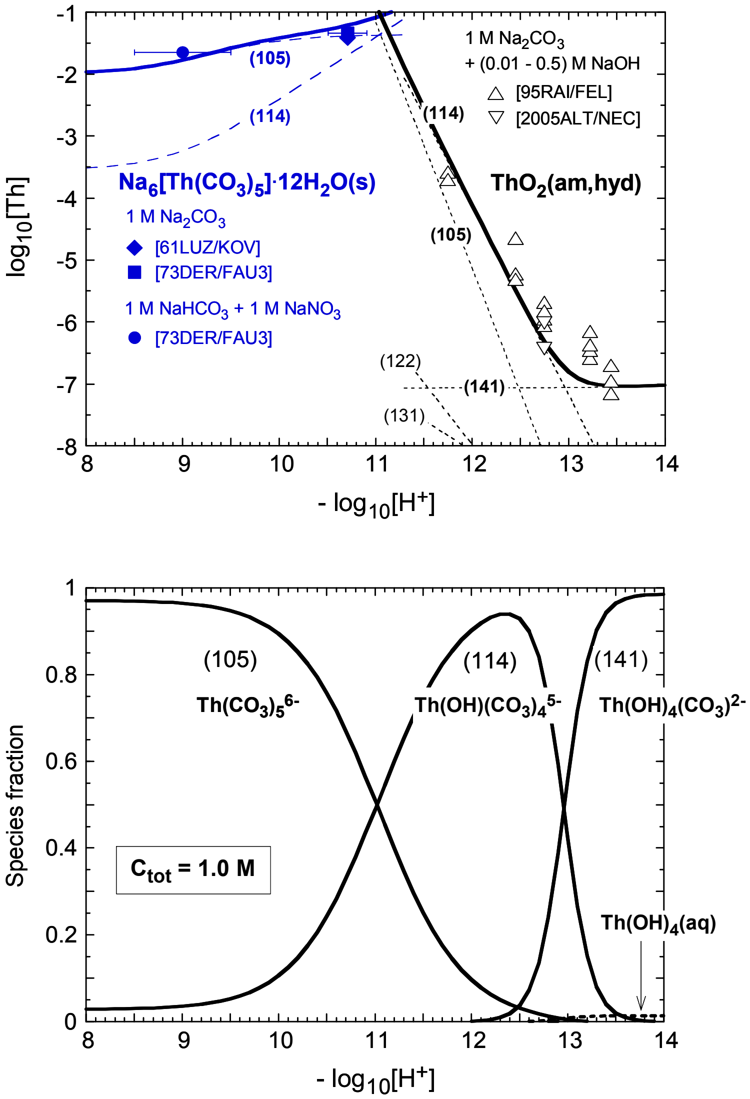
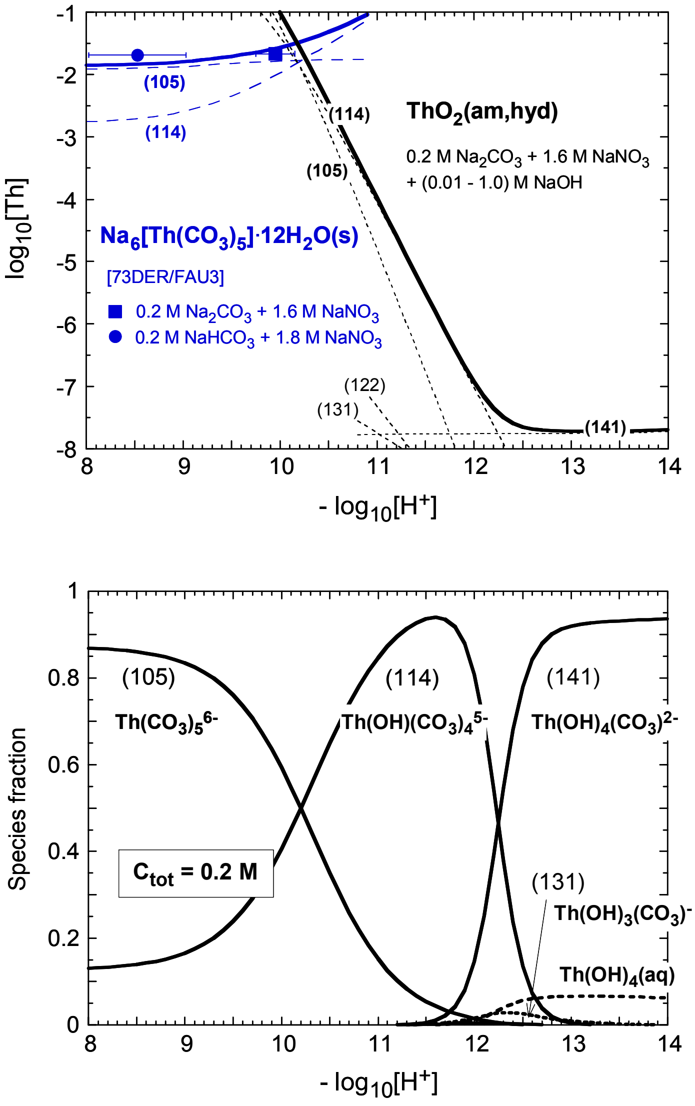


Figure XI-8: Solubility and speciation of thorium at a total carbonate concentration of C_{tot} = 0.2 M. Experimental data for $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ in 0.2 M $NaHCO_3$ / 1.8 M $NaNO_3$ and in 0.2 M Na_2CO_3 / 1.6 M $NaNO_3$ [1973DER/FAU3] and calculated solubility for ThO_2(am, hyd) in 0.2 M Na_2CO_3 / 1.6 M $NaNO_3$ containing 0.01 − 1.0 M NaOH. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review taking into accounting the variation of the solution composition and ionic strength.



Dervin and Faucherre [1973DER/FAU3] have also measured the solubility of $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s)$ as function of the carbonate and bicarbonate concentration, using a guanidinium nitrate ionic medium. The $C(NH_2)_3^+$ concentration was kept constant at 2.0 M. In the 2.0 M $[C(NH_2)_3]_2CO_3$-$C(NH_2)_3NO_3$ solutions with $[HCO_3^-]$ in the range 0.2 − 1.0 M, the solubility of $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s)$ remained constant at 1.57×10^{-3} M, yielding a conditional equilibrium constant of: $K_{s,5}(\text{XI.19}) = [C(NH_2)_3^+]^6\,[Th(CO_3)_5^{6-}] = 0.10\ M^7$ for the reaction:

$$[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s) \rightleftharpoons 6\,C(NH_2)_3^+ + Th(CO_3)_5^{6-} + xH_2O(l) \qquad (\text{XI.19})$$

In the $[C(NH_2)_3]_2CO_3$-$C(NH_2)_3NO_3$ solutions with $[C(NH_2)_3^+] = 2.0$ M and $[CO_3^{2-}] = 0.25 - 1.0$ M the ionic strength varies from $I = 2.25$ to 3.0 M. The solubility remained constant at 1.7×10^{-3} M, in the range $0.25\ M < [CO_3^{2-}] < 0.35$ M, indicating the predominance of $Th(CO_3)_5^{6-}$ in solution and a very similar value of $K_{s,5} = 0.11\ M^7$. At carbonate concentrations above 0.35, M the solubility increases and the slope of $\log_{10}[Th]_{tot}$ *vs.* $\log_{10}[CO_3^{2-}]$ apparently indicates an equilibrium between $Th(CO_3)_5^{6-}$ and $Th(CO_3)_6^{8-}$:

$$Th(CO_3)_5^{6-} + CO_3^{2-} \rightleftharpoons Th(CO_3)_6^{8-} \qquad (\text{XI.20})$$

As discussed above for the solubility of $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ in the corresponding Na_2CO_3-$NaNO_3$ and $NaHCO_3$-$NaNO_3$ solutions, it is clear that the activity coefficients do not remain constant at these high and varying carbonate concentrations. This review therefore does not accept the interpretation given by Dervin and Faucherre and concludes that the limiting Th(IV) carbonate complex is $Th(CO_3)_5^{6-}$, a conclusion that is supported by the available EXAFS data.

The solubility of $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s)$ is about 10 times lower than that of $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ in the corresponding sodium salt solutions. It is not possible to extrapolate the conditional solubility constant $\log_{10} K_{s,5} = -1.0$ at $I = 2.0$ M to zero ionic strength, because the ion interaction coefficients between $C(NH_2)_3^+$ and NO_3^-, HCO_3^-, CO_3^{2-}, and $Th(CO_3)_5^{6-}$ are not known.

XI.1.3.4 Additional studies of the thorium carbonate system

Bruno *et al.* [1987BRU/CAS2] and Grenthe and Lagerman [1991GRE/LAG2] performed potentiometric studies of the Th(IV)-hydroxide-carbonate system under CO_2 partial pressures of 0.3 and 1.0 bar ($[Th]_{tot} = 0.24 - 7.0$ mM, $-\log_{10}[H^+] = 2.5 - 5.0$ in 3.0 M $NaClO_4$). They noticed that the very steep curves of Z (average number of bonded OH^- per Th) *vs.* $\log_{10}[H^+]$ indicate the formation of complexes with high nuclearity, *e.g.* $"Th_8(OH)_{24}(CO_2)_2^{8+}" \equiv Th_8(OH)_{20}(CO_3)_2^{8+}$ and $"Th_{16}(OH)_{52}(CO_2)_{16}^{12+}" \equiv Th_{16}(OH)_{20}(CO_3)_{16}^{12+}$ which could explain the data at the lowest Th concentrations [1991GRE/LAG2]. The steep rise in the Z-curves take place at $-\log_{10}[H^+]$ around 3.3 where there should be no precipitation of Th(IV) hydrous oxide and no significant formation of mononuclear hydroxide-carbonate complexes *cf.*, Appendix A reviews of [1994OST/BRU] and [2005ALT/NEC]. A possible explanation suggested by this review is that hydrous oxides precipitate on the CO_2 gas-bubbles present in the study, that is a similar process to that used in flotation of ores. There is no attempt to make a quantitative evaluation of the carbonate data in [1991GRE/LAG2] and accordingly no quantitative information on the stoichiometry and equilibrium constants in the ternary Th(IV)-H_2O-CO_2(g) system at pH < 5.

Faucherre and Dervin [1962FAU/DER], [1962FAU/DER2], [1973DER/FAU2] have studied the complex formation in the thorium-carbonate system using different experimental methods. In [1962FAU/DER] they used cryoscopy and concluded that "it appears that the constitution of the complexes in the solutions studied is of the type [$Th(CO_3)_5^{6-}$]" ; however no thermodynamic data are given. In a second study [1962FAU/DER2] used potentiometry in attempt to determine the composition of the species formed. The experimental data were not rigorously analysed and no thermodynamic data were derived. In a third study [1973DER/FAU2] used cryoscopy, conductometry and ion exchange, but the information provided is limited to a suggestion that the limiting carbonate complex has the composition $[Th(CO_3)_6]^{8-}$, a conclusion not consistent with other observations as discussed in this review. Chernyaev *et al.* [1961CHE/GOL] describe the preparation of $(NH_4)_6[Th(CO_3)_5]\cdot 3H_2O$ and its thermal stability, but with no quantitative thermodynamic data. Ryabchikov *et al.* [1963RYA/VOL] have used high frequency titrations to establish that the stoichiometry of the limiting complex is $[Th(CO_3)_4]^{4-}$, not consistent with other observations. They also provide some crystallographic and thermogravimetric information. There are no thermodynamic data in this communication. Voliotis *et al.* [1975VOL/RIM2], [1975VOL/RIM3] demonstrate the coordination geometry of $[Th(CO_3)_5]^{6-}$ that occurs as isolated complexes in different solid phase of the type $M_6[Th(CO_3)_5]\cdot xH_2O$; where M is a univalent ion. The carbonate ligand is bonded through two oxygen atoms, resulting in a coordination number of ten for Th^{4+}. The same stoichiometry has been established in a number of solution chemical experiments at high carbonate concentrations and also in EXAFS studies of the Th(IV) limiting carbonate complex [1997FEL/RAI], [2006ALT/NEC] and the corresponding complexes of U(IV) [1998RAI/FEL], Np(IV) [1999RAI/HES], and Pu(IV) [1998CLA/CON], [1999RAI/HES2].

The mode of coordination of the carbonate ligand in solid phases has been inferred from IR spectra, [1962KAR/VOL], [1969KHA/MOL2] and [1982JOL/THO]; the conclusions in the first two of these studies are not in agreement with the known structure of the phases investigated. The third study made after the structure was known claims that the reported IR data are consistent with bidentate coordination of the carbonate ligand. Tolmachev [1944TOL] used UV spectrophotometry to suggest the formation of $Th(OH)_2(CO_3)_4^{6-}$. Only an abstract of this paper was available to the reviewers and the conclusions of this study have therefore not been accepted.

XI.1.3.5 Summary of selected thermodynamic data

The equilibrium constants selected in this review for solid and aqueous thorium carbonate compounds and the corresponding molar standard Gibbs energies of formation are summarised in Table XI-6.

Table XI-6: Equilibrium constants at zero ionic strength and molar standard Gibbs energies of formation selected for solid and aqueous thorium carbonate compounds at 25°C.

Solid phase	$\log_{10} K^{\circ}_{s,0}$	$\log_{10} K^{\circ}_{s,5}$	$\Delta_f G^{\circ}_m$ (kJ·mol^{-1})
$Na_6[Th(CO_3)_5]\cdot12H_2O$(cr)	-42.2 ± 0.8 [a]	-11.2 ± 0.4 [b]	-8002.6 ± 7.3
ThO_2(am, hyd, aged)	-47.5 ± 0.9 [c]		
Aqueous complex	**ε((1*yz*), Na^+) (kg·mol^{-1})**	**$\log_{10} \beta^{\circ}_{1yz}$ [d]**	**$\Delta_f G^{\circ}_m$ (kJ·mol^{-1})**
$Th(CO_3)_5^{6-}$	-0.30 ± 0.15	31.0 ± 0.7	-3521.2 ± 6.9
$Th(OH)(CO_3)_4^{5-}$	-0.22 ± 0.13	35.6 ± 0.5	-3176.8 ± 6.2
$Th(OH)_2(CO_3)_2^{2-}$	-0.1 ± 0.2	36.8 ± 0.5	-2285.1 ± 6.1
$Th(OH)_4(CO_3)^{2-}$	-0.1 ± 0.2	40.4 ± 0.6	-2092.2 ± 6.3

a: Reaction: $Na_6[Th(CO_3)_5]\cdot12H_2O(s) \rightleftharpoons 6Na^+ + Th^{4+} + 5CO_3^{2-} + 12H_2O(l)$

b: Reaction: $Na_6[Th(CO_3)_5]\cdot12H_2O(s) \rightleftharpoons 6Na^+ + Th(CO_3)_5^{6-} + 12H_2O(l)$

c: Reaction: $ThO_2(am, hyd, aged) + 2H_2O(l) \rightleftharpoons Th^{4+} + 4OH^-$

d: Reaction: $Th^{4+} + yOH^- + zCO_3^{2-} \rightleftharpoons Th(OH)_y(CO_3)_z^{4-y-2z}$

XI.1.3.6 Thorium thiocyanate

XI.1.3.6.1 Complexes with SCN^-

Thiocyanate solutions are extensively used analytically in various metal-metal separation methods, some of which include thorium. However, the quantitative information on chemical equilibria in the aqueous Th(IV)-SCN^- system is limited. Experimental investigations have been reported by Waggener and Stoughton [1950WAG/STO], Laubscher and Fouché [1971LAU/FOU], Sato *et al.* [1973SAT/KOT], Manouvrier and Devaure [1978MAN/DEV] and Livet and Musikas [1985LIV/MUS]; the latter study is only available as a conference contribution, *cf.* Appendix A.

The results reported by Waggener and Stoughton [1950WAG/STO] were given only in an ORNL quarterly report without any details and therefore could not be evaluated by this review. However, their value of $\beta_1 = 12.1$ M^{-1} ($\log_{10} \beta_1 = (1.08 \pm 0.08)$) listed in Table XI-7, recalculated to $I = 0$, $\log_{10} \beta_1^{\circ} = (2.44 \pm 0.16)$, is in fair agreement with the value $\log_{10} \beta_1^{\circ} = (2.0 \pm 0.5)$ from [1971LAU/FOU] selected by this review.

The equilibrium analysis in [1971LAU/FOU] was based on measurements of the distribution of trace amounts of Th(IV) between an aqueous phase containing different concentrations of thiocyanate and a benzene phase containing the extracting ligand, thenoyltrifluoroacetone (TTA) or dinonyl naphthalene sulphonic acid (DNNS). The hydrogen ion concentration was sufficiently high to prevent significant amounts of hydroxide complexes to be formed. The experimental distribution data cover the concentration range 0.00 M < [SCN$^-$] < 1.00 M in the TTA system and 0.00 M < [SCN$^-$] < 2.50 M in the DNNS system, respectively. The equilibrium constants deduced from these data are given in Table XI-7.

Table XI-7: Equilibrium constants deduced from the studies of [1971LAU/FOU], [1950WAG/STO] and [1985LIV/MUS].

Method	Ionic strength (mol·L^{-1})	β_1 (mol·L^{-1})$^{-1}$	β_2 (mol·L^{-1})$^{-2}$	β_3 (mol·L^{-1})$^{-3}$	β_4 (mol·L^{-1})$^{-4}$	References
DNNS	3.0 ^{a}	7.12 ± 1.11	33.9 ± 5.3	14.3 ± 7.3	32.4 ± 2.7	[1971LAU/FOU]
TTA	3.0 ^{a}	9.01 ± 0.62	25.1 ± 2.7	5.8 ± 2.6	-	[1971LAU/FOU]
TTA	1.0 ^{a}	12.1	60	-	-	[1950WAG/STO]
Raman spectroscopy	varying	25 ± 9	-	186 ± 39	-	[1978MAN/DEV]
Raman spectroscopy	varying, pH not reported	4.0 ± 0.6	5.0 ± 0.1	5.4 ± 0.1	1.4 ± 0.1	[1985LIV/MUS]

a: [H$^+$] = 0.50 M in (H$^+$/Na$^+$)(SCN$^-$/ ClO_4^-) media.

The values of β_1 and β_2 are in fair agreement between the two extraction systems, while the discrepancy is larger for β_3 and β_4; the authors suggest that this might be due to the formation of mixed Th(IV)-SCN$^-$-TTA complexes in the aqueous phase, but this is an *ad hoc* assumption. A large part of the ClO_4^- in the ionic medium has been replaced by SCN$^-$ in the range where β_3 and β_4 are determined, the equilibrium constants might then be strongly influenced by activity factor variations resulting from the changes in the ionic medium. The data in [1985LIV/MUS] have been made in a medium with variable ionic strength, in addition there is no information of the pH in the test solutions; the data have therefore not been accepted by this review.

This review has only accepted the values of β_1 and β_2 from [1971LAU/FOU] and selected their average and an uncertainty range that covers their respective uncertainties, β_1 = (8.0 ± 1.5) (mol·L^{-1})$^{-1}$, β_2 = (30 ± 10) (mol·L^{-1})$^{-2}$, $\log_{10} \beta_1$ = (0.90 ± 0.08) and $\log_{10} \beta_2$ = (1.48 ± 0.14) at I = 3.0 M. However the study by Sato *et al.*[1973SAT/KOT] strongly suggests that complexes with four or more coordinated ligands are formed at high SCN$^-$ concentrations. Manouvrier and Devaure [1978MAN/DEV] have studied the complex formation in the Th(IV) thiocyanate system using Raman spectroscopy. The experiments have been made at different pressures ranging from 0.1 − 300 MPa, by varying the ratio between SCN$^-$ and Th(IV) using high total concentrations of the reactants. The experimental data show conclusively that the SCN$^-$ ligand is coordinated through the nitrogen donor, but the deduction of the stoichiometry and equilibrium constants of the complexes formed is less clear; Manouvrier and Devaure report the formation of $Th(SCN)^{3+}$ and $Th(SCN)_3^+$ with equilibrium constants $\beta_1 = (25 \pm 9)\ (mol{\cdot}L^{-1})^{-1}$ and $\beta_3 = (186 \pm 39)\ (mol{\cdot}L^{-1})^{-3}$, respectively at 0.1 MPa. There is no indication in the studies of [1950WAG/STO] and [1971LAU/FOU] that $Th(SCN)_2^{2+}$ is a weak complex and this review suggests that its absence in the chemical model used in [1978MAN/DEV] is an artefact. The equilibrium constant for the first complex is consistent with values in [1950WAG/STO] and [1971LAU/FOU].

This review has based the selected equilibrium constants for the formation of $Th(SCN)^{3+}$ and $Th(SCN)_2^{2+}$ solely on the data from [1971LAU/FOU] in a 3.0 M perchlorate ionic medium. They have been recalculated to zero ionic strength using the ion interaction parameters $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ kg{\cdot}mol^{-1}$ and $\varepsilon(Na^+, SCN^-) = (0.05 \pm 0.01)\ kg{\cdot}mol^{-1}$ and assuming $\varepsilon(Th(SCN)^{3+}, ClO_4^-) = (0.50 \pm 0.10)\ kg{\cdot}mol^{-1}$ and $\varepsilon(Th(SCN)_2^{2+}, ClO_4^-) = \varepsilon(Np(SCN)_2^{2+}, ClO_4^-) = (0.38 \pm 0.20)\ kg{\cdot}mol^{-1}$.

The equilibrium constants and standard molar Gibbs energy of reaction for the formation of $Th(SCN)^{3+}$ and $Th(SCN)_2^{2+}$ selected by this review are:

$$\log_{10} \beta_1^{o} = (2.0 \pm 0.5);\ \Delta_r G_m^{o} = -(11.4 \pm 2.9)\ kJ{\cdot}mol^{-1}$$

$$\log_{10} \beta_2^{o} = (3.4 \pm 0.8);\ \Delta_r G_m^{o} = -(19.4 \pm 4.6)\ kJ{\cdot}mol^{-1}$$

where the uncertainty is primarily due to the uncertainties of the SIT coefficients used for the extrapolation to $I = 0$.

The Gibbs energies of formation of $Th(SCN)^{3+}$ and $Th(SCN)_2^{2+}$ have been calculated form the selected values of the Gibbs energy of reaction and the selected Gibbs energy of formation of Th^{4+} and SCN^-:

$$\Delta_f G_m^{o}(Th(SCN)^{3+}, 298.15\ K) = -(623.5 \pm 7.2)\ kJ{\cdot}mol^{-1}$$

$$\Delta_f G_m^{o}(Th(SCN)_2^{2+}, 298.15\ K) = -(538.8 \pm 10.6)\ kJ{\cdot}mol^{-1}.$$

There is no information on the enthalpy and entropy of reaction for the species formed in the Th(IV)-thiocyanate system.

XI.2 Silicon compounds and complexes

XI.2.1 Solid thorium silicides

There are four well-established intermetallic phases in this system, Th_3Si_2, ThSi, Th_3Si_5 and $ThSi_2$. The structural data on these compounds have been assembled by [1981CHI/AKH] and are shown in Table XI-8. In addition Brown and Norreys [1960BRO/NOR] found evidence for a phase of composition Th_6Si_{11}, with two polymorphs with a transition temperature of *ca.* 1573 K. The structural data in Table XI-8 suggest that they are defect structures of $ThSi_2$.

Table XI-8: Structural data for thorium silicides.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)
Th_3Si_2	Tetragonal	U_3Si_2	$a = 7.289$
	$P4/mbm$		$c = 4.149$
ThSi	orthorhombic	FeB	$a = 7.88$
	$Pnma$		$b = 4.148$
			$c = 5.896$
Th_3Si_5	hexagonal	AlB_2	$a = 3.897 – 3.896$
	$P6/mmm$		$c = 4.204 – 4.228$
Th_6Si_{11}	hexagonal	AlB_2	$a = 4.013$
< *ca.* 1573 K	$P6/mmm$		$c = 4.258$
Th_6Si_{11}	tetragonal	$ThSi_2$	$a = 4.01$
> *ca.* 1573 K	$I4_1/amd$		$c = 13.89$
$ThSi_2$	hexagonal	AlB_2	$a = 4.136$
< *ca.* 1573 K	$P6/mmm$		$c = 4.126$
$ThSi_2$	tetragonal	$ThSi_2$	$a = 4.135$
> *ca.* 1573 K	$I4_1/amd$		$c = 14.375$

There are two measurements of the enthalpy of formation of $ThSi_2$(cr) by direct combination of the elements in a calorimeter, by Robins and Jenkins [1955ROB/JEN] at 296 K and by Wang *et al.* [2000WAN/GUO] at 298.15 K. Fuller details are given in Appendix A. Neglecting the small difference in temperature, the average of three individual measurements by [1955ROB/JEN], using 98.7% pure thorium samples, yielded: $\Delta_f H_m^\circ$ ($ThSi_2$, cr, 298.15K) = $-(174.3 \pm 15.9)$ $kJ \cdot mol^{-1}$, where the uncertainty is calculated by this review. Wang *et al.* [2000WAN/GUO], made six measurements using purer (99.8%) thorium to give an average of $\Delta_f H_m^\circ$ ($ThSi_2$, cr, 298.15K) = $-(166.8 \pm 12.0)$ $kJ \cdot mol^{-1}$. The uncertainty limits reported by the authors have been doubled here so as to represent the 95% confidence interval.

The other thermodynamic data for thorium silicides are the Knudsen effusion measurements of silicon pressures from *ca.* 1685 – 1961 K in various diphasic fields by [1966ALC/COR]. As discussed in Appendix A, the only practical route to utilising these data is to adopt the activities, and thus Gibbs energy data, given by these authors, rather than try to reassess them, since this removes some the experimental uncertainty in the decomposition pressures. Even then there is some ambiguity in the results, since [1966ALC/COR] only define the Gibbs energies from Th(cr) and Si(cr), without defining the thorium allotrope, although the measurements span the α–β transformation temperature. The data given by [1981CHI/AKH], specified to be for the formation from α-Th and Si(l) seem to be derived from the values in [1966ALC/COR] assuming the latter refer to formation from α-Th, and we have made the same assumption, without further processing.

Given the ambiguity in the data, the following values, valid for 1685 to 1961 K, are given for information only.

$3\ \alpha\text{-Th} + 2\text{Si(cr)} \rightarrow \text{Th}_3\text{Si}_2\text{(cr)}$ $\quad \Delta_r G_m(T) = -270700 + 16.32\,T$

$\alpha\text{-Th} + \text{Si(cr)} \rightarrow \text{ThSi(cr)}$ $\quad \Delta_r G_m(T) = -122200 + 5.06\,T$

$3\ \alpha\text{-Th} + 5\text{Si(cr)} \rightarrow \text{Th}_3\text{Si}_5\text{(cr)}$ $\quad \Delta_r G_m(T) = -463200 + 12.05\,T$

$\alpha\text{-Th} + 2\text{Si(cr)} \rightarrow \text{ThSi}_2\text{(cr)}$ $\quad \Delta_r G_m(T) = -165300 + 2.43\,T$

The value of the enthalpy of formation of $ThSi_2$(cr), −165.3 kJ·mol^{-1} from these high temperature measurements (*ca.* 1750 K) supports the consistent calorimetric values determined near room temperature, noted above. The selected value is the weighted mean of the two calorimetric values:

$$\Delta_f H_m^\circ(\text{ThSi}_2,\ \text{cr},\ 298.15\ \text{K}) = -(169.5 \pm 9.6)\ \text{kJ·mol}^{-1}.$$

XI.2.2 Thorium silicate, $ThSiO_4$(cr)

$ThSiO_4$(cr) exists in two polymeric forms, thorite and huttonite. Thorite is tetragonal with $a = 7.1328$ Å, $c = 6.3188$ Å, [1978TAY/EWI], while huttonite is monoclinic, with $a = 6.80$ Å, $b = 6.96$ Å, $c = 6.54$ Å, $\beta = 104.55°$, [1951PAB/HUT]. However, the precise form of the polymorphism is still not clear. Huttonite is certainly the stable form at high temperatures and pressures, and there are two independent studies, [1964FIN/HAR] and [1997SEY/MON] which suggest that the equilibrium temperature is *ca.* (1490 ± 10) K, while in another study [1964DAC/ROY] the transformation is located at about 1273 K. The higher temperature range is supported by the recent results of Mazeina *et al.* [2005MAZ/USH] (see below and Appendix A) on the synthesis temperatures for the two forms.

There seems to be no direct evidence, however, that huttonite has ever been converted, even partially, to thorite under any conditions and indeed, Mumpton and Roy [1961MUM/ROY] have suggested that thorite may possibly be metastable at all temperatures and pressures despite its ready formation at temperatures below *ca.* (1490 ± 10) K.

Mazeina *et al.* [2005MAZ/USH] have obtained the standard enthalpies of formation of the two forms of thorite and huttonite, and, independently, the enthalpy of transition between these two polymorphs from high temperature calorimetry. Results were reported as averages of several experiments.

Crystals of the compounds were grown by the thermal gradient flux technique using $Li_2O·2WO_3$ as solvent, at 1473 K for thorite and at 1673 K for huttonite, from SiO_2(cr, α-quartz) with a reported purity greater than 99.9% and ThO_2(cr) with a reported purity greater than 99.99% (on the basis of the thorium content), thoroughly dried before use. Microprobe analyses indicated that the compounds were nearly stoichiometric – see Appendix A for details. Measurements of the enthalpy difference of samples of thorite and huttonite between 298.15 and 1774 K gives the enthalpy of the transition of thorite to huttonite, since thorite is transformed into huttonite at the high temperature. The experimental data give a value of $\Delta_{\mathrm{trs}}H_{\mathrm{m}}$ ((XI.21), 298.15 K) = (7.2 ± 7.4) kJ·mol^{-1} (see Appendix A) for the reaction:

$$\mathrm{ThSiO_4\ (thorite) \rightarrow ThSiO_4\ (huttonite)} \qquad \text{(XI.21)}$$

with the assumption that the heat capacities of the two polymorphs are the same.

For the determination of the enthalpies of formation of the two isomorphs, a custom-built Tian-Calvet calorimeter was used, operating at 1080 K. The solvent, contained in a platinum crucible, was $2\mathrm{PbO}\cdot\mathrm{B_2O_3}$. The reported results are derived from experiments in which samples at room temperature (25°C) were dropped into the solvent at the calorimeter temperature.

For the reactions

$$\mathrm{ThO_2(cr) + SiO_2(\alpha\text{-quartz}) \rightarrow ThSiO_4(thorite)} \qquad \text{(XI.22)}$$

and

$$\mathrm{ThO_2(cr) + SiO_2(\alpha\text{-quartz}) \rightarrow ThSiO_4(huttonite)} \qquad \text{(XI.23)}$$

values of $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ ((XI.22), 298.15 K) = (19.6 ± 2.0) kJ·mol^{-1} and $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ ((XI.23), 298.15 K) = (26.3 ± 3.0) kJ·mol^{-1} were obtained, giving for the transition:

$$\mathrm{ThSiO_4\ (thorite) \rightarrow ThSiO_4\ (huttonite)} \qquad \text{(XI.21)}$$

$\Delta_{\mathrm{trs}}H_{\mathrm{m}}^{\circ}$ ((XI.21), 298.15 K) = (6.7 ± 3.6) kJ·mol^{-1}, a value in agreement with that obtained from the heat content measurements, but more precise and involving fewer assumptions.

According to these results, both compounds are metastable towards quartz and thorium dioxide under standard conditions.

Use of the values selected in this review for $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ (ThO$_2$, cr, 298.15K) = – (1226.4 ± 3.5) kJ·mol^{-1} and $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ (SiO$_2$, α-quartz, 298.15 K) = −(910.7 ± 1.0) kJ·mol^{-1} yields the values:

$$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}\ (\mathrm{ThSiO_4},\ \text{thorite},\ 298.15\ \mathrm{K}) = -(2117.5 \pm 4.2)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}\ (\mathrm{ThSiO_4},\ \text{huttonite},\ 298.15\ \mathrm{K}) = -(2110.8 \pm 4.7)\ \mathrm{kJ\cdot mol^{-1}}$$

Schuiling *et al.* [1976SCH/VER] have estimated the Gibbs energy of formation of thorite at 1000K and 1 kbar pressure. In a series of compatibility experiments, they found that the two reactions:

$$\mathrm{CaTiO_3(perovskite) + ThSiO_4(thorite) \rightleftharpoons ThO_2(cr) + CaTiSiO_5(sphene)}$$

$$\mathrm{ThO_2(cr) + 0.5NaAlSi_3O_8(albite) \rightleftharpoons 0.5NaAlSiO_4(nepheline) + ThSiO_4(thorite)}$$

both have $\Delta_{\mathrm{r}}G_{\mathrm{m}} < 0$ at 1000 K and 1 kbar. From this, they infer that for the following reactions:

$$\mathrm{ThO_2(cr) + SiO_2\ (\alpha\text{-quartz}) \rightleftharpoons ThSiO_4(thorite)} \qquad \text{(XI.22)}$$

$$\mathrm{CaTiO_3(perovskite) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons CaTiSiO_5(sphene)} \qquad \text{(XI.24)}$$

$$\mathrm{0.5NaAlSiO_4(nepheline) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons 0.5NaAlSi_3O_8(albite)} \qquad \text{(XI.25)}$$

$\Delta_r G_m$ (XI.24) < $\Delta_r G_m$ (XI.22) < $\Delta_r G_m$ (XI.25) at 1000 K and 1 kbar.

We have used data from Robie and Hemingway [1995ROB/HEM] for reactions (XI.24) and (XI.25) to give the values in Table XI-9.

Table XI-9: Limiting Gibbs energies of reaction

Reaction	$\Delta_r G_m$ (1000 K, 1 bar) ($\mathrm{kJ \cdot mol^{-1}}$)	$\Delta_r G_m$ (1000 K, 1 kbar) ($\mathrm{kJ \cdot mol^{-1}}$)
(XI.24)	– 15.90 ± 3.70	– 15.96 ± 3.70
(XI.25)	– 9.70 ± 2.60	– 9.67 ± 2.60
(XI.22)	– 12.77 ± 6.84	– 12.82 ± 6.84*

*: Mean of $\Delta_r G_m$ (XI.24) and $\Delta_r G_m$ (XI.25).

This study would thus suggest that the value of $\Delta_r G_m$ ((XI.22), 1000 K, 1 bar) is – (12.8 ± 6.8) $\mathrm{kJ \cdot mol^{-1}}$. Since there are no values for the heat capacity of thorite, this value cannot be extrapolated to 298.15 K. However, comparison with the enthalpy of this reaction reported by [2005MAZ/USH], noted above, $\Delta_r H_m$ ((XI.22), 298.15 K) = 19.6 $\mathrm{kJ \cdot mol^{-1}}$, indicates that the entropy of Reaction (XI.22) is distinctly positive.

The only selected values are the enthalpies of formation from the study by [2005MAZ/USH]:

$$\Delta_f H_m^\circ\ (\mathrm{ThSiO_4}\text{, thorite, 298.15 K}) = -(2117.5 \pm 4.2)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_f H_m^\circ\ (\mathrm{ThSiO_4}\text{, huttonite, 298.15 K}) = -(2110.8 \pm 4.7)\ \mathrm{kJ \cdot mol^{-1}}.$$

XI.2.3 Aqueous complexes with H_4SiO_4(aq) and polynuclear Si species

No thermodynamic data for this system are available. However, X-ray absorption studies [2005RAI/YUI] of aqueous solutions in the Th-Si system under acidic conditions (pH ~ 1) and the solubility of $\mathrm{ThO_2{\cdot}}x\mathrm{H_2O}$ in highly alkaline conditions (pH 11 – 12) in the presence of ≥ 0.08 M soluble Si concentrations [2002PER/RIG] strongly suggest that thorium forms fairly strong complexes with silicate ions under these conditions. As discussed in Appendix A, the analysis of [2002PER/RIG] is far from unambiguous. However, one cannot exclude the formation of thorium complexes with polymeric silicate species and additional studies are necessary in order to decide if complexes of this type might be important at the high pH encountered in cement lined repositories.

XI.3 Thorium germanides

The phase diagram, structures and thermodynamic data have been treated by [1981CHI/AKH], and since there has been no further work published on this system, the present treatment follows closely their review. The phase diagram is still not well established, particularly around the $ThGe_2$ composition. The phases in Table XI-10 have been identified with some certainty, except that the high temperature polymorphism of $ThGe_2$ is not firmly established. The structural data are those quoted by [1981CHI/AKH], with some minor corrections from [1975FER].

Table XI-10: Structural data for thorium germanides.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)
Th_2Ge	tetragonal,	Al_2Cu	$a = 7.414$
	$I4/mcm$		$c = 6.081$
Th_3Ge_2	tetragonal,	U_3Si_2	$a = 7.95 - 7.98$
	$P4/mbm$		$c = 4.19 - 4.17$
ThGe	fcc, $Fm\bar{3}m$	NaCl	$a = 6.05 - 6.041$
Th_3Ge_5	hexagonal	AlB_2	$a = 4.065$
	$P6/mmm$		$c = 4.202$
$ThGe_2$	orthorhombic,	AlB_2	$a = 4.223$
< *ca.* 877 K	$Cmcm$		$b = 16.911$
			$c = 4.052$
$ThGe_2$	tetragonal	$ThSi_2$	$a = 4.13 - 4.18$
high temperature phase	$I4_1/amd$		$c = 14.20 - 14.23$
$Th_{0.9}Ge_2$	orthorhombic,	$ZrSi_2$	$a = 4.160$
	$Cm\bar{3}m$		$c = 16.642$
			$c = 4.023$

There are two sets of thermodynamic data for thorium germanides, which are not in good agreement. Wang *et al.* [2000WAN/GUO] measured the enthalpy of formation of $ThGe_2(cr)$ at 298.15 K by direct combination of the elements (at 1473 K), as described in Appendix A. The average of six measurements gave $\Delta_f H_m^\circ$ ($ThGe_2$, cr, 298.15 K) = $-(216.6 \pm 8.4)$ $kJ \cdot mol^{-1}$, where the authors' uncertainty limits have been doubled to correspond to a 95% uncertainty The other data are the Knudsen effusion measurements of germanium pressures from *ca.* 1330 − 1500 K in various diphasic fields by [1966ALC/COR]. However, as noted by [1981CHI/AKH], [1966ALC/COR] took the composition of the most Th-rich phase to be Th_3Ge, rather than the now established composition of Th_2Ge, and the most Ge-rich phase to be $ThGe_2$ rather than $Th_{0.9}Ge_2$. Chiotti *et al.* [1981CHI/AKH] have reinterpreted the measurements of [1966ALC/COR] to accord with the currently accepted phase diagram. Their revised values for the Gibbs energy of formation of the phases from 1330 − 1500 K are

$$2\,\alpha\text{-Th} + \text{Ge(cr)} \rightarrow \text{Th}_2\text{Ge(cr)} \qquad \Delta_r G_m\,(T) = -109077 + 3.948\,T$$

$$3\,\alpha\text{-Th} + 2\text{Ge(cr)} \rightarrow \text{Th}_3\text{Ge}_2\text{(cr)} \qquad \Delta_r G_m\,(T) = -209890 + 7.029\,T$$

$$\alpha\text{-Th} + \text{Ge(cr)} \rightarrow \text{ThGe(cr)} \qquad \Delta_r G_m\,(T) = -84768 + 3.353\,T$$

$$3\,\alpha\text{-Th} + 5\text{Ge(cr)} \rightarrow \text{Th}_3\text{Ge}_5\text{(cr)} \qquad \Delta_r G_m\,(T) = -329331 + 10.728\,T$$

$$\alpha\text{-Th} + 2\text{Ge(cr)} \rightarrow \text{ThGe}_2\text{(cr)} \qquad \Delta_r G_m\,(T) = -120625 + 3.351\,T$$

It will be seen that the enthalpy of formation of $ThGe_2$(cr) around 1400 K, – 120.6 kJ·mol^{-1}, derived from these measurements is very much less negative than the directly determined value noted above. It is difficult to explain this large discrepancy, especially as the data for $ThSi_2$(cr) from the two same studies agree rather well, as noted in Section XI.2.1. No values have been selected by the review for the thorium germanide phases.

XI.4 Thorium-tin compounds

Cirafici *et al.* [1983CIR/PAL] have studied the Th-Sn system, and no new phases have been reported since then.

There are four phases in the system, with structures given in Table XI-11 [1983CIR/PAL].

Table XI-11: Structural data for thorium tin compounds.

Phase	Symmetry, Space Group	Structural type	Lattice parameters (Å)
Th_5Sn_3	hexagonal, *P*6$_3$/*mcm*	Mn_5Si_3	$a = 9.332$ $c = 6.477$
Th_5Sn_4	hexagonal, *P*6$_3$/*mcm*	Ti_5Ga_4	$a = 9.643$ $c = 6.445$
$ThSn_2$	orthorhombic *Cmcm*	$ZrSi_2$	$a = 4.463$ $b = 17.062$ $c = 4.379$
$ThSn_3$	cubic, $Pm\bar{3}m$	$AuCu_3$	$a = 4.719$

For $ThSn_3$(cr), the results of [1983CIR/PAL] confirmed the structural data obtained earlier by [1958FER] who had reported a = 4.718 Å, while [1970HAV/DAM] gave a = 4.714 Å. This compound is isomorphous with USn_3, $ThPb_3$, $ThTl_3$, and $ThIn_3$. The most stable phase is Th_5Sn_3, which melts congruently at *ca.* 2073 K.

There are three thermodynamic measurements in this system, two involving $ThSn_3$(cr) and one Th_5Sn_3(cr). Kadochnikov *et al.* [1977KAD/LEB] measured the emf of the cell:

$$\text{Th(cr)} \mid \text{KCl-NaCl-3 wt\%ThCl}_4 \,\vdots\, \text{KCl-NaCl-3 wt\%ThCl}_4 \mid \text{Sn-Th(l)} + \text{compound}$$

from 952 to 1130 K. The actual compound present in the saturated solution was not identified, but was presumably $ThSn_3$(cr), since Cirafici *et al.* [1983CIR/PAL] report that this is stable up to 1228 K, where it undergoes a peritectic reaction to $ThSn_2$(cr) and liquid. The thorium potential in the diphasic region {Sn-Th(l) + $ThSn_3$(cr)} was given by:

$$[\Delta_f G_m]_{950\text{K}}^{1130\text{K}}(T) = -206517 + 51.677\,T \quad \text{J·mol}^{-1}$$

These data cannot be processed further without an assumption regarding the activity of tin in the saturated Sn-Th liquid. With the low solubility of thorium in Sn(l), also measured by [1977KAD/LEB] to be $\log_{10} x_{\text{Th}} = -4330/\text{T} + 2.2360$ from 950 to 1130 K, the chemical potential of tin in the melt will be close to the ideal value and if $ThSn_3$(cr) is indeed the phase in equilibrium with the saturated liquid, its Gibbs energy of formation (from Sn(l)) in the temperature range of the study by [1977KAD/LEB] is then calculated to be

$$[\Delta_f G_m]_{950\text{K}}^{1130\text{K}}(\text{ThSn}_3, \text{cr}, T) = -203377 + 48.762\,T \quad \text{J·mol}^{-1}$$

Kadochnikov *et al.* [1977KAD/LEB] estimated the uncertainties in the thorium potential to be only ±400 J·mol^{-1}, but the uncertainty in the enthalpy values is much higher, ±6300 J·mol^{-1}, as quoted by authors.

Palenzola and Cirafici [1975PAL/CIR] have measured the enthalpies of formation of $ThSn_3$(cr) by dynamic differential calorimetry (integration of DTA curves) from an appropriate mixture of the elements, held in a molybdenum container. As discussed in Appendix A, the DTA peak reached its maximum at 793 K. Palenzola and Cirafici [1975PAL/CIR] report the value of $\Delta_f H_m^o(\text{ThSn}_3, \text{cr}) = -(162 \pm 16)\ \text{kJ·mol}^{-1}$ to be that at 298.15 K, but make no mention of any corrections applied to the experimental value. We have therefore assumed the value to be that at the maximum in the DTA peak, 793 K and have doubled the uncertainty stated by the authors. However, in view of the uncertainties in the processing of the data from both these studies, these values are quoted for information only.

More recently Wang *et al.* [2000WAN/GUO] have measured the enthalpy of formation of the most stable compound in the system, Th_5Sn_3(cr). They used a direct reaction calorimeter operating at (1473 ± 2) K. All samples were held in BN crucibles in an argon atmosphere. For each run, both the unreacted mixture and the actual final product were dropped from 298.15 K to the reacting temperature and the enthalpies measured; the difference between these values therefore gives the enthalpy of formation at 298.15 K. For Th_5Sn_3(cr), the resultant value from six runs was:

$$\Delta_f H_m^o(\text{Th}_5\text{Sn}_3, \text{cr}, 298.15\ \text{K}) = -(510.4 \pm 32.0)\ \text{kJ·mol}^{-1}$$

where the authors' uncertainty limits have been doubled to correspond to a 95% uncertainty, and this is the selected value.

As expected from the phase diagram, the enthalpy of formation per gram-atom, – (63.8 ± 2.0) kJ·(gram-atom)$^{-1}$ is appreciably more negative than that for $ThSn_3$(cr), *ca.* – 40 kJ·(gram-atom)$^{-1}$ from the studies noted above.

XI.5 Thorium-lead compounds

There are three well-established compounds in this system, ThPb, $ThPb_2$ and $ThPb_3$; in addition, Gans *et al.* [1966GAN/KNA] found evidence for a phase of composition close to $ThPb_4$. The structures of $ThPb_2$ and $ThPb_4$ are not known; ThPb is body-centred tetragonal, space group $I4_1/amd$, with a = (4.545 ± 0.001) Å, c = (11.288 ± 0.006) Å, [1961BRO] while $ThPb_3$ is cubic, space group $Pm\bar{3}m$, $AuCu_3$ type. Values of a = (4.855 ± 0.001) Å [1958FER], [1961BRO] and 4.853 Å [1970HAV/DAM] have been reported.

The main thermodynamic data for this system are derived from the Knudsen effusion study by Gans *et al.* [1966GAN/KNA], who measured the vapour pressure of pure lead from 908 to 1178 K and the lead decomposition pressures in the four diphasic fields involving Th, ThPb, $ThPb_2$, $ThPb_3$ and $ThPb_4$, from 910 to 1263 K, depending on the phase field. Their measured vapour pressure of lead is in good agreement with the values derived from [1989COX/WAG]. Chiotti *et al.* [1981CHI/AKH] have reassessed these data, making small corrections to the derived equations for the decomposition pressures to obtain better agreement with the phase diagram. We have confirmed that the assessed values of [1981CHI/AKH] give a more consistent description of the system, and have adopted their derived values for the Gibbs energies of formation (from Pb(l)) of the four solid compounds, valid from *ca.* 900 to 1300 K:

$$\alpha\text{-Th} + \text{Pb(l)} \rightarrow \text{ThPb(cr)} \qquad \Delta_r G_m(T) = -\,63940 + 11.603\,T\ \text{J·mol}^{-1}$$

$$\alpha\text{-Th} + 2\text{Pb(l)} \rightarrow \text{ThPb}_2\text{(cr)} \qquad \Delta_r G_m(T) = -\,116080 + 41.937\,T\ \text{J·mol}^{-1}$$

$$\alpha\text{-Th} + 3\text{Pb(l)} \rightarrow \text{ThPb}_3\text{(cr)} \qquad \Delta_r G_m(T) = -\,167080 + 85.693\,T\ \text{J·mol}^{-1}$$

$$\alpha\text{-Th} + 4\text{Pb(l)} \rightarrow \text{ThPb}_4\text{(cr)} \qquad \Delta_r G_m(T) = -\,196770 + 112.450\,T\ \text{J·mol}^{-1}$$

Palenzona and Cirafici [1975PAL/CIR] have measured the enthalpy of formation of $ThPb_3$(cr) by dynamic differential calorimetry from a mixture of the elements under experimental conditions identical to those reported for $ThSn_3$(cr) (Section XI.4) and discussed in Appendix A. They report the value of $\Delta_f H^\circ_m$ ($ThPb_3$, cr) = – (117 ± 12) kJ·mol^{-1} to be that at 298.15 K, but make no mention of any correction applied to the experimental value. For this reason, we have doubled the uncertainty stated by the authors. Nevertheless, in view of these uncertainties in processing the data, the results of [1975PAL/CIR] are quoted for information only.

Poyarkov *et al.* [1976POY/LEB] have measured the solubility of thorium in Pb(l), and the thorium activities in saturated solutions, from 949 to 1043 K using the concentration cell of the type:

$$\text{Th(cr)} \mid \text{KCl-NaCl-3 wt\%ThCl}_4 \,\vdots\, \text{KCl-NaCl-3 wt\%ThCl}_4 \mid \text{Pb-Th(l)} + \text{compound}$$

The actual compound present in the saturated solution was not identified, but is assumed by this review to be $ThPb_4$(cr), as indicated by Gans *et al.* [1966GAN/KNA]. The solubility of thorium in lead in this temperature range is very small (0.23 at% at 1000 K), so the Gibbs energy of formation of $ThPb_4$(cr) (from Pb(l)) will be negligibly different from the thorium activity derived from the emf measurements, and thus $\Delta_f G_m(\text{ThPb}_4, \text{cr}, T) = -151870 + 56.646\,T\ \text{J·mol}^{-1}$, in the temperature range 949−1043 K. This gives a Gibbs energy of formation of $-95.24\ \text{kJ·mol}^{-1}$ at 1000 K, compared to $-84.32\ \text{kJ·mol}^{-1}$ from the pressure measurements of Gans *et al.*; the derived enthalpies and entropies of formation are also notably different. The latter data from the more complete study are preferred, but none of these values can be selected until the discrepancy is resolved.

XII Miscellaneous compounds and complexes

XII.1 Ternary and polynary oxides

XII.1.1 Thorium - Group 2 compounds

XII.1.1.1 Strontium thorate, $SrThO_3$(cr)

The early identification of $SrThO_3$(cr) by Naray-Szabo [1947NAR] has been questioned (see discussion below), but Purohit *et al.* [2000PUR/TYA] have suggested that it is formed by combustion of a sol-gel containing $Th(NO_3)_4$, $Sr(NO_3)$ and citric acid. They indicate that its structure is a monoclinic distortion of the ideal perovskite lattice, with $a = (6.319 \pm 0.004)$ Å, $b = (3.240 \pm 0.001)$ Å and $c = (4.928 \pm 0.003)$ Å, $\beta = (117.38 \pm 0.05)°$. The only thermodynamic data for $SrThO_3$(cr) are measurements by Ali (Basu) *et al.* [2001ALI/MIS] of the pressure of Sr(g) obtained by heating $SrThO_3$(cr) in a tungsten cell from 1677 to 2419 K by weight-loss Knudsen effusion. X-ray examination of the residue after partial decomposition showed that the condensed phases were different in different temperature ranges. As well as $SrThO_3$(cr), W(cr) and ThO_2(cr), the tungstate Sr_2WO_5(cr) was present from 1677 to 2047 K, but $SrWO_4$(cr) was found in experiments from 2138 to 2419 K. Since $SrWO_4$ would be molten at these higher temperatures, Energy Dispersive X-ray analysis was carried out to determine whether there was any solubility of thorium species in this melt. Less than 10% ThO_2 was detected, but it was not clear whether this was due to dissolution of *e.g.* of $SrThO_3$ or from interference from neighbouring ThO_2 particles. Thus $SrWO_4$(l) was treated as a pure phase in the subsequent analysis, as was ThO_2(cr), although the solubility of SrO in ThO_2(cr) at 2273 K is reported to be as high as 13 mol%. The error from these assumptions was estimated by the authors to be 2.6 $kJ\cdot mol^{-1}$. The authors discuss and dismiss the possible loss of oxygen to form phases such $SrWO_3$(cr) containing lower-valent tungsten.

The relevant reactions were thus assumed to be:

$$5SrThO_3(cr) + W(cr) \rightleftharpoons Sr_2WO_5(cr) + 5ThO_2(cr) + 3Sr(g) \qquad 1677 \text{ to } 2047 \text{ K} \qquad (XII.1)$$

and

$$4SrThO_3(cr) + W(cr) \rightleftharpoons SrWO_4(l) + 4ThO_2(cr) + 3Sr(g) \qquad 2138 \text{ to } 2419 \text{ K} \qquad (XII.2)$$

Measurements were also made below 1670 K, but the establishment of the equilibrium (probably with Sr_3WO_6(cr)) was too slow for the results to be reliable.

These measurements are analysed in detail in Appendix A. It was necessary to extrapolate the auxiliary data for the Gibbs energy of formation of the strontium tungstates from the measurement range (*ca.* 1100 − 1500 K) very considerably to the experimental temperature range, introducing further uncertainty into the analysis.

As discussed in Appendix A, these results correspond to a Gibbs energy of the formation reaction from the binary oxides:

$$\mathrm{SrO(cr) + ThO_2(cr) \rightleftharpoons SrThO_3(cr)} \qquad \text{(XII.3)}$$

given by the equations:

$$[\Delta_r G_m]_{1670\mathrm{K}}^{2040\mathrm{K}}\ \text{(XII.3)} = -\,3955 - 1.300\,T \ \ \mathrm{J{\cdot}mol^{-1}} \qquad \text{from Reaction (XII.1)}$$

and

$$[\Delta_r G_m]_{2135\mathrm{K}}^{2420\mathrm{K}}\ \text{(XII.3)} = -\,17583 + 4.033\,T \ \ \mathrm{J{\cdot}mol^{-1}} \qquad \text{from Reaction (XII.2)}$$

Considering the extrapolations involved, and the uncertain activities, especially for Reaction (XII.2), it is not surprising that the enthalpy and entropy values differ somewhat. However, the Gibbs energies of the formation reaction from the oxides at the intermediate temperature 2100 K, $-(6.7 \pm 4.0)$ and $-(9.1 \pm 10.0)$ kJ·mol^{-1} agree remarkably well. The uncertainties are those estimated by the authors.

The $\mathrm{SrThO_3(cr)}$ phase has a lower stability than $\mathrm{BaThO_3(cr)}$, as expected, but its enthalpy of formation is much more negative than the trends in the actinide(IV) mixed oxides would suggest. Indeed [1993FUG/HAI] estimated $\Delta_r H_m$((XII.3), 298.15K) to be (20.0 ± 8.5) kJ·mol^{-1}, and Smith and Welch [1960SMI/WEL] were unable to prepare $\mathrm{SrThO_3}$ by heating a mixture of $\mathrm{ThO_2(cr)}$ and $\mathrm{SrCO_3(cr)}$ in air at 1273 to 1923 K. These authors suggested that the XRD pattern attributed to $\mathrm{SrThO_3(cr)}$ by [1947NAR] fitted better to the two components SrO(cr) and $\mathrm{ThO_2(cr)}$. Similarly, Smith and Welch indicated that the diffraction pattern given by [1947NAR] for his reported $\mathrm{CaThO_3(cr)}$ agrees well with that for a mixture of $\mathrm{ThO_2}$ and hydrated lime. Keller [1976KEL] has also thrown doubt on some of the results of [1947NAR]. Although the sol-gel technique used by [2000PUR/TYA] and [2001ALI/MIS] provides intermediate products of much smaller particle size, and thus higher reactivity that could favour the completeness of the synthesis, we note that no detailed analyses to confirm the positive identification of the final product as $\mathrm{SrThO_3(cr)}$ were made in either of these papers.

The data from Reaction (XII.1) are the less uncertain; these correspond to the Gibbs energy of formation from the elements: $[\Delta_f G_m]_{1670\mathrm{K}}^{2040\mathrm{K}}$ ($\mathrm{SrThO_3}$, cr, T) = − 194680 + 36.23 T , where the standard state for strontium in this temperature range is Sr(g). However, owing to the uncertainties in the assessment noted above and in Appendix A and in the identification of $\mathrm{SrThO_3(cr)}$, these data are given for information only.

XII.1.1.2 Barium thorate, $\mathrm{BaThO_3(cr)}$

$\mathrm{BaThO_3(cr)}$ is the only known ternary oxide in the $\mathrm{BaO-ThO_2}$ system. Its structure is a distortion of the perovskite structure, but its diffraction pattern has been interpreted in various ways. Both Nakamura [1974NAK], in his detailed study, and Purohit *et al.* [2000PUR/TYA] describe it as an orthorhombic structure with $a = (6.345 \pm 0.002)$ Å, $b = (6.376 \pm 0.002)$ Å and $c = (8.992 \pm 0.002)$ Å, [1974NAK] with four pseudomonoclinic units ($a' = c' = 4.498$ Å, $b' = 4.496$ Å, $\beta' = 90.28°$). Smith and Welch [1960SMI/WEL], however, attributed the faint lines additional to those from the simple cubic cell to a larger cubic cell with a doubled parameter, $a = 8.895$ Å, while Bharadwaj *et al.* [1999BHA/MIS] noted that the diffraction pattern in their samples corresponded to a simple pseudo-cubic cell with $a = 4.499$ Å.

There are no low-temperature heat capacity measurements, but Venkata Krishnan *et al.* [2001VEN/NAG] have measured the heat capacity by a DSC technique from *ca.* 320 to 820 K. They fitted their results to the expression:

$$[C_{p,\mathrm{m}}]_{320\mathrm{K}}^{820\mathrm{K}}(\mathrm{BaThO_3, cr}, T) = 137.9046 + 5.272\times10^{-2}\,T - 2.432487\times10^{6}\,T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

However, as noted in Appendix A, this corresponds to a large $\Delta_{\mathrm{r}}C_{p,\mathrm{m}}$ of the formation reaction from the solid oxides in the range of temperature measurement; the calculated values are 20.0 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at 320 K and 50.9 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at 820 K. These large values must throw doubt on the validity of the results and these data are mentioned for information only, and have not been used to process the Gibbs energy data discussed below.

There are no experimental data for enthalpy of formation of $\mathrm{BaThO_3(cr)}$, but there are two measurements of the Gibbs energy of formation of $\mathrm{BaThO_3(cr)}$. Mishra *et al.* [1999MIS/ALI] have studied the decomposition pressure of BaO(g) from the reaction $\mathrm{BaThO_3(cr) \rightleftharpoons ThO_2(cr) + BaO(g)}$ by Knudsen effusion from 1770 to 2136 K. As discussed in Appendix A, these results correspond to a Gibbs energy of the formation reaction from the binary oxides:

$$\mathrm{BaO(cr) + ThO_2(cr) \rightarrow BaThO_3(cr)} \qquad \text{(XII.4)}$$

given by the equation:

$$[\Delta_{\mathrm{r}}G_{\mathrm{m}}]_{1770\mathrm{K}}^{2136\mathrm{K}}(\text{XII.4}) = -\,21420 - 3.058\,T \quad \mathrm{J\cdot mol^{-1}}$$

where the auxiliary data for the vapour pressure of pure BaO(cr) are taken from the data in [1994GUR/VEY] – see Appendix A. The small value of the entropy change of this all-solid reaction gives confidence in the experimental results. The estimated uncertainty in these Gibbs energy values is 6.0 $\mathrm{kJ\cdot mol^{-1}}$, since the uncertainty in $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$ (BaO, g, 298.15 K) is 3.0 $\mathrm{kJ\cdot mol^{-1}}$ [1994GUR/VEY].

Bharadwaj *et al.* [1999BHA/MIS] have studied the pressure of $\mathrm{Ba(OH)_2(g)}$ from the reaction $\mathrm{BaThO_3(cr) + H_2O(g) \rightleftharpoons ThO_2(cr) + Ba(OH)_2(g)}$ from 1548 to 1683 K by transpiration in various pressures of water vapour. As discussed in Appendix A, these results correspond to a Gibbs energy of the formation reaction from the binary oxides (Equation (XII.4)), given by the equation:

$$[\Delta_{\mathrm{r}}G_{\mathrm{m}}]_{1548\mathrm{K}}^{1683\mathrm{K}}(\text{XII.4}) = -\,29214 + 3.574\,T \quad \mathrm{J\cdot mol^{-1}}$$

where the auxiliary data for the reaction $\mathrm{BaO(cr) + H_2O(g) \rightleftharpoons Ba(OH)_2(g)}$ are taken from a recent study by [2001ALI/MIS2] using the same apparatus as [1999BHA/MIS] ((see Appendix A. However, there is a large uncertainty (-20 kJ·mol^{-1}) in the range of values of $\Delta_f H_m$ ($Ba(OH)_2$, g, 298.15 K) from other determinations, so we estimate the overall uncertainty in the above equation to be the same.

The temperature ranges of the two studies by [1999MIS/ALI] and [1999BHA/MIS] do not, in fact quite overlap, but at 1700 K, the respective values for the $\Delta_r G_m$ ((XII.4)) are $-(26.6 \pm 6.0)$ kJ·mol^{-1} and $-(23.1 \pm 20.0)$ kJ·mol^{-1}, and thus in reasonable agreement, although the small derived entropies of reaction are of opposite sign.

These values of $\Delta_r G_m$ (XII.4) are consistent with two estimates of the enthalpy of the formation reaction from the oxides at 298.15 K by [1983WIL/MOR] and [1993FUG/HAI]. Based on relationships between experimental enthalpies of formation of M(II)M'O3 perovskites and M' ionic radii, (M' = Ti, Mo, Hf, Zr, Tb, Pr, Ce, and U), Williams *et al.* [1983WIL/MOR] estimated $\Delta_r H_m$ ((XII.4), 298.15 K) = -20 kJ·mol^{-1} while Fuger *et al.* [1993FUG/HAI] suggested $-(31.0 \pm 8.5)$ kJ·mol^{-1} for the same reaction, based on a larger number of experimental results, especially on actinides. Since the entropy of Reaction (XII.4) will be small, the values of this Gibbs energy at higher temperatures should not be greatly different from the standard enthalpy of reaction.

The only value selected is the weighted mean of the two consistent values of $\Delta_r G_m$ (XII.4),*viz.*

$$\Delta_r G_m \text{ ((XII.4), 1700 K)} = -(26.3 \pm 5.7) \text{ kJ·mol}^{-1}$$

The corresponding Gibbs energy of formation from the elements is then:

$$\Delta_f G_m \text{ (BaThO}_3\text{, cr, 1700 K)} = -(1320.5 \pm 7.1) \text{ kJ·mol}^{-1}$$

the reference state for barium being Ba(l) at this temperature.

Because of the doubt expressed above in the $C_{p,m}$ data of $BaThO_3$(cr), especially the extrapolation to high temperatures, we have not processed the Gibbs energies data to derive values at 298.15 K**.**

XII.1.2 Thorium - Group 1 compounds

XII.1.2.1 Rubidium thorate, Rb_2ThO_3(cr)

Rb_2ThO_3(cr) is the only known ternary oxide in the Rb_2O-ThO_2 system. Hoppe and Seeger [1970HOP/SEE] reported the existence of a hexagonal structure for this compound, with a = 3.75 Å, c = 19.7 Å, Rb_2PbO_3 type and, more recently, the same group [1977BRU/HOP], reported a cubic modification, NaCl type, with a = (5.475 ± 0.005) Å, isomorphous with Cs_2ThO_3. The only thermodynamic data on Rb_2ThO_3(cr) derive from a study by Dash *et al.* [2005DAS/SIN] of the pressure of CO_2(g) in the reaction:

$$\mathrm{ThO_2(cr) + Rb_2CO_3(cr) \rightleftharpoons Rb_2ThO_3(cr) + CO_2(g)} \qquad \text{(XII.5)}$$

from 952 to 1098 K by a manometric technique.

The calculated decomposition pressures from ten experimental points are well represented by the equation $\log_{10} p_{\mathrm{CO_2}} / \mathrm{bar} = -\ 13031/T + 8.915$. The Gibbs energy of the above reaction is thus $\Delta_{\mathrm{r}}G_{\mathrm{m}}$ (XII.5) = 249476 − 170.680 T (J·mol^{-1}). The Gibbs energy of the reaction $\mathrm{Rb_2O(l) + CO_2(g) \rightleftharpoons Rb_2CO_3(cr)}$ over the experimental temperature range is given by − 413796 + 173.100 T (J·mol^{-1}); where the data are taken from [1982GLU/GUR], adjusted to 1 bar standard state. The Gibbs energy of the formation reaction of $\mathrm{Rb_2ThO_3(cr)}$ from the component oxides is thus:

$$\mathrm{Rb_2O(l) + ThO_2(cr) \rightarrow Rb_2ThO_3(cr)} \qquad \text{(XII.6)}$$

$$[\Delta_{\mathrm{r}}G_{\mathrm{m}}]^{1058\mathrm{K}}_{952\mathrm{K}}\ ((\text{XII.6}), T) = -\ 164320 + 2.420\,T\ \mathrm{J{\cdot}mol^{-1}}$$

Since the enthalpy of fusion of $\mathrm{Rb_2O}$ at 778 K is 20.0 kJ·mol^{-1} [1982GLU/GUR], the Gibbs energy change for the metastable reaction involving $\mathrm{Rb_2O(cr)}$ would be approximately −144320 − 23.287 T (J·mol^{-1}), with an appreciable positive entropy change. Combination of the values for Reaction (XII.6) with the values for $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ ($\mathrm{Rb_2O}$, l) from [1982GLU/GUR] and $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ ($\mathrm{ThO_2}$, cr) (this review) gives finally for the Gibbs energy of the formation reactions:

$$\mathrm{2Rb(l) + Th(cr) + 1.5O_2(g) \rightarrow Rb_2ThO_3(cr)} \qquad \text{(XII.7)}$$

$$[\Delta_{\mathrm{r}}G_{\mathrm{m}}]^{1058\mathrm{K}}_{952\mathrm{K}}\ ((\text{XII.7})\ T) = -1688657 + 276.470\,T\ \mathrm{J{\cdot}mol^{-1}}$$

and

$$\mathrm{2Rb(g) + Th(cr) + 1.5O_2(g) \rightarrow Rb_2ThO_3(cr)} \qquad \text{(XII.8)}$$

$$[\Delta_{\mathrm{r}}G_{\mathrm{m}}]^{1058\mathrm{K}}_{952\mathrm{K}}\ ((\text{XII.8}), T) = -\ 1831523 + 424.248\,T\ \mathrm{J{\cdot}mol^{-1}}$$

Both these equations are given since the pressure of Rb(g) over Rb(l) reaches 1 bar at *ca.* 967 K. The uncertainty in these values is estimated to be at least 11 kJ·mol^{-1}, mainly from the uncertainty in $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($\mathrm{Rb_2O}$, cr, 298.15 K) which is given as 8 kJ·mol^{-1} by [1982GLU/GUR]. These expressions correspond to a very negative value for the Gibbs energy of formation of $\mathrm{Rb_2ThO_3}$, in comparison with the results reported below (XII.1.2.2) for $\mathrm{Cs_2ThO_3}$.

Since there are no other thermodynamic data for $\mathrm{Rb_2ThO_3(cr)}$, no further processing of these results is possible, and no values are selected for the review.

XII.1.2.2 Caesium thorate, $\mathrm{Cs_2ThO_3(cr)}$

$\mathrm{Cs_2ThO_3(cr)}$ is the only known ternary oxide in the $\mathrm{Cs_2O}$-$\mathrm{ThO_2}$ system, and has been reported [1977BRU/HOP] as cubic, NaCl type, with a = 5.704 Å, isomorphous with the cubic form of $\mathrm{Rb_2ThO_3}$.

The only thermodynamic data on $Cs_2ThO_3(cr)$ derive from a study by Ali (Basu) *et al.* [2000ALI/MIS] of the decomposition pressure of $Cs_2ThO_3(cr)$ according to the reaction:

$$Cs_2ThO_3(cr) \rightleftharpoons ThO_2(cr) + Cs_2O(g) \qquad (XII.9)$$

from 1100 to 1254 K by weight-loss Knudsen effusion.

X-ray diffraction on partially evaporated samples showed them to be a mixture of $Cs_2ThO_3(cr)$ and $ThO_2(cr)$ as anticipated. The thermodynamic data for the Cs-O system indicate that there are quite negligible amounts of species other than $Cs_2O(g)$ in the vapour under the experimental conditions. The calculated decomposition pressures from ten experimental points are well represented by the equation $\log_{10} p_{Cs_2O} / \text{bar} = -13942/T + 6.939$. The Gibbs energy of the above reaction is thus $\Delta_r G_m$ ((XII.9), T) = $266916 - 132.842\,T$ ($J\cdot mol^{-1}$). The Gibbs energy of the vaporisation of $Cs_2O(l)$ over the experimental temperature range is given by $152692 - 107.587\,T$ ($J\cdot mol^{-1}$); where the data are taken from the equilibrium constant given in [1982GLU/GUR], adjusted to 1 bar standard state. The Gibbs energy of the formation reaction of $Cs_2ThO_3(cr)$ from the component oxides is thus:

$$Cs_2O(l) + ThO_2(cr) \rightarrow Cs_2ThO_3(cr) \qquad (XII.10)$$

$$[\Delta_r G_m]_{1100K}^{1254K}((XII.10), T) = -114224 + 25.254\,T\ J\cdot mol^{-1}$$

Since the entropy of fusion of Cs_2O is 26.042 $J\cdot mol^{-1}\cdot K^{-1}$, the entropy change for the metastable reaction involving $Cs_2O(cr)$ would be close to zero, which gives confidence in the experimental results. Combination of the values in the above equation with the values for $\Delta_f G_m^\circ$ (Cs_2O, l) [1982GLU/GUR] and $\Delta_f G_m^\circ$ (ThO_2, cr) (this review) gives finally:

$$[\Delta_f G_m]_{1100K}^{1254K}(Cs_2ThO_3, cr, T) = -1780323 + 441.26\,T\ J\cdot mol^{-1}$$

where the standard state for Cs is Cs(g) in this temperature range. The uncertainty in these values is estimated to be at least 20 $kJ\cdot mol^{-1}$, mainly from the uncertainty in $\Delta_f H_m^\circ$ (Cs_2O, g, 298.15 K) which is given as 15 $kJ\cdot mol^{-1}$ by [1982GLU/GUR].

Since there are no other thermodynamic data for $Cs_2ThO_3(cr)$, no further processing of these results is possible, and no values are selected for the review.

XII.2 Thorium minerals

XII.2.1 Common thorium minerals

The two Gmelin volumes on minerals [1990DIT/BAR], [1991BAR/DAH] provide a good review of thorium minerals.

In the earth's crust, thorium is about three times as abundant as uranium. In minerals, thorium is frequently associated with other quadrivalent species (Zr, Hf, Ce, and U), but also with tervalent lanthanides. Table XII-1 gives a list of common thorium containing minerals, extracted from the Mineralogical Database website[1]. In nature, $\mathrm{ThO_2}$ is found mostly as solid solutions with $\mathrm{UO_2}$. Conventionally, the name thorianite is used when the molar content of $\mathrm{ThO_2}$ is above 75%; uranothorianite is used for such solid solutions containing 25−75% $\mathrm{ThO_2}$; thorian uraninite is employed when the $\mathrm{ThO_2}$ content is 15−25%; uraninite is used when the $\mathrm{UO_2}$ content is above 85%.

Table XII-1: Common thorium minerals

Mineral name	Generic chemical formula	Th content (wt%) in a typical sample
Althupite	$\mathrm{ThAl(UO_2)_7(PO_4)_4(OH)_5\cdot 15(H_2O)}$	8.04
Arapovite	$\mathrm{(U,Th)(Ca,Na)_2(K1\text{-}x[\,]x)Si_8O_{20}}$, $x \sim 0.5$	7.07
Brabantite	$\mathrm{CaTh(PO_4)_2}$	50.22
Britholite-(Ce)	$\mathrm{(Ce,Ca,Th,La,Nd)_5(SiO_4,PO_4)_3(OH,F)}$	18.25
Brockite	$\mathrm{(Ca,Th,Ce)(PO_4)\cdot(H_2O)}$	31.55
Calciobetafite	$\mathrm{Ca_2(Ti,Nb)_2(O,OH)_7}$	5.88
Cerianite-(Ce)	$\mathrm{(Ce,Th)O_2}$	29.73
Cervandonite-(Ce)	$\mathrm{(Ce,Nd,La)(Fe^{+3},Fe^{+2},Ti^{+4},Al)_3SiAs(Si,As)O_{13}}$	3.66
Cheralite-(Ce)	$\mathrm{(Ce,Ca,Th)(P,Si)O_4}$	29.02
Chevkinite-(Ce)	$\mathrm{(Ce,La,Ca,Th)_4(Fe^{+2},Mg)_2(Ti,Fe^{+3})_3Si_4O_{22}}$	1.93
Ciprianiite	$\mathrm{Ca_4[(Th,U,Ln]_2(Al,Va)_2[Si_4B_4O_{22}](OH,F)_2}$	14.26
Coutinhoite	$\mathrm{Th_xBa_{1\text{-}2x}(H_2O)_y(UO_2)_2Si_5O_{13}\cdot H_2O}$	3.29
Dissakisite-(La)	$\mathrm{(Ca,Fe,Th)(REE,Ca)(Al,Cr,Ti)_2(Mg,Fe,Al)Si_3O_{12}(OH,F)}$ with La>Ce	3.98
Ekanite	$\mathrm{ThCa_2Si_8O_{20}}$	27.08
Eylettersite	$\mathrm{(Th,Pb)_{(1\text{-}x)}\ Al_3(PO_4,SiO_4)_2(OH)_6(?)}$	19.29
Fersmite	$\mathrm{(Ca,Ce,Na)(Nb,Ta,Ti)_2(O,OH,F)}$	2.97
Grayite	$\mathrm{(Th,Pb,Ca)PO_4\cdot(H_2O)}$	43.73
Huttonite	$\mathrm{ThSiO_4}$	71.59
IMA2004-001	$\mathrm{[(REE^{+}Y),U,Th,Ca,Fe](Nb,Ta,Ti)O_4}$	6.83
Ilimaussite-(Ce)	$\mathrm{(Ba,Na)_{10}K_3Na_4.5Ce_5(Nb,Ti)_6[Si_{12}O_{36}][Si_9O_{18}(O,OH)_{24}]O_6}$	1.04
Iraqite-(La)	$\mathrm{K(La,Ce,Th)_2(Ca,Na)_4(Si,Al)_{16}O_{40}}$	9.94
Karnasurtite-(Ce)	$\mathrm{(Ce,La,Th)(Ti,Nb)(Al,Fe^{+3})(Si,P)_2O_7(OH)_4\cdot 3(H_2O)(?)}$	6.18
Kivuite	$\mathrm{(Th,Ca,Pb)H_2(UO_2)_4(PO_4)_2(OH)_8\cdot 7(H_2O)}$	8.16
Kuannersuite-(Ce)	$\mathrm{Ba_6Na_2REE_2(PO_4)_6FCl}$	0.27
Kukharenkoite-(La)	$\mathrm{Ba_2(La,Th,Ce)(CO_3)_3F}$	10.87
Melanocerite-(Ce)	$\mathrm{(Ce,Th,Ca)_5(Si,B)_3O_{12}(OH,F)\cdot n(H_2O)(?)}$	5.14
Monazite-(Ce)	$\mathrm{(Ce,La,Nd,Th)PO_4}$	4.83
Monazite-(La)	$\mathrm{(La,Ce,Nd)PO_4}$	4.84
Monazite-(Nd)	$\mathrm{(Nd,Ce,La)(P,Si)O_4}$	4.82
Monazite-(Sm)	$\mathrm{SmPO_4}$	15.73

(Continued on next page)

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[1] Current web address (September 2007): www.webmineral.com

Table XII-1: (continued)

Mineral name	Generic chemical formula	Th content (wt%) in a typical sample
Mottanaite-(Ce)	$Ca_4(Ce,Ca)_2AlBe_2[Si_4B_4O_{22}]O_2$	2.30
Okanoganite-(Y)	$(Na,Ca)_3(Y,Ce)_{12}Si_6B_2O_{27}F_{14}$	1.66
Orthochevkinite	$(Ce,La,Ca,Na,Th)_4(Fe^{+2},Mg)_2(Ti,Fe^{+3})_3Si_4\,O_{22}$	7.93
Perrierite-(Ce)	$(Ce,La,Ca)_4(Fe^{+2},Mg)_2(Ti,Fe^{+3})_3Si_4O_{22}$	0.97
Polyakovite-(Ce)	$(Ce,La,Nd,Pr,Ca)_4(Mg,Fe^{++})(Cr,Fe^{+++})_2(Ti,Nb)_2Si_4O_{22}$	1.85
Polycrase-(Y)	$(Y,Ca,Ce,U,Th)(Ti,Nb,Ta)_2O_6$	6.22
Saryarkite-(Y)	$Ca(Y,Th)Al_5(SiO_4)_2(PO_4,SO_4)_2(OH)_7\cdot 6(H_2O)$	7.53
Steacyite	$K_{1-x}(Ca,Na)_2ThSi_8O_{20}(x=0.2\text{ to }0.4)$	25.29
Steenstrupine-(Ce)	$Na_{14}Ce_6Mn^{+2}Mn^{+3}Fe^{2+}{}_2(Zr,Th)(Si_6O_{18})_2(PO_4)_7\cdot 3(H_2O)$	1.85
Thorbastnasite	$Th(Ca,Ce)(CO_3)_2F_2\cdot 3(H_2O)$	45.57
Thorianite	ThO_2	87.88
Thorite	$ThSiO_4$	71.59
Thornasite	$Na_{12}Th_3[Si_8O_{19}]_4\cdot 18(H_2O)$	20.41
Thorogummite	$Th(SiO_4)_{1-x}(OH)_{4x}$	72.13
Thorosteenstrupine	$(Ca,Th,Mn)_3Si_4O_{11}F\cdot 6(H_2O)$	29.29
Thorutite	$(Th,U,Ca)Ti_2(O,OH)_6$	23.75
Tritomite-(Ce)	$(Ce,La,Ca,Y,Th)_5(Si,B)_3(O,OH,F)_{13}$	4.42
Tuliokite	$BaNa_6Th(CO_3)_6\cdot 6(H_2O)$	23.79
Turkestanite	$Th(Ca,Na)_2(K_{1-x},Va_x)Si_8O_{20}\cdot n(H_2O)$	21.11
Umbozerite	$Na_3Sr_4ThSi_8(O,OH)_{24}$	18.33
Uranopolycrase	$(U,Y)(Ti,Nb,Ta)_2O_6$	5.58
Vicanite-(Ce)	$(Ca,Ce,La,Th)_{15}\,As^{+5}(As^{+3}{}_{0.5},Na_{0.5})Fe^{+3}Si_6BO_{40}F_7$	9.08
Yttrialite-(Y)	$(Y,Th)_2Si_2O_7$	27.79
Yttrocrasite-(Y)	$(Y,Th,Ca,U)(Ti,Fe^{+3})_2(O,OH)_6$	7.79
Zirconolite-3O	$(Ca,Fe,Y,Th)Fe(Ti,Nb)_3Zr_2O_7$	3.61
Zirkelite	$(Ca,Th,Ce)Zr(Ti,Nb)_2O_7$	6.06

In addition, it should be noted that, although the generic formula of some minerals listed in Table XII-1 does not mention thorium, this element is often present in such minerals by substitution for quadrivalent or tervalent species, in percentages that may be in excess of 10%. This is, for instance, the case for Sm-monazites. Of course, in such substitutions charge balance must be maintained and the replacement of a tervalent ion by thorium must be accompanied by an equivalent increased amount of a lower-valent cation (often Ca^{2+}) in the structure.

The thorium content given in the third column of the list is that found for a typical sample.

XII.2.2 Specific minerals

XII.2.2.1 Thorite and huttonite, $ThSiO_4$(cr)

Section XI.2.2 includes a discussion of some thermodynamic properties of thorite, including a discussion of the thorite-huttonite phase transformation.

XII.2.2.2 Thorium brannerite, $ThTi_2O_6$(cr)

Thorium frequently substitutes for uranium in the mineral brannerite of generic formula (U, Ca, Ce)(Ti, Fe)$_2$O$_6$. Hence $ThTi_2O_6$(cr) is sometimes referred to as Th-brannerite. Its enthalpy of formation has been measured [2003HEL/NAV] (see Appendix A) by high temperature drop calorimetry at 976 K, using a sodium molybdate solvent with the composition $3Na_2O{\cdot}4MoO_3$. Drop solution enthalpic effects were measured by dropping pellets (about 5 mg) of the powdered samples from room temperature into the solvent at the calorimeter temperature. Solution enthalpies were measured after equilibration of sample pellets above the solvent at the calorimeter temperature. In this way, the heat content increments could be taken in account.

The Th-brannerite samples were prepared by sintering ball-mill mixed stoichiometric amounts of ThO_2(cr) and TiO_2(anatase) in air at 1773 K for more than 100 hours. X-ray powder diffraction of the compounds showed them to be monoclinic, space group *C2/m.* with a = (9.8046 ± 0.0008) Å, b = (3.8187 ± 0.0003) Å, c = (7.0229 ± 0.0005) Å, and β = (118.852 ± 0.005)°, with as expected, a slightly larger cell volume than that obtained for the corresponding uranium compound. Quantitative analyses by the Rietveld method indicated a sample composition of (0.991 ± 0.003) weight fraction $ThTi_2O_6$ and (0.009 ± 0.001) weight fraction ThO_2. These results were confirmed by back-scattered electron diffraction and electron microprobe analysis with wavelength dispersion spectroscopy. After correction for the small thorium dioxide impurity, a value of $(19.4 \pm 1.6)\ \text{kJ}\cdot\text{mol}^{-1}$ was reported for Reaction (XII.11) corresponding to the enthalpy of the formation reaction of thorium brannerite from the binary oxides,

$$ThO_2(\text{cr, 298.15 K}) + 2TiO_2(\text{rutile, 298.15 K}) \rightarrow ThTi_2O_6(\text{cr, 298.15 K}) \qquad (XII.11)$$

Taking their value, $(19.4 \pm 2.0)\ \text{kJ}\cdot\text{mol}^{-1}$, where the uncertainty has been recalculated by the review from individual uncertainties reported by [2003HEL/NAV], and making use of the values selected in this review for $\Delta_f H^\circ_m$ (ThO_2, cr, 298.15 K) = $-(1226.4 \pm 3.5)\ \text{kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H^\circ_m$ (TiO_2, rutile, 298.15 K) = $-(944.0 \pm 0.8)\ \text{kJ}\cdot\text{mol}^{-1}$ we calculate:

$$\Delta_f H^\circ_m(ThTi_2O_6, \text{cr, 298.15 K}) = -(3095.0 \pm 4.3)\ \text{kJ}\cdot\text{mol}^{-1}$$

which is the selected value.

This result indicates that Th-brannerite is entropy-stabilised and may be stable at high temperature only.

XII.2.3 General references for minerals

The following reference list concerns papers dealing with minerals of thorium, although few contain thermodynamic data. These references should be useful for readers interested in thorium minerals. They will also provide a source from which a more comprehensive list of minerals could be generated. Since this is a specialised area, these references are included hereunder rather than in the general bibliography.

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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.

[1908WOH/PLU]

The decomposition pressures of a large number of metallic sulphates were determined manometrically, using a porcelain container. The rapid equilibration to form $SO_3(g)$ was ensured by the presence of a platinum wire in the reaction tube.

Two sets of measurements were carried out for $Th(SO_4)_2(s)$. One sample, prepared from pure thorium nitrate, was studied at temperatures from 848 to 1058 K; these measurements gave somewhat scattered results. A second run involved a partially decomposed thorium sulphate, which gave essentially similar decomposition values (from 796 to 1073 K), which were less scattered than in the first experiment. From the close similarity of the equilibrium pressures in the two runs, the authors concluded that no oxysulphate was stable in this temperature range. There also seems to be the possibility that in the first set of experiments, the sulphate decomposed rapidly during the initial heating, and both studies involved an oxysulphate phase.

However, using the selected heat capacities for $Th(SO_4)_2(cr)$, we have made a second-law calculation of their results, assuming the reaction is that postulated by the authors,

$$Th(SO_4)_2(cr) \rightleftharpoons ThO_2(cr) + 2SO_2(g) + O_2(g)$$

to derive the enthalpy of formation and entropy of $Th(SO_4)_2(cr)$. Unfortunately, the values obtained $\Delta_f H^\circ_m(Th(SO_4)_2, cr, 298.15 K) = -2184.3$ kJ·mol^{-1} and $S^\circ_m(Th(SO_4)_2, cr, 298.15 K) = 453.7$ J·K^{-1}·mol^{-1} are not reasonable for $Th(SO_4)_2(cr)$. We thus conclude that the reaction studied was not that proposed by the authors, or some adventitious volatile material was present in their experiments for $Th(SO_4)_2(cr)$. This study has therefore not been considered further in the review.

[1910BAR]

See discussion in [1910KOP/HOL].

[1910KOP]

The enthalpies of solution of the tetrahydrate and the octahydrate of $Th(SO_4)_2$ were determined in *ca.* 1 M K_2CO_3 solution at *ca.* 15°C, to be $-(119.90 \pm 1.50)$ and $-(61.85 \pm 2.30)$ $kJ\cdot mol^{-1}$ respectively (statistical uncertainties only). If it is assumed that the (ill-defined) product formed by the reaction of the two hydrates is the same, and the small difference in temperature of the study from 298.15 K is ignored, the calorimetric data give for the hydration reaction:

$$Th(SO_4)_2\cdot 4H_2O(cr) + 4H_2O(l) \rightleftharpoons Th(SO_4)_2\cdot 8H_2O(cr) \tag{A.1}$$

$$\Delta_r H_m^o((A.1), 298.15\ K) = -(58.0 \pm 5.0)\ kJ\cdot mol^{-1}$$

where the uncertainty has been estimated by the review.

The temperatures at which the two hydrates coexist with the aqueous phase were found to be 42°C in water, and 30°C in 33 wt% H_2SO_4, 19.5 wt% HCl, and 31 wt% HNO_3 solutions. The activities of water (a_w) at 30°C in the last three solutions are calculated to be 0.702, 0.623 and 0.712 respectively from the data in [1984HAR/MOL] for H_2SO_4 and [1991PIT] for HNO_3 and HCl. With the mean value of $a_w = (0.679 \pm 0.069)$, the enthalpy of Reaction (A.1) is calculated to be $-(102.5 \pm 28.4)$ $kJ\cdot mol^{-1}$, the large uncertainty emanating from a combination of the very short temperature range and the uncertainty in the water activity in the acidic solutions. The calorimetric value is clearly to be preferred, but no value can be selected.

[1910KOP/HOL]

The data from [1910KOP/HOL], [1910BAR], [1911BAR], [1912BAR], and [1912WIR] for different chemical systems are compiled in [1965LIN2] and were used to partially validate the thorium sulphate aqueous phase model selected in this review. No thermodynamic data are given in these publications, but the data they contain were useful in determining the $\Delta_f G_m^o$ values for the reported solid phases. For details of the aqueous phase model, including the associated ion interaction parameters and the auxiliary data used in these calculations, and for $\Delta_f G_m^o$ values of different solids determined from this modelling, see the main text. In fitting these data at different temperatures, the $\Delta_f G_m^o$ value of H_2O and the temperature corrected value of the Debye-Hückel term at the experimental temperatures were used. The graphical comparisons of the data are provided in figures included in the main text. The details of the experimental data listed in these publications and of the concentrations of predicted species are reported in the following tables. In a limited number of cases involving very high ionic strengths, where the SIT model is not applicable, no predictions were made and thus only the experimental concentrations are listed in these cases.

Table A-1: Observed [1912BAR] and model-predicted concentrations at 25°C for the solubility of $Th(SO_4)_2 \cdot 9H_2O(cr)$ in Li_2SO_4 solutions (data plotted in Figure IX-5).

Experimental data (m)			Model predictions (m)				
Li^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
0.000	8.120×10^{-2}	4.060×10^{-2}	3.522×10^{-2}	9.410×10^{-6}	5.988×10^{-3}	2.777×10^{-2}	1.449×10^{-3}
4.680×10^{-1}	4.288×10^{-1}	9.740×10^{-2}	9.203×10^{-2}	8.334×10^{-6}	1.844×10^{-3}	2.995×10^{-2}	6.023×10^{-2}
8.960×10^{-1}	7.400×10^{-1}	1.460×10^{-1}	1.535×10^{-1}	1.129×10^{-5}	1.739×10^{-3}	3.183×10^{-2}	1.199×10^{-1}
1.270	1.011	1.880×10^{-1}	2.110×10^{-1}	1.286×10^{-5}	1.685×10^{-3}	3.347×10^{-2}	1.758×10^{-1}

Table A-2: Observed [1911BAR] and model-predicted concentrations at 16°C for the solubility of different thorium-sulphate solids in $(NH_4)_2SO_4$ solutions (data plotted in Figure IX-9).

Experimental data (m)			Model predictions (m)				
NH_4^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2 \cdot 9H_2O(cr)$							
0.000	6.560×10^{-2}	3.280×10^{-2}	3.280×10^{-2}	8.757×10^{-6}	5.651×10^{-3}	2.585×10^{-2}	1.294×10^{-3}
3.220×10^{-1}	3.196×10^{-1}	7.930×10^{-2}	6.498×10^{-2}	7.202×10^{-6}	1.885×10^{-3}	2.723×10^{-2}	3.586×10^{-2}
7.280×10^{-1}	6.120×10^{-1}	1.240×10^{-1}	1.122×10^{-1}	1.266×10^{-5}	1.889×10^{-3}	2.889×10^{-2}	8.138×10^{-2}
1.520	1.181	2.110×10^{-1}	2.168×10^{-1}	2.252×10^{-5}	2.054×10^{-3}	3.211×10^{-2}	1.826×10^{-1}
2.500	1.878	3.140×10^{-1}	3.843×10^{-1}	3.441×10^{-5}	2.319×10^{-3}	3.642×10^{-2}	3.455×10^{-1}
$Th(SO_4)_2.(NH_4)_2SO_4.4H_2O(cr)$							
2.500	1.878	3.140×10^{-1}	3.260×10^{-1}	2.439×10^{-5}	1.724×10^{-3}	2.873×10^{-2}	2.955×10^{-1}
4.240	2.608	2.440×10^{-1}	2.424×10^{-1}	5.871×10^{-6}	4.101×10^{-4}	9.004×10^{-3}	2.330×10^{-1}
5.340	3.134	2.320×10^{-1}	2.235×10^{-1}	2.932×10^{-6}	2.087×10^{-4}	5.236×10^{-3}	2.181×10^{-1}
$Th(SO_4)_2.2(NH_4)_2SO_4.2H_2O(cr)$							
5.340	3.134	2.320×10^{-1}					
6.840	3.730	1.550×10^{-1}					
7.440	3.992	1.360×10^{-1}					
$Th(SO_4)_2.3(NH_4)_2SO_4.3H_2O(cr)$							
8.020	4.226	1.080×10^{-1}					
10.56	5.358	3.900×10^{-3}					

Table A-3: Observed [1910BAR] and [1911BAR] and model-predicted concentrations at 16°C for the solubility of different thorium-sulphate solids in Na_2SO_4 solutions (data plotted in Figure IX-7).

Experimental data (m)			Model predictions (m)				
Na^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2.9H_2O(cr)$ [a]							
1.540×10^{-1}	1.590×10^{-1}	4.100×10^{-2}	4.616×10^{-2}	4.865×10^{-6}	2.026×10^{-3}	2.659×10^{-2}	1.754×10^{-2}
2.760×10^{-1}	2.500×10^{-1}	5.600×10^{-2}	5.987×10^{-2}	6.566×10^{-6}	1.908×10^{-3}	2.712×10^{-2}	3.084×10^{-2}
4.200×10^{-1}	3.960×10^{-1}	9.300×10^{-2}	7.613×10^{-2}	8.558×10^{-6}	1.869×10^{-3}	2.763×10^{-2}	4.662×10^{-2}
$Th(SO_4)_2\cdot[Na_2SO_4]\cdot6H_2O(cr)$							
4.200×10^{-1}	3.960×10^{-1}	9.300×10^{-2}	1.185×10^{-1}	1.791×10^{-5}	3.225×10^{-3}	4.300×10^{-2}	7.227×10^{-2}
5.780×10^{-1}	4.490×10^{-1}	8.000×10^{-2}	8.260×10^{-2}	8.552×10^{-6}	1.543×10^{-3}	2.412×10^{-2}	5.693×10^{-2}
8.160×10^{-1}	5.080×10^{-1}	5.000×10^{-2}	5.192×10^{-2}	3.862×10^{-6}	6.197×10^{-4}	1.106×10^{-2}	4.024×10^{-2}
1.320	7.240×10^{-1}	3.300×10^{-2}	3.054×10^{-2}	1.728×10^{-6}	2.173×10^{-4}	4.238×10^{-3}	2.608×10^{-2}
1.720	9.180×10^{-1}	2.800×10^{-2}	2.390×10^{-2}	1.150×10^{-6}	1.258×10^{-4}	2.554×10^{-3}	2.122×10^{-2}
2.160	1.130	2.500×10^{-2}	1.983×10^{-2}	8.166×10^{-7}	7.982×10^{-5}	1.669×10^{-3}	1.808×10^{-2}

a: The data reported by [1910BAR] and [1911BAR] indicate that the solubility controlling phase in the entire set is $Th(SO_4)_2\cdot[Na_2SO_4]\cdot6H_2O(cr)$. However, thermodynamic modelling and plotting of the data clearly show that the solubility controlling phase in the first two samples is $Th(SO_4)_2\cdot9H_2O(cr)$ and that the third sample is in equilibrium with both $Th(SO_4)_2\cdot9H_2O(cr)$ and $Th(SO_4)_2\cdot[Na_2SO_4]\cdot6H_2O(cr)$.

Table A-4: Observed [1911BAR] and model-predicted concentrations at 16°C for the solubility of different thorium-sulphate solids in K_2SO_4 solutions (data plotted in Figure IX-8).

Experimental data (m)			Model predictions (m)				
K^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2\cdot9H_2O(cr)$ [a]							
4.860×10^{-2}	1.029×10^{-1}	3.930×10^{-2}	3.479×10^{-2}	3.635×10^{-6}	2.532×10^{-3}	2.607×10^{-2}	6.184×10^{-3}
1.150×10^{-1}	1.610×10^{-1}	5.170×10^{-2}	4.230×10^{-2}	3.955×10^{-6}	2.019×10^{-3}	2.636×10^{-2}	1.392×10^{-2}
$Th(SO_4)_2\cdot K_2SO_4\cdot4H_2O(cr)$							
1.320×10^{-1}	2.167×10^{-1}	7.530×10^{-2}	7.385×10^{-2}	1.007×10^{-5}	4.024×10^{-3}	4.599×10^{-2}	2.383×10^{-2}
1.410×10^{-1}	1.889×10^{-1}	5.930×10^{-2}	5.877×10^{-2}	6.500×10^{-6}	2.772×10^{-3}	3.507×10^{-2}	2.092×10^{-2}
1.470×10^{-1}	1.785×10^{-1}	5.240×10^{-2}	5.206×10^{-2}	5.180×10^{-6}	2.265×10^{-3}	3.021×10^{-2}	1.958×10^{-2}
1.550×10^{-1}	1.578×10^{-1}	4.020×10^{-2}	4.230×10^{-2}	3.624×10^{-6}	1.624×10^{-3}	2.339×10^{-2}	1.728×10^{-2}
$Th(SO_4)_2\cdot2K_2SO_4\cdot2H_2O(cr)$							
1.582×10^{-1}	1.563×10^{-1}	3.860×10^{-2}	3.943×10^{-2}	3.234×10^{-6}	1.466×10^{-3}	2.155×10^{-2}	1.641×10^{-2}
1.708×10^{-1}	1.259×10^{-1}	2.050×10^{-2}	2.225×10^{-2}	1.422×10^{-6}	6.820×10^{-4}	1.128×10^{-2}	1.029×10^{-2}
2.118×10^{-1}	1.234×10^{-1}	8.730×10^{-3}	9.106×10^{-3}	4.665×10^{-7}	2.190×10^{-4}	4.066×10^{-3}	4.821×10^{-3}
3.550×10^{-1}	1.808×10^{-1}	1.650×10^{-3}	1.109×10^{-3}	4.635×10^{-8}	1.682×10^{-5}	3.569×10^{-4}	7.357×10^{-4}
$Th(SO_4)_2\cdot3.5K_2SO_4(cr)$							
4.640×10^{-1}	2.320×10^{-1}	6.360×10^{-4}	4.144×10^{-4}	1.607×10^{-8}	4.962×10^{-6}	1.102×10^{-4}	2.992×10^{-4}
5.540×10^{-1}	2.770×10^{-1}	7.080×10^{-5}	1.109×10^{-4}	4.020×10^{-9}	1.114×10^{-6}	2.555×10^{-5}	8.420×10^{-5}

a: The data reported by [1911BAR] indicates that the solubility controlling phase in these two samples is $Th(SO_4)_2\cdot K_2SO_4\cdot6H_2O$. However, modelling of these data suggests that the solubility controlling phase should be $Th(SO_4)_2\cdot9H_2O$.

Table A-5: Observed [1912BAR] and [1912WIR] and model-predicted concentrations at 25°C for the solubility of different thorium-sulphate solids in H_2SO_4 solutions (data plotted in Figure IX-6).

Experimental data (m)			Model predictions (m)				
H^+	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2\cdot9H_2O(cr)$							
0.000	8.200×10^{-2}	4.100×10^{-2}	3.515×10^{-2}	9.393×10^{-6}	5.979×10^{-3}	2.772×10^{-2}	1.445×10^{-3}
2.200×10^{-1}	2.000×10^{-1}	4.500×10^{-2}	4.072×10^{-2}	1.490×10^{-5}	4.396×10^{-3}	2.867×10^{-2}	7.636×10^{-3}
4.000×10^{-1}	2.940×10^{-1}	4.700×10^{-2}	4.508×10^{-2}	2.247×10^{-5}	4.840×10^{-3}	2.941×10^{-2}	1.081×10^{-2}
5.800×10^{-1}	3.870×10^{-1}	4.860×10^{-2}	4.900×10^{-2}	2.927×10^{-5}	5.282×10^{-3}	3.015×10^{-2}	1.354×10^{-2}
7.800×10^{-1}	4.870×10^{-1}	4.860×10^{-2}	5.310×10^{-2}	3.551×10^{-5}	5.743×10^{-3}	3.099×10^{-2}	1.633×10^{-2}
1.060	6.260×10^{-1}	4.800×10^{-2}	5.855×10^{-2}	4.189×10^{-5}	6.351×10^{-3}	3.217×10^{-2}	1.999×10^{-2}
1.640	9.080×10^{-1}	4.390×10^{-2}					
2.060	1.110	4.100×10^{-2}					
2.240	1.190	3.500×10^{-2}					
4.720	2.400	2.100×10^{-2}					
7.700	3.850	1.000×10^{-2}					
$Th(SO_4)_2\cdot8H_2O(cr)$							
12.10	6.050	2.500×10^{-3}					
14.14	7.070	1.500×10^{-3}					

Table A-6: Observed [1910KOP/HOL] and model-predicted concentrations at 30°C for the solubility of different thorium-sulphate solid in HCl solutions.

Experimental data (m)				Model predictions (m)				
H^+	Cl^-	Total SO_4	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
$Th(SO_4)_2\cdot8H_2O(cr)$								
0.000	0.000	1.014×10^{-1}	5.070×10^{-2}	2.343×10^{-2}	6.429×10^{-6}	4.327×10^{-3}	1.834×10^{-2}	7.550×10^{-4}
1.307	1.307	1.712×10^{-1}	8.560×10^{-2}	9.625×10^{-2}	1.529×10^{-2}	5.457×10^{-2}	2.468×10^{-2}	1.712×10^{-3}
2.048	2.048	1.686×10^{-1}	8.430×10^{-2}	1.207×10^{-1}	2.500×10^{-2}	6.489×10^{-2}	2.875×10^{-2}	2.080×10^{-3}
3.789	3.789	1.426×10^{-1}	7.130×10^{-2}					
5.110	5.110	1.228×10^{-1}	6.140×10^{-2}					
6.154	6.154	1.166×10^{-1}	5.830×10^{-2}					
$Th(SO_4)_2\cdot4H_2O(cr)$								
6.850	6.850	1.134×10^{-1}	5.670×10^{-2}					
6.850	6.850	1.150×10^{-1}	5.750×10^{-2}					
8.610	8.610	7.080×10^{-2}	3.540×10^{-2}					

[1911BAR]

See discussion in [1910KOP/HOL].

[1911CHA]

This early study is concerned with the preparation and the investigation of the properties of thorium metal and of a large number of compounds: oxide, hydroxide, various halides, oxyhalides, halogenocomplexes, their hydrates and adducts with ammonia. Elemental analyses were given for many of the compounds studied. Enthalpies of solution at 288 K of the metal in *ca.* 3.6 M HCl and of a number of compounds in *ca.* 16000 H_2O were reported. Values were given without any detail. Although the concentration of thorium in the calorimetric solutions was not specified in every case, it was assumed by this review to be the same throughout.

As the metal samples obtained in this study were reported to be only 92 − 96% pure, neither the enthalpy of solution of the metal nor its enthalpy of combustion to ThO_2(cr) will be considered further.

The enthalpy of solution of $ThCl_4$(cr) was given as −237.2 kJ·mol^{-1}. Using the values adopted in this review for $\log_{10}{}^{*}K^{\circ}_{s,0}$ ($Th(OH)_4$, am, 298.15 K) = (8.9 ± 1.1) (Section VII.4.1.1), for the equilibrium constants (Table VII-17) $\log_{10}{}^{*}\beta^{\circ}_{n,m}$ ($Th_m(OH)_n^{4m-n}$, aq, 298.15 K), and for the value $\log_{10}{}^{*}\beta^{\circ}_1$ ($ThCl^{3+}$, 298.15 K) = (1.70 ± 0.10) listed in Section VIII.2.2.1, and assuming that the results of Chauvenet are valid for 298.15 K, the distribution of thorium in the various species in a *ca.* 16000 H_2O medium is calculated to be:

Th^{4+}	$Th(OH)^{3+}$	$Th(OH)_2^{2+}$	$Th_2(OH)_2^{6+}$	$Th_2(OH)_3^{5+}$	$Th_4(OH)_{12}^{4+}$	$ThCl^{3+}$
28.93%	46.02%	4.62%	0.02%	1.17%	0.08%	19.16%

These calculations are for an ideal aqueous solution, which will be a satisfactory approximation at the concentrations involved.

As no enthalpies of formation values have been selected by this review for the minor species $Th_2(OH)_3^{5+}$ and $Th_4(OH)_{12}^{4+}$, and since the presence of $Th_2(OH)_2^{6+}$ can be considered as negligible, we have assumed, for the evaluation of the result of Chauvenet, that the most hydrolysed species is $Th(OH)_2^{2+}$ and have included under this the other minor (1% or less) species.

Thus we assume the dissolution reaction of $ThCl_4$ to be:

$$\begin{aligned}&ThCl_4(cr) + 0.5780\ H_2O\ (\text{in } ca.\ 16000\ H_2O(l)) \rightleftharpoons \\ &\quad (0.2893\ Th^{4+} + 0.4602\ Th(OH)^{3+} + 0.0589\ Th(OH)_2^{2+} + \\ &\quad 0.1916\ ThCl^{3+} + 3.8084\ Cl^- + 0.5780\ H^+)\ \text{in } ca.\ 16000\ H_2O(l) \qquad (A.2)\end{aligned}$$

To process Chauvenet's experimental value, we have therefore used the following auxiliary data: the enthalpy effect corresponding to the formation at infinite dilution of the various thorium hydrolytic species adopted in Table VII-15; $\Delta_f H_m$ (Th^{4+}, 298.15 K) = $-(768.7 \pm 2.3)$ kJ·mol^{-1}, assumed to be valid for the dilute medium used, and $\Delta_f H_m$ (Cl$^-$, *ca.* 4000 H_2O, 298.15 K) = $-(166.854 \pm 0.100)$ kJ·mol^{-1}. Also required is the enthalpy at infinite dilution of the reaction $\mathrm{Th}^{4+} + \mathrm{Cl}^- \rightleftharpoons \mathrm{ThCl}_3^+$, for which this review has not selected a value. However, [1968OHA/MOR] have suggested that this enthalpy effect is very small, and for the current comparison, we have used the value of (0.16 ± 2.00) kJ·mol^{-1} derived from the data given by [1982WAG/EVA], the uncertainty being conservatively estimated by this review. These values lead to $\Delta_f H_m^\circ$ ($ThCl_4$, cr, 298.15 K) = $-(1173.5 \pm 5.0)$ kJ·mol^{-1}, where the uncertainty does not include the unknown uncertainty of Chauvenet's determination. This value is to be compared with $\Delta_f H_m^\circ$ ($ThCl_4$, cr, 298.15 K) = $-(1186.3 \pm 1.3)$ kJ·mol^{-1} adopted in this review from more recent and better documented results. This may reveal a systematic difference between the results of Chauvenet and more recent data.

The enthalpies of solution in water of the thorium tetrachloride di-, tetra-, hepta-, and octahydrate were obtained as -171.88, -109.75, -61.5, and -47.91 kJ·mol^{-1}, respectively, under similar conditions to those for the anhydrous salt. With the logical assumption that the dissolution reaction was identical in all cases, the enthalpy of formation of these compounds can be obtained, from the comparison of their enthalpy of solution with that of the anhydrous salt obtained by Chauvenet, and $\Delta_f H_m^\circ$ ($ThCl_4$, cr, 298.15 K) = $-(1186.3 \pm 1.3)$ kJ·mol^{-1} selected in this review, using $\Delta_f H_m^\circ$ (H_2O, l, 298.15 K) = $-(285.830 \pm 0.040)$ kJ·mol^{-1}.

This yields $\Delta_f H_m^\circ$ ($ThCl_4 \cdot 2H_2O$, cr, 298.15 K) = $-(1822.4 \pm 12.0)$ kJ·mol^{-1}, $\Delta_f H_m^\circ$ ($ThCl_4 \cdot 4H_2O$, cr, 298.15 K) = $-(2456.2 \pm 12.0)$ kJ·mol^{-1} , $\Delta_f H_m^\circ$ ($ThCl_4 \cdot 7H_2O$, cr, 298.15 K) = $-(3361.9 \pm 12.0)$ kJ·mol^{-1}, and $\Delta_f H_m^\circ$ ($ThCl_4 \cdot 8H_2O$, cr, 298.15 K) = $-(3661.3 \pm 12.0)$ kJ·mol^{-1}, the large uncertainty limits being suggested by this review.

The enthalpy of solution of $ThOCl_2$(cr), $ThOBr_2$(cr), and $ThOI_2$(cr) in *ca.* 16000 H_2O were also reported as -117.78, -116.98, and -90.08 kJ·mol^{-1}, respectively. Use, as in the case of $ThCl_4$(cr) above, of the equilibrium constants for the hydrolysis of thorium, and, respectively, of $\log_{10} {}^*\beta_1^\circ$ (ThCl^{3+}, 298.15 K) = (1.70 ± 0.10) (Section VIII.2.2.1), $\log_{10} {}^*\beta_1^\circ$ (ThBr^{3+}, 298.15 K) = (1.37 ± 0.11) (Section VIII.3.2.1), and $\log_{10} {}^*\beta_1^\circ$ (ThI^{3+}, 298.15 K) = (1.25 ± 0.30) (Section VIII.4.2.1, based on the similar uranium species), allows the calculation of the distribution of thorium in the various species. This gives the approximate speciations given below.

Th^{4+}	$\mathrm{Th(OH)}^{3+}$	$\mathrm{Th(OH)}_2^{2+}$	$\mathrm{Th_2(OH)}_2^{6+}$	$\mathrm{Th_2(OH)}_3^{5+}$	$\mathrm{Th_4(OH)}_{12}^{4+}$	$\mathrm{Th(OH)_4}$(am) precipitate	ThBr^{3+}
For the dissolution of $ThOCl_2$(cr)							
5.36%	25.90%	7.89%	0.01%	1.13%	55.98%	1.89%	
For the dissolution of $ThOBr_2$(cr)							
5.50%	26.39%	7.99%	0.01%	1.16%	57.39%	0.67%	0.89%
For the dissolution of $ThOI_2$(cr)							
5.67%	26.96%	8.09%	0.01%	1.20%	58.07%		

Compared to the case of the dissolution of the halides, the increased complexity of the hydrolysis phenomena and the appearance of small amounts of $Th(OH)_4$(am) precipitate in the case of the dissolution of the oxychloride and the oxybromide do not permit us to treat the data on the three oxyhalides with sufficient accuracy for any values to be selected.

For the enthalpy of solution of $ThBr_4$(cr), Chauvenet reported a value of – 293.67 kJ·mol^{-1}. Calculation yields the following distribution of thorium in the various species in the solution:

Th^{4+}	$Th(OH)^{3+}$	$Th(OH)_2^{2+}$	$Th_2(OH)_2^{6+}$	$Th_2(OH)_3^{5+}$	$Th_4(OH)_{12}^{4+}$	$ThBr^{3+}$
33.52%	49.82%	4.67%	0.02%	1.28%	0.07%	10.62%

Neglect, as in the case of the chloride, of three minor hydrolysis products yields a dissolution reaction that can be written as:

$$\begin{aligned}&ThBr_4(cr) + 0.6190\, H_2O \text{ (in } ca.\ 16000\ H_2O(l)) \rightleftharpoons\\ &\quad (0.3352\,Th^{4+} + 0.4982\,Th(OH)^{3+} + 0.06040\,Th(OH)_2^{2+} + 0.1062\,ThBr^{3+}\\ &\quad + 3.8938\ Br^- + 0.6190\ H^+) \text{ in } ca.\ 16000H_2O(l)\end{aligned} \tag{A.3}$$

Use of the enthalpy of solution experimentally measured by Chauvenet (assumed to be valid at 298.15 K), $\Delta_{sol}H_m$ ($ThBr_4$, in *ca.*16000 H_2O, 298.15 K) = – 293.67 kJ·mol^{-1}, $\Delta_f H_m$ (Br^-, *ca.* 4000 H_2O, 298.15 K) = −(121.20 ± 0.15) kJ·mol^{-1}, and the same calculation procedure as for the dissolution of the tetrachloride (but neglecting the unknown, but likely to be negligible enthalpy effect, of the bromide complexation), leads to $\Delta_f H_m^\circ$ ($ThBr_4$, cr, 298.15 K) = – (932.6 ± 4.7) kJ·mol^{-1}, without consideration for the uncertainty in the experimental value reported by Chauvenet. This value is very distinctly less negative than that resulting from better documented more recent results adopted in this review, $\Delta_f H_m^\circ$ ($ThBr_4$, β, 298.15 K) = −(963.8 ± 2.0) kJ·mol^{-1}.

The enthalpies of solution in water of the thorium tetrabromide hepta-, deca- and dodecahydrate, respectively, were obtained as −94.35, −41.17, and −9.62 kJ·mol^{-1}, under similar conditions to those for the anhydrous salt. As in the case of the tetrachloride hydrates, the enthalpy of formation of these compounds can be obtained from the comparison of their enthalpy of solution with that of the anhydrous salt obtained by Chauvenet, and $\Delta_f H_m^\circ$ ($ThBr_4$, cr, 298.15 K) = −(963.8 ± 2.0) kJ·mol^{-1} selected in this review, using $\Delta_f H_m^\circ$ (H_2O, l, 298.15 K) = – (285.830 ± 0.040) kJ·mol^{-1}. This yields $\Delta_f H_m^\circ$ ($ThBr_4{\cdot}7H_2O$, cr, 298.15 K) = −(3163.9 ± 12.0) kJ·mol^{-1}, $\Delta_f H_m^\circ$ ($ThBr_4{\cdot}10H_2O$, cr, 298.15 K) = −(4074.6 ± 12.0) kJ·mol^{-1}, and $\Delta_f H_m^\circ$ ($ThBr_4{\cdot}12H_2O$, cr, 298.15 K) = – (4677.8 ± 12.0) kJ·mol^{-1}, the large uncertainty limits being suggested by this review.

Chauvenet does not report any result on ThI_4(cr) but only mentions the difficulty in obtaining this compound in a pure state. In addition to his result on the enthalpy of solution of $ThOI_2$(cr) (see above), he reports as −41.97 kJ·mol^{-1} the enthalpy of solution in water of a compound analysed as $ThOI_2 \cdot 3.5H_2O$ (or $Th(OH)_2I_2 \cdot 2.5H_2O$) and as − 35.31 $kJ \cdot mol^{-1}$, the enthalpy of solution of a species reported as $Th(OH)I_3 \cdot 10H_2O$. As these compounds were not unambiguously characterised and, in view of the difficulty of ascertaining the dissolution processes, these values are given here for information only.

Enthalpies of solution of large number of ternary chlorides of thorium with alkali metals and ammonium and of their hydrates were also reported, as well as that of adducts of $ThCl_4$ with ammonia. These results are outside the bounds of the present review.

[1912BAR]

See discussion in [1910KOP/HOL].

[1912WIR]

See discussion in [1910KOP/HOL].

[1925BRI]

Britton [1925BRI] performed potentiometric titrations of 0.001, 0.002 and 0.01 M $Th(NO_3)_4$, 0.01 M $ThCl_4$ and 0.01 M $Th(SO_4)_2$ solutions with 0.1 M NaOH from pH 3 to pH 12 at 15°C. The 0.01 M $Th(NO_3)_4$ solution was also titrated with 0.1 M NH_4OH. The hydroxide solutions were added in about 20 steps (equilibration intervals of 5 to 15 minutes) and pH was calculated from the emf measured with a hydrogen electrode against a normal calomel reference electrode.

The onset of (visible) precipitation in these titrations was observed at pH 3.51−3.60. This is in fair agreement with more recent solubility studies with ThO_2(am, hyd), *e.g.*, with [1963BIL/FUR] and [2002NEC/MUL] where the onset of precipitation / colloid formation in titrations at similar thorium concentrations was determined by light scattering or laser-induced breakdown detection.

The author noticed that less than four (3.24−3.58) equivalents of alkali are required for neutrality (pH 7) during the titrations and concluded that the precipitates were "basic salts" containing certain amounts of nitrate, chloride or sulphate, *e.g.*, $Th(OH)_{3.43}(NO_3)_{0.57}$. This early paper provides only qualitative information, and no equilibrium constants can be derived from the experimental data reported in [1925BRI].

[1927PRE/HIN]

Manometric measurements of the pressure of CO(g) in from mixtures of ThO_2(cr) + graphite, heated in a graphite furnace, were made at eight temperatures from 2057 to 2494 K. The equilibrium pressures were determined by interpolating the rate of reaction (as measured by the rate of change of pressure) to zero. The results were fitted to the equation:

$$\log_{10} p_{CO} / \text{bar} = 8.075 - 19325\, T^{-1}.$$

Using the equivalent of a manual DTA apparatus, the melting point of "ThC_2" was found to be *ca*. 2773 K, appreciably below the assessed melting point from more recent determinations (2883 ± 35) K [1984HOL/RAN].

[1928BEC]

After a rather long discussion of electronic, structural and thermodynamics interrelationships between compounds of polyvalent elements, the author reports density measurements on various sulphates, halides, and binary and ternary oxides, and also enthalpies of reaction of such salts with solutions of different compositions.

Of direct interest to this review is the measurement of the enthalpy effect accompanying the reaction of $Th(SO_4)_2(cr)$ with a solution of NaOH.

The concentration of the dissolution medium was not specified and apparently, only one experiment was reported (0.8925 g $Th(SO_4)_2$ reacted with 500 cm^3 of solution). The lack of proper identity of the thorium hydroxide precipitate resulting from the reaction adds to the difficulty in extracting meaningful conclusions from this experiment. In a quite unclear way Beck [1928BEC] derives from his experimental result a value of -483.3 $kJ\cdot mol^{-1}$ for the enthalpy of the reaction $ThO_2(cr) + 2SO_3 \rightleftharpoons Th(SO_4)_2(cr)$, at 291.15 K. The physical state of SO_3 to which this value applies is not stated, but is most probably gaseous.

With $\Delta_f H_m^\circ$ (SO_3, g, 298.15 K) = $-(395.9 \pm 0.7)$ $kJ\cdot mol^{-1}$ from [1989GUR/VEY], and $\Delta_f H_m^\circ$ (SO_3, cr, 298.15 K) = $-(454.7 \pm 1.5)$ $kJ\cdot mol^{-1}$, consistent with this value and the enthalpy of sublimation of $SO_3(cr)$, [1982WAG/EVA], this review obtains $\Delta_f H_m^\circ$ ($Th(SO_4)_2$, cr, 293.15 K) = -2502 or -2560 $kJ\cdot mol^{-1}$, according as to whether the tabulated value refers to $SO_3(g)$ or $SO_3(cr)$. The small difference in temperature is neglected, as well as the enthalpy of hydration of $ThO_2(cr)$, so the uncertainties are unknown, but appreciable. These values are given for information only, given the lack of detail in the paper, and the ill-defined derivation of the value tabulated therein.

[1929FRI2]

Experimental data are reported for the vapour pressures at 0°C and 15°C of solutions of $Th(NO_3)_4$, (and other solutions) at five different water-to-thorium molar ratios ranging from 24.46 to 16.48 and for the enthalpies of dilution of six solutions ranging from initial water-to-thorium molar ratios of 15.65 to 28.18, to a final ratio of 510 to 562.

Experimental enthalpies of dilution were correlated with vapour pressures data, and the limits of such correlations in the case of thorium nitrate solutions were outlined.

[1930CHA/SOU]

These authors investigated the chemical and thermal stability of different thorium nitrate solids. They identified $Th(NO_3)_4\cdot 5H_2O(cr)$ that formed as well defined crystals on slow evaporation at 15°C. The solid loses two molecules of water at 80°C and is transformed to $ThO(NO_3)_2{\cdot}0.5H_2O(cr)$ at 125°C. Further decomposition takes place at higher temperature. Heating under a gas phase composed of CO_2 and vapours from fuming nitric acid resulted in the formation of $Th(NO_3)_4{\cdot}2H_2O(cr)$ at 110°C. Solutions of the nitrate were titrated with NaOH and the reaction was followed by conductometry but no quantitative conclusions were drawn.

[1932NEU/KRO]

Neumann *et al.* [1932NEU/KRO] have measured the enthalpy of reaction of excess thorium (99% pure) with nitrogen at 298.15 K in an iron crucible in a bomb calorimeter. The overall N/Th of the reaction product was 0.69 − 0.87, but the main product was almost certainly $Th_3N_4(cr)$. From three experiments, these authors reported a value of $\Delta_f H_m$ (Th_3N_4, cr, 268.15 K) = −(1290.3 ± 16.3) $kJ{\cdot}mol^{-1}$, their uncertainty limits being for the 2σ confidence level. Experiments on the combustion of unpurified thorium (95% pure) in nitrogen in a platinum crucible, presumably after correction for the lower Th content, gave slightly smaller enthalpies of reaction.

Since there is no indication in the publication that a correction was made to convert the value to constant pressure, this correction (− 16.0 $kJ{\cdot}mol^{-1}$ (Th_3N_4)) has been applied. The similar adjustment made by [1975RAN] seems to be too small by a factor of three. Thus this measurement gives $\Delta_f H^\circ_m$ (Th_3N_4, cr, 298.15 K) = −(1306.3 ± 16.3) $kJ{\cdot}mol^{-1}$ from this source. The uncertainties include those from the ill-defined composition of the product.

[1932ROT/BEC]

The enthalpies of formation of eight oxides (SiO_2, TiO_2, ZrO_2, HfO_2, ThO_2, GeO_2, Nb_2O_5, and Ga_2O_3) were determined at 293 K.

The thorium metal sample (reportedly "free of carbon"), obtained from J.H. de Boer (van Arkel and de Boer process, presumably [1925ARK/BOE], although this reference is not explicitly cited) was almost certainly much purer than previous preparations reported in the literature, especially with regard to light elements, although it contained 0.1% W.

A total of five oxygen combustion experiments, using two calibrated equipments were carried out, with concordant results and led to a value of −(1224.2 ± 5.8) $kJ{\cdot}mol^{-1}$ for the enthalpy of formation of $ThO_2(cr)$ at 293 K.

[1934JAE/VEE]

The heat capacities of metallic thorium (containing 6.04 mass% ThO_2) and ThO_2 were measured in what is assumed to be a drop calorimeter. Two samples of thorium were used: a rod, which was found to contain 6.04 mass% ThO_2, and a powder, found to contain 26.8 mass% ThO_2. Even after correction for the presence of thoria, the results for the powder were *ca.* 27% greater than those for the rod and were discounted by the authors.

The results were fitted to the expression (t / ºC):

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Th, cr}, t) = 7.97816 + 0.45997 \times 10^{-3} t + 0.10014 \times 10^{-5} t^2 + 0.10493 \times 10^{-8} t^3 \\ \mathrm{cal{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

They agree reasonably well with more modern measurements using higher purity metal, but they were not included in the data fitting (see Section V.1.2)

The results for ThO_2 (671 − 1664 K) do not a have sensible variation with temperature, and have been discounted in view of the availability of more precise modern data.

[1934NEU/KRO]

The enthalpy of formation of Th_3N_4(cr) was determined from its enthalpy of combustion in 25 bar oxygen at 292 K in a bomb calorimeter. The compound was prepared by reacting 99% pure thorium metal filings with nitrogen as described in [1932NEU/KRO]. The measured weight gain corresponded to the formation of a material containing 99.03% Th_3N_4. The metal used in this study was the same as that used by the same group [1932NEU/KRO] for the direct determination of the heat of formation of Th_3N_4 from the elements.

Owing to the limited amount of material available, only one oxygen combustion could be realised. Analytical results showed that the combustion was close to 99% complete. For the reaction:

$$\mathrm{Th_3N_4(cr) + 3O_2(g) \rightleftharpoons 3ThO_2(cr) + 2N_2(g)} \quad \text{(A.4)}$$

the authors reported a value (at constant volume) of $-(2363.1 \pm 4.6)$ kJ·mol^{-1}.

Correction of this value to constant pressure (for a net decrease of 1 mol gas), yields $\Delta_r H_m$((A.4), 292 K) = $-(2371.1 \pm 4.6)$ kJ·mol^{-1}. The value at 298.15 K is assumed to be the same.

The authors used the enthalpy of formation of ThO_2(cr) as determined by [1932ROT/BEC], in combination with their experimental result to obtain the enthalpy of formation of Th_3N_4(cr). Using $\Delta_f H^{\circ}_m$ (ThO_2, cr, 298.15 K) = $-(1226.4 \pm 3.5)$ kJ·mol^{-1} accepted in this review, and neglecting the small difference in temperature of the measurement of the enthalpy of combustion, we obtain $\Delta_f H^{\circ}_m$ (Th_3N_4, cr, 298.1 K) = $-(1308.1 \pm 11.5)$ kJ·mol^{-1}.

The authors also measured the enthalpies of formation of nine other oxides and nitrides. Their results are in reasonable accord with the current values selected by [1998CHA].

[1939FIS/GEW2]

A variant of the boiling point method for samples which attack silica was developed, and used to measure the vapour pressures of $ThCl_4$(cr) and $ThCl_4$(l), $ThBr_4$(cr) and $ThBr_4$(l) and ThI_4(l). Samples were contained in a molybdenum bell, immersed in liquid tin, and the pressure within the bell was balanced by argon on the outside.

$ThCl_4$(cr) and $ThBr_4$(cr) were prepared in a silica apparatus from a mixture of "pure" ThO_2 and sugar-charcoal with a stream of chlorine and sulphur chlorides, or bromine containing nitrogen. ThI_4(cr) was prepared from the elements. All samples were purified by sublimation, and were stated to give analyses agreeing with the theoretical values within the uncertainties. No details of the analyses are given.

The melting points of $ThCl_4$, $ThBr_4$ and ThI_4 were found to be (1043 ± 2) K, (952 ± 3) K and (839 ± 2) K respectively, and the vapour pressures to be represented by the following equations ($\log_{10} p/\text{bar} = \text{A}/T + \text{B}$) for the given temperature ranges.

Phase	Temperature range / K	A	B
$ThCl_4$(cr)	974 − 1036	− 12910	11.425
$ThCl_4$(l)	1052 − 1186	− 7587	6.695
$ThBr_4$(cr)	903 − 950	− 9628	8.855
$ThBr_4$(l)	955 − 1126	− 7549	6.685
ThI_4(l)	856 − 1107	− 6892	6.215

[1939SAT]

The mean specific heats of "Th_3N_4(cr)", Li_3N(cr), Zn_3N_2(cr) were measured with an ice calorimeter over three temperature intervals from 273.2 to 373.7 K, 578.9 K and 776.2 K. The sample of Th_3N_4(cr) was prepared from the elements, initially at 1013 K, and subsequently at 1113 K for six hours. Analyses showed that it contained 5.78 wt% N, 2.65 wt% O and 91.57 wt% Th. With current atomic weights, this corresponds to 77.59 wt% Th_3N_4(cr), 21.87 wt% ThO_2(cr) and 0.54 wt% Th(cr). As noted by Rand [1975RAN], the overall composition corresponds to a composition of $Th_2N_{2.09}O_{0.84}$, close to Th_2N_2O, and it is not clear whether the sample was a mixture of Th_3N_4(cr) and ThO_2(cr), as assumed by Sato, or Th_2N_2O(cr) and Th_3N_4(cr), or of all three phases, with or without reciprocal solubility. The following calculation assumes, with the author, the first possibility.

The three measurements of the mean specific heat were corrected by the review for these impurities, using the selected heat capacity data for ThO_2(cr), and Th(cr). The mean heat capacities of Th_3N_4(cr) are thus calculated to be: 164.96 $\text{J·K}^{-1}\text{·mol}^{-1}$ for 273.2−373.7 K; 178.80 for 273.2−578.9 K and 273.2−776.2 K. These are represented by the following equation for the true heat capacities:

$$[C^{\circ}_{p,\text{m}}]^{800\text{K}}_{273.2\text{K}}\,(\text{Th}_3\text{N}_4, \text{cr}, T) = 133.97 + 0.1142\,T + 5.983\times10^{5}\,T^{-2} \quad \text{J·K}^{-1}\text{·mol}^{-1}$$

giving

$$C^{\circ}_{p,\mathrm{m}}(\mathrm{Th_3N_4, cr, 298.15\ K}) = 161.3\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

This is rather larger than the selected value (147.7 ± 8.0) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, and in view of the uncertainty in the phase composition of the sample, the data of [1939SAT] are not retained by this review.

[1941SOU]

Data are given for the heat content for thorium dioxide (to 1787 K). Impure thoria was purified from rare earths metals by dissolution in concentrated HCl and iodate precipitation, to give samples of 99.4% and 99.1% purity. No correction was made for the impurities. The samples were contained in a Pt-Rh cylinder and dropped into a copper block, whose temperature was monitored. The enthalpy increments were fitted to a four term extended Kelley equation from which the heat capacity was derived.

[1941STR/ZUM]

Strotzer and Zumbusch [1941STR/ZUM] have measured the sulphur decomposition pressures over a sample of composition $\mathrm{ThS_{2.19}}$ at four temperatures from 924 to 1027 K. Based on their structural and analytical studies, they took this to be a mixture of $\mathrm{ThS_2}$(cr) and $\mathrm{Th_3S_7}$(cr). However, we have preferred the interpretation of Graham and McTaggart [1960GRA/MCT] and assumed the higher sulphide to be $\mathrm{Th_2S_5}$(cr). With corrections to the total pressure of sulphur vapour for the presence of 4 − 6% higher sulphur polymers in the vapour (see Section IX.1.1.8), the results indicate that the enthalpy of formation of $\mathrm{Th_2S_5}$(cr) is *ca.* 8.3 $\mathrm{kJ{\cdot}mol^{-1}}$ more negative than that of $\mathrm{ThS_2}$(cr) around 1000 K.

[1944TOL]

Only an short abstract was available to the reviewers; the author uses UV spectra to suggest the formation of the species $\mathrm{Th(OH)_2(CO_3)_4^{6-}}$, presumably in a solution with high carbonate concentration. It is not obvious to the reviewers how this assignment was made and this information has not been considered reliable.

[1947ROB/LEV]

The vapour pressures of aqueous solutions of $\mathrm{K_3Fe(CN)_6}$ and $\mathrm{Th(NO_3)_4}$ were determined by the isopiestic method. The osmotic and activity coefficients were determined from these data. Ions of high negative charges cause greater deviation from ideal behaviour than ions of high positive charge. It is postulated that this effect is due to the extensive hydration of the positive ions in contrast to the negative ions.

[1948MOE/SCH]

The paper describes an analytical method and does not provide any thermodynamic data.

[1948SOU]

Souchay has studied hydrolysis and the formation of polynuclear complexes of a number of different metal ions, including Th(IV), using cryoscopy. The method requires high total concentrations of the solute (in this case 0.4 M thorium nitrate) to which different amounts of NaOH were added. Souchay interpreted his result as the formation of a single tetranuclear complex $\mathrm{Th_4(OH)_8^{8+}}$. There is no information on the pH in the system and as a result of later investigations discussed in the present review, it is well established that no single species can describe the hydrolysis of Th. There are no thermodynamic data reported and the data do not provide supporting evidence for the formation of a tetranuclear Th hydroxide complex.

[1949DOD/ROL]

The authors have studied the complex formation between Th(IV) and fluoride using the redox couple Fe(III)/Fe(II) as indicator electrode. In a separate experiment they determined the fluoride complexes formed by $\mathrm{Fe^{3+}}$ (the fluoride complex formation of $\mathrm{Fe^{2+}}$ is negligible under the conditions used). From the known equilibrium data for the iron system they then calculated the free fluoride concentration from the measured redox potential in test solutions that in addition to Fe(III)/Fe(II) also contained Th(IV); the indicator system acts as a fluoride selective electrode.

The experiments were made at 25.00°C in a $\mathrm{HClO_4}$-$\mathrm{NaClO_4}$ ionic medium with the ionic strength 0.50 M. The concentration of $\mathrm{H^+}$ was varied in the different titrations and ranged from 0.03 to 0.30 M. All experimental details are carefully described.

The Fe(III)-$\mathrm{F^-}$ titrations were described with the following set of equilibrium constants for the reactions:

$$\mathrm{Fe^{3+} + HF(aq) \rightleftharpoons FeF^{2+} + H^+} \qquad {}^*K_1 = (189 \pm 5)$$

$$\mathrm{FeF^{2+} + HF(aq) \rightleftharpoons FeF_2^+ + H^+} \qquad {}^*K_2 = (10.4 \pm 0.4)$$

$$\mathrm{FeF_2^+ + HF(aq) \rightleftharpoons FeF_3(aq) + H^+} \qquad {}^*K_3 \approx 0.58$$

$$\mathrm{Fe^{3+} + H_2O(l) \rightleftharpoons FeOH^{2+} + H^+} \qquad {}^*K_\mathrm{h}$$

$$\mathrm{HF(aq) \rightleftharpoons H^+ + F^-} \qquad K_4$$

$$\mathrm{HF(aq) + F^- \rightleftharpoons HF_2^-} \qquad K_5$$

The equilibrium constants ${}^*K_\mathrm{h}$, K_4 and K_5 taken from the literature are so small that they do not affect the values of the equilibrium constants ${}^*K_n$, $n = 1-3$. The latter are also in good agreement with previous studies discussed in [1949DOD/ROL].

The thorium experiments were made at a hydrogen ion concentration of approximately 0.05 M. The experimental $\bar{n}_\mathrm{F}$ *vs.* $[\mathrm{F^-}]$ curves had a break at $\bar{n}_\mathrm{F} \approx 2$ where $\mathrm{ThF_4(s)}$, presumably hydrated, was formed. The most accurate data were obtained in the range $1 < \bar{n}_\mathrm{F} < 2$, which means that the equilibrium constant for the formation of $\mathrm{ThF^{3+}}$

is somewhat less precise than that for the formation of ThF_2^{2+}. Analysis of the data gave the following result:

$$\mathrm{Th}^{4+} + \mathrm{HF(aq)} \rightleftharpoons \mathrm{ThF}^{3+} + \mathrm{H}^+ \qquad {}^*K_1 = (4.5 \pm 0.5) \times 10^4$$

$$\mathrm{ThF}^{3+} + \mathrm{HF(aq)} \rightleftharpoons \mathrm{ThF}_2^{2+} + \mathrm{H}^+ \qquad {}^*K_2 = (650 \pm 15)$$

$$\mathrm{ThF}_2^{2+} + \mathrm{HF(aq)} \rightleftharpoons \mathrm{ThF}_3^{+} + \mathrm{H}^+ \qquad {}^*K_3 = (32 \pm 2)$$

The authors also used the test solutions where precipitation of $\mathrm{ThF_4(s)}$ occurred to determine the solubility constant, ${}^*K_s$, for the reaction:

$$\mathrm{ThF_4{\cdot}4H_2O(s)} + 2\mathrm{H}^+ \rightleftharpoons \mathrm{ThF}_2^{2+} + 2\mathrm{HF(aq)} + 4\mathrm{H_2O(l)} \qquad {}^*K_s = (5.9 \pm 0.5) \times 10^{-8}\ \mathrm{M}.$$

This is a precise experimental study and the equilibrium analysis made by the authors is accepted by this review.

[1949WES/ROB3]

The enthalpies of solution at 298.15 K of pure anhydrous $\mathrm{ThCl_4(cr)}$ in 1.000, 6.000, and 9.000 M HCl solutions were found to be $-(240.25 \pm 0.42)$, $-(185.23 \pm 0.42)$, and $-(146.15 \pm 0.42)$ $\mathrm{kJ{\cdot}mol^{-1}}$, respectively. The $\mathrm{ThCl_4}$ concentrations were approximately 0.005 M.

The $\mathrm{ThCl_4(cr)}$ used was purified by high-vacuum sublimation in quartz to eliminate oxychloride and loaded into the semi-microcalorimeter bulbs in a dry box. The sample used was of high purity as judged from the thorium and chlorine analyses which were given as 62.8% Th and 37.8% Cl (theoretical: 62.07% Th and 37.93% Cl) as determined by the analytical section of the authors' laboratory. No X-ray analysis was given, and the material is assumed to be the β polymorph normally obtained without long annealing at low temperatures. The presence of small amounts of the most likely impurity, $\mathrm{ThOCl_2}$, would have had a very small effect on the enthalpies of solution.

These data are used in the determination of $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}(\mathrm{Th}^{4+}, 298.15\ \mathrm{K})$ in conjunction with results from [1950EYR/WES], [1969SMI/THA], and [1973FUG/BRO].

[1950DAY/STO]

The authors have used a liquid-liquid extraction method with thenoyltrifluoroacetone (TTA) as the extracting ligand to study the complex formation between Th^{4+} and different organic and inorganic ligands. The characteristics of the experimental method are described in the main text of this review. The experiments have been made at 25°C using an aqueous phase with a constant hydrogen ion concentration and ionic strength of 0.50 M; the organic phase was 0.25 M TTA dissolved in benzene. Thorium was present in trace concentration, 10^{-6} M. The following ligands were investigated Cl^-, NO_3^-, ClO_3^-, BrO_3^-, IO_3^-, F^-, mono-, di- and tri-chloroacetate and formate. The total concentrations of the ligands were varied, while keeping $[H^+]$ constant. The experimental equilibrium constants are given in Table A-7.

Table A-7: Equilibrium constants reported in [1950DAY/STO].

Reaction	Equilibrium constant
$Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+$	4.3×10^4
$Th^{4+} + 2HF(aq) \rightleftharpoons ThF^{3+} + 2H^+$	3.1×10^7
$Th^{4+} + IO_3^- \rightleftharpoons ThIO_3^{3+}$	7.6×10^2 M^{-1}
$Th^{4+} + 2\ IO_3^- \rightleftharpoons Th(IO_3)_2^{2+}$	6.2×10^4 M^{-2}
$Th^{4+} + 3\ IO_3^- \rightleftharpoons Th(IO_3)_3^{+}$	1.4×10^7 M^{-3}
$Th^{4+} + BrO_3^- \rightleftharpoons ThBrO_3^{3+}$	6.4 M^{-1}
$Th^{4+} + 2\ BrO_3^- \rightleftharpoons Th(BrO_3)_2^{2+}$	8.2 M^{-2}
$Th^{4+} + ClO_3^- \rightleftharpoons ThClO_3^{3+}$	1.84 M^{-1}
$Th^{4+} + NO_3^- \rightleftharpoons ThNO_3^{3+}$	4.73 M^{-1}
$Th^{4+} + Cl^- \rightleftharpoons ThCl^{3+}$	1.76 M^{-1}
$Th^{4+} + ClCH_2COOH \rightleftharpoons Th(ClCH_2COO)^{3+} + H^+$	1.33 M^{-1}
$Th^{4+} + Cl_2CHCOOH \rightleftharpoons Th(Cl_2CHCOO)^{3+} + H^+$	5.74 M^{-1}
$Th^{4+} + 2Cl_2CHCOOH \rightleftharpoons Th(Cl_2CHCOO)_2^{2+} + 2H^+$	12.7 M^{-2}
$Th^{4+} + Cl_3CCOOH \rightleftharpoons Th(Cl_3CCOO)^{3+} + H^+$	8.23 M^{-1}
$Th^{4+} + 2Cl_3CCOOH \rightleftharpoons Th(Cl_3CCOO)_2^{2+} + 2H^+$	26.7 M^{-2}

The fluoride complexes were also investigated in a nitrate ionic medium and the authors note that the distribution coefficients are lower than in a perchlorate medium, suggesting formation of a ternary complex $ThF(NO_3)^{2+}$. This review suggests that a more probable explanation is that the effect is due to changes in activity coefficients between the two media and therefore does not accept the suggestion of formation of ternary complexes. No equilibrium constant was determined for acetate and formate complexes because of indications of coextraction of a Th-TTA-acetate/formate complex, (so-called synergistic extraction).

The dissociation constants for tri- di- and mono-chloroacetic acids are 0.2, 0.05 and 0.0014 M, respectively. The experimental procedures and data analysis used in this study are satisfactory and the numerical values of the proposed equilibrium constants are therefore considered to be reliable, but are not selected since data on organic ligands are not included in the present review. However, the equilibrium constants for the weak complexes require extensive changes in the ionic medium and the observed variation in distribution coefficients could therefore also be a result of activity coefficient variations.

The authors have not made any error estimates of the constants, but this review estimates an uncertainty of ten percent in the constants accepted.

As discussed in previous volumes of this series it is difficult to distinguish between complex formation and activity factor variations in systems where weak complexes are formed, owing to the large changes in the composition of the ionic medium required to have a measurable effect in these systems. We will illustrate this point by a more detailed discussion of experimental data for the Th^{4+}-Cl^-, ClO_3^-, BrO_3^-, and NO_3^- systems, studied using liquid-liquid extraction with thenoyltrifluoroacetone (HL) as extractant; two different methods will be described. The experimental data are from [1950DAY/STO] and [1952WAG/STO].

The phase equilibrium is given by the reaction:

$$Th^{4+}(aq) + 4HL(org) \rightleftharpoons ThL_4(org) + 4H^+(aq) \qquad (A.5)$$

and the equilibrium constant at $I = 0$ in both aqueous and organic phase is given by:

$$\begin{aligned}\log_{10} K^{\circ} = {} & \log_{10}[ThL_4(org)] - \log_{10}[Th^{4+}] + 4\log_{10}[H^+] - 4\log_{10}[HL(org)] \\ & + \log_{10}\gamma_{ThL_4(org)} - \log_{10}\gamma_{Th^{4+}} + 4\log_{10}\gamma_{H^+} - 4\log_{10}\gamma_{HL(org)} \end{aligned} \qquad (A.6)$$

As thorium is usually a trace component and the composition of the organic phase and hence the activity coefficients of the organic species are constant (independent of the aqueous phase), Equation (A.6) can be rewritten as:

$$\log_{10}{}'K^{\circ} = \log_{10}[ThL_4(org)] - \log_{10}[Th^{4+}] + 4\log_{10}[H^+] - \log_{10}\gamma_{Th^{4+}} + 4\log_{10}\gamma_{H^+} \qquad (A.7)$$

where $\log_{10}{}'K^{\circ} = \log_{10} K^{\circ} + 4\log_{10}[HL(org)] + 4\log_{10}\gamma_{HL(org)} - \log_{10}\gamma_{ThL_4(org)}$ is the equilibrium constant for a given composition of the organic phase and $I = 0$ in the aqueous phase. Applying the SIT to mixed $HClO_4$-HX media, *e.g.*, for the data from [1950DAY/STO] at $I = 0.5$ M with $X^- = Cl^-$, ClO_3^-, BrO_3^-, and NO_3^-, Eq. (A.7) becomes:

$$\begin{aligned}\log_{10}{}'K^{\circ} = {} & \log_{10}[ThL_4(org)] - \log_{10}[Th^{4+}] + 4\log_{10}[H^+] + 16D \\ & + \{4\,\varepsilon(H^+, ClO_4^-) - \varepsilon(Th^{4+}, ClO_4^-)\}\, m_{ClO_4^-} + \{4\,\varepsilon(H^+,X^-) - \varepsilon(Th^{4+},X^-)\}\, m_{X^-}\end{aligned} \qquad (A.8)$$

The distribution coefficient D of thorium is defined by:

$$D = \frac{[Th]_{org}}{[Th]_{aq}} \qquad (A.9)$$

where $[Th]_{org} = [ThL_4(org)]$ and $[Th]_{aq} = [Th^{4+}] + [ThX^{3+}] + [ThX_2^{2+}] + \ldots$ are the molar thorium concentrations in the organic and aqueous phase, respectively.

Method 1 (complexation model used in [1950DAY/STO] and [1952WAG/STO]). In a series of extraction experiments at constant H^+ concentration and constant ionic strength, *e.g.*, in $(H/Na)ClO_4$-$(H/Na)Cl$ mixtures with $I = [ClO_4^-] + [X^-]$, the changes in the measured distribution coefficients are interpreted as being due to the formation of ThX_n^{4-n} complexes:

$$Th^{4+} + nX^- \rightleftharpoons ThX_n^{4-n} \qquad (A.10)$$

with

$$[\text{Th}]_{\text{aq}} = [\text{Th}^{4+}] + \Sigma\,[\,\text{ThX}_n^{4-n}\,] = [\text{Th}^{4+}]\,(1 + \Sigma\,\beta_n\,[\text{X}^-]^n) \qquad \text{(A.11)}$$

where β_n is the conditional formation constant of the complex ThX_n^{4-n} which is given by:

$$\beta_n = [\,\text{ThX}_n^{4-n}\,] \,/\, [\text{Th}^{4+}]\,[\text{X}^-]^n \qquad \text{(A.12)}$$

Combination of Equations (A.9)−(A.12) yields the relation:

$$\frac{1}{D} = \frac{1}{D_{\text{o}}}(1 + \sum \beta_n\ [\text{X}^-]^n) \qquad \text{(A.13)}$$

where D_{o} is the distribution coefficient in pure perchlorate solution at (I = [ClO_4^-], [X^-] = 0). Equation (A.13) is then applied to calculate the conditional formation constants β_n. The constant ionic strength (I = [ClO_4^-] + [X^-]) is usually considered as sufficient to keep the activity coefficients of the aqueous species constant. However, as the distribution coefficient and thermodynamic equilibrium constant $\log_{10}{}'K^\circ$ are related by:

$$\begin{aligned}\log_{10}D + \log_{10}(1 + \sum \beta_n\ [\text{X}^-]^n) = {} & \log_{10}{}'K^\circ - 16D - 4\log_{10}[\text{H}^+] \\ & - \{4\,\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-)\}\, m_{\text{ClO}_4^-} - \{4\,\varepsilon(\text{H}^+,\text{X}^-) - \varepsilon(\text{Th}^{4+},\text{X}^-)\}\, m_{\text{X}^-}\end{aligned}$$

this complexation model implies the (incorrect) assumptions that $\varepsilon(\text{H}^+, \text{ClO}_4^-) = \varepsilon(\text{H}^+,\text{X}^-)$ and $\varepsilon(\text{Th}^{4+}, \text{ClO}_4^-) = \varepsilon(\text{Th}^{4+},\text{X}^-)$.

Method 2 (strict ion interaction model). In distinction to the complexation model, the ion interaction model takes into account the fact that the SIT coefficients $\varepsilon(\text{M}^{z+}, \text{ClO}_4^-)$ differ from $\varepsilon(\text{M}^{z+}, \text{X}^-)$ but ignores the formation of complexes ($[\text{Th}]_{\text{aq}} = [\text{Th}^{4+}]$). The equations for $\log_{10}D$ (at $I_{\text{m}} = m_{\text{ClO}_4^-} + m_{\text{X}^-}$) and $\log_{10}D_{\text{o}}$ (at $m_{\text{X}^-} = 0$ and $I_{\text{m}} = m_{\text{ClO}_4^-} + m_{\text{X}^-} = (m_{\text{ClO}_4^-})_{\text{o}}$) are thus:

$$\begin{aligned}\log_{10}D = {} & \log_{10}{}'K^\circ - 16D - 4\log_{10} m_{\text{H}^+} - \{4\,\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-)\}\, m_{\text{ClO}_4^-} \\ & - \{4\,\varepsilon(\text{H}^+,\text{X}^-) - \varepsilon(\text{Th}^{4+},\text{X}^-)\}\, m_{\text{X}^-} \qquad \text{(A.14)}\end{aligned}$$

and

$$\log_{10}D_{\text{o}} = \log_{10}{}'K^\circ - 16D - 4\log_{10} m_{\text{H}^+} - \{4\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{Th}^{4+}, \text{ClO}_4^-)\}\,(m_{\text{ClO}_4^-})_{\text{o}} \qquad \text{(A.15)}$$

with

$$m_{\text{ClO}_4^-} = (m_{\text{ClO}_4^-})_{\text{o}} - m_{\text{X}^-} \qquad \text{(A.16)}$$

Combination of Eqs. (A.14)−(A.16) gives:

$$\begin{aligned}\log_{10} D = {} & \log_{10} D_{\text{o}} - \{\varepsilon(\text{Th}^{4+}, \text{ClO}_4^- - \varepsilon(\text{Th}^{4+}, \text{X}^-)\}\, \text{m}_{\text{X}-} \\ & + 4\{\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{H}^+, \text{X}^-)\}\, \text{m}_{\text{X}-} \qquad \text{(A.17)}\end{aligned}$$

Thus the solvent extraction data at constant ionic strength can be interpreted by taking into account only the changing composition of the HClO_4-HX media. For the data from

[1950DAY/STO] at I = 0.5 M with $\mathrm{Cl^-}$, $\mathrm{ClO_3^-}$, $\mathrm{BrO_3^-}$ and $\mathrm{NO_3^-}$ and the known values of $\varepsilon(\mathrm{H^+}, \mathrm{ClO_4^-}) = (0.14 \pm 0.02)\ \mathrm{kg{\cdot}mol^{-1}}$ and $\varepsilon(\mathrm{Th^{4+}}, \mathrm{ClO_4^-}) = (0.70 \pm 0.10)\ \mathrm{kg{\cdot}mol^{-1}}$, Eq. (A.17) becomes:

$$\log_{10} D = \log_{10} D_{\mathrm{o}} - (0.14 \pm 0.13)\, m_{\mathrm{X^-}} + \{\varepsilon(\mathrm{Th^{4+}}, \mathrm{X^-})\} - 4\varepsilon(\mathrm{H^+}, \mathrm{X^-})\}\, m_{\mathrm{X^-}}. \qquad \text{(A.18)}$$

The values of $\{\varepsilon(\mathrm{Th^{4+}}, \mathrm{X^-})\} - 4\varepsilon(\mathrm{H^+}, \mathrm{X^-})\}$ obtained by linear regression, Figure A-1 to Figure A-4, are summarised in Table A-8 (last column) and compared to the values of $\{\varepsilon(\mathrm{Th^{4+}}, \mathrm{X^-})\} - 4\varepsilon(\mathrm{H^+}, \mathrm{X^-})\}$ that can be calculated from the known individual SIT coefficients (preceding column). The values for $\mathrm{X^-} = \mathrm{Cl^-}$ and $\mathrm{ClO_3^-}$ are in the expected range while the values for $\mathrm{X^-} = \mathrm{NO_3^-}$ and $\mathrm{BrO_3^-}$ are far outside the expected range. The results for the nitrate system are in strong contradiction to the TBP extraction study of [2006NEC/ALT] where the distribution coefficients could be described without nitrate complexes over a wide range of nitrate concentrations (0.05 − 3.0 M $\mathrm{NaNO_3}$ containing 0.01 − 0.02 M $\mathrm{HNO_3}$). The experimental data could be described by the activity coefficients calculated with the SIT and $\varepsilon(\mathrm{Th^{4+}}, \mathrm{NO_3^-}) = (0.31 \pm 0.12)\ \mathrm{kg{\cdot}mol^{-1}}$. On the other hand it is well known that nitrate complexes are formed by the tetravalent actinides as discussed in [1992GRE/FUG] and [2001LEM/FUG]. There is no evidence for coextraction of $\mathrm{HNO_3}$ or $\mathrm{HClO_4}$ in TTA-systems, which would change the activity of the species in the organic phase which are assumed to be constant. Coextraction is, however, known in TBP systems.

Table A-8: SIT coefficients obtained from linear regression (Figure A-1 to Figure A-4).

X	$\varepsilon(\mathrm{Th^{4+}}, \mathrm{X^-})$ [a] ($\mathrm{kg{\cdot}mol^{-1}}$)	$\varepsilon(\mathrm{H^+}, \mathrm{X^-})$ [a] ($\mathrm{kg{\cdot}mol^{-1}}$)	$\{\varepsilon(\mathrm{Th^{4+}}, \mathrm{X^-}) - 4\,\varepsilon(\mathrm{H^+}, \mathrm{X^-})\}$ ($\mathrm{kg{\cdot}mol^{-1}}$)	
$\mathrm{ClO_4^-}$	0.70 ± 0.10 [b]	0.14 ± 0.02	0.14 ± 0.13	
$\mathrm{Cl^-}$	0.25 ± 0.03	0.12 ± 0.01	– 0.23 ± 0.05	– 0.39 ± 0.14 [c]
$\mathrm{ClO_3^-}$				– 0.41 ± 0.14 [c]
$\mathrm{BrO_3^-}$				– 1.43 ± 0.14 [c]
$\mathrm{NO_3^-}$	0.11 ± 0.02	0.07 ± 0.01	– 0.17 ± 0.05	– 0.91 ± 0.14 [c]
	0.31 ± 0.12 [b]	0.07 ± 0.01	0.03 ± 0.13	

a: From [1980CIA], [1992GRE/FUG], except otherwise stated.

b: Selected by this review, from [2006NEC/ALT].

c: $\{\varepsilon(\mathrm{Th^{4+}}, \mathrm{X^-})\} - 4\,\varepsilon(\mathrm{H^+}, \mathrm{X^-})\}$ calculated from the results in [1950DAY/STO].

Figure A-1: Distribution coefficients of Th in solvent extraction studies with TTA and aqueous $HClO_4$-HCl media at I = 0.5 M; experimental data [1950DAY/STO] and predicted values of $\log_{10}D$ (left side) and $1/D$ (right side) as a function of m_{Cl^-}

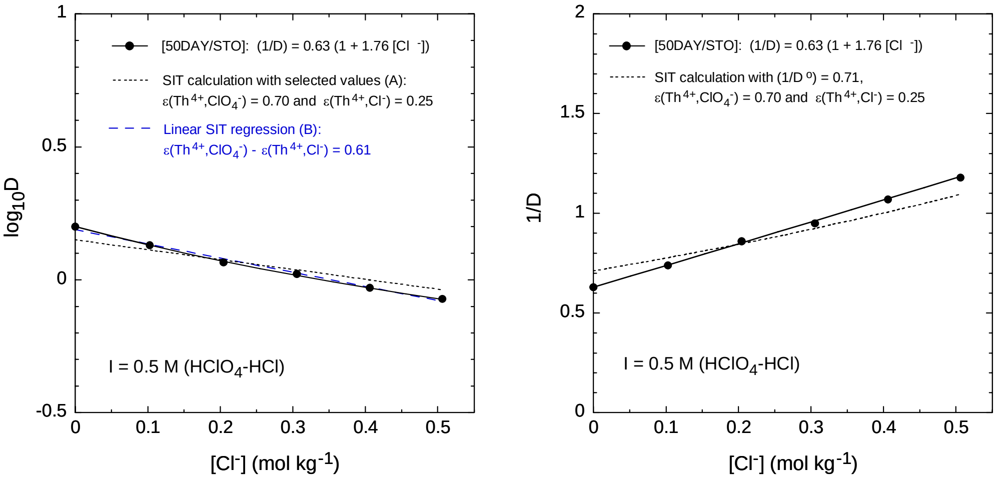


Figure A-2: Distribution coefficients of Th in solvent extraction studies with TTA and aqueous $HClO_4$-$HClO_3$ media at I = 0.5 M; experimental data [1950DAY/STO] and predicted values of $\log_{10}D$ (left side) and $1/D$ (right side) as a function of $m_{ClO_3^-}$.

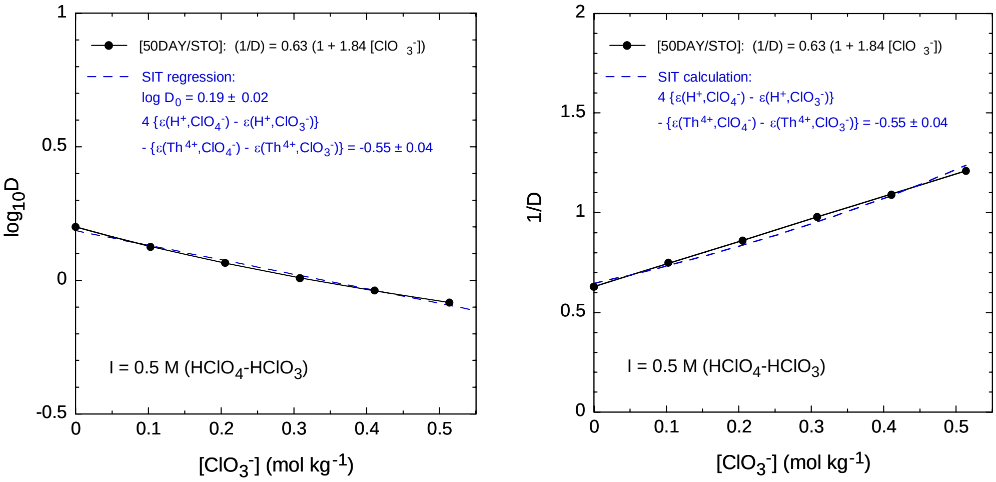


Figure A-3: Distribution coefficients of Th in solvent extraction studies with TTA and aqueous $HClO_4$-$HBrO_3$ media at *I* = 0.5 M; experimental data [1950DAY/STO] and predicted values of $\log_{10}D$ (left side) and $1/D$ (right side) as a function of $m_{\mathrm{BrO}_3^-}$.

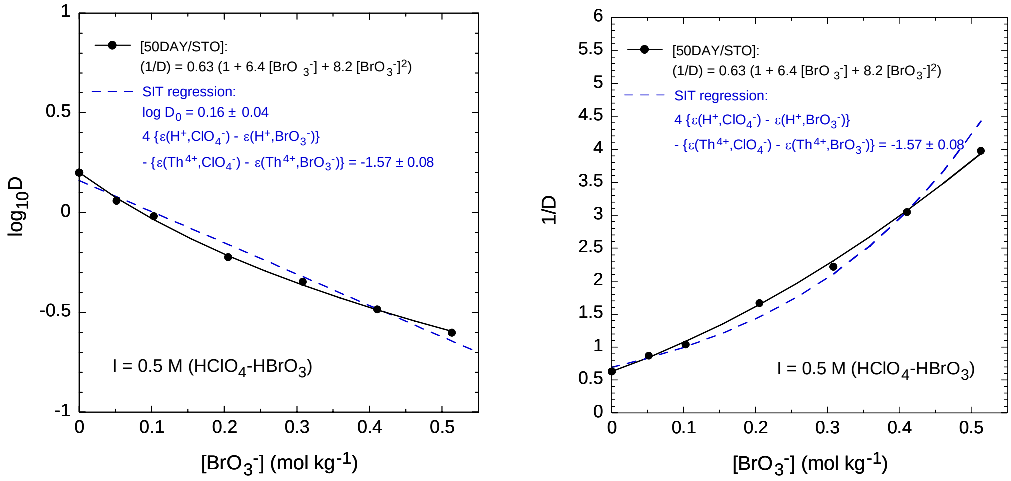
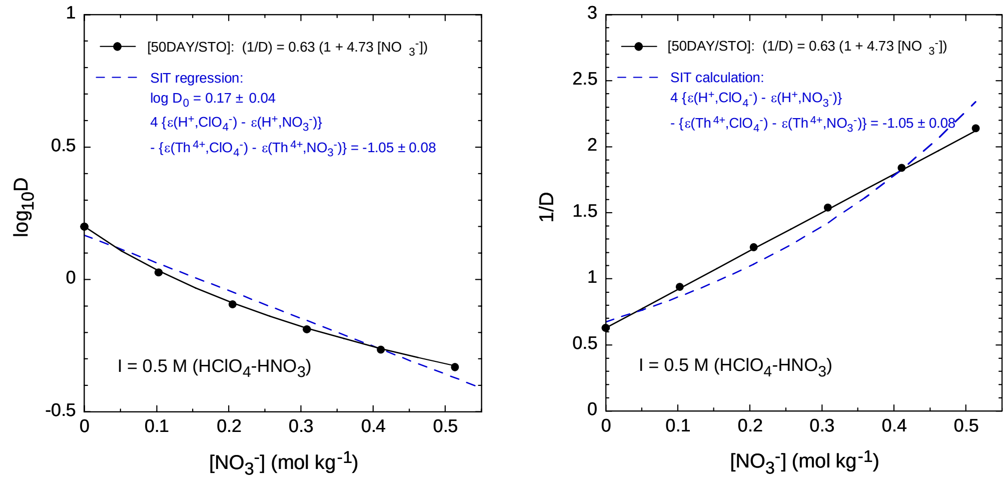


Figure A-4: Distribution coefficients of Th in solvent extraction studies with TTA and aqueous $HClO_4$-HNO_3 media at *I* = 0.5 M; experimental data [1950DAY/STO] and predicted values of $\log_{10}D$ (left side) and $1/D$ (right side) as a function of $m_{\mathrm{NO}_3^-}$.



The same equilibrium system has also been studied using a nonlinear fitting code (NONLINT-SIT, described in Appendix D) with the experimental values of 1/*D* *vs.* [X$^-$], where *D* is the distribution coefficient between the organic and aqueous phases, fitted to determine the unknown interaction coefficients or the chemical potentials of the aqueous complexes. This approach took into account the changes in the chemical potential of the organic phase as a result of the changes in the Th content of the organic phase and used the code that included all of the appropriate SIT ion-interaction parameters to fit the data. This method has been used for both the data in [1950DAY/STO] and the more extensive data for the chloride system in [1952WAG/STO]; the results are given in Table A-9 and in more detail in the Appendix A entry for [1952WAG/STO]. The results in Table A-9 show that both methods provide similar best fitted values for $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$. The estimated $\varepsilon(\mathrm{Th}^{4+},\mathrm{ClO}_3^-)$ values based on linear regression (Figure A-2) and NONLINT-SIT (Figure VIII-10), 0.15 and 0.22 kg·mol^{-1} respectively, are also similar.

Table A-9: The $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ values based on reanalyses of literature data for the chloride system from [1950DAY/STO] and [1952WAG/STO] using linear regression and the NONLINT-SIT model.

Ionic strength (M)	Source of data	Best fit $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ (kg·mol^{-1})^a	
		NONLINT-SIT	Linear regression
0.5	[1950DAY/STO]	0.20 ± 0.12	0.09 ± 0.04
0.5	[1952WAG/STO]	– 0.04 ± 0.16	– 0.09 ± 0.16
0.7	[1952WAG/STO]	0.08 ± 0.10	0.07 ± 0.10
1.0	[1952WAG/STO]	0.13 ± 0.16	0.15 ± 0.05
2.0	[1952WAG/STO]	0.23 ± 0.12	0.27 ± 0.02
4.0	[1952WAG/STO]	0.26 ± 0.22	0.32 ± 0.02
6.0	[1952WAG/STO]	0.25 ± 0.10	0.24 ± 0.02

a: NEA value for this parameter is (0.25 ± 0.03) kg·mol^{-1}.

Both methods show that when data for nitrate and bromate systems are interpreted based on only the changes in activity coefficients rather than the formation of aqueous complexes, the fitted $\varepsilon(\mathrm{Th}^{4+},\mathrm{NO}_3^-)$ and $\varepsilon(\mathrm{Th}^{4+},\mathrm{BrO}_3^-)$ values are too negative, suggesting that the interactions between Th^{4+} and NO_3^- or BrO_3^- must include the formation of complexes. The results from [1950DAY/STO] for the nitrate system are very different from those recently presented in [2006NEC/ALT] and are not appropriate for nitrate concentrations above 0.5 M and are not accepted by this review (see Section X.1.3.3 and [2006NEC/ALT] for further details).

The bromate data in [1950DAY/STO] when interpreted using NONLINT-SIT that included all of the appropriate ion interaction parameters to fit the $\Delta_f G_m^\circ / RT$ value for ThBrO_3^{3+} showed that all the data can be fitted well (Figure VIII-12) with

$\Delta_f G_m^o / RT$ ($ThBrO_3^{3+}$) = −(280.981 ± 0.066) ($\log_{10} \beta_1^o$ = (1.897 ± 0.028)). This is contrary to the interpretations presented in [1950DAY/STO], which also included $Th(BrO_3)_2^{2+}$ species. This review finds no need to consider species other than $ThBrO_3^{3+}$ when appropriate ion-interaction parameters (Table VIII-25) are included in the analysis and thus the $Th(BrO_3)_2^{2+}$ species should not be included in modelling this system with the selected values.

[1950EYR/WES]

This is an excellent study of the enthalpy of solution at 298.15 K of two samples of Th(cr) with 0.3 and 0.5 wt% impurities in 6.004 molar HCl containing 0.005 M Na_2SiF_6; the latter is required to avoid the formation of small amounts of insoluble residues. The average value obtained was −(760.2 ± 0.8) kJ·mol^{-1}. The enthalpy of solution of $ThCl_4$(cr) in the same medium was also measured to be −(186.52 ± 0.33) kJ·mol^{-1}, while a value of −(185.27 ± 0.25) kJ·mol^{-1} was reported for the dissolution in 6.004 M HCl in the absence of Na_2SiF_6.

The analytical data on the $ThCl_4$ were listed as 62.8% Th and 37.8% Cl as given by the manufacturers (theoretical: 62.07% Th and 37.93% Cl).

These results are used, in conjunction with the results of [1949WES/ROB3], [1969SMI/THA], and [1973FUG/BRO], to evaluate $\Delta_f H_m^o$ (Th^{4+}) and $\Delta_f H_m^o$ ($ThCl_4$, β).

[1951MAL/CAM]

Dissociation pressures were measured in the Th-H system for the range of compositions up to *ca.* $ThH_{1.90}$ at temperatures from 924 to 1149 K. The thorium used contained about 0.2% impurities, chiefly oxygen (0.16%) and carbon (0.04%). In common with other investigators, the authors found that the dissociation pressure in the diphasic field {Th(cr) + ThH_{2-x}(cr)} increased with H/Th, possibly due to the effect of impurities or the failure to attain true equilibrium. The mean value of the enthalpy of solution from $ThH_{0.5}$(cr) to $ThH_{1.65}$(cr) in this temperature range was: −(143.5 ± 2.9) kJ·mol^{-1}, where, following [1984FLO/HAS], the uncertainty in this value has been increased from the authors' quoted value of 0.8 kJ·mol^{-1}. This corresponds to a value of −(148.1 ± 5.0) kJ·mol^{-1} at 298.15 K.

[1951ZEB/ALT]

The complex formation between Th(IV) and chloride, fluoride, nitrate, phosphate and sulphate has been studied using liquid-liquid extraction with thenoyltrifluoroacetone (TTA) as the extractant. The experiments have been made at 25°C at hydrogen ion concentrations sufficiently high (0.0875−2.00 M) to prevent hydrolysis of Th^{4+}. The chloride complexes have been studied in a medium of constant ionic strength 4.00 M using mixtures of $NaClO_4$ and NaCl at [H^+] = 0.100 M. The nitrate complexes have been studied in a mixture of $NaNO_3$ and $NaClO_4$ at [H^+] = 0.075 M and I = 5.97 M. The sulphate complexes were studied in a mixture of $NaHSO_4$, $NaClO_4$ and $HClO_4$ at [H^+] = 0.500, 1.00 and 1.99 M and ionic strength 2.00 M. The phosphate complexes were studied at varying concentrations of phosphoric acid in a mixture of $HClO_4$ and $NaClO_4$ ($[H^+]$ = 0.25, 0.50, 1.00 and 2.00 M) at ionic strength 2.00 M. The fluoride complexes were studied under the same conditions as used by Dodgen and Rollefson [1949DOD/ROL]. The experimental methods are described in detail and the distribution coefficient of TTA at different hydrogen ion concentrations has been determined. The authors have also tested the stoichiometry of the extracted Th-TTA complex and confirmed that it is $Th(TTA)_4$. The fluoride study gives equilibrium constants $K(A.19) = 5.0\times10^4$ and $K(A.20) = 2.9\times10^7$ that are in good agreement with those reported in [1949DOD/ROL] for the reactions:

$$Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+ \qquad (A.19)$$

$$Th^{4+} + 2HF(aq) \rightleftharpoons ThF_2^{2+} + 2H^+ \qquad (A.20)$$

These constants have been accepted by this review; however, Zebroski *et al.* do not report uncertainty estimates and this review has therefore assigned an uncertainty of 10% to the constants.

The chloride and nitrate complexes are weak and it is then very difficult, or impossible, to decide if the variation in the measured distribution coefficients are due to complex formation or variation in activity coefficients. Zebroski *et al.* [1951ZEB/ALT] have described the distribution coefficient in the chloride system using four different complexes $ThCl_n^{4-n}$, with equilibrium constants $K_1 = 1.30$; $K_2 = 0.12$; $K_3 = 0.037$; $K_4 = 0.014$; this review considers these constants as fitting parameters and they are therefore not accepted. Zebroski *et al.* [1951ZEB/ALT] report the formation of two nitrate complexes $Th(NO_3)^{3+}$ and $Th(NO_3)_2^{2+}$ up to the highest nitrate concentration 4.93 M; their equilibrium constants are 2.83 and 1.91, respectively. This review does not accept these constants because of the high ionic strength and the large changes in the ionic medium in this study.

The sulphate system was described using the equilibria:

$$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+ \qquad (A.21)$$

$$Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2H^+ \qquad (A.22)$$

The equilibrium constants are $K(A.21) = 159$ and $K(A.22) = 2850$. The experimental distribution coefficients for the experiments at $[H^+] = 1.99$ M fall somewhat above the calculated distribution curve obtained using the data at $[H^+] = 0.50$ and 1.00 M. Zebroski *et al.* suggested that this was due to the formation of the complex $Th(SO_4)(HSO_4)^+$ with the equilibrium constant $K(A.23) = 800\ M^{-1}$ for the reaction:

$$Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(SO_4)(HSO_4)^+ + H^+ \qquad (A.23)$$

This constant has not been accepted by this review, as the complex was not confirmed in [1959ZIE]; in addition the substantial change in the ionic media at the different H^+ values might also result in ionic medium dependent distribution coefficients. The equilibrium constants $K(\text{A.21}) = 159$ and $K_2(\text{A.22}) = 2850$ are accepted by this review; the equilibrium constants for the reactions:

$$\text{Th}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{ThSO}_4^{2+} \tag{A.24}$$

$$\text{Th}^{4+} + 2\,\text{SO}_4^{2-} \rightleftharpoons \text{Th(SO}_4)_2\text{(aq)} \tag{A.25}$$

calculated using the experimentally determined dissociation constant for HSO_4^-, $K = 0.084$ M, are $\beta(\text{A.24}) = (1.89 \pm 0.20)\times 10^3\ \text{M}^{-1}$, and $\beta(\text{A.25}) = (4.04 \pm 0.4)\times 10^5\ \text{M}^{-2}$. These constants are accepted by this review that has also estimated the uncertainty.

The phosphate system has been described using the equilibria:

$$\text{Th}^{4+} + \text{H}_3\text{PO}_4 \rightleftharpoons \text{Th(H}_3\text{PO}_4)^{4+} \qquad K = 78\ \text{M}^{-1} \tag{A.26}$$

$$\text{Th}^{4+} + \text{H}_3\text{PO}_4 \rightleftharpoons \text{Th(H}_2\text{PO}_4)^{3+} + \text{H}^+ \qquad K = 150 \tag{A.27}$$

$$\text{Th}^{4+} + 2\text{H}_3\text{PO}_4 \rightleftharpoons \text{Th(H}_2\text{PO}_4)(\text{H}_3\text{PO}_4)^{3+} + \text{H}^+ \qquad K = 1.4\times 10^4\ \text{M}^{-1} \tag{A.28}$$

$$\text{Th}^{4+} + 2\text{H}_3\text{PO}_4 \rightleftharpoons \text{Th(H}_2\text{PO}_4)_2^{2+} + 2\text{H}^+ \qquad K = 8.0\times 10^3 \tag{A.29}$$

This set of equilibrium constants describes the experimental data very well, but as pointed out by Zebroski *et al.* this is not sufficient proof to exclude the formation of species like $\text{Th(HPO}_4)^{2+}$ and $\text{Th(H}_3\text{PO}_4)_2^{4+}$. The previous NEA reviews on uranium, [1992GRE/FUG], neptunium and plutonium, [2001LEM/FUG] and [2003GUI/FAN] have not selected any equilibrium constants for M(IV) phosphate complexes; Zebroski *et al.* [1951ZEB/ALT] give all necessary experimental details and also a detailed analysis of the experimental data and this study is therefore accepted by this review.

[1952EYE/SEL]

This paper reports an extensive study of the Th-Se system. From thermal, metallographic, X-ray, and chemical analyses, four phases were identified in this binary system: ThSe(cr), which exists over a narrow solid-solution range; Th_2Se_3(cr), which has again a narrow solid-solution range; $\text{Th}_7\text{Se}_{12}$(cr); ThSe_2(cr), which loses Se when heated above 1273 K, being degraded to $\text{ThSe}_{1.7}$(cr). On the basis of X-ray powder diffraction data, the structure of the compounds could be identified and lattice parameters were given. Similarities and differences with the other thorium and actinide chalcogenides were discussed.

A tentative phase diagram was given for compositions from Th to $\text{ThSe}_{1.7}$. Above ThSe_2(cr), a further compound Th_3Se_7(cr) was reported but its structure could not be identified.

The ternary compound ThOSe(cr) was found as a contaminant in the system, most probably arising from the 0.5% oxygen contamination in the thorium metal used. ThOSe(cr) was also prepared by heating an equimolar mixture of ThO_2(cr) and

$ThSe_2$(cr) *in vacuo* at 1223 K. ThOSe(cr) was found to be isomorphous with thorium and uranium oxysulphides.

[1952HUB/HOL]

Precise measurements of the heats of combustion of thorium and uranium metals, and of uranium dioxide have been made and the enthalpies of formation of ThO_2(cr), UO_2(cr) and U_3O_8(cr) have been calculated.

A bomb calorimeter operating under 25 atm O_2 pressure was used for these determinations. The energy equivalent of the instrument had been determined using the combustion of benzoic acid. The details of the method and apparatus had been previously described. The thorium metal was in the form of 0.025 cm sheet and strands of 0.012 cm wire were used as fuse wire. Analysis of a portion the sheet showed that it contained 0.12% oxygen, 0.01% carbon, less than 0.01% iron and beryllium and no other metallic impurities in significant amounts.

The metal was burnt on sintered ThO_2 discs supported on a platinum platform. A total of 16 runs were made using samples ranging between 1.90 and 2.97 g in mass. Completeness of the combustion, which ranged between 99.74 and 99.99%, was determined by treating the combustion products with HCl and measuring the amount of hydrogen evolved. As it is well known that thorium metal leaves a residue upon dissolution in HCl, an empirical correction factor was determined from the gas evolved in the reaction of acid with weighed thorium metal samples. In the correction of the combustion results for the impurities contained in the metal, it was assumed that oxygen was present as ThO_2 and that the other impurities were present in the elemental form, neglecting the enthalpy of formation of carbides and alloys. After correction from the experimental temperature of 297.35 to 298.15 K, accounting for the deviation of oxygen from an ideal gas behaviour and converting from ΔE to $\Delta_f H_m$, the standard enthalpy of formation of formation of ThO_2 at 298.15 K was reported as $-(1226.9 \pm 1.5)$ kJ·mol^{-1}. Use of contemporary atomic masses leads to a value of $-(1226.4 \pm 1.5)$ kJ·mol^{-1}.

This value was adopted by CODATA [1989COX/WAG] with uncertainty limits increased to ± 3.5 kJ·mol^{-1}.

[1952MOE/QUI]

The authors describe the synthesis of $Th_2P_2O_6$ and have measured the solubility in HCl; the solubility in 1 M hydrochloric acid is 2.5×10^{-5} M demonstrating that the phase is sparingly soluble. There are no other thermodynamic data in this study.

[1952NOT/WIL]

Dissociation pressures were measured in the thorium-hydrogen system, as a function of composition, from *ca.* 573 to *ca.* 1073 K, and the structures of the two compounds formed, ThH_2(cr) and $ThH_{3.75\pm x}$(cr) were studied by X-ray diffraction. Since this work was carried out some years before the publication date, the thorium metal used was not of the highest quality. Dissolution measurements showed that it certainly contained some combined thorium, probably ThO_2(cr), since the metal was cast in a BeO crucible. The metal used also contained *ca.* 0.03 wt% Zn, since it had been purified by alloying with zinc, followed by decomposition at 1873 K.

The structure of ThH_2 was indexed as a pseudotetragonal body-centred cell, ZrH_2 type with a = (4.09 ± 0.03) Å, c = (5.02 ± 0.03) Å. Most modern references describe this structure with a face-centred cell, for which the equivalent a parameter would be a = (5.78 ± 0.04) Å. The higher hydride was cubic, as indicated by [1953ZAC]. The lattice parameter increases with H/Th ratio, from (9.10 ± 0.02) Å for $ThH_{2.49}$ to (9.15 ± 0.02) Å for compositions approaching $ThH_{3.75}$.

In the dissociation pressure measurements, equilibrium was approached from both sides. Pressures were measured either manometrically or with a McLeod gauge. Steady pressures were attained in 5 to 10 minutes in the Th-ThH_2 system, but only after 1 to 5 hours when the higher hydride was involved (longer at 573 K), and even so the pressures from the decomposition side were very much larger than those from the absorption side. For both systems, the pressures in the “diphasic” region increased with H/Th ratio, indicating that impurities are playing a role in the “equilibria”. The following equations (converted from those reported in torr) for the decomposition pressures, (calculated from the relatively flat region of the individual) isotherms as a function of temperature: Th-ThH_2, $\log_{10} p/\text{bar} = -7700/T + 6.665$, ThH_2-$ThH_{3.75}$: $\log_{10} p/\text{bar} = -4220/T + 6.625$. These data form the basis of the selected values for the enthalpies of formation of $ThH_{3.75}$(cr).

[1952SHA]

This was the first serious study of the vapour pressure of thoria. Weighed tungsten filaments coated with thoria were in heated *in vacuo* for a known period and the resultant mass loss determined directly. The brightness temperature of the filament was measured pyrometrically, and corrected to true temperature from a calibration curve obtained from another thoria-coated filament to which a Mo-W thermocouple was welded. Similar measurements were made using a molybdenum filament, with results indistinguishable from those from tungsten filaments.

Thirteen measurements were made from *ca.* 2060 to 2250 K, and the derived vapour pressures, assumed to be due to ThO_2(g) only, were given by the equation equivalent to $\log_{10} p/\text{bar} = -37100/T + 8.655$. Although it is now known that there is also an appreciable proportion of ThO(g) and O(g) in the vapour, as well as the predominant ThO_2(g), the major source of error was in the temperature measurements. The author found it difficult to get pyrometer readings reproducible to better than ± 20 K, especially at the higher temperatures; the corrections from brightness to true temperatures must also be somewhat uncertain. Nevertheless, these results agree well with the corpus of later, better defined, experiments.

[1952WAG/STO]

This is a careful experimental study wherein all details necessary for analysis of the experimental data are reported. Waggener and Stoughton have determined the complex formation in the Th^{4+}-Cl^- system using liquid-liquid extraction with TTA (thenoyltrifluoroacetone) as the extracting ligand and benzene as the organic solvent. The concentration of thorium is at the trace level and the experiments were made at 25°C at six different ionic strengths; the composition of the test solutions is shown in Table A-10. The total anion concentration of $[Cl^-] + [ClO_4^-]$ is equal to the ionic strength.

Table A-10: Compositions of test solutions.

Ionic strength (M)	$[H^+]$ (M)	$[Cl^-]$ concentration range (M)	$[Na^+]$ concentration range (M)
0.50	0.20	0.00 – 0.50	0.30 – 0.00
0.70	0.20	0.00 – 0.50	0.50 – 0.00
1.00	0.20	0.00 – 1.00	0.80 – 0.00
2.00	0.20	0.00 – 2.00	1.80
4.00	0.32	0.00 – 4.00	3.68
6.00	0.32	0.00 – 2.00	5.68

The experimental data were analysed by Waggener and Stoughton using a chloride complex model and their reported equilibrium constants are given in Table A-11.

Table A-11: Values of equilibrium constants reported by [1952WAG/STO].

Ionic strength (M)	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})
0.50	2.24	–	–	–
0.70	1.78	–	–	–
1.00	1.53	–	–	–
2.00	1.21	0.10	0.20	–
4.00	1.70	0.14	0.10	0.018
6.00	2.10	0.55	0.35	–

The authors do not report any uncertainty in the equilibrium constants; this review estimates the uncertainty in β_1 to at least 10% based on the uncertainty in the measured distribution coefficients. Waggener and Stoughton note the close agreement between their data and those in [1951ZEB/ALT] at the ionic strength 4.00 M; this is a good indicator for the experimental accuracy in both of these studies. In previous reviews it has been repeatedly pointed out that it is not possible to distinguish between complex formation and activity factor variations when analysing solution chemical data obtained with "standard" solution chemical methods (liquid-liquid distribution, ion-exchange, potentiometry *etc*.). This review has therefore reinterpreted the data of Waggener and Stoughton assuming that the experimental variations are due to activity factor variations when perchlorate is replaced by chloride. Two slightly different approaches that used the SIT ion-interaction theory were utilised and are discussed in detail under the Appendix entry for [1950DAY/STO]. The activity factor variations have been estimated using the SIT model with interaction coefficients given in Table A-12. The final results based on best fits to these data with both of these methods are summarised under [1950DAY/STO] and show that both approaches provide similar results. Therefore, the detailed analyses done with only one of these approaches (NONLINT-SIT) are presented in the tables and figures that follow. The tables list the experimental data extracted from [1952WAG/STO], including concentrations of thorium in the organic (Th_{org}) and the aqueous (Th_{aq}) and other constituents important in calculations, and predicted concentrations when a best fitted value of $\varepsilon(Th^{4+}, Cl^-)$ from the data is used in calculations. The figures show the comparison of experimental and predicted concentrations of Th(aq) or $1/D$, where D is the distribution coefficient of Th(IV) between the aqueous and organic phases, as a function of the molality of chloride concentrations when $\varepsilon(Th^{4+}, Cl^-) = 0.25$ kg·mol^{-1} or that best fitted to the data are used.

Table A-12: SIT ion-interaction parameters and dimensionless molar Gibbs free energies of formation of species used in interpreting [1952WAG/STO] data for the estimation of activity factors in the Th^{4+}-Cl^- system.

Species	ε (kg·mol^{-1})	References
H^+-Cl^-	0.12 ± 0.01	Appendix B
H^+- ClO_4^-	0.14 ± 0.02	Appendix B
Th^{4+}-Cl^-	0.25 ± 0.03	Appendix B [a]
Th^{4+}- ClO_4^-	0.70 ± 0.10	This review, Section VI.3.1
Na^+-Cl^-	0.03 ± 0.01	Appendix B
Na^+- ClO_4^-	0.01 ± 0.01	Appendix B
Na^+-OH^-	0.04 ± 0.01	Appendix B
	$\Delta_f G^o_m / RT$	
Th^{4+}	– 284.305	This review [b]

a: Predictions for [1952WAG/STO] data were made with $\varepsilon(Th^{4+}, Cl^-) = 0.25$ kg·mol^{-1} or a value fitted with NONLINT-SIT for different ionic strengths. The best fitted $\varepsilon(Th^{4+}, Cl^-)$ values for I_c equal to 0.5, 0.7, 1.0, 2.0, 4.0, and 6.0 M are –(0.04 ± 0.16), (0.08 ± 0.10), (0.13 ± 0.16), (0.23 ± 0.12), (0.26 ± 0.22), (0.25 ± 0.10) kg·mol^{-1}, respectively.

b: $\Delta_f G^o_m / RT$ values for other species ($H_2O, Na^+, Cl^-, ClO_4^-$ and OH^-) included in modelling were calculated from the values in Table IV-1.

- *SIT modelling calculation for thorium chloride system:*

Table A-13: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 0.5 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-) = -(0.04 \pm 0.16)\ \mathrm{kg{\cdot}mol^{-1}}$ and the other thermodynamic data listed in Table A-12. Selected data from this table are plotted in Figure A-5.

		Experimental [1952WAG/STO], I_c = 0.5 M						Predicted				
		Concentrations (m)						Concentrations (m)				
m/c^a	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	1/*D*	1/*D*	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.027	0.205	7.551	2.719	0.3081	0.00	0.5135	0.36	0.44	0.205	3.131	0.00352	0.787
1.027	0.205	7.496	2.774	0.3081	0.00	0.5135	0.37	0.43	0.205	3.108	0.00352	0.787
1.027	0.205	7.442	2.828	0.3081	0.00	0.5135	0.38	0.43	0.205	3.085	0.00352	0.787
1.027	0.205	7.415	2.855	0.3081	0.00	0.5135	0.39	0.43	0.205	3.074	0.00352	0.787
1.025	0.205	7.348	2.902	0.3075	0.05125	0.4613	0.40	0.47	0.205	3.260	0.00323	0.785
1.025	0.205	7.295	2.955	0.3075	0.05125	0.4613	0.41	0.46	0.205	3.236	0.00323	0.785
1.024	0.205	7.186	3.054	0.3072	0.1024	0.4096	0.43	0.50	0.205	3.427	0.00297	0.783
1.024	0.205	7.121	3.119	0.3072	0.1024	0.4096	0.44	0.50	0.205	3.396	0.00297	0.783
1.023	0.205	6.766	3.464	0.3069	0.1535	0.3581	0.51	0.51	0.205	3.469	0.00272	0.781
1.023	0.205	6.717	3.513	0.3069	0.1535	0.3581	0.52	0.51	0.205	3.444	0.00272	0.781
1.023	0.205	6.643	3.587	0.3069	0.1535	0.3581	0.54	0.50	0.205	3.406	0.00272	0.781
1.021	0.204	6.748	3.462	0.3063	0.2042	0.3063	0.51	0.57	0.204	3.698	0.00250	0.780
1.021	0.204	6.717	3.493	0.3063	0.2042	0.3063	0.52	0.56	0.204	3.681	0.00250	0.780
1.021	0.204	6.673	3.537	0.3063	0.2042	0.3063	0.53	0.56	0.204	3.657	0.00250	0.780
1.020	0.204	6.538	3.662	0.3060	0.2550	0.2550	0.56	0.61	0.204	3.850	0.00229	0.778
1.020	0.204	6.497	3.703	0.3060	0.2550	0.2550	0.57	0.60	0.204	3.826	0.00229	0.778
1.020	0.204	6.456	3.744	0.3060	0.2550	0.2550	0.58	0.59	0.204	3.802	0.00230	0.778
1.020	0.204	6.435	3.765	0.3060	0.2550	0.2550	0.59	0.59	0.204	3.789	0.00229	0.778
1.018	0.204	6.423	3.757	0.3054	0.3054	0.2036	0.59	0.66	0.204	4.041	0.00211	0.776
1.018	0.204	6.359	3.821	0.3054	0.3054	0.2036	0.60	0.65	0.204	4.001	0.00211	0.776
1.018	0.204	6.280	3.900	0.3054	0.3054	0.2036	0.62	0.63	0.204	3.952	0.00211	0.776
1.018	0.204	6.222	3.958	0.3054	0.3054	0.2036	0.64	0.62	0.204	3.915	0.00211	0.776
1.016	0.203	6.256	3.904	0.3048	0.3556	0.1524	0.62	0.71	0.203	4.205	0.00194	0.774
1.016	0.203	6.214	3.946	0.3048	0.3556	0.1524	0.64	0.70	0.203	4.177	0.00194	0.774
1.016	0.203	6.102	4.058	0.3048	0.3556	0.1524	0.67	0.68	0.203	4.101	0.00194	0.774
1.016	0.203	6.066	4.094	0.3048	0.3556	0.1524	0.68	0.67	0.203	4.077	0.00194	0.774
1.015	0.203	5.556	4.594	0.3045	0.4060	0.1015	0.83	0.65	0.203	4.010	0.00178	0.772
1.015	0.203	5.442	4.708	0.3045	0.4060	0.1015	0.87	0.63	0.203	3.928	0.00178	0.772
1.015	0.203	5.385	4.765	0.3045	0.4060	0.1015	0.89	0.62	0.203	3.887	0.00178	0.772
1.013	0.203	6.037	4.093	0.3039	0.4559	0.05065	0.68	0.85	0.203	4.652	0.00164	0.770
1.013	0.203	5.789	4.341	0.3039	0.4559	0.05065	0.75	0.79	0.203	4.461	0.00164	0.770
1.013	0.203	5.675	4.455	0.3039	0.4559	0.05065	0.79	0.76	0.203	4.373	0.00164	0.770
1.013	0.203	5.643	4.487	0.3039	0.4559	0.05065	0.80	0.75	0.203	4.349	0.00164	0.770
1.012	0.202	5.619	4.501	0.3036	0.5060	0.00	0.80	0.85	0.202	4.647	0.00151	0.768
1.012	0.202	5.456	4.664	0.3036	0.5060	0.00	0.86	0.80	0.202	4.512	0.00151	0.768

a: Based on estimated conversion factors for mixtures of electrolytes.

Figure A-5: Observed [1952WAG/STO] and NONLINT-SIT predictions for I_c = 0.5 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ as shown in the figure and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/D as a function of chloride concentrations

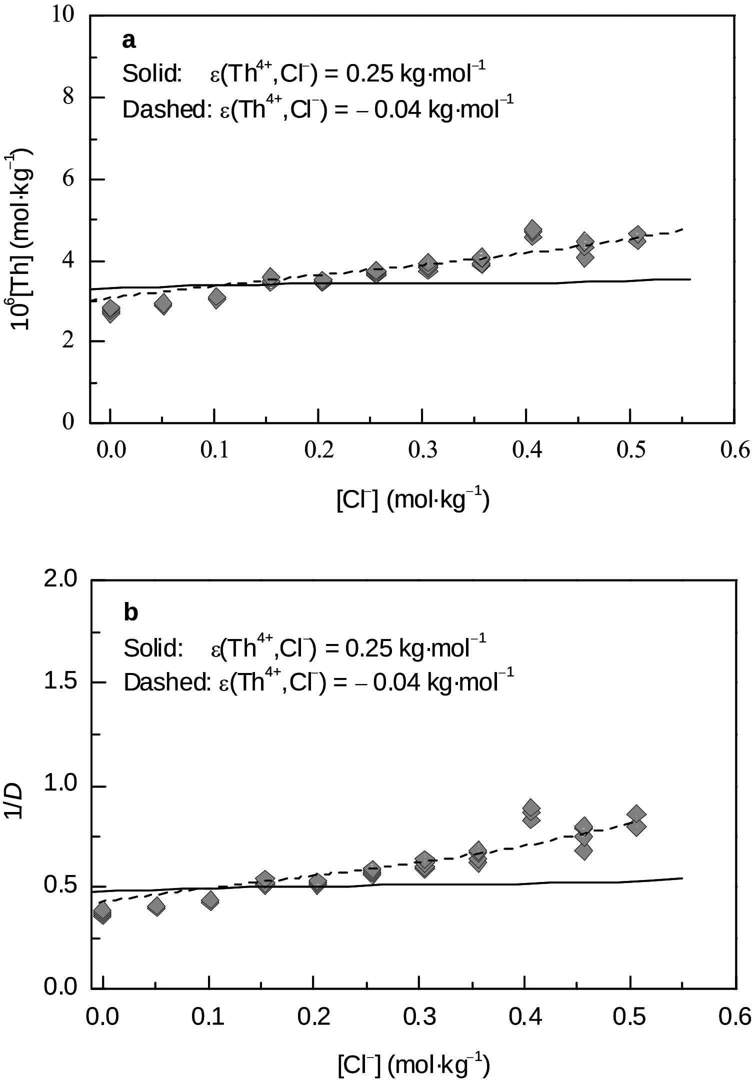


Table A-14: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 0.7 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ = (0.08 ± 0.10) kg·mol^{-1} and other thermodynamic data listed in Table A-12. Selected data plotted in Figure A-6.

Experimental [1952WAG/STO], I_c = 0.7 M								Predicted				
	Concentrations (m)								Concentrations (m)			
m/c[a]	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.037	0.207	6.960	3.410	0.5185	0.00	0.7259	0.49	0.60	0.207	3.881	0.00289	0.815
1.037	0.207	6.849	3.521	0.5185	0.00	0.7259	0.51	0.58	0.207	3.819	0.00289	0.815
1.037	0.207	6.756	3.614	0.5185	0.00	0.7259	0.54	0.57	0.207	3.767	0.00290	0.815
1.035	0.207	6.756	3.594	0.5175	0.05175	0.6728	0.53	0.63	0.207	3.981	0.00269	0.813
1.035	0.207	6.656	3.694	0.5175	0.05175	0.6728	0.56	0.61	0.207	3.922	0.00269	0.813
1.035	0.207	6.613	3.737	0.5175	0.05175	0.6728	0.57	0.60	0.207	3.897	0.00269	0.813
1.034	0.207	6.463	3.878	0.517	0.1034	0.6204	0.60	0.64	0.207	4.043	0.00250	0.811
1.034	0.207	6.422	3.918	0.517	0.1034	0.6204	0.61	0.64	0.207	4.018	0.00250	0.811
1.034	0.207	6.363	3.977	0.517	0.1034	0.6204	0.63	0.63	0.207	3.981	0.00250	0.811
1.033	0.207	6.396	3.934	0.5165	0.1550	0.5682	0.62	0.70	0.207	4.248	0.00232	0.809
1.033	0.207	6.112	4.218	0.5165	0.1550	0.5682	0.69	0.65	0.207	4.060	0.00232	0.809
1.033	0.207	6.059	4.271	0.5165	0.1550	0.5682	0.71	0.64	0.207	4.025	0.00232	0.809
1.031	0.206	6.248	4.062	0.5155	0.2062	0.5155	0.65	0.74	0.206	4.383	0.00216	0.807
1.031	0.206	6.211	4.099	0.5155	0.2062	0.5155	0.66	0.73	0.206	4.357	0.00216	0.807
1.031	0.206	6.174	4.136	0.5155	0.2062	0.5155	0.67	0.72	0.206	4.331	0.00215	0.807
1.030	0.206	5.985	4.315	0.515	0.2575	0.4635	0.72	0.76	0.206	4.455	0.00201	0.805
1.030	0.206	5.971	4.329	0.515	0.2575	0.4635	0.73	0.76	0.206	4.445	0.00201	0.805
1.028	0.206	5.824	4.456	0.514	0.3084	0.4112	0.77	0.80	0.206	4.577	0.00186	0.803
1.028	0.206	5.737	4.543	0.514	0.3084	0.4112	0.79	0.78	0.206	4.508	0.00187	0.803
1.028	0.206	5.695	4.585	0.514	0.3084	0.4112	0.81	0.77	0.206	4.475	0.00186	0.803
1.026	0.205	5.691	4.569	0.513	0.3591	0.3591	0.80	0.85	0.205	4.720	0.00173	0.801
1.026	0.205	5.555	4.705	0.513	0.3591	0.3591	0.85	0.81	0.205	4.607	0.00174	0.801
1.025	0.205	5.352	4.898	0.5125	0.4100	0.3075	0.92	0.85	0.205	4.708	0.00161	0.799
1.025	0.205	5.327	4.923	0.5125	0.4100	0.3075	0.92	0.84	0.205	4.686	0.00162	0.799
1.025	0.205	5.284	4.966	0.5125	0.4100	0.3075	0.94	0.83	0.205	4.648	0.00161	0.799
1.023	0.205	5.376	4.854	0.5115	0.4604	0.2558	0.90	0.95	0.205	4.989	0.00150	0.797
1.023	0.205	5.336	4.894	0.5115	0.4604	0.2558	0.92	0.94	0.205	4.952	0.00150	0.797
1.023	0.205	5.323	4.907	0.5115	0.4604	0.2558	0.92	0.93	0.205	4.940	0.00150	0.797
1.023	0.205	5.287	4.943	0.5115	0.4604	0.2558	0.94	0.92	0.205	4.906	0.00150	0.797
1.022	0.204	5.180	5.040	0.511	0.5110	0.2044	0.97	0.99	0.204	5.097	0.00140	0.795
1.022	0.204	5.097	5.123	0.511	0.5110	0.2044	1.01	0.96	0.204	5.015	0.00140	0.795
1.022	0.204	5.059	5.161	0.511	0.5110	0.2044	1.02	0.95	0.204	4.978	0.00140	0.795

a: Based on estimated conversion factors for mixtures of electrolytes.

Figure A-6: Observed [1952WAG/STO] and NONLINT-SIT predictions for I_c = 0.7 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ as shown in the figure and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/*D* as a function of chloride concentrations

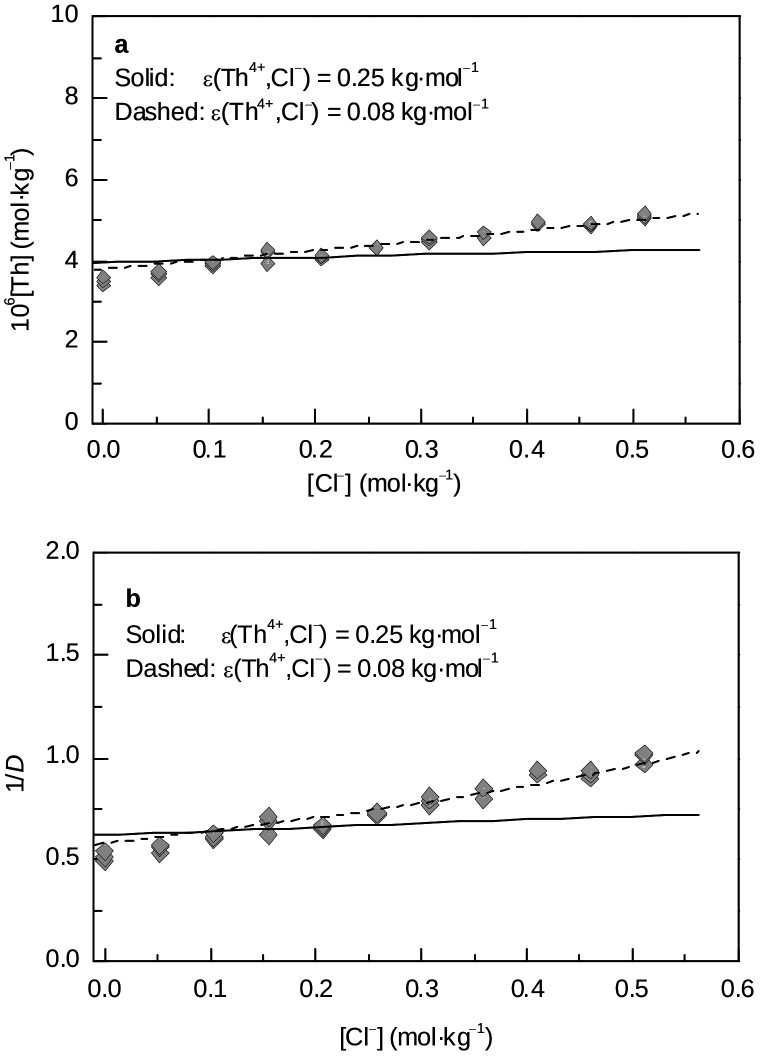


Table A-15: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 1.0 M based on $\varepsilon(\text{Th}^{4+},\text{Cl}^-)$ = (0.13 ± 0.16) kg·mol^{-1} and other thermodynamic data listed in Table A-12. Selected data plotted in Figure A-7.

Experimental [1952WAG/STO], I_c = 1.0 M								Predicted				
Concentrations (m)									Concentrations (m)			
m/c^a	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.051	0.210	6.610	3.900	0.8408	0.00	1.051	0.59	0.68	0.210	4.253	0.00279	0.874
1.048	0.210	6.201	4.279	0.8384	0.1048	0.9432	0.69	0.73	0.210	4.435	0.00243	0.869
1.045	0.209	5.838	4.612	0.836	0.209	0.836	0.79	0.80	0.209	4.638	0.00211	0.864
1.042	0.208	5.725	4.695	0.8336	0.3126	0.7294	0.82	0.94	0.208	5.048	0.00184	0.860
1.039	0.208	5.328	5.062	0.8312	0.4156	0.6234	0.95	1.01	0.208	5.211	0.00160	0.855
1.036	0.207	5.424	4.936	0.8288	0.5180	0.518	0.91	1.31	0.207	5.880	0.00140	0.850
1.034	0.207	4.809	5.531	0.8272	0.6204	0.4136	1.15	1.28	0.207	5.805	0.00122	0.846
1.031	0.206	4.840	5.470	0.8248	0.7217	0.3093	1.13	1.68	0.206	6.466	0.00107	0.841
1.028	0.206	4.356	5.924	0.8224	0.8224	0.2056	1.36	1.67	0.206	6.437	0.00093	0.837
1.025	0.205	3.912	6.338	0.82	0.9225	0.1025	1.62	1.66	0.205	6.390	0.00082	0.833
1.022	0.204	3.488	6.732	0.8176	1.022	0.00	1.93	1.60	0.204	6.293	0.00072	0.828
1.051	0.210	6.565	3.945	0.8408	0.00	1.051	0.60	0.67	0.210	4.224	0.00279	0.874
1.048	0.210	6.023	4.457	0.8384	0.1048	0.9432	0.74	0.70	0.210	4.308	0.00243	0.869
1.045	0.209	5.649	4.801	0.836	0.2090	0.836	0.85	0.75	0.209	4.488	0.00211	0.864
1.042	0.208	5.663	4.757	0.8336	0.3126	0.7294	0.84	0.92	0.208	4.994	0.00184	0.860
1.039	0.208	5.169	5.221	0.8312	0.4156	0.6234	1.01	0.95	0.208	5.056	0.00160	0.855
1.036	0.207	4.933	5.427	0.8288	0.5180	0.518	1.10	1.07	0.207	5.348	0.00140	0.850
1.034	0.207	4.575	5.765	0.8272	0.6204	0.4136	1.26	1.15	0.207	5.522	0.00122	0.846
1.031	0.206	4.314	5.996	0.8248	0.7217	0.3093	1.39	1.27	0.206	5.764	0.00107	0.841
1.028	0.206	4.196	6.084	0.8224	0.8224	0.2056	1.45	1.52	0.206	6.201	0.00093	0.837
1.025	0.205	3.648	6.602	0.82	0.9225	0.1025	1.81	1.39	0.205	5.959	0.00082	0.833
1.022	0.204	3.351	6.869	0.8176	1.022	0.00	2.05	1.45	0.204	6.046	0.00072	0.828

a: Based on estimated conversion factors for mixtures of electrolytes.

Figure A-7: Observed [1952WAG/STO] and NONLINT-SIT predictions for I_c = 1.0 M based on $\varepsilon(\mathrm{Th^{4+}, Cl^-})$ as shown in the figure and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/*D* as a function of chloride concentrations

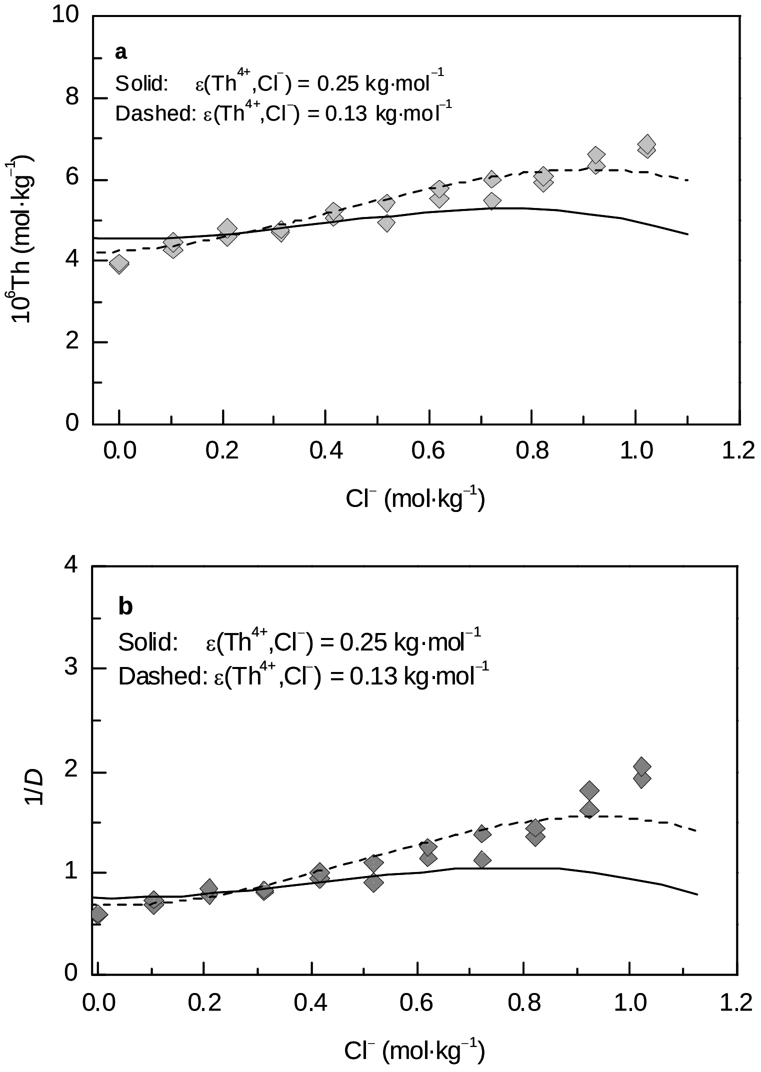


Table A-16: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 2.0 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ = (0.23 ± 0.12) $\mathrm{kg \cdot mol^{-1}}$ and other thermodynamic data listed in Table A-12. Selected data plotted in Figure A-8.

Experimental [1952WAG/STO], I_c = 2.0M								Predicted				
	Concentrations (m)								Concentrations (m)			
m/c^a	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.106	0.221	5.614	5.446	1.991	0.00	2.212	0.97	1.19	0.221	6.001	0.00629	1.189
1.106	0.221	5.475	5.585	1.991	0.00	2.212	1.02	1.12	0.221	5.852	0.00629	1.189
1.100	0.220	4.933	6.067	1.980	0.2200	1.98	1.23	1.33	0.220	6.277	0.00490	1.173
1.100	0.220	4.846	6.154	1.980	0.2200	1.98	1.27	1.28	0.220	6.166	0.00490	1.173
1.093	0.219	4.425	6.505	1.967	0.4372	1.749	1.47	1.56	0.219	6.657	0.00382	1.157
1.087	0.217	4.041	6.829	1.957	0.6522	1.522	1.69	1.96	0.217	7.203	0.00299	1.142
1.087	0.217	3.924	6.946	1.957	0.6522	1.522	1.77	1.81	0.217	6.995	0.00299	1.142
1.081	0.216	3.568	7.242	1.946	0.8648	1.297	2.03	2.28	0.216	7.517	0.00234	1.127
1.081	0.216	3.454	7.356	1.946	0.8648	1.297	2.13	2.06	0.216	7.277	0.00234	1.127
1.074	0.215	3.159	7.581	1.933	1.074	1.074	2.40	2.66	0.215	7.809	0.00185	1.112
1.068	0.214	2.774	7.906	1.922	1.282	0.8544	2.85	3.09	0.214	8.068	0.00146	1.097
1.062	0.212	2.279	8.341	1.912	1.487	0.6372	3.66	2.74	0.212	7.779	0.00115	1.083
1.056	0.211	2.233	8.327	1.901	1.690	0.4224	3.73	5.45	0.211	8.923	0.00092	1.070
1.056	0.211	2.209	8.351	1.901	1.690	0.4224	3.78	5.09	0.211	8.827	0.00091	1.070
1.049	0.210	1.847	8.643	1.888	1.888	0.2098	4.68	4.46	0.210	8.567	0.00073	1.056
1.049	0.210	1.621	8.869	1.888	1.888	0.2098	5.47	2.53	0.210	7.520	0.00073	1.056
1.043	0.209	1.696	8.734	1.877	2.086	0.00	5.15	7.25	0.209	9.166	0.00058	1.043
1.043	0.209	1.617	8.813	1.877	2.086	0.00	5.45	5.17	0.209	8.740	0.00058	1.043

a: Based on estimated conversion factors for mixtures of electrolytes.

Figure A-8: Observed [1952WAG/STO] and NONLINT-SIT predictions for $I_c = 2.0$ M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^{-})$ as shown in the figure and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/*D* as a function of chloride concentrations

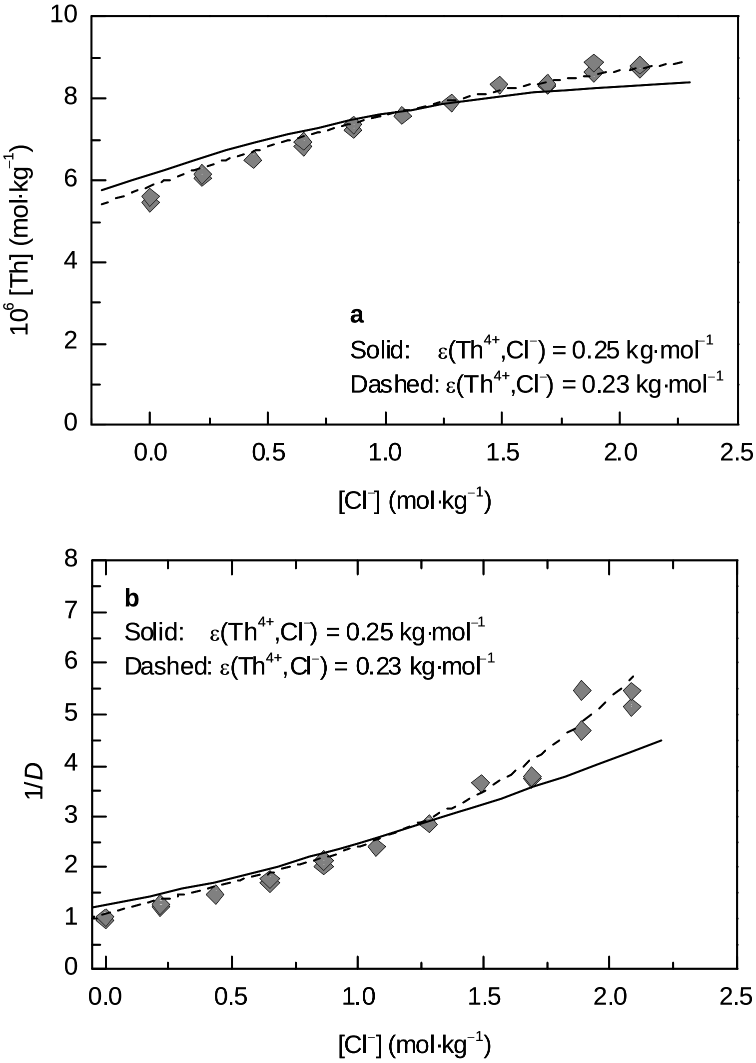


Table A-17: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 4.0 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ = (0.26 ± 0.22) $\mathrm{kg \cdot mol^{-1}}$ and other thermodynamic data listed in Table A-12. Selected data plotted in Figure VIII-8.

Experimental [1952WAG/STO], I_c = 4.0 M								Predicted				
	Concentrations (m)								Concentrations (m)			
m/c[a]	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	$1/D$	$1/D$	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.236	0.396	9.810	2.550	4.548	0.00	4.944	0.26	0.26	0.396	2.570	0.19190	2.698
1.236	0.396	9.581	2.779	4.548	0.00	4.944	0.29	0.25	0.396	2.510	0.19201	2.698
1.218	0.390	8.066	4.114	4.482	0.609	4.263	0.51	0.38	0.390	3.347	0.09361	2.566
1.218	0.390	7.758	4.422	4.482	0.609	4.263	0.57	0.36	0.390	3.219	0.09360	2.566
1.200	0.384	6.818	5.182	4.416	1.200	3.600	0.76	0.58	0.384	4.404	0.04647	2.442
1.200	0.384	6.704	5.296	4.416	1.200	3.600	0.79	0.56	0.384	4.331	0.04639	2.442
1.182	0.378	5.656	6.164	4.35	1.773	2.955	1.09	0.90	0.378	5.597	0.02350	2.326
1.182	0.378	5.629	6.191	4.35	1.773	2.955	1.10	0.89	0.378	5.570	0.02350	2.327
1.164	0.373	4.392	7.248	4.284	2.328	2.328	1.65	1.29	0.373	6.558	0.01211	2.218
1.164	0.373	4.279	7.361	4.284	2.328	2.328	1.72	1.22	0.373	6.389	0.01209	2.218
1.157	0.370	3.883	7.687	4.258	2.545	2.083	1.98	1.43	0.370	6.802	0.00934	2.177
1.157	0.370	3.831	7.739	4.258	2.545	2.083	2.02	1.38	0.370	6.711	0.00934	2.177
1.150	0.368	3.722	7.778	4.232	2.760	1.840	2.09	1.98	0.368	7.643	0.00722	2.137
1.150	0.368	3.674	7.826	4.232	2.760	1.840	2.13	1.91	0.368	7.545	0.00723	2.137
1.143	0.366	3.412	8.018	4.206	2.972	1.600	2.35	2.53	0.366	8.192	0.00561	2.099
1.143	0.366	3.266	8.164	4.206	2.972	1.600	2.50	2.18	0.366	7.841	0.00561	2.099
1.136	0.364	2.943	8.417	4.18	3.181	1.363	2.86	2.63	0.364	8.230	0.00436	2.061
1.136	0.364	2.905	8.455	4.18	3.181	1.363	2.91	2.51	0.364	8.123	0.00437	2.061
1.129	0.361	2.720	8.570	4.155	3.387	1.129	3.15	3.62	0.361	8.845	0.00341	2.024
1.129	0.361	2.675	8.615	4.155	3.387	1.129	3.22	3.36	0.361	8.699	0.00341	2.024
1.122	0.359	2.397	8.823	4.129	3.590	0.8976	3.68	4.13	0.359	9.031	0.00267	1.987
1.122	0.359	2.382	8.838	4.129	3.590	0.8976	3.71	4.00	0.359	8.975	0.00267	1.987
1.114	0.357	2.232	8.908	4.1	3.788	0.6684	3.99	6.64	0.357	9.682	0.00209	1.950
1.114	0.357	2.228	8.912	4.1	3.788	0.6684	4.00	6.55	0.357	9.664	0.00209	1.951
1.107	0.354	1.919	9.151	4.074	3.985	0.4428	4.77	6.49	0.354	9.592	0.00164	1.916
1.107	0.354	1.899	9.171	4.074	3.985	0.4428	4.83	6.02	0.354	9.492	0.00165	1.916
1.100	0.352	1.806	9.194	4.048	4.180	0.2200	5.09	17.03	0.352	10.39	0.00130	1.883
1.100	0.352	1.741	9.259	4.048	4.180	0.2200	5.32	10.22	0.352	10.02	0.00130	1.883
1.093	0.350	1.579	9.351	4.022	4.372	0.00	5.92	20.86	0.350	10.43	0.00103	1.850
1.093	0.350	1.497	9.433	4.022	4.372	0.00	6.30	9.53	0.350	9.892	0.00103	1.850

a: Based on estimated conversion factors for mixtures of electrolytes.

Table A-18: Observed [1952WAG/STO] and NONLINT-SIT predicted concentrations for I_c = 6.0 M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-)$ = (0.25 ± 0.10) kg·mol^{-1} and other thermodynamic data listed in Table A-12. Selected data plotted in Figure A-9.

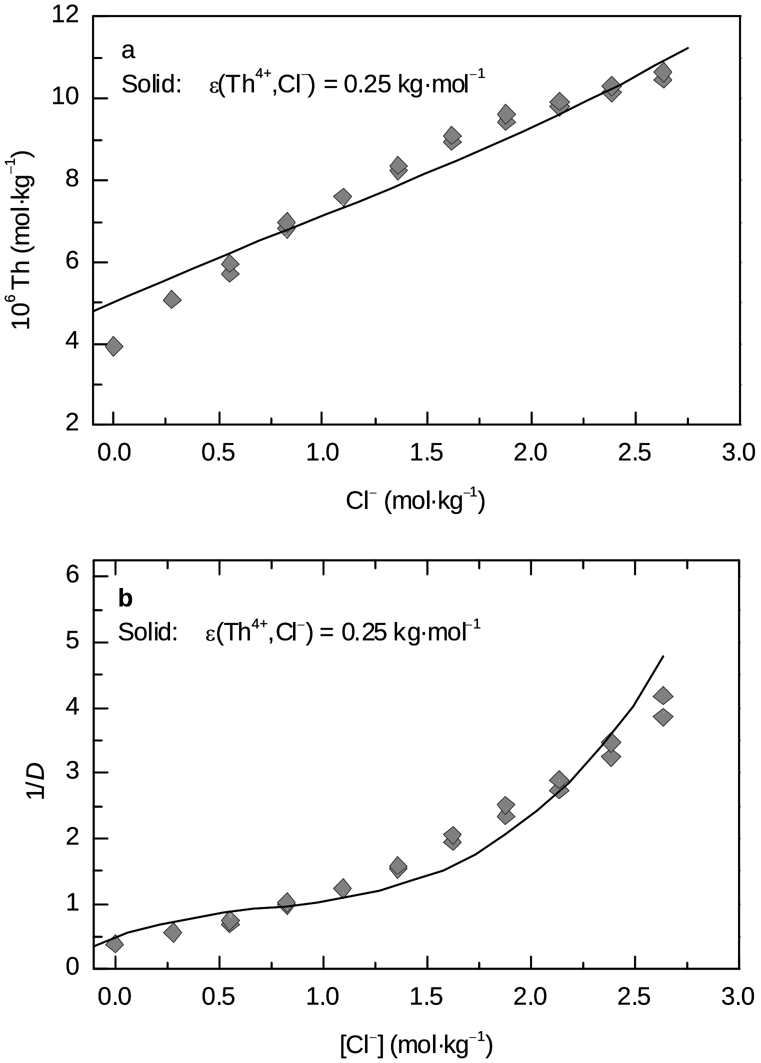
Experimental [1952WAG/STO], I_c = 6.0 M								Predicted				
	Concentrations (m)								Concentrations (m)			
m/c[a]	H^+	$Th_{org}\times10^6$	$Th^{4+}\times10^6$	Na^+	Cl^-	ClO_4^-	1/*D*	1/*D*	H^+	$Th^{4+}\times10^6$	$\gamma_{Th^{4+}}$	γ_{H^+}
1.405	0.450	10.11	3.942	7.980	0.00	8.430	0.39	0.56	0.450	5.054	30.505	8.020
1.405	0.450	10.11	3.942	7.980	0.00	8.430	0.39	0.56	0.450	5.054	30.505	8.020
1.396	0.447	8.892	5.068	7.929	0.2792	8.097	0.57	0.66	0.447	5.565	21.064	7.784
1.396	0.447	8.892	5.068	7.929	0.2792	8.097	0.57	0.66	0.447	5.565	21.064	7.784
1.388	0.444	8.165	5.715	7.884	0.5552	7.773	0.70	0.85	0.444	6.394	14.731	7.570
1.388	0.444	7.931	5.949	7.884	0.5552	7.773	0.75	0.81	0.444	6.211	14.752	7.570
1.379	0.441	6.965	6.825	7.833	0.8274	7.447	0.98	0.97	0.441	6.786	10.266	7.351
1.379	0.441	6.827	6.963	7.833	0.8274	7.447	1.02	0.93	0.441	6.651	10.259	7.351
1.370	0.438	6.116	7.584	7.782	1.096	7.124	1.24	1.17	0.438	7.390	7.167	7.137
1.362	0.436	5.383	8.237	7.736	1.362	6.810	1.53	1.45	0.436	8.057	5.056	6.944
1.362	0.436	5.259	8.361	7.736	1.362	6.810	1.59	1.37	0.436	7.871	5.058	6.944
1.353	0.433	4.586	8.944	7.685	1.624	6.494	1.95	1.67	0.433	8.469	3.558	6.745
1.353	0.433	4.436	9.094	7.685	1.624	6.494	2.05	1.53	0.433	8.192	3.553	6.745
1.344	0.430	4.012	9.428	7.634	1.882	6.182	2.35	2.10	0.430	9.099	2.512	6.553
1.344	0.430	3.829	9.611	7.634	1.882	6.182	2.51	1.83	0.430	8.684	2.514	6.553
1.336	0.428	3.563	9.797	7.588	2.138	5.878	2.75	2.88	0.428	9.919	1.793	6.379
1.336	0.428	3.426	9.934	7.588	2.138	5.878	2.90	2.50	0.428	9.538	1.793	6.379
1.327	0.425	3.122	10.15	7.537	2.389	5.573	3.25	3.99	0.425	10.61	1.274	6.199
1.327	0.425	2.969	10.30	7.537	2.389	5.573	3.47	3.17	0.425	10.09	1.277	6.199
1.318	0.422	2.712	10.47	7.486	2.636	5.272	3.86	5.69	0.422	11.21	0.911	6.026
1.318	0.422	2.539	10.64	7.486	2.636	5.272	4.19	3.92	0.422	10.50	0.912	6.026

a: Based on estimated conversion factors for mixtures of electrolytes.

Figure A-9: Observed [1952WAG/STO] and NONLINT-SIT predictions for $I_c = 6.0$ M based on $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-) = (0.25 \pm 0.10)$ kg·mol^{-1} and other thermodynamic data listed in Table A-12.

(a) aqueous thorium concentrations as a function of chloride concentrations

(b) 1/*D* as a function of chloride concentrations



The conclusion from these calculations and those summarised under [1950DAY/STO] is that the experimental data can be described well both with the complex formation (as shown in [1952WAG/STO]) and the activity coefficient model. This review has used the complex formation model and the SIT to calculate the equilibrium constant $\log_{10} \beta_1^\circ = (1.70 \pm 0.10)$ as shown in Figure VIII-9 (Section VIII.2.2.1). This value is in reasonable agreement with the one obtained in [1952WAG/STO] using the Debye-Hückel term only, $\log_{10} \beta_1^\circ = 1.38$. The final issue is: How do we describe the experimental data and what method should be used in chemical modelling? The experimental data from [2005HEN/TUT] demonstrate unequivocally that chloride complexes are formed; this fact and the use of the complex formation model in previous volumes in this series is the reason why this review prefers the complex formation model. However, the uncertainty in the equilibrium constants is large and the only chemical conclusion that can be supported is that the thorium(IV) chloride complexes are very weak and therefore of minor importance in systems where ligands that form stronger complexes are present. It should also be emphasised that modelling the Th-Cl systems should either use ion-interaction parameter or ion complexes but not both.

[1953EYR/WES]

The enthalpy of solution of thorium sesquisulphide in 6.000 M HCl media was determined at 298.15 K according to reaction:

$$Th_2S_3(cr) + 8H^+ \text{ (in 6.000 M HCl +) } \rightarrow \{2Th^{4+} + 3H_2S\} \text{ (in 6.000 M HCl) } + H_2(g),$$

leading to the standard enthalpy of formation of this compound.

Preliminary tests indicated that (96.95 ± 0.20)% of the samples dissolved in the medium used, leaving a (3.05 ± 0.20)% residue of a mixture of ThOS and ThO_2. It was also shown by titrimetry that the H_2S produced by the dissolution, corresponded to a compound with a S/Th ratio of (1.500 ± 0.005). Gravimetric analyses for the thorium in the individual calorimetric solutions were also carried out, as well as determinations of the amount of H_2S remaining in each of these solutions (about 94%). Corrections were made by the authors for the partial loss of H_2S to the gas phase and the evolution of hydrogen in the dissolution reaction. These corrections included the saturation of the evolving gases by the components of the HCl solutions

Three dissolution experiments were carried out in 6.000 M HCl and three others in the same medium containing 0.005 M Na_2SiF_6. No detectable heat effect was detected due to the presence of Na_2SiF_6, which, however, appeared to increase the rate of dissolution. As the same authors [1950EYR/WES] had established as −(1.25 ± 0.42) $kJ\cdot mol^{-1}$ the effect of the presence of 0.005 M Na_2SiF_6 in the dissolution of Th(cr) in 6.000 M HCl, we have treated separately the two sets of data for the dissolution of $Th_2S_3(cr)$.

In carrying the correction for the partial evaporation of H_2S we have used the value selected in this review, (18.0 ± 1.6) $kJ\cdot mol^{-1}$ for the process $H_2S(aq) \rightleftharpoons H_2S(g)$

corresponding to the hypothetical standard state of unit molality, as such data are not available in 6.000 M HCl. Eyring and Westrum [1953EYR/WES] had used for this process a value of 19.2 kJ·mol^{-1}; this leads to a minute correction in the enthalpies of solution: $-(556.1 \pm 0.4)$ and $-(555.8 \pm 0.4)$ kJ·mol^{-1}, in the absence and presence of 0.005 M Na_2SiF_6, respectively. The use of $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl) = $-(758.957 \pm 1.600)$ kJ·mol^{-1} (see Section VI.1) and $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl$-$0.005 M Na_2SiF_6) = $-(760.207 \pm 1.700)$ kJ·mol^{-1} (taking into account the influence of the fluorosilicate ion, $-(1.25 \pm 0.42)$ kJ·mol^{-1}, see Section VIII.2.1.3.1) and of the selected value for $\Delta_f H_m$ (H_2S, aq, 298.15 K) = $-(38.6 \pm 1.5)$ kJ·mol^{-1} leads, for $\Delta_f H_m$ (Th_2S_3, cr, 298.15 K) to the values $-(1077.6 \pm 5.5)$ and $-(1080.4 \pm 5.6)$ kJ·mol^{-1} from the 6.000 M HCl and (6.00 + 0.005 M Na_2SiF_6) media, respectively. In these calculations, small effects due to the dilution of the media by the reacting species were neglected, the thorium concentration in the solutions being in the millimolar range.

[1953GRI/SKO]

The heat capacity of Th(cr) was measured from 18 to 300 K, at 3$-$4 K intervals. A thorium rod, 7.5 cm long × 3.8 cm diameter was used for the measurements. The major impurities in the metal were 0.04% N, 0.06% O and 0.028% Si (mass%). The original experimental data are not given, only smoothed data at 20 to 300 K being tabulated. The authors state that agreement of the experimental data with the smoothed curve was generally well within 0.1%, but deviations of up to 0.2% were observed between 135 and 155 K. The uncertainties in $C_{p,m}$ are estimated by the authors to be 1% at 20 K, decreasing to 0.3% at 30 K and 0.1% above 35 K. For the entropy calculation, $C_{p,m}$ was extrapolated below 20 K using a Debye function with a Debye temperature of 141.6 K, the mean value from 18 to 28 K. The entropy calculated by the authors is S°_{m} (Th, cr, 298.15 K) = 53.39 J·K^{-1}·mol^{-1}; no uncertainty is given.

[1953OSB/WES]

The heat capacity of ThO_2 was determined in an adiabatic calorimeter from 10.2 to 305.4 K. The heat capacity and entropy at 298.15 K were calculated to be (61.76 ± 0.06) and (65.24 ± 0.08) J·K^{-1}·mol^{-1} respectively; when corrected for the modern atomic weight of thorium, these become 61.74 and 65.23 J·K^{-1}·mol^{-1}. The sample of thoria used was ground from electrically-fused material, and was analysed to have a Th content of (87.54$-$87.93) mass% (theoretical 87.88). Chemical analysis showed the total content of lanthanide elements to be < 150 ppm, similar to the total content of other metals, measured spectroscopically. 53 heat capacity measurements were made, extending from 10.2 to 305.4 K. For the entropy calculations, the heat capacity was extrapolated to 0 K using a Debye function. The heat capacity and entropy from this excellent study were adopted by the review.

[1954ALL/YOS]

The reaction of Th(cr) with iodine from 1395 to 1706 K was investigated by passing iodine vapour, entrained in an inert gas, over the metal in a molybdenum tube. The iodine content of the gas stream both before and after reaction was determined by measurement of the optical density at wavelengths in the 4300 − 4800 Å range, and the partial pressure of the metallic iodide (assumed to be $ThI_4(g)$) was determined by difference. The measurements at the highest temperature (1706 K) gave optical densities greater than unity and were rejected, as were those at the lowest temperature (1395 K), because of the very low, and thus uncertain, optical density. The remaining four measurements were assumed to refer to the equilibrium $Th(cr) + 4I(g) \rightleftharpoons ThI_4(g)$, and the enthalpy and entropy of this reaction at the mean temperature are derived. However, the experimental $\Delta_r S_m$ (1515 K), −628 $J\cdot K^{-1}\cdot mol^{-1}$ (as calculated by the review) is much more negative than that calculated from the selected thermal functions, −306 $J\cdot K^{-1}\cdot mol^{-1}$. This indicates that the reaction was more complex than that assumed (probably involving lower gaseous iodides) and/or that equilibrium was not achieved. These data are not used in the assessment.

[1954EYE/SEL]

This paper reports an extensive study of the Th-Te system. The ThTe, $ThTe_2$, $ThTe_{2.66}$, and ThOTe phases were prepared and identified from X-ray and chemical analyses. ThTe is simple cubic with the CsCl-type structure (unlike ThS and ThSe, which have the NaCl structure) while ThOTe is tetragonal, isostructural with ThOSe and ThOS. The tellurides are all degraded well below 1273 K when heated *in vacuo*. The Th-Te system is not analogous to the Th-S and the Th-Se systems.

[1954FAU]

Faucherre has studied the solution chemistry of a number of ions known to form basic (*i.e.*, containing coordinated oxide and hydroxide in the solid compounds) salts using pH titrations and measuring the free hydrogen ion concentration. A graphical method was used to analyse the experimental data. The reliability of the methods used by Faucherre can be tested by comparison with the data obtained for the hydrolysis of Bi(III), where there are both experimental and structure chemical data available, *cf.* [1976BAE/MES]. Faucherre suggests that the predominant hydrolysis product is $Bi_4O_4^{4+} \equiv Bi_4(OH)_8^{4+}$, as compared to the very well documented $Bi_6(OH)_{12}^{6+}$. This review concludes that the methods used by Faucherre are not satisfactory, hence we do not accept the evidence for the formation of $Th_4(OH)_8^{8+}$ based on his experimental data.

[1954FER/KAT]

The hydrates of $Th(NO_3)_4(cr)$ and ternary system $Th(NO_3)_4(cr)$-H_2O-HNO_3 were investigated at 298.15 K, by the wet residues method. At this temperature, the stable hydrates are the penta- and tetrahydrate. The ternary system is depicted. The invariant point of the pentahydrate-tetrahydrate-aqueous phases is at 17.70 wt% water and 28.67 wt% $Th(NO_3)_4$ and that of the tetrahydrate-$Th(NO_3)_4$-aqueous phases is at 5.10% water and 21.13% $Th(NO_3)_4$. The authors discuss in some detail the various lower and higher hydrates, but conclude that there is no conclusive evidence that any of these are stable at 298.15 K. The anhydrous solid isolated from the low-water region of the ternary system, of composition suggested by the extrapolation of the ‘wet-residues’ tie-lines, $Th(NO_3)_4{\cdot}2HNO_3$, showed the same XRD pattern as the addition product of $Th(NO_3)_4$ and nitrogen dioxide, isolated previously.

[1954GAY/LEI]

Gayer and Leider [1954GAY/LEI] studied the solubility of Th(IV) hydroxide in $HClO_4$ and NaOH solutions at 25°C. The solid, designated as thorium hydroxide $ThO(OH)_2(s)$, was precipitated from thorium perchlorate solution by adding an excess of NaOH, washed with water and used for solubility experiments in following media:

(1): 0.020 − 0.811 m $HClO_4$

(2): Dilute $HClO_4$ (pH = 3.12 - 3.44)

(3): 0.010 − 0.865 m NaOH (prepared and stored under N_2 atmosphere)

After shaking the samples 5−7 days for equilibration, the Th concentrations were determined colorimetrically. After allowing the solid to settle 3−5 days, aliquots were taken from the clear supernatant without filtration or centrifugation to remove polymeric or colloidal species.

- *Solubility in acidic solutions*

For series (1) only the initial $HClO_4$ concentrations are reported, but not the equilibrium pH or $-\log_{10}[H^+]$ values. These data are not useful, because the measured Th concentrations are only 2−3 times lower than the initial H^+ concentrations (*e.g.*, [Th] = 0.04 $mol{\cdot}kg^{-1}$ in initially 0.1 m $HClO_4$); since H^+ is consumed by the dissolution of thorium hydroxide, there is no information on the equilibrium H^+ concentration.

In series (2), pH is measured with a glass electrode which is roughly calibrated against two buffer solutions at pH 4 and pH 7. The equilibrium thorium concentrations were found to decrease from $\log_{10}[Th] = -1.42$ at pH 3.12 to $\log_{10}[Th] = -2.00$ at pH 3.4. The equilibrium constants calculated by Gayer and Leider [1954GAY/LEI] for the reactions:

$$ThO(OH)_2(s) + H^+ \rightleftharpoons ThO(OH)^+ + H_2O(l) \qquad (A.30)$$

$$ThO(OH)_2(s) + 2H^+ \rightleftharpoons ThO^{2+} + 2H_2O(l) \qquad (A.31)$$

$$ThO(OH)_2(s) \rightleftharpoons ThO^{2+} + 2OH^- \qquad (A.32)$$

are $\log_{10}{}^{*}K^{\circ}_{s,1}$ (A.30) = 1.51, $\log_{10}{}^{*}K^{\circ}_{s,2}$ (A.31) = 4.74 and $\log_{10}K^{\circ}_{s,2}$ (A.32)= − 23.26, respectively. They are based on the assumptions $\gamma_{ThO(OH)^+} = \gamma_{H^+}$ and $\gamma_{ThO^{2+}} = (\gamma_{H^+})^2$;

where γ_{H^+} is calculated with the Debye-Hückel equation. These equilibrium constants are not accepted by this review. It is known from potentiometric studies that $\mathrm{ThO(OH)}^+$ and ThO^{2+} (equivalent to $\mathrm{Th(OH)}_3^+$ and $\mathrm{Th(OH)}_2^{2+}$) are not the predominant Th(IV) hydroxide complexes at the H^+ and Th concentrations of the solubility studies (1) and (2). Since ionic strength is not kept constant and the pH values, which are not very accurate, vary only in a narrow range, these results are not re-evaluated in the present review. However, it should be noted that the solubility data of [1954GAY/LEI] at pH 3.1 – 3.4 are consistent with solubility data for $\mathrm{ThO_2}$(am, hyd) in numerous studies over more extended pH ranges at I = 0.1, 0.5 or 0.6 M [1964NAB/KUD], [1978RYA/RAI], [1989MOO], [1991FEL/RAI], [2000RAI/MOO], [2002NEC/MUL].

- Solubility in alkaline solutions

From a linear plot of the equilibrium thorium concentrations in NaOH solutions above 0.38 molal (Figure 1 in [1954GAY/LEI]), Gayer and Leider postulated the formation of anionic hydroxide complexes according to the reactions.

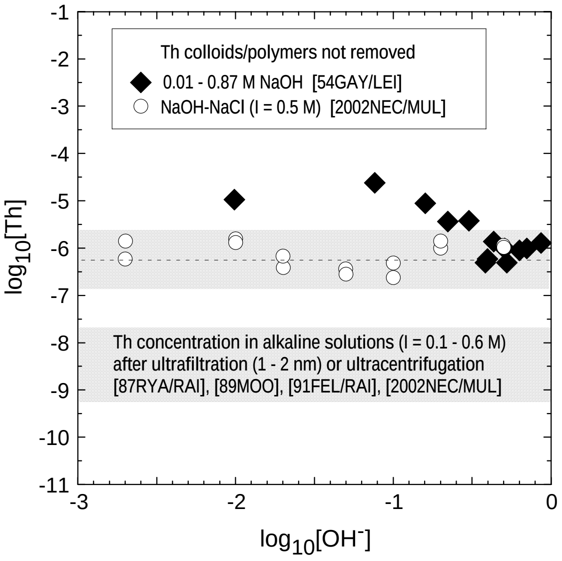
$$\mathrm{ThO(OH)_2(s) + OH^- \rightleftharpoons HThO_3^- + H_2O(l)}\ \text{(equal to } \mathrm{Th(OH)_5^-}\text{)} \qquad \text{(A.33)}$$

$$\mathrm{ThO(OH)_2(s) + 2OH^- \rightleftharpoons ThO_3^{2-} + 2H_2O(l)}\ \text{(equal to } \mathrm{Th(OH)_6^{2-}}\text{)} \qquad \text{(A.34)}$$

The equilibrium constants, calculated assuming $\gamma_{\mathrm{HThO_3^-}} = \gamma_{\mathrm{OH^-}}$ and $\gamma_{\mathrm{ThO_3^{2-}}} = (\gamma_{\mathrm{OH^-}}\ \gamma_{\mathrm{NaOH}})^2$, are $\log_{10} K^{\circ}_{s,5}$(A.33) = $\log_{10} K^{\circ}_{s,6}$(A.34) = –5.80. These values are not accepted by the present review.

As demonstrated in a number of later solubility studies with thorium hydroxide or $\mathrm{ThO_2}$(am, hyd) at constant ionic strength (I = 0.1, 0.5 or 0.6 M) [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [2002NEC/MUL], there is no evidence for the formation of anionic Th(IV) hydroxide complexes at high pH which would cause an increase of the solubility; in these studies the solubility was found to be constant at a level of $\log_{10}$ [Th] = –(8.5 ± 0.8) from pH 6 up to pH 13.5. Figure A-10 demonstrates that Gayer and Leider's solubility data in NaOH solutions, shown in a logarithmic plot of $\log_{10}$ [Th] *vs.* $\log_{10}$ [$\mathrm{OH^-}$], provide no indication for the formation of anionic Th(IV) hydroxide complexes. There is only a scatter due to the fact that, as mentioned above, Gayer and Leider [1954GAY/LEI] have taken the aliquots for Th concentration measurements without filtration or centrifugation to remove polymeric or colloidal species. Their equilibrium thorium concentrations are considerably higher than those measured by other authors after ultracentrifugation or ultrafiltration [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [2002NEC/MUL]. The data in NaOH solutions above 0.3 molal are comparable with those measured by Neck *et al.* [2002NEC/MUL] in the clear supernatant of the samples, *i.e.*, as done in [1954GAY/LEI] without removal of colloids. The equilibrium thorium concentrations coming from neutral Th(IV) polymers or small colloids in neutral and alkaline solution, also at higher ionic strength, have been discussed in [2004ALT/NEC] and found to be constant at a level of $\log_{10}$ [Th] = –(6.3 ± 0.6), independent of ionic strength and pH in the range pH = 6 – 14.

Figure A-10: Solubility data determined by Gayer and Leider [1954GAY/LEI] and Neck *et al.* [2002NEC/MUL] with ThO_2(am, hyd) in NaOH and NaOH-NaCl solutions without removal of polymeric/colloidal Th(IV) species. Thorium concentrations measured in comparable solubility studies after ultrafiltration (1 − 2 nm) [1987RYA/RAI], [1989MOO], [1991FEL/RAI] or ultracentrifugation [2002NEC/MUL] are indicated for comparison by the lower hatched area.



[1954HIE]

This study of the hydrolysis of Th(IV) has been made at 25°C, using potentiometric technique in a 1M $(Na)ClO_4$ ionic medium. Full experimental details, including all experimental data are reported. Test solutions with six different total concentration of thorium, Th_{tot} = 1, 2, 5, 10 and 20 mM were investigated over the $-\log_{10}[H^+]$ range 2.0 to 4.0. The experiments were made as titrations by adding known volumes of a standardised NaOH solution; the authors point out that the small amounts of carbonate present in these were not important for the interpretation as it is removed as CO_2 by bubbling nitrogen gas through the test solutions. The acid excess in the Th stock-solution was determined by potentiometric titration giving high confidence in the accuracy of the analytical total concentration of H^+, H_{tot}. The experiments were continued until a precipitate was formed as indicated by drifting emf-values. In order to establish if true equilibrium had been obtained some titrations were also made in the reverse direction (increasing $[H^+]$). The emf potentials began to drift around

$-\log_{10}[H^+] = 3.0$ and the test solutions were distinctly opaque at $-\log_{10}[H^+] = 4.7$ at $[Th]_{tot} = 2$ mM. The emf values were corrected for the hydrogen ion dependent diffusion potentials.

The values of $\bar{n}_{OH}$ ranges from approx 0 to 2.7 and all data were used in the graphical analysis. From the plots of $\bar{n}_{OH}$ *vs.* $-\log_{10}[H^+]$ the author suggested that the complexes formed were of the "core-and-link" type, $Th\{(OH)_3Th\}_n^{(4+n)+}$, where Th is the core and "$(OH)_3Th$" the link. This model implies an unlimited series of complexes that can be described using a two-parameter approximation:

$$(n+1)Th^{4+} + 3nH_2O \rightleftharpoons Th\{(OH)_3Th\}_n^{(4+n)+} + 3nH^+ \qquad k_n$$

The ratio k_{n+1}/k_n is the equilibrium constant for the addition of a new link:

$$Th\{(OH)_3Th\}_n^{(4+n)+} + Th^{4+} + 3H_2O \rightleftharpoons Th\{(OH)_3Th\}_{n+1}^{(5+n)+} + 3H^+$$

In this two-parameter approximation three different models were tested, $k_n = k_0k^n$, $k_n = k_0nk^n$ and $k_n = k_0k^n/n$. Hietanen found that the experimental data could be described equally well by these models with k_0 between 0.5 to 1.0 for the first two models and about 0.1 for the third. The value of $\log_{10}k$ for the three models were -7.50, -7.65 and -9.15, respectively. The "core-and-link" model is related to chain structures found in solid state for so called "basic salts", thorium hydroxide sulphate and thorium hydroxide chromate ([1949SIL/LUN], [1950LUN]). However, in solution systems, a model with a very large number of complexes does not make chemical sense and the model was also abandoned in later studies.

The experimental data indicate quite clearly that polynuclear complexes are formed and that only small amounts of mononuclear complexes are present in the system under the experimental conditions used. The experimental data were reanalysed using least-squares methods as discussed in [1964HIE/SIL].

[1954HOC/JOH]

The vapour pressure over ThO_2(cr) (no analysis given) in a tantalum cell was determined by Knudsen effusion from 2398 to 2676 K, and with admixed W(cr) from 2389 to 2661 K; the pressures were the same in the two cases. The authors note that some decomposition to ThO(g) did occur at the highest temperatures. However, it is now known that under these conditions, the oxygen potential is so low that the major species in the vapour is ThO(g) rather than ThO_2(g) over the whole temperature range, and these results are discussed under ThO(g) in Section VII.1.1.

The authors suggested that the material formed from ThO_2 and Th at 2150 K, which had an fcc cell parameter of 4.31 Å was ThO(cr). However, this lattice constant is much smaller than the cell sizes of the firmly established U(C,N,O) and Pu(C,N,O) phases, and could not have been ThO(cr), pure or impure.

[1954KRA/HOL]

The hydrolysis of Th(IV) was studied at 25°C in 1 M (Na)ClO_4; the experimental data cover the Th_{tot} concentration range from 2.5×10^{-4} to 1.5×10^{-2} M and the $-\log_{10}[H^+]$ range from 2.3 to 3.7. The values of $\bar{n}_{OH}$ vary from 0.03 to about 2.5. The investigators checked the reversibility of the titration data, if precipitation occurred and also arranged the experiment in such a way that the variation in the activity factors was minimised. They also noted that equilibrium was rapidly attained and that the solutions remained clear at $\bar{n}_{OH} < 2$. Experimental data are reported, but the number of reported experimental points is much smaller than in the study by Hietanen [1954HIE]; more data are given in Figure 3 of [1965BAE/MEY]. The analysis of the data has been made using approximations and graphical methods and the reported equilibrium constants therefore do not have the highest accuracy. The reported values are: $\log_{10} {}^*\beta_{1,1} = -4.3$, $\log_{10} {}^*\beta_{2,1} = -7.8$ and $\log_{10} {}^*\beta_{2,2} = -4.8$.

The authors mention ultracentifugation experiments that indicate the formation of tetranuclear species at $\bar{n}_{OH}$ slightly less than 2 and the formation of aggregates with a much higher nuclearity at $\bar{n}_{OH} > 2$. The primary experimental data $\bar{n}_{OH}(-\log_{10}[H^+])$ in this study agree well with those in [1954HIE]. The chemical model and the deduced equilibrium constants were also checked using the Oak Ridge least squares program by Rush as described in the comments to [1965BAE/MEY].

[1954LOH/OSB]

ThF_4(cr) was prepared from a pure sample of electrically fused ThO_2(cr) by hydrofluorination at 1023 K for 132 h, until a constant weight was attained. Analyses for thorium and fluorine were in excellent agreement with the theoretical values. The heat capacities of a 91 g sample were measured from 5.5 to 298.2 K and are given in a table and a graph. At 298.15 K, $C^{\circ}_{p,m}(ThF_4, cr) = (110.71 \pm 0.13)\ J \cdot K^{-1} \cdot mol^{-1}$ and $S^{\circ}_{m}(ThF_4, cr) = (142.06 \pm 0.17)\ J \cdot K^{-1} \cdot mol^{-1}$.

[1955PAN/HSE]

The hydrolysis of Th(IV) has been studied at 25°C and different constant concentrations of sodium perchlorate (0.05, 0.1, 0.3 and 0.5 M) by diluting 10.0 mM test solutions of Th(IV) with the ionic medium. The experimental quantities are the pH change and the change in Th(IV) concentration. The glass electrode used was calibrated against pH buffer solutions but the conversion of H^+ activities to H^+ concentrations is not reported in [1955PAN/HSE].

The experimental data were interpreted using two mononuclear complexes, $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$. The reported equilibrium constants are given in Table A-19. The authors have not taken the presence of polynuclear complexes into account and they are predominant in the 10 mM test solution in the pH range studied (approx. 2.7 − 4.1). For these reasons the equilibrium constants are not accepted by the present review.

Table A-19: Equilibrium constants reported in [1955PAN/HSE]

Ionic strength (M)	$\log_{10}{}^*\beta_1$	$\log_{10}{}^*\beta_2$
0.5	– 4.26	– 8.28
0.3	– 4.12	– 8.19
0.1	– 4.00	– 8.14
0.05	– 3.92	– 8.11
0 [a]	– 3.89 [a]	– 8.09 [a]
Pure water	– 3.77	– 8.09

[a] The equilibrium constants at zero ionic strength given in [1955PAN/HSE] were derived by extrapolating $\log_{10}{}^*\beta_n$ plotted against $I^{1/2}$ to $I = 0$.

[1955ROB/JEN]

These authors used reaction calorimetry to measure the enthalpies of formation of a number of silicides of Ti, Zr, V, Ta, Mo, W, and Th. For the disilicides, the authors compared the enthalpies of formation and the character of the metal bonding.

Metals and silicon in powdered form were used as starting materials. The major impurities in Si were Al (0.1%), B (< 0.01%), and Fe (< 0.01%), while the thorium sample was reported as containing 98.7% Th, 0.15% Fe, a trace of Si, and the balance thorium oxide. For calorimetry the mixtures of powders in the appropriate stoichiometric ratio were compacted at 20 tons per square inch (2.75 kbar) so as to obtain cylinders 10 mm in diameter and 20 mm high.

The calorimeter (operating at (296 ± 1) K) was calibrated using the aluminothermic reaction $Cr_2O_3 + 2Al \rightleftharpoons Al_2O_3 + 2Cr$ for which a enthalpy change value of $-539.7\ kJ\cdot mol^{-1}$ was reported (a 10% excess Al was assumed not to take part to the reaction), which compares to a literature value of $-536.0\ kJ\cdot mol^{-1}$ [1982WAG/EVA]. A mixture of the same composition was used to initiate the reaction to form the silicides.

For $\Delta_f H^\circ_m$ ($ThSi_2$, cr), three determinations were reported, yielding -177.8, -178.2, and $-166.9\ kJ\cdot mol^{-1}$. X-ray examination showed that the reacted product was “mainly a $ThSi_2$ phase and some ThO_2”, the latter being already present in the starting metal powder. These results, assumed to be valid for 298.15 K, are included in the discussion of the basis for the selection of the enthalpy of formation of $ThSi_2$(cr) (Section XI.2.1).

[1956CHU/STE]

This paper reports the solubilities of the thorium and uranyl phosphates; only the Th(IV) studies will be discussed here. The authors have measured the solubility of two different Th(IV) phosphate solids, $Th_3(PO_4)_4$(s) and $Th(HPO_4)_2$(s) as a function of pH in nitric and sulphuric acid solutions. The solid phases used have been analysed using elemental analysis prior to the solubility experiments, but there is no X-ray data, or information on the composition of the solids after equilibration. The experiments have been made at 19−20°C without an additional ionic medium; the time for equilibration was investigated. The experimental data for $Th_3(PO_4)_4(s)$ were collected at three different pH values, 1.80−2.45, sufficiently low to reduce the importance of hydrolysis. The Th(IV) concentration at equilibrium was measured either using a colorimetric method or by using a Th tracer; the two methods give essentially the same result, but we will discuss only those obtained by the first method. The solubility of Th varies between 3.5 and 0.70 mM in the nitrate solutions but is significantly larger in sulphuric acid, 4.5−1.5 mM, presumably as a result of the formation of sulphate complexes. However the authors have not analysed this. The reported solubility product refers to the reaction:

$$Th_3(PO_4)_4(s) \rightleftharpoons 3Th^{4+} + 4PO_4^{3-}$$

and this value has been calculated from the experimental solubility and total concentration of phosphate at equilibrium using the protonation constants in the H^+- PO_4^{3-} system that differs significantly from the values selected in this review. The authors report $\log_{10} K_s = -(78.0 \pm 1.0)$ in H_2SO_4 solutions and $\log_{10} K_s = -(79.2 \pm 0.8)$ in HNO_3 solutions; these values have not been accepted by the present review, because of poor characterisation of the solid phase in the equilibrium solutions, the lack of information on activity coefficients, doubtful values of the protonation constants of phosphate, too few experimental data and neglect of the formation of Th(IV) complexes with OH^-. The proposed equilibrium constant is much larger than the value proposed in [1994BAG/FOU], $\log_{10} K^{\circ}_{s,0} = -(112 \pm 2.1)$.

The solubility of $Th(HPO_4)_2(s)$ was also studied in nitric and sulphuric acid, but only at two different pH values for each acid. The calculated equilibrium constant for the reaction:

$$Th(HPO_4)_2(s) \rightleftharpoons Th^{4+} + 2HPO_4^{2-}$$

is $\log_{10} K_s = -(26.6 \pm 0.2)$ in nitric acid and $\log_{10} K_s = -(20.9 \pm 0.4)$ in sulphuric acid. When the experiments were repeated using a tracer marked solid, the value $\log_{10} K_s = -19.9$ was obtained, but it is not clear from the paper if these experiments were made in nitric or sulphuric acid. For the same reasons as stated above the proposed solubility product for $Th(HPO_4)_2(s)$ is not accepted by this review. Moskvin *et al.* [1967MOS/ESS] also determined the solubility product for $Th(HPO_4)_2(s)$, where they have taken the formation of phosphate complexes into account; their reported solubility product is $\log_{10} K_s = -26.89$.

[1956FER/KAT]

These authors report the measurement of the enthalpy of solution of $Th(NO_3)_4{\cdot}4H_2O(cr)$ and $Th(NO_3)_4{\cdot}5H_2O(cr)$ in water and in number of organic solvents. They observed, as expected, that the relative enthalpies of solution approximately parallel the base strength of the solvents. The authors also reported the enthalpy of solution of $\mathrm{Th(NO_3)_4(cr)}$. Analytical results were briefly mentioned for the two hydrates, and an earlier reference [1955FER/KAT] was given for details on the anhydrous salt.

The calorimetric apparatus and procedure were described. Performances were verified using the enthalpy of solution of $\mathrm{Na_2CO_3(cr)}$ in 200 $\mathrm{H_2O}$. Calorimetric results at 298.15 K were reported based on two or three determinations. The enthalpy of solution of the anhydrous salt in 2500 $\mathrm{H_2O}$ was given as -145.2 kJ·mol^{-1}. This review estimates the uncertainty of this value to be ±2.0 kJ·mol^{-1}. The tetra- and pentahydrates were dissolved in 350 $\mathrm{H_2O}$ and the corresponding enthalpies of solution were reported as $-(32.01)$ kJ·mol^{-1} and $-$ 14.85 kJ·mol^{-1}, respectively. Based on the discussion by the authors, this review estimates the uncertainty on these values to ± 1.70 kJ·mol^{-1}.

Using the value adopted in this review for the equilibrium constants (Table VII-17) $\log_{10} {}^{*}\beta^{\circ}_{n,m}$ ($\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$, aq, 298.15 K), the value $\log_{10} {}^{*}\beta^{\circ}_{1}$ ($\mathrm{Th(NO_3)^{3+}}$, 298.15 K) = (1.3 ± 0.2) and $\log_{10} {}^{*}\beta^{\circ}_{2}$ ($\mathrm{Th(NO_3)_2^{2+}}$, 298.15 K) = (2.3 ± 0.4) (as selected in Section X.1.3.3), calculations of the speciation (assuming ideal aqueous solution) indicate that the dissolution reactions can be approximately represented by:

$$\begin{aligned}
\mathrm{Th(NO_3)_4(cr)} + 2500\,\mathrm{H_2O(l)} \rightleftharpoons\ & 0.2387\,\mathrm{Th^{4+}} + 0.3370\,\mathrm{Th(NO_3)^{3+}} + \\
& 0.2384\,\mathrm{Th(NO_3)_2^{2+}} + 0.1730\,\mathrm{Th(OH)^{3+}} + \\
& 0.0079\,\mathrm{Th(OH)_2^{2+}} + 0.0024\,\mathrm{Th_2(OH)_3^{5+}} + \\
& 3.1861\,\mathrm{NO_3^-} + 0.1962\,\mathrm{H^+} \quad \text{in } 2499.8040\ \mathrm{H_2O(l)}
\end{aligned}$$

$$\begin{aligned}
\mathrm{Th(NO_3)_4{\cdot}4H_2O(cr)} + 350\,\mathrm{H_2O(l)} \rightleftharpoons\ & 0.0284\,\mathrm{Th^{4+}} + 0.2050\,\mathrm{Th(NO_3)^{3+}} + \\
& 0.7426\,\mathrm{Th(NO_3)_2^{2+}} + 0.0223\,\mathrm{Th(OH)^{3+}} + \\
& 0.0011\,\mathrm{Th(OH)_2^{2+}} + 0.0003\,\mathrm{Th_2(OH)_3^{5+}} + \\
& 2.3098\,\mathrm{NO_3^-} + 0.0254\,\mathrm{H^+} \quad \text{in } 353.9746\ \mathrm{H_2O(l)}
\end{aligned}$$

$$\begin{aligned}
\mathrm{Th(NO_3)_4{\cdot}5H_2O(cr)} + 350\ \mathrm{H_2O(l)} \rightleftharpoons\ & 0.0285\ \mathrm{Th^{4+}} + 0.2053\ \mathrm{Th(NO_3)^{3+}} + \\
& 0.7421\,\mathrm{Th(NO_3)_2^{2+}} + 0.0224\ \mathrm{Th(OH)^{3+}} + \\
& 0.0011\,\mathrm{Th(OH)_2^{2+}} + 0.0003\,\mathrm{Th_2(OH)_3^{5+}} + \\
& 2.3105\,\mathrm{NO_3^-} + 0.0255\ \mathrm{H^+} \quad \text{in } 354.974\ \mathrm{H_2O(l)},
\end{aligned}$$

neglecting very minor amounts of the higher hydrolysis species.

As can be seen, the nitrate complexes are, in the main, the dominant thorium species in solution. As there are no experimental values for the enthalpy of formation of these complexes (for either thorium or uranium), only the difference between the enthalpies of solution of the pentahydrate and the tetrahydrate has been used (see Section X.1.3.2) in conjunction with other results, to evaluate $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}$ ($\mathrm{Th(NO_3)_4{\cdot}4H_2O}$, cr, 298.15 K).

[1956FOM/MAI]

Tributyl phosphate (TBP) forms uncharged complexes with tetravalent actinides in organic solvents in equilibrium with nitric acid solution, a fact that is used in reprocessing of spent nuclear fuel in the Purex process. The chemistry is complicated by the simultaneous extraction of both HNO_3-TBP and An(IV)-TBP complexes. Fomin and Maiorova present a detailed experimental investigation of the complex formation in the Th(IV)-nitrate system using the distribution of Th(IV) between an aqueous $H(NO_3, ClO_4)$ phase and an organic phase containing 1 M TBP in benzene. The experiments have been made at a temperature of (20 ± 2)°C and a constant ionic strength of 2.00 M $H(NO_3, ClO_4)$. This is a careful experimental study where the authors provide all the important experimental details. For the extraction from pure nitrate solution they have quantified the co-extraction of HNO_3 and also determined the composition of the extracted uncharged complex in the organic phase, $Th(NO_3)_4(TBP)_2(org)$, and the equilibrium constant for the distribution equilibrium:

$$Th^{4+} + 4NO_3^- + 2TBP(org) \rightleftharpoons Th(NO_3)_4(TBP)_2(org) \qquad K = (36 \pm 2)\ M^{-6}.$$

However, the co-extraction of the complexes $HClO_4(TBP)_p$ and $Th(ClO_4)_4(TBP)_n(org)$ was not taken into account by the authors. From the variation of the distribution coefficient of Th(IV) between the aqueous and the organic phase they then deduced the equilibrium constants for the reactions:

$$Th^{4+} + nNO_3^- \rightleftharpoons Th(NO_3)_n^{4-n} \qquad n = 1-4.$$

The nitrate concentration in the aqueous phase varied between 0.226 and 1.717 M and a total of five test solutions were investigated. Even if the measurements and data analysis in [1956FOM/MAI] are made with careful attention to details, this is not sufficient to determine precise values of the four equilibrium constants using a total of five different nitrate concentrations. Fomin and Maiorova propose for the reactions:

$$Th^{4+} + NO_3^- \rightleftharpoons ThNO_3^{3+} \qquad \beta_1 = (6.0 \pm 0.5)\ M^{-1}$$

$$Th^{4+} + 2NO_3^- \rightleftharpoons Th(NO_3)_2^{2+} \qquad \beta_2 = (13 \pm 1)\ M^{-2}$$

$$Th^{4+} + 3NO_3^- \rightleftharpoons Th(NO_3^-)_3^{+} \qquad \beta_3 = (10 \pm 0.5)\ M^{-3}$$

$$Th^{4+} + 4NO_3^- \rightleftharpoons Th(NO_3)_4(aq) \qquad \beta_4 = (5.5 \pm 0.5)\ M^{-4}.$$

These equilibrium constants have been calculated assuming the activity coefficients for reactants and products to be constant. However, this is not the case when the composition of the aqueous phase is varied as in the system studied by [1956FOM/MAI]. Accordingly it is not possible to distinguish between the formation of weak complexes and activity variations. Moreover, the assumption of constant activity coefficients is incorrect for the thorium complex in the organic phase because the composition of the organic thorium complex in the TBP-benzene phase varies when $HClO_4$ is successively replaced by HNO_3. The complexes $Th(ClO_4)_4(TBP)_n(org)$ and $Th(NO_3)_4(TBP)_2(org)$ are in equilibrium with pure perchlorate or nitrate aqueous phases, respectively; mixed complexes are probably formed when thorium is extracted from $HClO_4$-HNO_3 mixtures. This effect was not taken into account by

[1956FOM/MAI]. The equilibrium constants proposed for the thorium nitrate complexes are therefore considerably overestimated and not accepted by this review.

[1957LAN/MIE]

The observed exothermic enthalpies of dilution of dilute aqueous solutions of $AlCl_3$, $Th(NO_3)_4$, and $UO_2(NO_3)_2$ are attributed to the hydrolysis of the salts. Addition of the appropriate acid represses the hydrolysis and leads to endothermic enthalpies of dilution. No quantitative thermodynamic information can be derived from this paper.

[1958BEA/MCT]

These authors studied the reactions of the chalcogenides of Ti, Zr, Hf and Th with a series of inorganic and organic reagents. They also gave a number of heats of formation based on combustion calorimetry.

Among results, given without any experimental details, values for the standard enthalpies of formation of Th_2S_3(cr), Th_2Se_3(cr), and Th_2Te_3(cr) were listed as -996, -937, and -628 $kJ\cdot mol^{-1}$, respectively. As recognised by the authors themselves, the difficulties in obtaining complete and unambiguous reactions with such systems are considerable. In the case of sulphides, the formation of SO_3, or of sulphuric acid, if any moisture is present, can lead to large errors. In the case of the heavier chalcogenides, sublimation of the chalcogen is also possible.

These results are mentioned in this review for information only.

[1958DAR/KEN]

The vapour pressures of ThF_4(cr) and ThF_4(l) were determined, by effusion for the solid (1055 to 1297 K) and the boiling point method for the liquid (1437 to 1595 K). Mass-spectrometric studies showed that the monomer is the only important species in the vapour.

The sample of ThF_4 used was well characterised by X-ray and chemical analysis for thorium; volatile impurities were negligible. The melting point was found to be (1383 ± 2) K, in agreement with an earlier value.

The vapour pressure of the solid was determined by mass-loss effusion from a nickel cell, from 1055 to 1297 K. Corrosion tests showed negligible reaction between Ni and ThF_4, even in the molten state. In one run, the effusate was collected on a tantalum cylinder and was found to be ThF_4, by chemical and X-ray analysis.

The boiling point method was used for the measurements on the liquid, from 1437 to 1595 K, again from a nickel container, the upper temperature limit being determined by the loss of strength of the nickel cell.

Masses corresponding to ThF_{4-n}, $n = 0$ to 4, were observed in the mass-spectrometric analysis, with ThF_4 being predominant. As for similar materials, the lower fluorides were attributed to fragmentation in the mass-spectrometer. There was no evidence for polymeric species.

These data have been processed by second and third-law methods in Section VIII.1.1.2.2.

[1958LEF]

Lefèbvre [1958LEF] reinterpreted potentiometric data from [1954HIE] and [1954KRA/HOL] in 1 M $NaClO_4$. Using his own calculation program, the author proposed the following complexes and equilibrium constants (given without uncertainties): $\log_{10}{}^*\beta_{2,1}(Th(OH)_2^{2+}) = -7.47$, $\log_{10}{}^*\beta_{2,2}(Th_2(OH)_2^{6+}) = -4.56$ and $\log_{10}{}^*\beta_{12,5}(Th_5(OH)_{12}^{8+}) = -29.5$. For $\bar{n}_{OH} > 2.3$ he claimed the predominance of a heptanuclear complex $Th_7(OH)_n^{28-n}$ with n between 18 and 21.

The paper [1958LEF] does not contain new experimental data and the proposed speciation scheme and equilibrium constants are not accepted by this review. The potentiometric data of [1954HIE] and [1954KRA/HOL] have been evaluated subsequently by Baes *et al.* [1965BAE/MEY] and Hietanen and Sillén [1968HIE/SIL] who found a consistent model and equilibrium constants for the hydrolysis of thorium in 1 M $NaClO_4$ solution. Their model, including the complexes (n,m) = (1,1), (2,1), (2,2), (8,4) and (15,6), is selected in the present review.

[1958MAI/FOM]

Tributyl phosphate in benzene was used to extract thorium from aqueous solutions of 1.7 molar ionic strength containing H^+, NO_3^-, HSO_4^-, Na^+, and ClO_4^-. The required concentration of nitrate was obtained by $NaNO_3$, H^+ by $HClO_4$ and the ionic strength by the addition of $NaClO_4$. Two series of experiments were made with the total concentration of H^+ equal to 0.3 and 1.7 M, respectively; the HSO_4^- concentration ranged up to 0.05 M and that of nitrate up to 1.7 M. The temperature of the extractions is not reported.

The authors provide detailed information on the graphical methods used to deduce stoichiometry and equilibrium constants of the complexes formed in this ternary system and also experimental distribution coefficients. As discussed in [1956FOM/MAI] the authors have not taken the co-extraction of ClO_4^- and NO_3^- into the organic phase into account and the nitrate data are therefore unreliable. As sulphate is not co-extracted into the organic phase and the variation in the concentration of perchlorate is small, the activity of the species in the organic phase will be nearly constant and the experiments thus provide reliable information on the equilibrium constants of the sulphate complexes. The analysis of the experimental data is satisfactory. The nitrate system has been described assuming constant activity coefficients where the Th^{4+}- NO_3^- interactions are described using four complexes $Th(NO_3)_n^{4-n}$. As discussed in this review, this does not provide a unique model in systems where weak complexes are formed and where the ionic composition of the test solutions have been varied significantly in the course of the experiment.

The authors calculated values of equilibrium constants for several reactions reported in the Table A-20.

Table A-20: Values of equilibrium constants at 1.7 M ionic strength.

Reaction	$\log_{10} K$
$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+$	2.30
$Th^{4+} + 2\ HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2\ H^+$	3.40
$Th^{4+} + HSO_4^- + NO_3^- \rightleftharpoons Th(NO_3)(SO_4)^+ + H^+$	3.29
$Th^{4+} + HSO_4^- + 2\ NO_3^- \rightleftharpoons Th(NO_3)_2(SO_4)(aq) + H^+$	3.04
$Th^{4+} + HSO_4^- + 3\ NO_3^- \rightleftharpoons Th(NO_3)_3(SO_4)^- + H^+$	2.70

Assuming that the data presented by these authors pertain to 25°C and that we can use the SIT parameters given below as an estimate for the description of the ion interactions in the mixed $(HClO_4)$-$(H,Na)NO_3$ ionic medium (1.7 M or 1.85 m), this review calculated the values of $\log_{10} {}^*\beta_n^\circ$ with the SIT model from the $\log_{10} {}^*\beta_n$ reported by [1958MAI/FOM] using the relationship $\log_{10} {}^*\beta_n^\circ = (\log_{10} {}^*\beta_n - \Delta z^2 D + \Delta\varepsilon I_m) \pm (\sigma\Delta\varepsilon I_m)$. The SIT ion interaction parameters used in these calculations included $\varepsilon(Th^{4+}, ClO_4^-) \approx \varepsilon(H^+, HSO_4^-) = (0.70 \pm 0.10)$, $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$, and $\varepsilon(ThSO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)$ kg·mol^{-1} (for details about the selection of these parameters see Section IX.1.3.2). The $\log_{10} {}^*\beta_1^\circ$ and $\log_{10} {}^*\beta_2^\circ$ values for the binary sulphate system thus determined are (4.29 ± 0.27) and (5.75 ± 0.21). These $\log_{10} {}^*\beta_n^\circ$ values are very close to the values calculated from several other sources (*e.g.* [1959ZIE], [1951ZEB/ALT], [1972PAT/RAM]) and are accepted by this review.

The suggested composition and equilibrium constants for the ternary complexes are strongly dependent on the model used to describe the ion interactions and these data are not accepted by this review.

[1959GAG/MAS2]

These authors prepared various hydrates of thorium fluoride by precipitation from nitrate solutions using HF(aq), followed by controlled thermal treatment. Although full analysis of the samples was mentioned, no detailed analytical results were given. It was shown by these authors that careful vacuum dehydration of their samples up to 523 K did not alter their structure, as shown by their X-ray diffraction patterns and that they could be easily hydrated back to their initial water content. Examples found in the literature of hydrates with a similar behaviour are given. They measured calorimetrically the enthalpies of rehydration of the (presumably metastable) anhydrous $ThF_4(cr)$ phases obtained by dehydration of $ThF_4{\cdot}2.5H_2O(cr)$ and of $ThF_4{\cdot}0.5H_2O(cr)$. These enthalpies of rehydration were reported to be $-(8.673 \pm 0.017)$ and $-(4.912 \pm 0.021)$ kJ·mol^{-1}, respectively.

It is interesting to note that in an adjacent paper [1959GAG/MAS], the same authors report a value of $-(25.48 \pm 0.05)$ kJ·mol^{-1} for the enthalpy of hydration of UF_4(cr) to $UF_4·0.4H_2O$(cr).

[1959HIE/SIL2]

The study has been made in a "self-medium", where the ionic medium cation consists of Th^{4+}. The experiments, potentiometric titrations have been made in test solutions of varying total concentration of protons, H_{tot}, in a $-\log_{10}[H^+]$ range where the value of $\bar{n}_{OH}$ is less than 0.1. Hence, the free metal ion concentration is approximately equal to Th_{tot} and it is straightforward to make the necessary corrections for the amount of hydroxide complexes formed. From experiments of this type it is only possible to determine the sum of the concentrations of Th complexes that contain a given number of hydroxide ions (one and two in this study); it is not possible to determine the nuclearity of the complexes without additional information. The experimental data obtained refers to reactions of the type

$$Th^{4+} + nH_2O(l) \rightleftharpoons \text{“}Th(OH)_n\text{”} + nH^+$$

where "$[Th(OH)_n]$" $= \sum m[Th_m(OH)_n^{4m-n}]$, the summation over m being from $m = 1$ to N (where N is the highest value for the nuclearity) for a given value of n.

In the present study, Hietanen and Sillén provide convincing evidence for the formation of complexes containing one and two coordinated hydroxides. By using additional information on the equilibrium constants for the mononuclear hydroxide complexes of Th(IV) they suggest that the complexes formed are binuclear, that is $Th_2(OH)^{7+}$ and $Th_2(OH)_2^{6+}$. The equilibrium constants for these complexes at 25°C are: $\log_{10} {}^*\beta_{1,2} = -(2.8 \pm 0.2)$ and $\log_{10} {}^*\beta_{2,2} = -(5.02 \pm 0.04)$ in 0.5 M $ThCl_4$; $\log_{10} {}^*\beta_{1,2} = -(2.9 \pm 0.2)$ and $\log_{10} {}^*\beta_{2,2} = -(5.09 \pm 0.04)$ in 0.7 M $ThCl_4$ + 2.2 M NaCl. The experimental technique and data analysis are described in detail. It is not possible to extrapolate the equilibrium constants to zero ionic strength and therefore no constants have been selected by this review.

[1959HIG]

Higashi measured the solubility of thorium hydroxide at room temperature from the direction of oversaturation. Thorium nitrate solutions (3×10^{-3} M, pH 2.5) were titrated with 0.1 M NaOH to pH values in the range 4 − 8. After precipitation of $Th(OH)_4$(s), the Th concentration and pH were measured after 30 minutes, 12 hours, 1, 2, 3, 7, 15, 30 and 100 days. No ionic medium was used in the experiments and the pH was measured using a glass electrode, but with no information about calibration procedures. Thorium concentrations were measured by a colorimetric method after filtration through filter paper, which is not sufficient to remove the colloidal and large polynuclear species $Th_m(OH)_{4m}(aq)$.

The author refers to the literature available at the time concerning the formation of Th(IV) hydroxide complexes, but does not use this information for the interpretation of the experimental data. It is obvious from Figure 4 in [1959HIG] that the reaction

$$Th(OH)_4(s) + 4H^+ \rightleftharpoons Th^{4+} + 4H_2O(l)$$

alone cannot describe the experimental data as also recognised by the author. For the quantitative evaluation of the Higashi's data it is helpful that the titration of 3×10^{-3} M $Th(NO_3)_4$ solutions with 0.1 M NaOH from pH 2.5 to 4−8 leads to $Th(OH)_4$ suspensions at approximately constant ionic strength, $I = 0.01$ M ($NaNO_3$). Assuming that the pH values given by the authors refer to the activity scale, this review converts pH into H^+ concentrations ($\log_{10}[H^+]$) with the activity coefficient of $\log_{10}\gamma_{H^+} = -0.04$ calculated with the SIT for $I = 0.01$ M. Using the hydrolysis constants and ion interaction coefficients selected in this review, the solubility measured after 1−7 days corresponds to solubility constants $\log_{10}{}^{*}K^{\circ}_{s,0}$ decreasing from 10.0 to 9.0. Re-evaluation of the data measured after 100 days (solid line in Figure A-11) yields $\log_{10}{}^{*}K^{\circ}_{s,0} = (8.7 \pm 0.4)$ and $\log_{10} K_{s,(4m,m)} = -(6.8 \pm 0.2)$ for the reaction:

$$Th(OH)_4(am) \rightleftharpoons (1/m)\,Th_m(OH)_{4m}(aq).$$

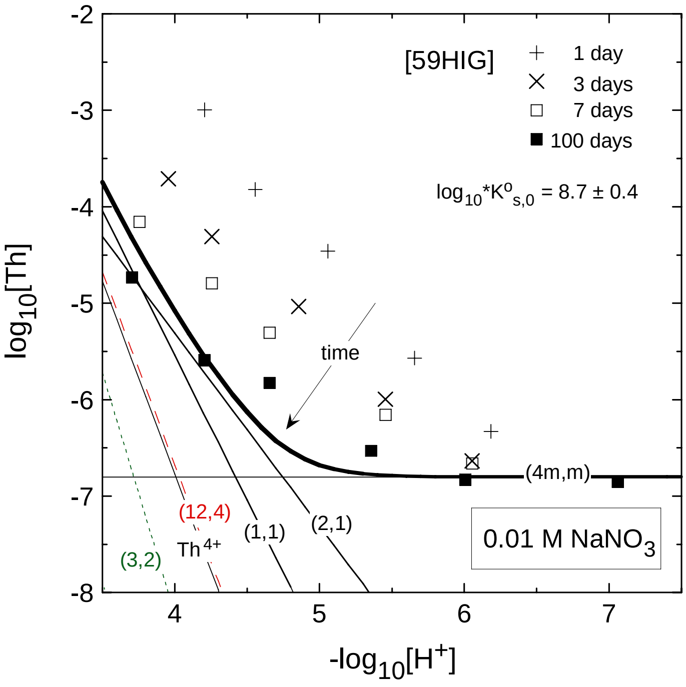
These two values are in reasonable agreement with the equilibrium constants recalculated by this review from numerous more recent data in chloride and perchlorate media. The results of [1959HIG] clearly demonstrate the very large effect of ageing as shown in Figure A-11 for the data measured after 1, 3, 7, and 100 days. This effect is more pronounced at lower pH and higher Th concentrations in solution. Ascribing the effect of ageing to an increase of particle size, due to recrystallisation *via* solution (dissolution-precipitation equilibria), explains that the increase of particle size is enhanced by the higher Th concentrations at low pH. This also indicates that the solubility data at different time and pH do not refer to a phase with a well-defined molar Gibbs energy.

[1959KIN/WEL]

This report describes heat-capacity measurements between 53 and 296 K for a sample of $ThS_2(cr)$, for which the analyses gave Th = 78.54 wt%, S = 21.43 wt%, corresponding to a composition of $ThS_{1.974}$. The heat capacity was extrapolated to 298.15 K to give $C^{\circ}_{p,m}(ThS_2, cr, 298.15 K) = (70.29 \pm 0.50)\ J\cdot K^{-1}\cdot mol^{-1}$. The standard entropy was calculated to be $S^{\circ}_{m}(ThS_2, cr, 298.15 K) = (96.23 \pm 1.70)\ J\cdot K^{-1}\cdot mol^{-1}$, where the heat capacity was extrapolated from 53 to 0 K using a combination of Einstein and Debye functions.

Similar measurements were made on samples of CeS(cr) and $Ce_2S_3(cr)$ which do not concern this review.

Figure A-11: Solubility of thorium hydroxide determined by Higashi [1959HIG] from oversaturation after 1, 3, 7, and 100 days. The calculated lines are based on the hydrolysis constants and ion interaction coefficients selected in this review, $\log_{10}{}^{*}K^{\circ}_{s,0} = 8.7$, and $\log_{10} K_{s,(4m,m)} = -6.8$.



[1959MIT2]

The heat capacities of Th, U, Be, Na and a Pb-Bi alloy were determined from 323 to 973 K by two methods, the precise details of which are not clear. For thorium (99.81% purity), two measurements were made at 323 and 373 K by comparing the cooling rate with an unspecified standard, and ten measurements from 523 to 973 K in an electron radiation calorimeter. The uncertainties in the values were estimated by the author to be 1.5−2%.

The derived heat capacity values have an unusually high temperature coefficient and since there are many other, better documented data, these results have not been included in the data fitting.

[1959PET/WES]

The solubility of hydrogen in Th(cr) was examined from 573 to 1073 K by equilibration of saturated samples and subsequent analysis. The solubility increased from about

1 atom% at 573 K to about 20 atom% at 1073 K, being given by the expression $\log_{10}(\text{atom\% H}) = -1732/T + 2.966$ for crystal bar thorium metal (main impurities: 170 ppm C, 200 ppm O and 135 ppm Fe).

[1959TAN/LU4]

A solution with constant $Th(NO_3)_4$ concentration of 0.0251 M was mixed with different concentrations of NaF at (25 ± 0.1)°C to obtain molar ratios of F to Th of 1 to 10. The solubility and solid phase characterisations of the resulting precipitates were investigated at pH values ranging from 2.52 to 6.30. The solubility results are presented in a tabular form. The authors did not detect any soluble Th at F:Th ratios of > 4.0 and the aqueous Th concentrations at F:Th ratios of < 1.5 are very similar to the Th added initially. The authors report the presence of colloids at F:Th ratios of < 3.8. The authors do not report any thermodynamic data, nor can any thermodynamic data be calculated because of the paucity of data points (only 4 points), lack of evidence for the presence of solid phase, and of equilibrium in this system. However, the authors provide convincing evidence, based on chemical, thermogravimetric, and X-ray diffraction analyses, that the compound that precipitates at higher NaF concentrations is $NaThF_5{\cdot}H_2O$.

[1959TAN/LU5]

The authors used test solutions consisting of $Th(NO_3)_4$ or mixtures of $Th(NO_3)_4$ and NaF to increase the solubility of $CaF_2(s)$. From the measured solubility they could then determine the equilibrium constants for the fluoro complexes of Th(IV). The ionic strength of the solutions was not controlled and varied from about 0.1 to 5 M. No evidence is presented as to whether equilibrium is attained, or not. The number of data points on which the thorium fluoro complexes are based is very limited. The data reported by the authors correspond to average values of $\log_{10} K_1 = 5.92$ and $\log_{10} K_2 = 8.68$ for the reactions $Th^{4+} + F^- \rightleftharpoons ThF^{3+}$ and $Th^{4+} + 2F^- \rightleftharpoons ThF_2^{2+}$ respectively and for reasons stated above, these values are not accepted by this review.

[1959TAN/LU6]

This paper describes the aqueous concentrations and solid phases observed upon addition of KF or NH_4F to solutions of 0.0025 M $Th(NO_3)_4$ at 25°C. The concentrations of KF or NH_4F varied from 0.0025 to 0.025 M. The authors report Th, F, pH, and specific conductance in a tabular form and also report chemical compositions and XRD data. Their data indicate the presence of similar compounds in both the K and NH_4 fluoride systems and report the formation of normal thorium fluorides (ThF_4) and complex double salts of the type MTh_2F_9 and M_2ThF_6 with the progressive increase in F concentrations in relation to $Th(NO_3)_4$. The authors neither report any thermodynamic constants nor can any such data be extracted from this study due to the difficulties similar to those discussed under the other studies reported by these authors ([1959TAN/LU4], [1959TAN/LU5]).

[1959ZIE]

The equilibrium constants for the reactions:

$$\mathrm{Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+} \tag{A.35}$$

$$\mathrm{Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2H^+} \tag{A.36}$$

have been determined at ionic strength 2.00 M using two different total concentrations of H^+, 1.00 and 2.00 M. The experiments were made using cation exchange at 25°C. At 1.00 M H^+ the test solutions were a mixture of $HClO_4$, H_2SO_4 and $NaClO_4$; at 2.00 M H^+ the test solutions were a mixture of $HClO_4$ and H_2SO_4. The total concentration of Th was around 10^{-5} M. The ion-exchange data were properly evaluated by assuring constant activity factors of the sorbed species by working at a constant load of the ion exchanger and taking both the sorption of Th^{4+} and $ThSO_4^{2+}$ into account. The data analysis indicated that the sorption of $ThSO_4^{2+}$ was negligible.

Zielen reports the following equilibrium constants for reactions (A.35) and (A.36):

$K((\mathrm{A.35}), 1.00\ \mathrm{M\ H^+}) = (167 \pm 9)$; $K((\mathrm{A.36}), 1.00\ \mathrm{M\ H^+}) = (3.63 \pm 0.21) \times 10^3$;

$K((\mathrm{A.35}), 2.00\ \mathrm{M\ H^+}) = (164 \pm 18)$; $K((\mathrm{A.36}), 2.00\ \mathrm{M\ H^+}) = (3.49 \pm 0.44) \times 10^3$.

These constants and their reported uncertainty at the 95% confidence limit are accepted by this review.

Zielen makes a comment on the formation of the complex $Th(SO_4)(HSO_4)^+$ suggested in [1951ZEB/ALT] and concludes that their data provide no evidence for the formation of this species; the present review agrees with this conclusion.

In a set of calorimetric experiments Zielen has determined the enthalpy of reaction for (A.35) and (A.36), together with the enthalpy of protonation of SO_4^{2-}. In order to evaluate the latter, Zielen used a dissociation constant of 0.084 for HSO_4^- from [1951ZEB/ALT]; this value is in fair agreement with the value 0.078 calculated at ionic strength 2.00 using the equilibrium constant and the ionic interaction coefficients selected in the NEA-TDB reviews. The proper corrections for heats of dilution and bulb breaking have been made in the calorimetric experiments. No test of the accuracy of the calorimetric procedure was made. However the measured enthalpy of protonation of sulphate, (5.54 ± 0.17) $\mathrm{kcal \cdot mol^{-1}}$ ((23.18 ± 0.71) $\mathrm{kJ \cdot mol^{-1}}$) is in good agreement with the value 23.44 $\mathrm{kJ \cdot mol^{-1}}$, calculated from the enthalpy of formation of SO_4^{2-} and HSO_4^- selected in the NEA-TDB reviews. The experimental enthalpy of reaction for (A.35) and (A.36) from [1959ZIE]:

$$\Delta_r H_m((\mathrm{A.35}), 298.15, I = 2\ \mathrm{M}) = -(2.26 \pm 0.21)\ \mathrm{kJ \cdot mol^{-1}}$$

$$\Delta_r H_m((\mathrm{A.36}), 298.15, I = 2\ \mathrm{M}) = -(5.98 \pm 0.39)\ \mathrm{kJ \cdot mol^{-1}}$$

are accepted by this review.

This review calculated the values of $\log_{10}{}^{*}\beta_n^{\circ}$ at 25°C with the SIT model from the $\log_{10}{}^{*}\beta_n^{m}$ reported by [1959ZIE] using the relationship:

$$\log_{10}{}^{*}\beta_n^{\circ} = (\log_{10}{}^{*}\beta_n^{m} - \Delta z^2 D + \Delta\varepsilon I_m) \pm (\sigma\Delta\varepsilon I_m).$$

The SIT ion interaction parameters used in these calculations included $\varepsilon(\mathrm{Th}^{4+}, \mathrm{HSO}_4^-) \approx \varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4^-) = (0.70 \pm 0.10)$, $\varepsilon(\mathrm{H}^+, \mathrm{ClO}_4^-) = (0.14 \pm 0.02)$, and $\varepsilon(\mathrm{ThSO}_4^{2+}, \mathrm{ClO}_4^-) = (0.3 \pm 0.1)$ kg·mol^{-1} (for details about the selection of these parameters see Section IX.1.3.2). The $\log_{10}{}^{*}\beta_1^{\circ}$ (A.35) and $\log_{10}{}^{*}\beta_2^{\circ}$ (A.36) values thus determined are (4.15 ± 0.32) and (5.76 ± 0.25). These $\log_{10}{}^{*}\beta_n^{\circ}$ values are very similar to the values calculated from several other sources (*e.g.*, [1958MAI/FOM], [1951ZEB/ALT], [1972PAT/RAM]) and were used in deriving the final value selected in this review for these reactions. The experimental Th concentrations at different sulphate concentrations are compared in Table A-21 with the concentrations predicted by the aqueous phase model selected in this review (see Section IX.1.3.2).

Table A-21: Observed [1959ZIE] and predicted concentrations at 25°C for ion-exchange studies in 2.2 m $\mathrm{HClO_4}$-$\mathrm{H_2SO_4}$ media (data are plotted in Figure IX-3). Predicted concentrations are based on NONLINT-SIT modeling calculations using the thermodynamic data reported in Tables IX-2 and IX-5.

Experimental data (m)				Model predictions (m)				
H^+	SO_4^{2-} total	ClO_4^-	Th total	Th total	Th^{4+}	ThSO_4^{2+}	$\mathrm{Th(SO_4)_2(aq)}$	$\mathrm{Th(SO_4)_3^{2-}}$
2.204	1.173×10^{-3}	2.203	3.735×10^{-9}	3.514×10^{-9}	3.212×10^{-9}	2.987×10^{-10}	2.794×10^{-12}	0
2.204	2.358×10^{-3}	2.202	3.982×10^{-9}	3.824×10^{-9}	3.212×10^{-9}	6.007×10^{-10}	1.129×10^{-11}	0
2.204	4.716×10^{-3}	2.199	4.723×10^{-9}	4.461×10^{-9}	3.213×10^{-9}	1.203×10^{-9}	4.512×10^{-11}	1.150×10^{-13}
2.204	7.074×10^{-3}	2.197	5.008×10^{-9}	5.123×10^{-9}	3.213×10^{-9}	1.808×10^{-9}	1.015×10^{-10}	3.880×10^{-13}
2.204	9.432×10^{-3}	2.195	5.651×10^{-9}	5.808×10^{-9}	3.213×10^{-9}	2.414×10^{-9}	1.805×10^{-10}	9.197×10^{-13}
2.204	1.178×10^{-2}	2.193	6.909×10^{-9}	6.518×10^{-9}	3.213×10^{-9}	3.021×10^{-9}	2.819×10^{-10}	1.794×10^{-12}
2.204	2.244×10^{-2}	2.182	1.012×10^{-8}	1.004×10^{-8}	3.215×10^{-9}	5.793×10^{-9}	1.022×10^{-9}	1.239×10^{-11}
2.204	4.496×10^{-2}	2.161	1.939×10^{-8}	1.920×10^{-8}	3.217×10^{-9}	1.178×10^{-8}	4.101×10^{-9}	9.959×10^{-11}
2.204	5.609×10^{-2}	2.150	2.523×10^{-8}	2.460×10^{-8}	3.218×10^{-9}	1.481×10^{-8}	6.379×10^{-9}	1.933×10^{-10}
2.204	6.733×10^{-2}	2.139	3.019×10^{-8}	3.064×10^{-8}	3.219×10^{-9}	1.790×10^{-8}	9.191×10^{-9}	3.344×10^{-10}
2.204	7.845×10^{-2}	2.129	3.799×10^{-8}	3.725×10^{-8}	3.220×10^{-9}	2.102×10^{-8}	1.248×10^{-8}	5.289×10^{-10}
2.204	8.991×10^{-2}	2.118	4.349×10^{-8}	4.468×10^{-8}	3.222×10^{-9}	2.427×10^{-8}	1.639×10^{-8}	7.961×10^{-10}
2.204	1.009×10^{-1}	2.107	4.862×10^{-8}	5.245×10^{-8}	3.223×10^{-9}	2.745×10^{-8}	2.065×10^{-8}	1.126×10^{-9}
2.204	1.122×10^{-1}	2.096	5.749×10^{-8}	6.102×10^{-8}	3.224×10^{-9}	3.074×10^{-8}	2.551×10^{-8}	1.547×10^{-9}
2.204	1.683×10^{-1}	2.042	1.102×10^{-7}	1.136×10^{-7}	3.230×10^{-9}	4.784×10^{-8}	5.733×10^{-8}	5.214×10^{-9}
2.204	2.243×10^{-1}	1.989	1.796×10^{-7}	1.836×10^{-7}	3.236×10^{-9}	6.620×10^{-8}	1.018×10^{-7}	1.235×10^{-8}

There is a close agreement between the predicted and the experimental data. Graphical comparisons are presented in Figure IX-3, Section IX.1.3.2.

[1960DAN]

The author has measured the distribution of trace amount of Th(IV) between an aqueous phase and a nitrate-loaded anion exchanger to determine equilibrium constants in the Th(IV)-nitrate system. The method used to evaluate the experimental data are from Marcus and Coryell [1959MAR/COR]. The experimental study was made by measuring the distribution coefficient for Th(IV) between an ion-exchanger and test solutions in which the concentration of $LiNO_3$ was varied between 1.55 and 8.44 M; there is no information on the temperature at which the experiments were performed. The ionic strength of the test solutions is not constant and the activity coefficients of reactants and products will therefore vary; the variation in the (single-ion) activity coefficient of NO_3^- has been assumed to be the same as the mean activity coefficient of $LiNO_3$. When the concentration of the $LiNO_3$ in the aqueous phase varies, the invasion of $LiNO_3$ into the ion exchanger will vary, leading to different concentrations (and activity) of $LiNO_3$ in the resin phase, a factor that also must be taken into account when evaluating the experimental data (the method to do this is from Marcus and Coryell).

The net result of the experimental study is a distribution curve $\log_{10}D$ *vs* the activity of NO_3^-, a curve that has a maximum where the concentration of the uncharged complex $Th(NO_3)_4(aq)$ has its maximum value. The decrease of $\log_{10}D$ at lower nitrate concentration is due to the dissociation of the uncharged complex to form cationic complexes; the decrease at higher nitrate concentrations to the formation of anionic complexes. The experimental method is accordingly very similar to the measurement of the distribution of an uncharged complex between an aqueous and an organic phase. The important difference is that the control of the activity factors is much more difficult in the anion exchange method.

Danon reports equilibrium constants for the following reactions:

$$Th(NO_3)_4(aq) \rightleftharpoons Th(NO_3)_3^+ + NO_3^- \qquad \log_{10}K = 0.22$$

$$Th(NO_3)_4(aq) + NO_3^- \rightleftharpoons Th(NO_3)_5^- \qquad \log_{10}K = -(0.80 \pm 0.17)$$

$$Th(NO_3)_4(aq) + 2NO_3^- \rightleftharpoons Th(NO_3)_6^{2-} \qquad \log_{10}K = -(1.70 \pm 0.22).$$

Danon points out that the data can also be described with a model where no cationic complexes are formed. The key conclusion of this study is that the uncharged complex $Th(NO_3)_4(aq)$ is predominant when the activity of the nitrate is about 0.5 M and that anionic complexes are formed at higher nitrate activities. In the analysis of the experimental data, Danon has not considered the variation of the activity coefficients of the thorium species participating in the reactions and there is no justification for this approximation. Because of this, the present review has not accepted the equilibrium constants proposed by Danon. It should be noted that the experimental mean-activity coefficients of thorium nitrate solutions can be well described by the simple SIT model without any assumptions of complexes up to nitrate concentrations of 3.5 m ([2006NEC/ALT], see Figure X-1). However, there is structural evidence for the formation of nitrate coordination, *cf.* Section X.1.3.3 and [1968JOH], [1968JOH2], [1991JOH/MAG].

[1960DAR]

The equilibrium pressures of SiF_4 for the reaction:

$$ThF_4(cr) + SiO_2(cr) \rightleftharpoons ThO_2(cr) + SiF_4(g)$$

were measured from 871 to 1077 K.

ThF_4(cr) was purified by heating *in vacuo* at 873 K for 16 h, giving material with 75.3 and 25.4 wt% Th and F, as compared with the theoretical values of 75.33 and 24.67. Finely particulate SiO_2 was prepared from SiF_4(g) and fired at 1073 K. ThO_2 powder of 99.8 wt% purity was heated to 973 K *in vacuo.*

Seventeen measurements were made on hydraulically pressed mixtures of equimolar amounts of ThF_4(cr) and SiO_2(cr), broken into *ca.* 1 mm cubes, and gave equilibrium pressures of SiF_4(g) in 2 − 4 h. There was satisfactory agreement between the pressures approached from pressures higher and lower than the equilibrium value.

There are two minor problems with interpreting these data. Firstly, the polymorph of silica involved in the reaction is unknown. However, the Gibbs energies of formation of the polymorphs of silica do not differ greatly and we have taken the phases to be α- or β-quartz (although it is more likely to have been an amorphous form) and increased the uncertainty of the derived enthalpy of formation.

A more serious problem is that ThF_4(cr) and SiO_2(cr) are not the equilibrium phases in this system, since $ThOF_2$(cr) is a stable phase, although its preparation needs temperatures of 1173 − 1273 K. Darnell in fact found traces of $ThOF_2$(cr) in his quenched samples. However, the pressures in two measurements of the reverse reaction (ThO_2 reacting with SiF_4(g)) were in good accord with those of the forward reaction. Moreover, Darnell also measured the pressures in the reaction of SiO_2 and $ThOF_2$(cr) (presumably from the reaction $2ThOF_2(cr) + SiO_2(cr) \rightleftharpoons 2ThO_2(cr) + SiF_4(g)$) which are lower than those in the current study. However, these data are not quoted by the author.

The reaction involved was thus probably that postulated by the author, $ThOF_2$(cr) not being formed for kinetic reasons. The data have been processed by the third-law method to give a value for $\Delta_f H_m$ (ThF_4, cr, 298.15 K).

[1960DAR2]

The equilibrium pressure of ThF_4 from the decomposition of $ThOF_2$ was measured in a Knudsen effusion cell from 1109 to 1286 K. The $ThOF_2$ was prepared by heating a mixture of fine ThO_2(cr) and ThF_4(cr) powders to 1173 K in an argon atmosphere for 16 h. The decomposition pressures were only about a factor of two smaller than the vapour pressure of pure ThF_4(cr) measured by the same authors [1958DAR/KEN], and agree excellently with those measured more recently by Lau *et al.* [1989LAU/HIL]. The results were processed by the second-law to give the enthalpy of formation and standard entropy of the oxyfluoride. The oxyfluoride is only marginally stable with respect to ThO_2(cr) and ThF_4(cr).

[1960DAR/MCC]

The vapour pressure of Th(cr) was measured at 1757 − 1956 K by the Langmuir method. Special purification of the thorium was necessary since traces of ThO_2 react with Th to give ThO(g). The vapour pressure equation is $\log_{10} p(\text{Th})/\text{bar} = -(28780 \pm 620)/T + (5.997 \pm 0.333)$.

This is a good study which recognised the importance of ThO(g) in the vaporisation even of nominally high purity thorium, before the application of mass-spectrometry to such systems. Residual oxygen in the vacuum system is also gettered by Th(cr) to form ThO(g). Darnell *et al.* attempted to reduce the oxygen contamination (initially ~ 1000 ppm) of their sample by volatilisation of ThO(g) for 200 h at 1883 K; however their sample still contained 30 ppm oxygen, and subsequent work by Ackermann and Rauh [1972ACK/RAU] suggest that their measured pressures are too high by about a factor of three, due to residual ThO(g) in the vapour. Second and third-law analyses of their data by this review give $\Delta_f H^\circ_m$ (Th, g, 298.15 K) = (561.5 ± 23.7) $\text{kJ}\cdot\text{mol}^{-1}$ and (581.5 ± 5.0) $\text{kJ}\cdot\text{mol}^{-1}$ respectively, somewhat lower than the selected value, owing to the presence of ThO(g) in the vapour.

[1960FIL/TEK]

The solubility of ThP_2O_7(s) at 20°C was determined in solutions of $Na_4P_2O_7$ and also in three acid solutions, by using a radioactive thorium tracer. The solid phase was characterised by elemental analysis prior to the equilibration and also after equilibrium had been attained.

In one set of experiments the authors measured the solubility as a function of the total concentration of HCl, HNO_3 and H_2SO_4, respectively. For a variation of the total concentrations of acid in the range 0.1 − 0.5 M the solubility varied between 4×10^{-4} and 8×10^{-4} M in the sulphuric acid system; between 0.5×10^{-4} and 5×10^{-4} M in the nitric acid system and between 0.1×10^{-4} and 2×10^{-4} M in the hydrochloric acid system. As the chloride and nitrate complexes of Th(IV) are weak one would not expect that the solubility would be systematically different in these two systems. The solubility in the sulphuric acid is only a factor of two larger than the solubility in the nitrate system and here one would expect a larger difference because of the strong sulphate complexation. The authors have not made any attempt to calculate the solubility product of the solid. The experiments in the $Na_4P_2O_7$ test solutions were made at four different total concentrations of $Na_4P_2O_7$ of 0.0237, 0.0475, 0.0055 and 0.2040 M, but with no information on the pH in the test solutions used; the measured solubility in these solutions was 0.0205, 0.0433, 0.0320 and 0.0077 M, respectively. The variation in the solubility is small, the pH unknown and it is therefore not possible to determine a solubility product from these data. The measured solubility in [1960FIL/TEK] differs very significantly from that obtained in [1967MER/SKO], in 0.1 M $HClO_4$. Filinov *et al.* observed that a mixed solid phase consisting of $Th_2P_2O_7(s)$ and $Na_4Th(P_2O_7)_2(s)$ is formed at concentrations of $Na_4P_2O_7$ higher than 0.0475 M. The authors compared conductivity measurements in pure $Na_4P_2O_7$ solutions and test solutions of $Na_4Th(P_2O_7)_2$ and derived an "approximate" equilibrium constant of $\log_{10} K = -(5.25 \pm 0.17)$ for the dissociation of $Th(P_2O_7)_2^{4-}$ into $ThP_2O_7(aq) + P_2O_7^{4-}$. This value corresponds to a stepwise complexation constant of $\log_{10} K_2 = (5.25 \pm 0.17)$ for the reaction:

$$ThP_2O_7(aq) + P_2O_7^{4-} \rightleftharpoons Th(P_2O_7)_2^{4-}.$$

They also note that the reaction takes place with a decrease of about 1.5 pH units. The present review suggests that this is an indication that ternary complexes containing hydroxide might be formed. The pH in the $Na_4P_2O_7$ test solutions vary between approximately 8.8 and 9.5 and in this range the concentration of protonated $H_xP_2O_7^{x-4}$ species is significant. These facts demonstrate that the stoichiometry of the complexes formed has not been ascertained and accordingly no equilibrium constants can be determined. The only conclusion to be drawn from this study is qualitative, that complexes are formed in the Th(IV)-pyrophosphate system.

[1960LAN/DAR]

Landis and Darnell [1960LAN/DAR] attempted to obtain the Gibbs energy of formation of $ThI_4(cr)$ by measuring the 'equilibrium' pressure of $TiI_4(g)$ in the reaction:

$$ThI_4(cr) + TiO_2(cr) \rightleftharpoons ThO_2(cr) + TiI_4(g)$$

from 637 to 745 K by Knudsen effusion. However, as with the similar reaction involving the fluorides (with silica), $ThI_4(cr)$ and $ThO_2(cr)$ can never coexist in true equilibrium. This effect is much more serious in the present case since $ThOI_2(cr)$ is quite stable with respect to decomposition to $ThO_2(cr)$ and $ThI_4(cr)$, whereas $ThOF_2(cr)$ is only just stable with respect to the similar decomposition. In fact, in the light of present knowledge on the stabilities of $ThI_4(cr)$ and $ThOI_2(cr)$ (see Sections VIII.4.1.2 and VIII.4.1.5) it is clear that the initial reaction between the reactants used:

$$2ThI_4(cr) + TiO_2(cr) \rightleftharpoons 2ThOI_2(cr) + TiI_4(g)$$

will have an equilibrium pressure in excess of one atmosphere even at room temperature. Thus $ThOI_2(cr)$ was probably formed during the initial heating and the reaction studied by Landis and Darnell was most likely

$$2ThOI_2(cr) + TiO_2(cr) \rightleftharpoons 2ThO_2(cr) + TiI_4(g) \qquad (A.37)$$

Their Gibbs energies near the centre of their temperature range are represented by the equation:

$$[\Delta_r G_m]_{640\text{K}}^{750\text{K}} ((\text{A}.37), T) = 208332 - 230.147\,T\ (\text{J}\cdot\text{mol}^{-1}).$$

The scatter in the experimental data is quite pronounced and the temperature range quite short, so these values have appreciable uncertainty. However, the derived enthalpy of reaction at 700 K, (208.3 ± 10.5) kJ·mol^{-1} overlaps, within the combined uncertainties, with that calculated for Reaction (A.37), (194.7 ± 10.4) kJ·mol^{-1}, assuming the heat capacity of $ThOI_2$(cr) is the mean of those of ThO_2(cr) and ThI_4(cr). The data have, therefore, been used to provide an estimate of the entropy of $ThOI_2$(cr) – see Section VIII.4.1.5.

[1960MAT/ABR]

This paper presents a different approach to study hydrolysis; the authors have used the well-known fact that the addition of metal ions to lyotropic colloids of AgI, AgBr and AgCl results in coagulation, where the coagulation point is determined by the charge of the metal ion (or a charged complex). The metallic ion concentration where coagulation takes place can be estimated from the turbidity of the test solutions. An important feature of this method is that only very small concentrations of metal ions are necessary; in this study the thorium concentrations are in the range 10^{-6} M. Matijević *et al.* noticed that the coagulation point varied with pH and ascribed this to a change in charge of the species causing the coagulation. At pH < 4 they suggested that the metal species had a charge of +4 and at pH around 7 a charge of +3. It is reasonable to assume that only mononuclear hydroxide complexes are formed at these low Th-concentrations and pH < 5. At low pH, the observations are consistent with proposed hydrolysis data, but not at high pH. At pH > 5 the Th concentration of 10^{-6} M exceeds the solubility of $Th(OH)_4$(am) by 1 – 2.5 orders of magnitude which result in the formation of approximately uncharged Th(IV) polymers/colloids which remain dissolved in solution (*cf.* [2004ALT/NEC]), if they are not sorbed on the container walls. This study does not provide quantitative information on equilibrium constants, but gives qualitative support for the formation of hydroxide complexes.

The authors also noticed that a reversal of charge of the colloids could take place, but not in test solutions containing Th^{4+}, only at higher pH where thorium hydroxide complexes were formed. This observation is important for the modelling of Th sorption on colloidal systems. For negatively charged colloids like AgI, AgBr and AgCl the presence of coordinated hydroxide groups seems to result in a strong sorption of positively charged thorium hydroxide complexes and accordingly charge reversal of the colloids.

[1960MAY/OWE]

Mayer *et al.* reported enthalpy increment data for $Th(SO_4)_2(cr)$ from 623 to 897 K, from which they derived the following heat capacity equation, assumed to apply down to 298.15 K:

$$[C_{p,\mathrm{m}}]_{298.15\,\mathrm{K}}^{900\,\mathrm{K}}\,(\mathrm{Th(SO_4)_2},\ \mathrm{cr},\ T) = 104.6 + 23.096\times10^{-2}\,T \qquad (\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}})$$

These data have been adopted.

The authors also report the decomposition pressures for the reaction $Th(SO_4)_2(cr) \rightleftharpoons ThO_2(cr) + 2SO_2(g) + O_2(g)$ from 908 to 1057 K. Although Mayer *et al.* did not show that the $SO_2(g)/O_2(g)$ ratio was 2:1, to demonstrate unambiguously that the above equilibrium was in fact being studied, they did analyse the samples after the experiments and could not detect any solid solution or oxysulphate. The equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons SO_3(g)$ was established in the gas phase by the presence of a platinum coil in the gas stream. The equilibrium constants for the reaction calculated by the review, including the correction for the presence of the small amount of $SO_3(g)$, using values from Table IV-1 and [1989GUR/VEY], agree closely with those given in the paper. Lacking a reliable entropy value for $Th(SO_4)_2(cr)$, we are forced to utilise a second-law treatment of the data, recognising that the derived values must have considerable uncertainty owing to the small temperature interval. With the thermal data for $ThO_2(cr)$ from the present assessment and for $SO_2(g)$ and $O_2(g)$ from the Table IV-1, we finally derive the following values: S°_{m} ($Th(SO_4)_2$, cr, 298.15 K) = (146.3 ± 4.9) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ ($Th(SO_4)_2$, cr, 298.15 K) = $-(2543.2 \pm 4.9)$ $\mathrm{kJ{\cdot}mol^{-1}}$ and hence $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}$ ($Th(SO_4)_2$, cr, 298.15 K) = $-(2307.4 \pm 5.1)$ $\mathrm{kJ{\cdot}mol^{-1}}$. However, as discussed in Section IX.1.3.1, this Gibbs energy of formation corresponds to a very low (hypothetical) solubility of $Th(SO_4)_2(cr)$ to (predominantly) $Th(SO_4)_2(aq)$ and thus has not been selected by the review. The reason for the considerable discrepancy is not clear.

[1960MUH/VAU]

Aqueous solutions of $MOX_2{\cdot}8H_2O$, where M = Zr, Hf and X = Cl or Br have been studied using large angle X-ray scattering. The total concentrations of the test solutions were 0.5, 1.0, 1.5 and 2 m for $HfOCl_2$ and 2 molal for the remaining solutions. The radial distribution functions have been derived and used to deduce a structure model that is the same for all systems and consists of a square arrangement of metal ions, linked by double hydroxide bridges. The coordination number of the M^{4+} ions is eight, four bridging OH^- ions and four water molecules; the halide ions are located in the second coordination sphere. The M–M distance is 3.57 Å and the M–O distance 2.24 Å, the same as in crystalline $ZrOCl_2{\cdot}8H_2O$. The authors suggest a square antiprism geometry around M, this is chemically reasonable, but information of this type cannot be deduced from these experimental data. Because of the chemical similarity between Zr, Hf and Th, this study provides a model for the structure of tetranuclear $[Th_4(OH)_8]^{8+}$ hydroxide complex.

[1960WAL]

The heat capacity of high-purity thorium wires (*ca*. 150 ppm non-metallic elements) has been measured from room temperature to 1273 K, using an electrical pulse-heating method. The sample was held *in vacuo* in a furnace, at 1273 K, and cooled slowly at *ca*. 40 K·hr^{-1}, during which it was periodically pulsed electrically and the rate of temperature change monitored. The heat capacity was evaluated at about 25 data points for each of ten pulses used, but the only a table of the fitted values at round temperatures are given. The uncertainty in $C_{p,\text{m}}$ is estimated by the authors to be 2% at most.

As noted in Section V.1.2 although these data agree well with one set of low-temperature data (by [1953GRI/SKO]) near room temperature, the results of subsequent measurements indicate that they are somewhat too high over the whole temperature range, and they have not been included in the data fitting.

[1960YOS]

In this Progress Report, Yosim reports preliminary details of a study of the decomposition pressure of ThI_4(g) above ThI_3(cr) and ThI_2(cr) (presumably, in practice, the {ThI_3(cr) + ThI_2(cr)} and {ThI_2(cr) + Th(cr)} diphasic fields). At an unspecified temperature, the pressures of ThI_4(g) above the two compounds/phase fields are reported to be 0.15−0.20 and 0.004 times the sublimation pressure of pure ThI_4(cr). He suggests that the results indicate that the Gibbs energy of formation of ThI_4(cr), ThI_3(cr), ThI_2(cr) per iodine atom are very similar, which would be consistent with the phase diagram of [1964SCA/WYL].

There is insufficient detail in the paper to derive any more quantitative data from this study

[1961BUC/BER]

Samples of ThF_4 and $ThCl_4$ were heated to 1475 and 950 K respectively to observe their infrared spectrum. The observed values of the stretching frequencies were 520 and 335 cm^{-1} respectively. The values for the zirconium and hafnium halides agreed closely with earlier measurements. The frequencies of the bending vibration, also active in the infrared, were lower than the cut-off (*ca.* 200 cm^{-1}) of the CsI prism used in the spectrometer.

[1961CAT/RAU]

In a mass-spectrometric study of the vapour effusing from a sample of US(cr) contained in tungsten, Cater *et al.* [1961CAT/RAU] tentatively attributed a weak peak at mass number 264 to ThS(g) from adventitious thorium impurity in the system.

[1961CHE/GOL2]

The paper describes the preparation of $[NH_4]_6[Th(CO_3)_5]\cdot 3H_2O$ and the characterisation of this phase; no thermodynamic data are reported.

[1961DAR/MCC]

The evaporation behaviour of the Th-O system was studied from 1984 to 2564 K, using mass-loss Knudsen effusion measurements on the dioxide phase and {liquid metal + dioxide} mixtures.

The thorium used was stated to be of 99.8% purity, but no details of the analysis are given. The mass effusion rate from ThO_2(cr) contained in a thoria-lined tungsten effusion cell was measured from 2268 to 2593 K (13 points) and from mixtures of Th(cr, l) and ThO_2(cr) from 1984 to 2564 K (35 points, rather scatted data). A mass-spectrometric study of the vaporisation from {Th(l) + ThO_2(cr)} mixtures from tungsten cells showed that the vapour was predominantly ThO(g), but at 2125 K, ion currents attributed to Th(g) were observed. The vaporisation of ThO_2(cr) was not apparently studied mass-spectrometrically, and the reaction was assumed to be simple vaporisation to ThO_2(g). The derived equations for the pressures were $\log_{10} p_{\mathrm{ThO_2(g)}}/\mathrm{bar} = -(22.210 \pm 680)/T + (4.69 \pm 0.31)$ from {Th(l) + ThO_2(cr)} mixtures (corrections were made for the calculated contributions of Th(g) and ThO_2(g) to the total pressure) and $\log_{10} p_{\mathrm{ThO_2(g)}}/\mathrm{bar} = -(35.460 \pm 1140)/T + (8.17 \pm 0.47)$ from ThO_2(cr).

The authors also determine the solubility of oxygen in Th(l), reporting values of 3.5 wt% ThO_2 at 2090 K and of 8.2 wt% ThO_2 at 2450 K. These values are reasonably consistent with the later data of Benz [1969BEN].

These data have been used by the review to calculate the Gibbs energies of formation of ThO(g) and ThO_2(g), by third-law processing. For ThO(g), the calculated value of $\Delta_f H_m^\circ$ (ThO, g, 298.15 K) is $-(28.6 \pm 23.3)$ kJ·mol^{-1}, where the uncertainty is the 2σ statistical value only. Inclusion of the experimental uncertainties is estimated to increase this to 23.5 kJ·mol^{-1}. For ThO_2(g), the calculated value of $\Delta_f H_m^\circ$ (ThO_2, g, 298.15 K) is $-(459.5 \pm 12.0)$ kJ·mol^{-1}, where the uncertainty is again the 2σ statistical value only. Inclusion of the experimental uncertainties is estimated to increase this to 15.0 kJ·mol^{-1}. But this value of $\Delta_f H_m^\circ$ (ThO_2, g, 298.15 K) does not take into account the fact that there are small amounts of ThO(g) and O(g) in the vapour, so will be slightly too low.

[1961HAR/MOO]

The authors report measurements of the enthalpies of combustion of UOS(cr), ThOS(cr), α-US_2(cr), and ThS_2(cr). ThOS(cr) and ThS_2(cr) were prepared from reaction of ThO_2(cr) in flowing H_2S(g) in a graphite crucible at 1773 K. Although they report that the powder diffraction data show no impurities and that the products were analysed using various methods, no details of these analyses are given. Also mentioned are the measurements of the average $C_{p,\mathrm{m}}$ values necessary for the calculation of the enthalpies of formation at 298.15 K. The $C_{p,\mathrm{m}}$ values reported for the thorium compounds are $[C_{p,\mathrm{m}}]^{773\mathrm{K}}_{298.15\mathrm{K}}$ (ThO$_2$, cr) = (74.1 ± 2.2) J·K^{-1}·mol^{-1}, $[C_{p,\mathrm{m}}]^{773\mathrm{K}}_{298.15\mathrm{K}}$ (ThOS, cr) = (76.6 ± 2.3) J·K^{-1}·mol^{-1}, and $[C_{p,\mathrm{m}}]^{773\mathrm{K}}_{298.15\mathrm{K}}$ (ThS$_2$, cr) = (72.8 ± 2.2) J·K^{-1}·mol^{-1}, where the authors' given uncertainties (1.5%) have been doubled. However, the selected data for ThO$_2$(cr), based on a number of consistent studies (see Section VII.1.2.2) give a mean heat capacity of 69.9 J·K^{-1}·mol^{-1} for this temperature range, so the authors may have underestimated their errors. It will be noted also that the mean heat capacities do not follow the sequence expected for a series of non-magnetic solids, $C^{\circ}_{p,\mathrm{m}}$ (ThO$_2$,cr) < $C^{\circ}_{p,\mathrm{m}}$ (ThOS, cr) < $C^{\circ}_{p,\mathrm{m}}$ (ThS$_2$,cr).

The following enthalpies of formation for the two thorium compounds are given without any details of the experimental results or method of calculation: $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (ThOS, cr, 298.15 K) = −(862 ± 26) kJ·mol^{-1} and $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (ThS$_2$, cr, 298.15 K) = – (816 ± 24) kJ·mol^{-1}. However, the value of $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (ThS$_2$, cr) is almost certainly too negative, since these values would indicate that the enthalpy of the decomposition reaction:

$$2\mathrm{ThOS(cr)} \rightleftharpoons \mathrm{ThO_2(cr)} + \mathrm{ThS_2(cr)} \qquad \text{(A.38)}$$

becomes $\Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}$ ((A.38), 298.15 K) = −(318 ± 57) kJ·mol^{-1}, using $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}$ (ThO$_2$, cr, 298.15 K) = −(1226.4 ± 3.5) kJ·mol^{-1} selected in this review. Since the entropy change in this all-solid reaction will be small, this would imply ThOS(cr) would never be easily formed from these solids (*cf.* [1984AMO/BLA2]). In view of these notable inconsistencies, the data of [1961HAR/MOO] are not considered in this review.

[1961HOC/JOH]

The enthalpies (referred to 0°C) of Al$_2$O$_3$ (corundum) and of ThO$_2$(cr) were determined in the range 1555 to 2278 and 1456 to 2753 K, respectively by drop calorimetry.

The sample of thoria used was the same as that used in the vapour pressure study [1954HOC/JOH] by the same authors. No further analysis is given. It was held in a tantalum container, with which "only very slight reaction was observed between ThO$_2$ and the tantalum holder".

Six measurements were made, extending from 1456 to 2753 K. They agree very well with other experimental data and were included in the data fitting.

[1961KOV/BAG2]

The solubility of Th(OH)$_4$(s) was measured at 22°C in test solutions of different pH adjusted in the range of 3 to 5 by adding HNO$_3$ to thorium hydroxide suspensions in water and 0.5 to 4 M KNO$_3$. After 24 hours of equilibration and phase separation by filtration or centrifugation (no further details given), thorium concentrations were measured colorimetrically using the organic reagent "thoron". No information is given on the determination of pH. The measured thorium concentrations were ascribed exclusively to

Th^{4+} without considering hydrolysis and the solubility product is calculated according to:

$$K_{sp} = [\mathrm{Th}^{4+}]\, K_\mathrm{w}{}^4 \times 10^{4\mathrm{pH}}$$

as a function of pH and Th concentration. From the linear extrapolation of the $-\log_{10} K_{sp}$ values in water to [Th] = 0, the authors derived the solubility product at zero ionic strength $\log_{10} K^\circ_{sp} = -44.7$. Applying similar graphical procedures to the $-\log_{10} K_{sp}$ values determined in 0.5−4 M KNO_3 the authors obtained an average value of $\log_{10} K^\circ_{sp} = -44.0$.

The calculated solubility products are based on erroneous assumptions and inadequate extrapolation procedures and the primary experimental data are not given. Only the experimental data in the experiments without background electrolyte (varying ionic strength) are shown in Figure 3 of [1961KOV/BAG2]. However, this figure is too small to extract the data. Therefore no quantitative information can be drawn from this study. When the pH in the test solutions decreased from about 3.6 to 3.2, there was a sharp increase in the solubility of thorium to a maximum value of about 3.5 mM. A further decrease in pH to 2.2 did not result in any additional increase in solubility.

[1961LUZ/KOV2]

The solubility in the system Th-Na_2CO_3-H_2O has been studied as a function of the total concentration of Na_2CO_3 at 25°C using $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ as the initial solid phase. The molality of Na_2CO_3 varied from 0.79 to 2.8 $\mathrm{mol\cdot kg^{-1}}$ and the concentration of dissolved Th and the composition of the solid phase in equilibrium with the solution were analysed. In the concentration range $0.79 < m_{\mathrm{Na_2CO_3}} < 2.4$ $\mathrm{mol\cdot kg^{-1}}$ the data indicate that the only solid phase present is $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$; at higher carbonate concentrations solid Na_2CO_3 is also present. Luzhnaya and Kovaleva observed that the solubility of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ decreased with increasing carbonate concentration; the only possible reasons for this is the increase of the concentration of $[Na^+]$ and changes in the activity coefficients. This review has therefore used the experimental data to calculate the concentration product $[Na^+]^6\,[Th(CO_3)_5]$ using the experimental data in Table 1 of [1961LUZ/KOV2]. The solubility constant $\log_{10} K^\circ_{s,5}$ at zero ionic strength for the reaction:

$$\mathrm{Na_6[Th(CO_3)_5]\cdot 12H_2O(s) \rightleftharpoons 6Na^+ + Th(CO_3)_5^{6-} + 12H_2O(l)} \qquad (A.39)$$

is calculated from the experimental data in 0.79−2.8 m Na_2CO_3 solution according to

$$\log_{10} K^\circ_{s,5} = 6\log_{10}[\mathrm{Na^+}] + \log_{10}[\mathrm{Th(CO_3)_5^{6-}}] - 42D + 6\,\varepsilon(\mathrm{Na^+},\mathrm{CO_3^{2-}})\cdot m_{\mathrm{CO_3^{2-}}} + \varepsilon(\mathrm{Th(CO_3)_5^{6-}},\mathrm{Na^+})\cdot m_{\mathrm{Na^+}} + 12\log_{10}a_w \qquad (A.40)$$

with $\varepsilon(\mathrm{Na^+},\mathrm{CO_3^{2-}}) = -(0.08 \pm 0.03)$ $\mathrm{kg\cdot mol^{-1}}$ and $\varepsilon(\mathrm{Th(CO_3)_5^{6-}},\mathrm{Na^+}) = -(0.30 \pm 0.15)$ $\mathrm{kg\cdot mol^{-1}}$.

Table A-22: Evaluation of $\log_{10} K^{\circ}_{s,5}$ ($Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$) from the solubility data of [1961LUZ/KOV2] at (25.0 ± 0.1)°C.

Solution composition (wt%)			Molality m_i (mol·kg^{-1} H_2O)					
Na_2CO_3	$Th(CO_3)_5$	H_2O	Na_2CO_3	$Th(CO_3)_5^{6-}$	I_m	a_w	$\log_{10} K_{s,5}$	$\log_{10} K^{\circ}_{s,5}$ [c]
22.55[a]	0.38	77.07	2.76	0.0093[b]	8.48	0.904		
22.60[a]	0.53	76.87	2.77	0.0130[b]	8.59	0.904		
22.70[a]	0.86	76.44	2.80	0.0211	8.85	0.903	2.87	– 12.36 ± 0.98[d]
22.97[a]	0.96	76.07	2.85	0.0237	9.04	0.902	2.97	– 12.35 ± 1.00[d]
22.81[a]	0.86	76.33	2.82	0.0212	8.90	0.903	2.89	– 12.38 ± 0.99[d]
20.02	1.01	78.98	2.39	0.0240	7.68	0.917	2.54	– 12.03 ± 0.84[d]
18.67	1.09	80.24	2.20	0.0255	7.12	0.923	2.35	– 11.88 ± 0.77[d]
14.57	1.34	84.09	1.63	0.0299	5.53	0.942	1.70	– 11.53 ± 0.57[d]
10.88	1.64	87.48	1.17	0.0352	4.26	0.958	0.99	– 11.33 ± 0.41
8.59	2.05	89.36	0.91	0.0431	3.63	0.968	0.53	– 11.25 ± 0.32
7.60	2.20	90.20	0.79	0.0458	3.35	0.971	0.29	– 11.25 ± 0.28

a: Solid Na_2CO_3 present (saturated solution).

b: $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ completely dissolved.

c: The large uncertainties arise from the ionic strength corrections (error propagation accounting for the uncertainties of the SIT coefficients)

d: At $I > 5$ mol·kg^{-1}, which is outside the validity range of the SIT, the calculated $\log_{10} K^{\circ}_{s,5}$ values show a systematic increase. They are not considered in the mean value accepted by this review.

For the calculation of the solubility constant and ionic strength, the increase of the Na^+ concentration and ionic strength caused by the dissolution of $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ is taken into account. The mean value from data at $I <$ 5 mol·kg^{-1}, $\log_{10} K^{\circ}_{s,5} = -(11.3 \pm 0.3)$, is used together with similar values derived from the study of [1973DER/FAU3] to select thermodynamic data for this solid phase.

[1961VIC/DOU2]

The enthalpy of thorium dioxide relative to 273.15 K was measured at ten temperatures from 323 to 1173 K. A Bunsen ice drop calorimeter was used to make the measurements on two samples of widely different bulk densities. The corresponding heat-capacity values for the higher density sample are represented within their uncertainty (estimated to be ± 0.3 to 0.5%) by the following equation:

$$C^{\circ}_{p,\mathrm{m}}(T) = 71.366 + 7.556\times10^{-3}\,T - 10.529\times10^{5}\,T^{-2} \quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}.$$

At 298.15 K this equation agrees well with previously reported low-temperature measurements made with an adiabatic calorimeter [1953OSB/WES]. Values of heat content, heat capacity, entropy, and Gibbs energy function are tabulated from 298.15 to 1200 K. These data were included in the data fitting.

[1962FAU/DER]

The constitution of the limiting complex in the Th(IV)-carbonate system has been determined using potentiometric titrations (measuring the free hydrogen ion concentration at different carbonate concentrations). The experiments have been made in a KNO_3 ionic medium, and the authors have only determined the equivalence point where the limiting complex is formed, but no equilibrium constants. The authors have tested different models and their titration curves are only consistent with the stoichiometry $Th(CO_3)_5^{6-}$; the compositions $Th(CO_3)_4^{4-}$, $Th(CO_3)_6^{8-}$ and $Th(CO_3)_4(OH)_2^{6-}$ were ruled out. There are few experimental details in this short communication and the experimental data can therefore not be reinterpreted by this review. However, the study seems well done and the suggested stoichiometry is considered reliable by this review.

[1962FAU/DER2]

The constitution of the thorium(IV) carbonate complex formed at high carbonate concentration has been determined by cryoscopy. This is a method that provides information about the number of solute particles in solution and for the case of complex formation reactions, the change in this number as a result of complex formation, *e.g.* for the reaction $Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-}$ there is a decrease of five. The authors have determined the molar freezing point depression and this is used to test the stoichiometry of the complexes formed. One important conclusion from this study is that the experimental data are only consistent with the stoichiometry $Th(CO_3)_5^{6-}$. Experimental data of this type cannot be made in a medium of constant ionic strength and it is also not possible to determine equilibrium constants. However, the proposed stoichiometry is in agreement with that proposed in a large number of other studies.

[1962KAR/VOL]

The authors have used IR spectroscopy and suggested that the compound $Na_6[Th(CO_3)_5]\cdot 12H_2O$ is a double-salt with the composition $Na_4[Th(CO_3)_4]\cdot Na_2CO_3\cdot 12H_2O$; X-ray structure data [1975VOL/RIM2], [1975VOL/RIM3] clearly demonstrate that this conclusion is in error and this review does not consider the use of qualitative IR data for structure and bonding assignments as reliable. There are no thermodynamic data in this study.

[1962NIK/LUK]

The solubility of thorium tetrafluoride was investigated as a function of $HClO_4$ molarity. The solid was precipitated by reacting thorium nitrate with hydrofluoric acid. The solid was suspended in test solutions with five fixed concentrations of $HClO_4$ ranging from 0.1 to 1.1 M at 25°C. The suspensions were stirred for 12 hours. Filtered solutions (unspecified pore size) were analysed for thorium gravimetrically by precipitation of the hydroxide and weighing as ThO_2. The authors report solubility in terms of ThF_4 ($g\cdot L^{-1}$) as a function of the $HClO_4$ concentrations. They also report the pH values for these samples. From these data they calculated the solubility product for the solid and the value of the equilibrium constant for ThF^{3+}. The values they report are based on data obtained in this study and the values of fluoride and hydroxide complexes of thorium from the literature, which in turn are based on different chemical systems and different ionic strengths.

This study was not conducted at a fixed ionic strength, so evidence for the equilibrium with the solid phase is lacking. As the reported values for the solubility product of ThF_4(cr, hyd) vary by 1.5 orders of magnitude, and values of thorium fluoride and hydrolysis constants from different chemical systems and ionic strengths were combined, this review does not consider the calculated solubility product (4.5×10^{-26} $(\text{mol}\cdot\text{L}^{-1})^5$) to be reliable.

[1962PEP/NAM]

This is a detailed study of the extraction equilibria in the toluene-Th(IV)-hydrogen 2-ethylhexyl phosphonate-Cl^-- NO_3^- systems. There is no quantitative information on the formation of complexes between thorium and Cl^- or NO_3^- in the aqueous phase, only a qualitative statement that $Th(NO_3)^{3+}$ and $Th(NO_3)_2^{2+}$ complexes are extracted to a much greater extent than the corresponding chloride complexes.

[1962PET/REX]

This paper mainly concerns the diffusion of hydrogen in the ThH_{2-x}(cr) phase, but the composition of this phase was also determined as a function of temperature and pressure of hydrogen from 773 to 1073 K. Crystal bar thorium, whose principal impurities were 0.145 wt% C and 0.19 wt% O was used. By using these data the diffusion coefficients of hydrogen in ThH_{2-x}(cr) were calculated from previous measurements of the parabolic reaction rate constants. Although no values for the equilibrium pressures in the {Th(cr) + ThH_{2-x}} region were quoted by the authors, Flotow *et al.* [1984FLO/HAS] have derived these values from the paper, and these are discussed in Section VII.2.1.2.2.

[1962PRA/DEY]

Prasad and Dey [1962PRA/DEY] performed potentiometric titrations of 0.005 to 0.05 M $ThCl_4$ solutions with NaOH solutions of different concentrations from pH 3 to pH 11 − 12 and reverse titrations by adding 0.04 and 0.08 M $ThCl_4$ to the NaOH test solutions at 27°C. Ionic strength was not kept constant and the calibration of the glass-calomel electrode system used to measure pH is not mentioned. The authors report only the qualitative results that precipitation occurs already at $\bar{n}_{OH} < 4$ (which is concluded from the inflection points of the titration curves) and that precipitation is complete near pH 7, independent of the thorium concentration. No thermodynamic data can be derived from this study.

[1963ACK/RAU]

The evaporation behaviour of the Th-O system was studied at *ca.* 2200 to 2900 K. The results of the effusion measurements of the dioxide phase and {liquid metal + dioxide} mixtures and a mass spectrometric investigation of the former were combined to yield an internally consistent set of thermodynamic data for the system.

The thorium used was of 99% purity, as established by spectroscopic analysis. The mass effusion rate from ThO_2(cr) contained in a tungsten effusion cell was measured from 2180 to 2871 K, both by collection, plus activation analysis, and, over a much smaller temperature range, by using a vacuum thermobalance. The results agreed excellently.

The solid dioxide evaporates congruently at all temperatures. Above 2800 K, the thoria in equilibrium with Th(l) showed a measurable but thermodynamically insignificant hypostoichiometry to a composition of $ThO_{1.998}$. The "effective" pressure, (*i.e.* the pressure assuming the vapour is composed entirely of ThO_2) is given by the equation $\log_{10} p_\mathrm{e}/\mathrm{bar} = -35500/T + 8.265$.

A mass-spectrometric study of the vaporisation from ThO_2(cr) from tungsten cells at temperatures from *ca.* 2500 to 2825 K showed that the vapour in fact contains similar amounts of ThO(g) and ThO_2(g).

In a limited study of the pressure of ThO(g) from Th(l) + ThO_2 mixtures, there were problems with movement of Th(l) out of or through the containing ThO_2 cup due to dissolution of ThO_2 in the melt, but reasonable success was achieved for the initial period of the runs.

These data were used to calculate the Gibbs energies of formation of ThO(g) and ThO_2(g), which are not quoted here, since there are now better data for the thermal functions of many of the substances concerned – see Sections VII.1.1.2 and VII.1.3.2. The data in this publication were also re-evaluated by [1973ACK/RAU2], using better defined values for $\Delta_\mathrm{f}G_\mathrm{m}$(ThO, g).

The reaction occurring in thoriated tungsten filaments was also discussed.

[1963ALL/MCD]

The authors have used a liquid ion exchanger, di-*n*-decylamine sulphate to determine the stepwise equilibrium constants at 25°C for the reactions:

$$\mathrm{Th(SO_4)_2(aq)} + \mathrm{SO_4^{2-}} \rightleftharpoons \mathrm{Th(SO_4)_3^{2-}} \qquad \text{(A.41)}$$

$$\mathrm{Th(SO_4)_2(aq)} + 2\mathrm{SO_4^{2-}} \rightleftharpoons \mathrm{Th(SO_4)_4^{4-}} \qquad \text{(A.42)}$$

The experiments have been made by varying the total concentrations of Th(IV) from 6.00×10^{-6} to 64.8×10^{-6} M in a mixed H_2SO_4-Na_2SO_4 medium with varying ionic strength. The acidity is sufficiently high to avoid significant hydrolysis of thorium. The composition of the organic phase has been kept very nearly constant in the different test solutions, ensuring that the activity of the extracted uncharged complex $Th(SO_4)_2$ is constant; as the two phases are in equilibrium the activity of this species in the aqueous phase is also constant. The experiments are made in such a way that $[Th(SO_4)_2]_{org}$ is kept constant by varying the total concentrations of thorium and sulphate. The equilibrium constants for Equations (A.41) and (A.42), $K_{2,3}$ and $K_{2,4}$ respectively, were calculated by using the mass balance equation:

$$Th_{tot} = [Th(SO_4)_2] + [Th(SO_4)_2][SO_4^{2-}]K_{2,3}G_{3,2} + [Th(SO_4)_2][SO_4^{2-}]^2K_{2,4}G_{4,2} \qquad (A.43)$$

$G_{3,2}$ and $G_{4,2}$ are activity correction factors calculated by using the Debye-Hückel term for the reactions and assuming this to be equal to unity for the uncharged complex. The total concentration of thorium is so low that it does not have any significant effect on the mass balance for sulphate. Allen and McDowell report $K_{2,3}$ (A.41) = (5.7 ± 1.2) and $K_{2,4}$(A.42) = (0.054 ± 0.009), where the errors are at the 95% confidence limit and refer to zero ionic strength.

The changes in the composition of the aqueous phase in these experiments are very large from 0.094 M H_2SO_4/0.006 M Na_2SO_4 to 0.190 M H_2SO_4/1.30 M Na_2SO_4 and there is no reason to assume that the simple Debye-Hückel term will provide an accurate description the variation in the activity coefficients of sulphate and the negatively charged Th(IV) complexes. The experimental data in [1963ALL/MCD] therefore need to be reinterpreted.

The NONLINT-SIT code (Appendix D) was used for this, with $\Delta_f G_m^o / RT$ values of $-(598.638 \pm 0.737)$ for $ThSO_4^{2+}$ and of $-(906.869 \pm 0.622)$ for $Th(SO_4)_2(aq)$, selected in this review. These values are based on several other sources and ion interaction parameters $\varepsilon(Na^+, SO_4^{2-})$ and $\varepsilon(Na^+, HSO_4^-)$ from [2003GUI/FAN], and making the reasonable assumptions that the ion interaction parameters $\varepsilon(H^+, Th(SO_4)_3^{2-})$ and $\varepsilon(H^+, HSO_4^-)$ are approximately equal, respectively to $\varepsilon(Li^+, SO_4^{2-})$ and $\varepsilon(H^+, ClO_4^-)$ (as reported by [2003GUI/FAN]). The values of $\Delta_f G_m^o / RT$ for $Th(SO_4)_3^{2-}$ and $\varepsilon(Na^+, Th(SO_4)_3^{2-})$ were fitted simultaneously using the known equilibrium constants for the formation of $Th(SO_4)^{2+}$ and $Th(SO_4)_2(aq)$ and the interaction coefficients mentioned above (for details see Section IX.1.3.2). These analyses provided a $\Delta_f G_m^o / RT$ value of $-(1209.432 \pm 0.086)$ for $Th(SO_4)_3^{2-}$ and $\log_{10} \beta_3^o$ = (10.748 ± 0.076), and $\varepsilon_1(Na^+, Th(SO_4)_3^{2-})$ = (0.091 ± 0.038) $kg \cdot mol^{-1}$, which were selected in this review. Predicted concentrations, using the aqueous phase model selected in this review, are compared against the experimental data in Figure IX-2 (see Section IX.1.3.2) and the details are provided in Table A-23. A close agreement is observed between the predicted and experimentally observed Th concentrations. These comparisons (Figure IX-2) show that $Th(SO_4)_3^{2-}$ is the dominant species in this experiment and this species was selected for calculations involving solubilities of different Th-sulphate solids (Section IX.1.3.3) where this species is dominant and is needed for interpretation of solubility data.

Table A-23: Observed [1963ALL/MCD] and predicted aqueous thorium concentrations at 25°C for solvent extraction studies in Na_2SO_4 (data are plotted in Figure IX-2).

Experimental concentrations (m)			Predicted concentrations (m)				
Na^+ total	SO_4^{2-} total	Th total $\times10^5$	Th total $\times10^5$	Th^{4+} $\times10^5$	$ThSO_4^{2+}$ $\times10^5$	$Th(SO_4)_2(aq)$ $\times10^5$	$Th(SO_4)_3^{2-}$ $\times10^5$
1.210×10^{-2}	1.010×10^{-1}	6.003×10^{-1}	6.479×10^{-1}	1.497×10^{-4}	5.971×10^{-2}	4.619×10^{-1}	1.261×10^{-1}
3.620×10^{-2}	1.170×10^{-1}	6.363×10^{-1}	6.732×10^{-1}	1.389×10^{-4}	5.453×10^{-2}	4.619×10^{-1}	1.566×10^{-1}
8.040×10^{-2}	1.420×10^{-1}	7.393×10^{-1}	7.230×10^{-1}	1.282×10^{-4}	4.836×10^{-2}	4.619×10^{-1}	2.126×10^{-1}
1.710×10^{-1}	1.920×10^{-1}	8.793×10^{-1}	8.469×10^{-1}	1.181×10^{-4}	4.073×10^{-2}	4.619×10^{-1}	3.442×10^{-1}
1.910×10^{-1}	2.020×10^{-1}	9.523×10^{-1}	8.778×10^{-1}	1.164×10^{-4}	3.945×10^{-2}	4.619×10^{-1}	3.763×10^{-1}
2.620×10^{-1}	2.430×10^{-1}	1.060	9.915×10^{-1}	1.163×10^{-4}	3.650×10^{-2}	4.619×10^{-1}	4.930×10^{-1}
3.730×10^{-1}	3.040×10^{-1}	1.210	1.185	1.177×10^{-4}	3.329×10^{-2}	4.619×10^{-1}	6.899×10^{-1}
7.290×10^{-1}	4.970×10^{-1}	1.830	1.843	1.328×10^{-4}	2.897×10^{-2}	4.619×10^{-1}	1.352
9.430×10^{-1}	6.110×10^{-1}	2.160	2.265	1.413×10^{-4}	2.766×10^{-2}	4.619×10^{-1}	1.775
1.137	7.140×10^{-1}	2.620	2.651	1.485×10^{-4}	2.689×10^{-2}	4.619×10^{-1}	2.162
1.333	8.200×10^{-1}	2.930	3.056	1.541×10^{-4}	2.628×10^{-2}	4.619×10^{-1}	2.568
1.725	1.028	3.780	3.913	1.624×10^{-4}	2.532×10^{-2}	4.619×10^{-1}	3.426
1.924	1.134	4.320	4.379	1.649×10^{-4}	2.490×10^{-2}	4.619×10^{-1}	3.892
2.124	1.241	4.800	4.873	1.662×10^{-4}	2.450×10^{-2}	4.619×10^{-1}	4.386
2.324	1.351	5.450	5.388	1.659×10^{-4}	2.415×10^{-2}	4.619×10^{-1}	4.902
2.520	1.455	6.060	5.925	1.656×10^{-4}	2.380×10^{-2}	4.619×10^{-1}	5.439
2.720	1.561	6.780	6.511	1.647×10^{-4}	2.343×10^{-2}	4.619×10^{-1}	6.026

[1963BIL/FUR]

Bilinski *et al.* [1963BIL/FUR] report the titration of thorium nitrate solutions ($[Th]_{tot} = 3\times10^{-5}$ to 0.1 M) with KOH solutions of varying concentrations at (20 ± 0.1)°C. The onset of precipitation was measured by a tyndallometric (light scattering) method as a function of the total metal concentration and pH. The lower limit for the detection of precipitation was at $[Th]_{tot} = 3\times10^{-5}$ M. A glass electrode was used for pH measurements; however, neither its calibration nor the pK_w values or activity coefficients used to convert the measured pH values into $\log_{10}[OH^-]$ are mentioned.

The solubility curve of thorium hydroxide shown in Figure 5 in [1963BIL/FUR], where $\log_{10}[Th]_{tot}$ is plotted against pH measured after 24 hours in the thorium hydroxide suspensions, is evaluated by slope analysis and described by the following reactions and equilibrium constants:

pH 3.1 to 3.4: $$Th(OH)_4(s) \rightleftharpoons Th^{4+} + 4OH^- \qquad \log_{10} K_{s,0} = -(45.7 \pm 0.2)$$

pH 3.5 to 4.1: $$Th(OH)_4(s) \rightleftharpoons (1/n)\left((Th(OH)_2^{2+})_n\right) + 2OH^- \qquad \log_{10} K_{s,2} = -(24.3 \pm 0.2)$$

The possible formation of $Th(OH)^{3+}$ and other polynuclear species than (4,2) and (8,4) was neglected. The authors also neglected the fact that the activity coefficients depend strongly on the initial thorium nitrate concentration since no background electrolyte was added to maintain the ionic strength constant. The variation of ionic strength along the solubility curve does not allow the simple slope analysis to be used. A cumulative hydrolysis constant of ${}^{*}\beta_2 = 1.029 \times 10^{-7}$ ($\log_{10} {}^{*}\beta_2 = -6.99$) is given in the abstract of [1963BIL/FUR]. The calculation of this value, which is not consistent with the difference between $\log_{10} K_{s,2}$ and $\log_{10} K_{s,0}$, is not explained. For these reasons the equilibrium constants calculated in [1963BIL/FUR] are not accepted by this review.

Additional titration experiments in the presence of $10^{-5} - 10^{-2}$ M carbonate at $[Th]_{tot} = 4 \times 10^{-4}$ M led to a decrease of the turbidity at pH 9 − 10.4, partly even to clear solutions, due to the formation of thorium complexes with carbonate. However, these results do not allow a quantitative interpretation.

[1963GIN/EFI]

Gingerich and Efimenko have measured mass-spectrometrically the pressures of the elemental phosphorus species over thorium phosphides from $ThP_{0.63}$ to $ThP_{1.27}$ from 1131 to 2243 K. The authors indicate that their measured phosphorus pressures are too low, at least for the higher phosphide compositions, owing to slow diffusion in the surface layers. A further reason for suspecting these data is that, as noted by [1975RAN], above 1900 K, the equilibrium constants for the reaction $P_2(g) \rightleftharpoons 2P(g)$ are 4 to 9 times greater than those calculated from the assessed data by the Gurvich *et al.* [1989GUR/VEY] and much greater at lower temperatures. The three measurements of the $P_4(g)$ pressures (from 1416 to 1482 K) are even further from equilibrium. These factors suggest that equilibrium was not attained in this study, even at the highest temperatures, and the data from this study have not been used by the review.

[1963LIN]

In this quite detailed Progress Report, Linevsky reports the results of IR spectra of ThO_2 molecules condensed in a solid argon matrix, using both normal ThO_2 and a sample enriched in ^{18}O (*ca.* 45%). By a comparison of the observed peaks, the symmetric and anti-symmetric stretch frequencies for $Th^{16}O_2$ were identified at υ_1 = 786.8 cm^{-1} and υ_3 = 734.5 cm^{-1} respectively. From the corresponding frequencies for $Th^{18}O_2$, 743.8 cm^{-1} and 659.9 cm^{-1}, the O-Th-O apex angle was estimated to be 106°, with an unspecified, but large, uncertainty (due to the large mass ratio of the Th and O atoms). Doublets due to the ThO(g) molecule were also observed. Linevsky further suggests that the υ_2 bending frequency is below the lower limit of their instrumentation, 180 cm^{-1}, since no peaks were observed in this region.

[1962MAT/MIL]

The paper provides information on precipitation curves of colloids when K_2HPO_4 solutions is added to solutions of Th(IV) nitrate. This study provides no thermodynamic information.

[1963RYA/VOL]

The paper contains a brief review of older studies of thorium carbonate systems, a high-frequency titration study to establish the stoichiometry of the limiting complex and finally the preparation and characterisation of some solid carbonate phases. The high-frequency titration is the part of main interest for this review. The experiment consists of a titration where the current through a titration cell is measured as a function of the ratio between the total concentrations of Th(IV) and carbonate. The titration curves display sudden changes in slope at different ratios Th(IV)/carbonate and this is used as an indicator for the stoichiometry of the complexes formed. In the present case the titration curve when ammonium carbonate is titrated with thorium nitrate, is linear at low values of the ratio and bends at a ratio 1:4. The curve is then linear until a ratio slightly larger than 1:2. In the reverse titration there is a sharp bend in the curve at a ratio Th(IV)/carbonate = 2, but only a gradual change of the slope at higher values. There is no justification why the curve should display a sudden change in slope at a certain ratio; on the contrary in stepwise complex formation reactions one would in general expect a gradual change of properties. For this reason the present review does not accept the stoichiometry proposed by Ryabchikov *et al.* The characterisation of the solid phases has been made by X-ray powder diffraction and thermogravimetry and the authors conclude, based on these data, that the solid phase $M_6[Th(CO_3)_5]\cdot12H_2O$; M = Na, K, is the double salt $M_4[Th(CO_3)_4]\cdot M_2CO_3.12H_2O$; this conclusion is erroneous as shown by the known single crystal structure of the compound with M = Na, [1975VOL/RIM3], [1975VOL/RIM4].

[1963VOR/DAN]

The authors report the rates of evaporation of ThO_2(cr) at *ca.* 1803, 2023 and 2233 K, (the data are only reported graphically) but do not convert these to vapour pressures, unlike their similar study on UO_2(cr) in the same paper. If the data for ThO_2 are converted to pressures using the Langmuir equation, the ratio of the experimental pressures to those calculated from the final assessed data are respectively 38, 5.6 and 0.19, a variability reflected in the very large uncertainty of the derived third-law enthalpy of sublimation quoted in Section VII.1.2.2. These data have been included in the weighted average, but with that very large uncertainty.

[1963WIS/EGA]

This is a study of the thermodynamic properties of solutions of the actinides and some fission products in liquid bismuth. For dissolution of thorium, the cell

$$\text{Th(cr)} \mid \text{LiCl-KCl (eutectic)} + 5\%\ \text{ThCl}_4 \mid \text{Bi-Th(l)}$$

was used. Values of the emf are quoted for 1073 K only, the mole fraction of thorium in the Th-Bi melt varying from 0.00135 to 0.0080 (six different values). The derived values of the thorium potential in this range correspond to an excess Gibbs energy of solution of thorium of $-(118.0 \pm 0.8)$ $\text{kJ}\cdot\text{mol}^{-1}$, the uncertainty showing the range of values only.

[1963YEN/LI]

For this study of the properties of $ThOCl_2$(cr), ThO_2 was obtained by heating to 873 K a thorium oxalate precipitated from a thorium nitrate solution. $ThCl_4$(cr) was prepared by chlorinating ThO_2 at 873 to 923 K with a "mixture of S_2Cl_2 (SCl_2) vapour and Cl_2". $ThOCl_2$(cr) was obtained by direct reaction of ThO_2 and $ThCl_4$. Analyses yielded the compositions $ThCl_{3.98\pm0.02}$ and $ThOCl_{1.98\pm0.03}$.

The phase diagram of the ThO_2-$ThCl_4$ system was investigated in order to prove the existence of $ThOCl_2$(cr) and to demonstrate that the compound could be obtained from the reaction of ThO_2 with $ThCl_4$. The melting point of $ThCl_4$ was 1040−1043 K for different batches, in agreement with earlier data. A eutectic at 988 K was observed from 50 to 100 mol% $ThCl_4$, presumed to be between $ThOCl_2$(cr) and $ThCl_4$(cr) but the details of the other parts of the diagram are not clear.

The enthalpy of formation of $ThOCl_2$(cr) at 298.15 K was obtained from the comparison of the enthalpies of solution of $ThCl_4$(cr) and $ThOCl_2$(cr) in 0.1 M NaOH, under the same conditions, in order to eliminate the uncertainties associated with the formation of the thorium hydroxide precipitate.

The experimental reactions were:

$$\text{ThOCl}_2\text{(cr)} + \{2\text{NaOH}+\text{H}_2\text{O}\}\ (\text{in NaOH}\cdot 550\,\text{H}_2\text{O}) \rightleftharpoons \{\text{Th(OH)}_4\text{(ppt)} + 2\text{NaCl}\}\ (\text{in NaOH}\cdot 550\,\text{H}_2\text{O}) \qquad \text{(A.44)}$$

$$\text{ThCl}_4\text{(cr)} + 4\,\text{NaOH}\ (\text{in NaOH}\cdot 550\,\text{H}_2\text{O}) \rightleftharpoons \{\text{Th(OH)}_4\text{(ppt)} + 4\text{NaCl}\}\ (\text{in NaOH}\cdot 550\,\text{H}_2\text{O}) \qquad \text{(A.45)}$$

$$\Delta_{\text{r}} H^{\text{o}}_{\text{m}}\,(\text{A.44}) = -(129.33 \pm 1.38)\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{r}} H^{\text{o}}_{\text{m}}\,(\text{A.45}) = -(336.64 \pm 2.03)\ \text{kJ}\cdot\text{mol}^{-1}.$$

The authors also measured the vapour pressure of $ThCl_4$(g) at four temperatures from 953 to 1025 K by the modified boiling point method, and, more extensively, the pressure of $ThCl_4$(g) in the decomposition reaction $2ThOCl_2(cr) \rightleftharpoons ThO_2(cr) + ThCl_4(g)$ from 1040 to 1182 K. For the latter, the pressures were given by

$\log_{10} p_{\mathrm{ThCl_4}}$ /bar = − (72500 / 4.575 T) + 12.64. The results were processed by the review by the second-law to give the enthalpy of formation and standard entropy of the oxychloride.

All these results are used, in conjunction with other studies, in the evaluation of the enthalpy of formation of $ThOCl_2$(cr) in Section VIII.2.1.6.

[1964ARO]

Thermodynamic data in the Th–C system were obtained from measurements on solid electrochemical cells of the following types, at 1073 to 1273 K:

$$\mathrm{Th + ThF_4 \,|\, CaF_2 |\, ThF_4 + “ThC_2” + C}$$

$$\mathrm{Th + ThF_4 \,|\, CaF_2 |\, ThF_4 + “ThC_2”+ “ThC”}$$

$$\mathrm{Th + ThF_4 \,|\, CaF_2 |\, ThF_4 + ThC_{1-x} + Th}$$

from which the chemical potentials in the relevant diphasic fields can be determined. Further processing of these data is complicated by the varying and ill-defined phase boundaries of the carbide phases, but the derived data for the Gibbs energies of ThC_{2-x} are discussed in Section XI.1.1.4.

[1964CAT/THO]

The authors attempted to measure the vaporisation of ThS from by effusion from a tantalum cell 1935 to 2464 K, but found that the measured “pressures” were unreasonably high, due to “flow” of ThS over the surface of the container, despite the temperatures being well below the melting point of ThS(cr) (> 2600 K), and give an estimated equation for the effective pressure, based on the measured slope of their (incorrect) measurements and an estimated entropy of vaporisation. These data have been processed in a somewhat different way in Section IX.1.1.3, following the analysis of Rand [1975RAN], as corrected by [1984GRO/DRO].

[1964EGA]

The Gibbs energy of formation of “ThC_2” at 973 to 1243 K was determined using a solid-state emf cell Th,ThF_4(s)|CaF_2(s)|ThF_4, “ThC_2”,C with molybdenum electrodes. The dicarbide + graphite +ThF_4 mixture was prepared by heating Th + excess graphite, heating to 1923 K for 30 min, crushing, admixing ThF_4(cr) and repelleting. Four to seven days were required for equilibrium to be attained.

[1964HIE/SIL]

This preliminary paper of Hietanen and Sillén on the hydrolysis of Th(IV) in 3 M (Na)Cl medium is discussed together with a later paper of these authors [1968HIE/SIL] where the results of both studies are evaluated and discussed more detailed.

[1964HOL/GRE]

Torsion effusion measurements were made of the pressures of CO(g) in the reaction of ThO_2 and graphite $ThO_2 + 2C(cr) \rightleftharpoons$ “ThC_2” + 2CO(g) from *ca.* 1560 to 1680 K. Samples of ThO_2(cr) were held in graphite effusion cells heated in a molybdenum furnace. Measurements of the vapour pressure of zinc were used to calibrate the torsion wire, rather than an absolute determination. The measured pressures varied slightly with orifice area, but when extrapolated to zero orifice size were given by the equation: $\log_{10} p_{CO} / \text{bar} = -21830\, T^{-1} + 8.45$ in the range 1560 to 1680 K. These results are included in the comparison of similar studies in Section XI.1.1.4.

[1964JAC/BAR]

A mass spectrometric investigation of the vaporisation processes of solid ThC_2(s), contained in a graphite Knudsen cell is reported. ‘ThC_2’(cr) was prepared from the elements by arc-melting, and characterised by X-ray diffraction immediately after preparation. The initial thorium contained *ca.* 1% ThO_2, but the oxygen was presumably removed during arc melting, since no ThO(g) was found in the mass-spectrometric studies. Ion intensities were converted to partial pressures by calibration with both silver and molybdenum.

The partial pressures of Th(g) and ThC_2(g) in equilibrium with the carbon-saturated solid were of comparable magnitude in the temperature range investigated, 2371 − 2642 K. The authors do not, curiously, give pressures of both Th(g) and ThC_2(g) at the same temperature. Instead, they report individual pressures of ThC_2(g) at one set of temperatures (2371 − 2641 K) for the reaction:

$$ThC_2(\text{cr, carbon saturated}) \rightleftharpoons ThC_2(g) \tag{A.46}$$

and pressures of Th(g) in the reaction

$$ThC_2(\text{cr, carbon saturated}) \rightleftharpoons Th(g) + 2C(cr) \tag{A.47}$$

at a different set of temperatures (2411 − 2642 K).

The data were analysed by the authors by both second- and third-law methods, using estimated thermal functions for both ThC_2(cr) and ThC_2(g), with reasonable agreement for both the above reactions. However, as noted in Sections XI.1.1 and XI.1.2, most of the thermodynamic data for both these species are uncertain. The authors assumed that the ThC_2(g) molecule had the linear C=Th=C structure, and the electronic contribution to the partition function for ThC_2(g) was based on that for the Th^{2+}(g) ion. Both of these assumptions are now almost certainly incorrect, see below.

The uncertainty from the data for ThC_2(cr) can be removed by subtracting the fitted linear Gibbs energies for the Reactions (A.46) and (A.47) above, to give that for the reaction:

$$\mathrm{ThC_2(g)} \rightarrow \mathrm{Th(g)} + 2\mathrm{C(cr)} \quad \text{(A.48)}$$

$$[\Delta_{\mathrm{r}} G^{\circ}_{\mathrm{m}}]^{2560\,\mathrm{K}}_{2350\,\mathrm{K}}\,((\mathrm{A.48}), T) = 67632 - 29.325\,T \quad \mathrm{J{\cdot}mol^{-1}}$$

As discussed in Section (XI.1.2.1), recent calculations by Kovács and Konings [2008KOV/KON] suggest that $\mathrm{ThC_2(g)}$ is not linear, but has an asymmetric L-shaped structure. With the thermal functions and vibration frequencies calculated from this structure, and an electronic contribution to the partition function based on that for ThO(g), the third law enthalpy of formation of $\mathrm{ThC_2(g)}$ from the data of [1964JAC/BAR] is calculated to be $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}$ ($\mathrm{ThC_2}$, g, 298.15 K) = (784.7 ± 9.2) $\mathrm{kJ{\cdot}mol^{-1}}$, where the uncertainty does not include those from the experimental difficulties (conversion from ion intensities to pressures, *etc.*) and in the estimated electronic contribution for $\mathrm{ThC_2(g)}$.

Moreover, the experimental and calculated entropies of Reaction (A.48) at 2500 K are distinctly different (29.3 *vs.* 61.6 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$). In view of these inconsistencies, no data are selected for $\mathrm{ThC_2(g)}$ for this review.

[1964NAB/KUD]

Nabivanets and Kudritskaya studied the solubility of an amorphous $\mathrm{Th(OH)_4(am)}$ precipitate in 0.1 M $\mathrm{NaClO_4}$ at (17 ± 1)°C. The solubility was measured in the pH range 3.4 to 7.0 after equilibration times of 3 − 6 days. The Th concentrations were determined colorimetrically after centrifugation for 1 hour at 10000 rpm with a usual laboratory centrifuge. The measured solubilities, which decrease from 1.6×10^{-3} M at pH 3.40 to 5×10^{-7} M at pH 5.35 − 7.00, were described by assuming only the presence of mononuclear Th(IV) hydroxide complexes. The stepwise equilibrium constants for the reactions:

$$\mathrm{Th(OH)}_{n-1}^{4-n+1} + \mathrm{OH^-} \rightleftharpoons \mathrm{Th(OH)}_{n}^{4-n},$$

were calculated by slope analysis. The following final results, *i.e.*, the solubility product $\log_{10} K_{s,0}$ for the reaction:

$$\mathrm{Th(OH)_4(am)} \rightleftharpoons \mathrm{Th^{4+}} + 4\mathrm{OH^-} \quad \text{(A.49)}$$

and the formation constants $\log_{10} \beta_n(\mathrm{Th(OH)}_n^{4-n})$ for the reactions

$$\mathrm{Th^{4+}} + n\mathrm{OH^-} \rightleftharpoons \mathrm{Th(OH)}_n^{4-n} \quad \text{(A.50)}$$

were reported in [1964NAB/KUD]:

$$\log_{10} K_{s,0}\,(\mathrm{A.49}) = -41.14$$
$$\log_{10} \beta_1\,((\mathrm{A.50}), n = 1) = (9.40 \pm 0.24)$$
$$\log_{10} \beta_2\,((\mathrm{A.50}), n = 2) = (18.25 \pm 0.37)$$
$$\log_{10} \beta_3\,((\mathrm{A.50}), n = 3) = (26.74 \pm 0.41)$$
$$\log_{10} \beta_4\,((\mathrm{A.50}), n = 4) = (34.82 \pm 0.44).$$

The solubility data at pH < 5.4 are consistent with corresponding data reported in other solubility studies with $Th(OH)_4(am)$ or $ThO_2(am, hyd)$. However, the constant, pH-independent Th concentration of $\log_{10}[Th] = -(6.30 \pm 0.02)$ measured at pH 5.4 to 7.0 is more than two orders of magnitude higher than corresponding data obtained after 1−2 nm ultrafiltration or ultracentrifugation [1987RYA/RAI], [1989MOO], [1991FEL/RAI], [2000RAI/MOO], [2002NEC/MUL]. Neck *et al.* have shown that the centrifugal force used in the study of Nabivanets and Kudritskaya [1964NAB/KUD] is not sufficient to remove small Th(IV) colloids; this requires ultracentrifugation, *e.g.*, at 90000 rpm corresponding to 5×10^5 g [2002NEC/MUL], [2004ALT/NEC]. It is noteworthy that Th concentrations in neutral and alkaline solutions were found to be exactly the same ($\log_{10}[Th] = -(6.3 \pm 0.5)$ [2004ALT/NEC]) when aliquots were taken from the supernatant solution without filtration or centrifugation. They must be ascribed to colloidal or polynuclear species $(4m,m) = Th_m(OH)_{4m}(aq)$.

As ultracentrifugation and potentiometric studies have shown that polynuclear species are predominant at the thorium concentrations and pH values in the saturated solutions of [1964NAB/KUD], the reported equilibrium constants for mononuclear hydroxide complexes have no chemical significance. Using the hydrolysis constants and ion interaction coefficients selected in the present review, the solubility data of Nabivanets and Kudritskaya at pH 3.5−4.5 have been reinterpreted (Figure A-12). The complex $Th_4(OH)_{12}^{4+}$ is found to be predominant along the solubility curve. The solubility constants recalculated from the data in 0.1 M $NaClO_4$,

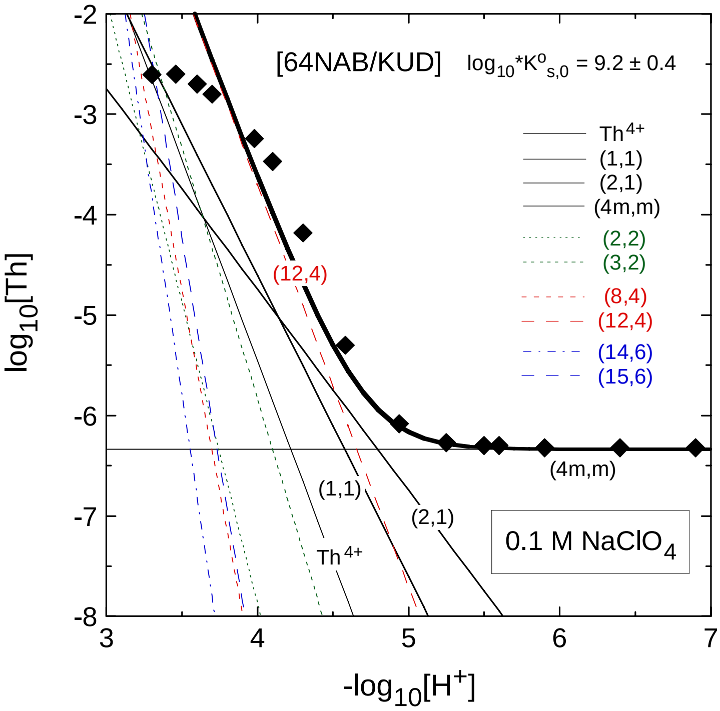
$$\log_{10} {}^{*}K_{s,0} = (10.5 \pm 0.4)\ (\log_{10} K_{s,0} = -(44.7 \pm 0.4)),$$

correspond to following equilibrium constants at zero ionic strength:

$$\log_{10} {}^{*}K^{\circ}_{s,0} = (9.2 \pm 0.4)\ (\log_{10} K^{\circ}_{s,0} = -(46.8 \pm 0.4)).$$

Because of the large scatter of solubility data for amorphous Th(IV) precipitates, this review did not carry out temperature corrections for the hydrolysis constants used and the solubility constant calculated from the data at 17°C [1964NAB/KUD] are compared to the standard state temperature of 298.15 K (25°C).

Figure A-12: Solubility of thorium hydroxide determined by Nabivanets and Kudritskaya [1964NAB/KUD] at 17°C in 0.1 M $NaClO_4$. The calculated lines are based on the hydrolysis constants and ion interaction coefficients selected in this review, $\log_{10} {}^{*}K^{\circ}_{s,0} = 9.2$, and $\log_{10} K_{s,(4m,m)} = -6.3$.



[1964NAB/KUD2]

Only a document in Russian was available to the reviewers and only a few comments can therefore be made on this paper. The electrodialysis experiments seem to give, at best, qualitative information on the speciation and will not be further discussed. The ion-exchange experiments have been made using the Fronaeus method where the distribution of thorium between an aqueous solution and a cation exchanger is measured as a function of the ligand concentration. When analysing the data, the distribution coefficient of both Th^{4+} and the positively charged complexes are taken into account. The experiments have been made at an ionic strength of 4 M in a medium of the composition: (4.00 − L) M $HClO_4$ and L M HCl or HNO_3. The concentration of L varies from 0.25 to 4.00 M, and one must therefore expect large variations of the activity coefficients of reactants and products. These have not been taken into account by the authors who report equilibrium constants for the formation of five chloride complexes and six nitrate complexes that are listed in Table A-24. There is no information on the temperature of the experiments; this review assumes that it is 20 − 25°C.

Table A-24: Equilibrium constants for the formation of Th(IV)-chloride and nitrate complexes at room temperature obtained by the cation exchange method.

Complex	β_n	Complex	β_n
$ThCl^{3+}$	1.60 M^{-1}	$Th(NO_3)^{3+}$	3.55 M^{-1}
$ThCl_2^{2+}$	0.16 M^{-2}	$Th(NO_3)_2^{2+}$	2.10 M^{-2}
$ThCl_3^{+}$	0.14 M^{-3}	$Th(NO_3)_3^{+}$	0.50 M^{-3}
$ThCl_4(aq)$	0.035 M^{-4}	$Th(NO_3)_4(aq)$	0.19 M^{-4}
$ThCl_5^{-}$	0.0035 M^{-5}	$Th(NO_3)_5^{-}$	0.032 M^{-5}
		$Th(NO_3)_6^{2-}$	0.0040 M^{-6}

These data can at best be used to estimate the first equilibrium constants, β_1; the other proposed constants have no chemical significance. It is of interest to compare these equilibrium constants with those obtained for Pu^{4+} by Grenthe and Norén [1960GRE/NOR] using the same method and the same ionic medium; they report β_1 = 1.4 and 5.5 for the chloride and nitrate systems, respectively (and also equilibrium constants for higher complexes that are not reliable as they are strongly influenced by medium effects). This review notes that the nitrate complexes are significantly stronger than the chloride complexes in agreement with the LAXS observations in [1991JOH/MAG]. However, in view of the large medium changes that occur, no equilibrium constants are selected. Figure A-13 and A-14 show the distribution diagrams calculated for the Th^{4+}-Cl^- and the Th^{4+}-NO_3^- systems using the constants given by [1964NAB/KUD2]. These show that the higher complexes ThX_n^{4-n}, $n > 2$, are formed only when the anion concentrations are larger than 1 M.

Figure A-13: Distribution diagram for the thorium-chloride system using the equilibrium constants from [1964NAB/KUD2]. The complexes ThCl_n^{4-n}, $n > 1$ are not accepted by this review and are best considered as fitting constants in the method used.

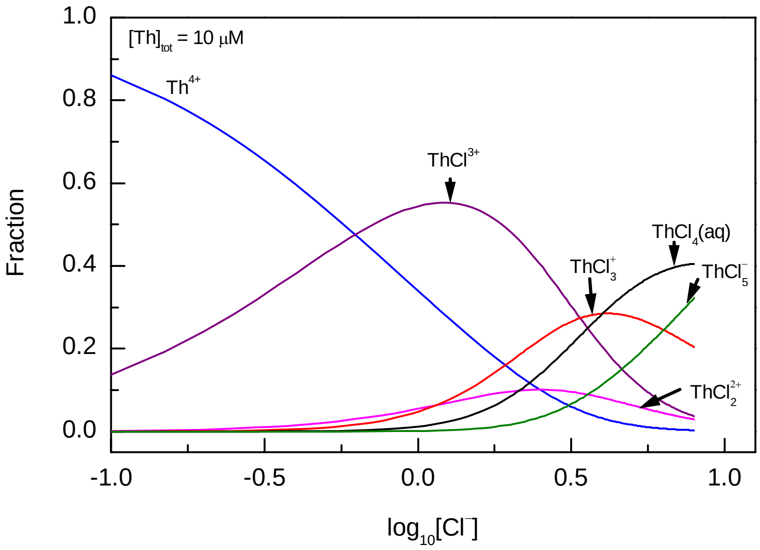
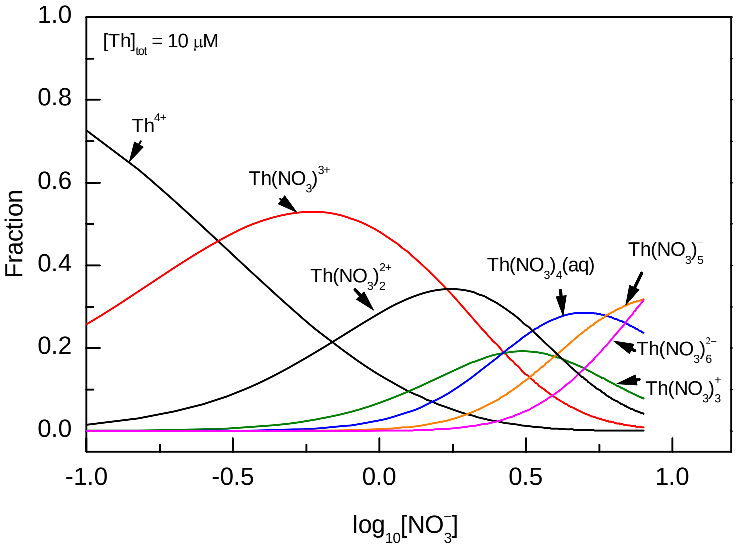


Figure A-14: Distribution diagram for the thorium-nitrate system using the equilibrium constants from [1964NAB/KUD2]. The complexes $\mathrm{Th(NO_3)}_n^{4-n}$, $n > 2$ are not accepted by this review and are best considered as fitting constants in the method used.



[1964SCA/WYL]

These authors have studied in detail the lower iodides of thorium using X-ray powder diffractometry, differential thermal analysis and microscopic examination.

Electrolytic thorium metal samples, containing 100−104 ppm oxygen, 6−15 ppm nitrogen, 5−6 ppm hydrogen, less than 600 ppm chlorine, and insignificant amounts of other impurities were used as starting material, together with iodine purified by distillation and condensation in a vacuum. High purity thorium obtained by the carbide-iodide process was also used for the critical experiments. It contained less than 25 ppm of each carbon, oxygen and nitrogen. The thorium tetraiodide used in the synthesis of the lower iodides was obtained by direct combination of the elements in Pyrex containers, and used after sublimation *in vacuo*.

The lower iodides were obtained by reacting, in tantalum or platinum containers, the tetraiodide and thorium metal (reduced to a powder form by several hydriding-dehydriding cycles) in the appropriate ratios. All transfers, weighings, and other operations were carried out in an evacuable glove box whose argon atmosphere could be maintained at a dew point of 213 K or better. Essentially conventional powder X-ray diffraction, microscopy and DTA techniques were used. Through the use of classical wet analytical methods, the I/Th molar ratios accurate to ±0.02 were reported for the various di-and triiodides samples, including those submitted to thermal analysis.

The α and β (high temperature) forms of ThI_2 were indexed on the basis of two distinct hexagonal cells, with a = 8.00 Å and c = 7.87 Å for the α form, and a = 9.21 Å and c = 3.74 Å for the β form. The structure of the β form has since been more definitely determined by [1968GUG/JAC], based on single crystal data.

The differential thermal analysis results leading to a tentative Th-I phase diagram show that ThI_3(cr) and ThI_2(cr) undergo peritectic transformations as follows: ThI_3 into β-ThI_2 and liquid at 1019 K and β-ThI_2 into Th metal plus liquid at 1137 K; in each case, the liquid has a I/Th ratio substantially less than 4. The transformation of α- to β-ThI_2 occurs sluggishly at 873 to 973 K. The existence of another iodide of Th at I/Th *ca.* 3.3−3.4 suggested subsequently by [1967GER/KRU] is considered as doubtful by [1964SCA/WYL].

[1965ARO/SAD]

The chemical potential of thorium relative to Th(cr) were calculated from the emf measurements in the single phase monocarbide region between $ThC_{0.66}$ and $ThC_{0.96}$. The cells were of the type Th, $ThF_4|CaF_2|ThF_4$, ThC_x. Measurements were made at 1073 to 1223 K. The chemical potential at 1173 K decreases from −1.7 $kJ\cdot mol^{-1}$ at $ThC_{0.66}$ to – 83.3 $kJ\cdot mol^{-1}$ at $ThC_{0.96}$. The thermodynamic data are discussed in connection with theories of chemical bonding.

These results are of limited interest for the present review, and are mentioned for information only.

[1965BAE/MEY]

The hydrolysis of Th(IV) has been studied at 0 and 95°C in 1 m (Na)ClO$_4$ using potentiometric titration technique. In addition the experimental data in [1954KRA/HOL] have been re-evaluated using the same least-squares method as the 0 and 95°C data. This is a precise experimental study representing the state of the art. The authors have checked the reversibility of their titrations and the possible occurrence of precipitation. They note that the equilibria are slowly attained in some test solutions and ascribe this to the formation of a hydrous oxide as a result of local high pH at the entry of the sodium hydroxide titrant. A transient precipitation usually occurred when an increment of base was added to thorium solutions. Normally this precipitate, produced by local excess of base, dissolves more or less readily on mixing, depending on the pH. No difficulty from this effect was noted in the measurements below $\bar{n}_{\mathrm{OH}} = 1.8$ at 95°C; however, at 0°C it appeared that the precipitate so formed did not readily redissolve. The authors report their primary experimental data and also test a number of different chemical models (their Table IV). The complexes $\mathrm{Th(OH)^{3+}}$ and $\mathrm{Th(OH)_2^{2+}}$ are always included in these models. Based on $\sigma(\bar{n}_{\mathrm{OH}})$ they suggest that a minimum of five complexes is necessary to describe the experimental data. All of them contain $\mathrm{Th(OH)^{3+}}$, $\mathrm{Th(OH)_2^{2+}}$, $\mathrm{Th_2(OH)_2^{6+}}$ and two other species, the composition of which was decided based on the least-squares fitting. The best additional species are $\mathrm{Th_3(OH)_6^{6+}}$ and $\mathrm{Th_6(OH)_{15}^{9+}}$ or $\mathrm{Th_4(OH)_8^{8+}}$ and $\mathrm{Th_6(OH)_{15}^{9+}}$; the latter were selected by the authors to describe the speciation at all temperatures investigated. The equilibrium constants are given in Table A-25. These equilibrium constants have also been evaluated with the LETAGROP least-squares program using the experimental data from [1954KRA/HOL]. The difference between the constants is much larger than the estimated standard deviations, indicating that the latter have to be treated with caution. The maximum concentration of $\mathrm{Th(OH)_2^{2+}}$ is so small that this complex cannot be safely identified through these data.

Table A-25: Equilibrium constants, $-\log_{10}{}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ for the "best" hydrolysis model based on data from [1954KRA/HOL] and [1965BAE/MEY] in 1 m (Na)ClO$_4$.

t (°C)	$-\log_{10}{}^{*}\beta_{1,1}$	$-\log_{10}{}^{*}\beta_{2,1}$	$-\log_{10}{}^{*}\beta_{2,2}$	$-\log_{10}{}^{*}\beta_{8,4}$	$-\log_{10}{}^{*}\beta_{15,6}$	$\sigma(\bar{n}_{\mathrm{OH}})$
0	4.32 ± 0.02	8.48 ± 0.03	5.60 ± 0.02	22.79 ± 0.02	43.84 ± 0.02	0.0117
25	4.15 ± 0.04	7.70 ± 0.03	4.61 ± 0.02	19.01 ± 0.02	36.76 ± 0.02	0.0145
95	2.29 ± 0.02	4.50 ± 0.01	2.55 ± 0.03	10.49 ± 0.03	20.63 ± 0.02	0.0154

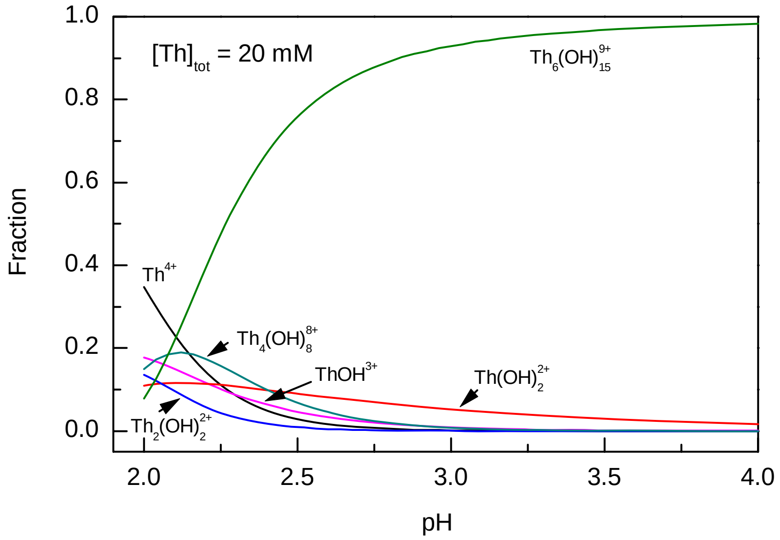
The enthalpy and entropy of reaction has been calculated from the temperature dependence of the equilibrium constants given in Table A-25. In the calculation the authors assumed a constant value of $\Delta_{\mathrm{r}}C_{p,\mathrm{m}}$. The results are given in Table A-26.

Table A-26: Enthalpy, entropy and heat capacity of reaction for the hydrolysis reactions of Th(IV) in 1 m (Na)ClO_4. In the last two columns are given the enthalpy and entropy of reaction divided by the number of OH-groups in the complex.

Species	$\Delta_r H_m$ ($kJ\cdot mol^{-1}$)	$\Delta_r S_m$ ($J\cdot K^{-1}\cdot mol^{-1}$)	$\Delta_r C_{p,m}$ ($J\cdot K^{-1}\cdot mol^{-1}$)	$\Delta_r H_m / n_{OH}$ ($kJ\cdot mol^{-1}$)	$\Delta_r S_m / n_{OH}$ ($J\cdot K^{-1}\cdot mol^{-1}$)
$ThOH^{3+}$	25	4	937	25	4
$Th(OH)_2^{2+}$	58	46	1272	29	23
$Th_2(OH)_2^{6+}$	62	119	4	31	60
$Th_4(OH)_8^{8+}$	241	446	452	30	56
$Th_6(OH)_{15}^{9+}$	454	819	1000	30	55

It is not satisfactory to determine three parameters from three experimental data and the values given in Table A-26 should therefore be used with caution; the uncertainty estimated by the authors (about 1 $kJ\cdot mol^{-1}$ in $\Delta_r H_m$; and 80 $J\cdot K^{-1}\cdot mol^{-1}$ in $\Delta_r C_{p,m}$) seems too optimistic. However, it is interesting to note that the enthalpy and entropy of reaction per OH-group is very nearly the same in all complexes and also similar to the values found for U(IV) [1962BAE/MEY]. The relative stability of the various complexes changes significantly with a change of temperature as seen by comparing the speciation diagrams in Figure A-21 at 25°C and in Figure A-15 at 95°C.

Figure A-15: The speciation in the Th(IV) hydroxide system at 95°C.



The experimental data also includes solubility measurements at 95°C; oversaturated Th solutions were spiked with crystalline $ThO_2(cr)$ and equilibrated for 10 to 100 days. The composition of the solid was identified by electron microscopy. Equilibrium was attained after ten days in test solutions with $-\log_{10}[H^+] = 2-2.6$, while test solutions in the range $-\log_{10}[H^+] < 2$ required longer equilibration times. The data were analysed and could be well described using the equilibrium constants for the two mononuclear complexes $ThOH^{3+}$ ($\log_{10}{}^*\beta_{1,1} = -2.26$) and $Th(OH)_2^{2+}$ ($\log_{10}{}^*\beta_{2,1} = -4.54$) from the potentiometric study at 95°C. The solubility constant $\log_{10}{}^*K_{s,0}$ (1.0 m $NaClO_4$, 95°C) = 4.26 is calculated for the reaction:

$$ThO_2(s) + 4H^+ \rightleftharpoons Th^{4+} + 2H_2O(l).$$

The solubility data in [1965BAE/MEY] are about 0.5−0.8 $\log_{10}$-units higher than those obtained by Rai *et al.* [2000RAI/MOO] in the same pH range in 0.1 M NaCl with a microcrystalline $ThO_2(s)$ solid, which resulted from the transformation of ThO_2(am, hyd) suspensions after heating for 52−76 days at 90°C. The difference might be due to ionic strength effects or to differences in crystallinity, *i.e.*, particle size.

[1965HEN/TYR]

This paper of Hentz and Tyree is discussed together with [1966HEN/JOH], a related paper from the same group.

These two communications present investigations of Th(IV) hydrolysis using ligh-scattering and ultracentrifugation. The light-scattering experiments have been made in the Th_{tot} range 10 to 100 mM at pH ranging from 2.07 to 3.25. The interpretation of the light-scattering data is at best qualitative as indicated by the statement in [1965HEN/TYR] that the species $Th(OH)(ClO_4)_2^+$ is formed at $\bar{n}_{OH} = 1$. At this value of $\bar{n}_{OH}$ a range of different polynuclear complexes is present in the test solutions, as shown by potentiometric and other equilibrium studies. At $\bar{n}_{OH}$ equal to 1.6 and 2.0 the average nuclearity is approximately 2.3 and 2.9, respectively, in qualitative agreement with the titration data. At higher values of $\bar{n}_{OH} \approx 3$, large aggregates with 140 to 150 Th atoms are formed, presumably colloids. The authors indicate that the observations at the lower values of $\bar{n}_{OH}$ refer to equilibrium systems, but that slow kinetics cannot be ruled out at higher pH. No equilibrium constants are reported. The ultra-centrifugation data [1966HEN/JOH] gives similar information as the light scattering data, but also in this case only the qualitative information that the nuclearity of Th(IV) complexes increases with increasing Th_{tot}; no equilibrium constants are reported. An important observation is that the polynuclear hydroxide complexes in chloride media are more prone to further aggregation (colloid formation ?) than the complexes formed in perchlorate media; this is in agreement with the break-down detection studies of Neck *et al.* [2002NEC/MUL], [2003BIT/MUL]. There is an extensive increase of aggregation with time in chloride media, while the perchlorate solutions do not change much over several years, particularly in solutions with $\bar{n}_{OH} < 1.5$.

[1965LIN2]

This contains a comprehensive compilation of published solubility data for thorium compounds prior to 1965. Raw experimental data for sulphate compounds of thorium from many different sources ([1910KOP/HOL], [1910BAR], [1911BAR], [1912BAR], [1912WIR]) are presented in this publication and were used by [1992FEL/RAI] and this review to determine $\Delta_f G_m^o$ values for several different solids important in Li_2SO_4, $(NH_4)_2SO_4$, Na_2SO_4, K_2SO_4, H_2SO_4, HCl and H_2SO_4 systems based on Pitzer and SIT models. For details see the review under [1910KOP/HOL] and main text, Section IX.1.3.3.

[1965OLS/MUL]

The nitrogen decomposition pressures for of ThN_{1-x}(cr) to give Th(l) + N_2(g) were measured from 2689 to 3063 K. ThN was found to melt congruently at (3063 ± 30) K under a nitrogen pressure just under 1 bar. The presence of oxygen as an impurity in the ThN(cr) has a large effect on the melting point and decomposition pressure. The decomposition pressure-temperature relation for pure ThN is given by: $\log_{10} p/\text{bar} = 8.095 - 33{,}224/T + 0.958 \times 10^{-17}\,T^5$. These authors suggest that ThN(cr) has only a small homogeneity range.

[1965SCA/TUR]

This paper concerns the synthesis of thorium oxyiodide and its study by X-ray diffractometry, optical and electron microscopy, visible and infrared spectroscopy, and solution calorimetry leading to a determination of its enthalpy of formation.

The compound was synthesised by reaction of thorium dioxide with a 20% excess molten thorium iodide. Most of the excess thorium iodide was sublimed from the product. Analytical results yielded 45.5% Th and 51.41% I (theoretical 46.2% Th and 50.6% I). The X-ray powder diffraction pattern was given but the data could not be indexed on the basis of a unit cell with orthorhombic or higher symmetry.

A value of $-(169.9 \pm 1.7)$ kJ·mol^{-1}, the average of four concordant measurements, was reported for the enthalpy of solution of the compound in 1 M HCl, after correction of individual measurements by 1.2 to 1.6 kJ·mol^{-1}, for the presence of 3 − 5 wt% thorium iodide in the oxyiodide. The amount of this impurity was determined by analysis for thorium and iodine of individual calorimetric solutions. For this correction, the authors used a “preliminary” value of −314 kJ·mol^{-1} for the enthalpy of solution of ThI_4(cr) in 1 M HCl. No further details on this value were given.

These results are the basis for the selection of the enthalpy of formation of $ThOI_2$(cr) by this review.

[1965SHC/SEM]

The total vapour pressures over the oxides ZrO_2, HfO_2, and ThO_2 were determined at *ca.* 2573 to 3023 K by isothermal evaporation and the partial pressures of the gaseous oxides $MO_2(g)$ and MO(g) at these temperatures were established by mass spectroscopy on the basis of ZrO_2^+/ZrO^+ ratios. The following equations are given for the pressures of ThO(g) and $ThO_2(g)$ over stoichiometric $ThO_2(cr)$:

$$\log_{10} p_{\mathrm{ThO(g)}} / \mathrm{bar} = -33300 / T + 7.10 \qquad 2573-2973\ \mathrm{K}$$

$$\log_{10} p_{\mathrm{ThO_2(g)}} / \mathrm{bar} = -35180 / T + 7.87 \qquad 2573-2773\ \mathrm{K}$$

These data are discussed in Sections VII.1.1.2 and VII.1.3.2.

[1965TAK/WES2]

The heat capacity of a sample of thorium dicarbide was measured by adiabatic calorimetry from 5 to 350 K and was found to be of normal sigmoid shape without transitions or thermal anomalies. The sample was a composite of seven different samples, prepared from the elements and annealed at 5 h at 2273 K, crushed and reheated to "above 2273 K" for a further 5 h to obtain a sample of uniform composition. The C/Th ratio was analysed to be (1.98 ± 0.03), the major impurity being 0.79 wt% carbon, for which the heat capacities were corrected. There is no mention of oxygen contamination or analysis. At 298.15 K, the values of $C^{\circ}_{p,\mathrm{m}}$ for $ThC_{1.98}$ and (S°_{m}(298.15 K) − S_{m}(0 K)) are (56.9 ± 0.2) and (68.7 ± 0.3) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ respectively, where the uncertainties have been increased from the 0.1% quoted in the paper to account for uncertainties in the composition of the sample.

[1965WES/TAK2]

The heat capacity of arc-melted buttons of hypostoichiometric "ThC_2" was measured by adiabatic calorimetry from 6 to 346 K and was found to be of normal sigmoid shape without transitions or thermal anomalies. The calorimetric sample was a mixture from a series of analysed samples, prepared from the elements. The weighted overall composition of the mixed calorimetric sample was calculated from the analyses to be 96.91 mol% $ThC_{1.93}$, 2.43 mol% WC, 0.46 mol% ThO_2, 0.19 mol% "ThH_3" and 0.012 mol% Th_3N_4, for which the measured heat capacities were corrected. Of course, there is the possibility that some, at least, of the impurities were dissolved in the main dicarbide phase. At 298.15 K, the values of $C^{\circ}_{p,\mathrm{m}}$ for $ThC_{1.93}$ and (S°_{m}(298.15 K) − S_{m}(0 K)) are (56.7 ± 0.2) and (68.5 ± 0.3) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ respectively, where the uncertainties have been increased from the 0.1% quoted in the paper to account for uncertainties in the composition of the mixed sample.

[1966ALC/COR]

Mass-loss effusion studies have been made of the vaporisation of compounds of thorium and uranium with silicon and germanium, and of other compounds of U with Pb, Sn, In, and Ga. Gibbs energies of formation are reported for the compounds $ThSi_2$, Th_3Si_5, ThSi, Th_3Si_2 for the temperature range *ca.* $1685 < T < 1961$ K and $ThGe_3$,

$ThGe_2$, Th_3Ge_5, ThGe, Th_3Ge_2, and Th_3Ge for the temperature range *ca.* $1330 < T <$ 1500 K. The data are presented only in graphical form and derived equations for the Gibbs energies of formation.

For all the alloys except that containing 37.5 at.% Si, corresponding to the phase field {liquid thorium, saturated with silicon + Th_3Si_2(cr)}, the pressures of thorium in the vapour were negligible. For this alloy, the individual pressures of Th(g) and Si(g) were measured by analysis of the condensed vapours, and the activity of thorium determined by comparing the measured p(Th) to that of their own measurements of the vapour pressure of pure thorium. However, there are no details of these measurements, merely a statement that the results were "in close agreement" with those of Darnell *et al.* [1960DAR/MCC]. It is noted in Section V.2.2 that the results of these authors are too high by a factor of three, probably because of residual oxygen contamination and consequent formation of ThO(g). This suggests that the Th-Si alloys used by Alcock *et al.* may also have contained appreciable oxygen, which would appear in the gas phase as both ThO(g) and SiO(g). In the absence of mass-spectrometric data, oxygen analyses or individual data values, it is impossible to correct for this effect, and it is preferable to use the thorium and silicon activities reported by Alcock *et al.,* rather than recalculate their results using the assessed data for the vapour pressures of the pure elements.

An additional source of uncertainty in the Th-Si study lies in the phase diagram at the temperature of the measurements. The authors found no evidence for separate phase fields due to the presence of Th_6Si_{11} as suggested by Brown and Norreys [1960BRO/NOR]. Alcock *et al.* interpreted their data in this region of the diagram in terms of one compound of composition Th_3Si_5, and we have also done this.

[1966ARO/AUS]

The authors report nitrogen pressures in the diphasic region ThN(cr) + Th_3N_4(cr) from *ca.* 1723 to 2073 K.

Samples of the nitride prepared by heating thorium metal in nitrogen at 773 to 1173 K had a N/Th molar ratio of (1.319 ± 0.002) as determined by the weight change. After correction for the 0.11 wt% oxygen present in the metallic thorium (assumed to form ThO_2(cr)), the composition of the thorium nitride becomes $ThN_{1.31}$. Aronson and Auskern [1966ARO/AUS] were not able to index the X-ray diffraction pattern obtained from the maroon-coloured product.

Nitrogen decomposition pressure measurements were made in the diphasic region ThN-Th_3N_4 from 1723 to 2073 K. The pressures ranged from 7×10^{-3} to 0.03 bar and equilibrium values were attained in (0.5−2) h. The pressures measured for both increasing and decreasing temperatures differed only slightly. The data were not sufficiently accurate to determine whether narrow ranges on non-stoichiometry exist in ThN and Th_3N_4, but there was some sluggishness in obtaining equilibrium in samples close to ThN.

No individual measurements are reported but the variation of $\log_{10} p_{\mathrm{N_2}}$ / bar with reciprocal temperature given in their Figure 2, was accurately linear. The Gibbs energy expression for the reaction:

$$6\mathrm{ThN(cr)} + \mathrm{N_2(g)} \rightleftharpoons 2\mathrm{Th_3N_4(cr)} \qquad \text{(A.51)}$$

was calculated by the authors to be:

$$[\Delta_{\mathrm{r}} G_{\mathrm{m}}]_{1723\,\mathrm{K}}^{2023\,\mathrm{K}}\ ((\mathrm{A.51}),\ T) = -\ (304.2 \pm 8.4) + (0.1368 \pm 0.0084)\ T\ \mathrm{kJ \cdot mol^{-1}}$$

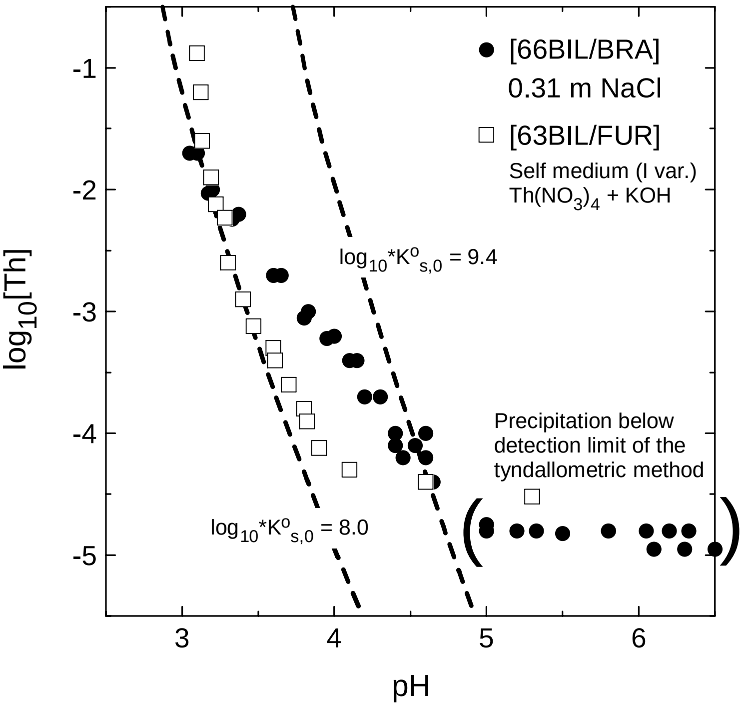
where the uncertainty includes those from experimental considerations as well as the reproducibility of the measurements. Both phases were assumed to be stoichiometric, which as noted in Section X.1.1.1 is probably true at the lower temperatures of the experimental range, but not, possibly at the higher temperatures.

[1966BIL/BRA]

This is a qualitative study of precipitation of zirconium and thorium in 50% seawater (salinity = 18.29‰; *ca.* 0.31 m NaCl), where the onset of precipitation was measured using a tyndallometric method. Bilinski and Branica [1966BIL/BRA] report "titration curves" where the onset of precipitation is measured as a function of pH and the total metal concentration ($[\mathrm{Th}]_{\mathrm{tot}} = 10^{-5} - 0.02$ M) at 20°C. The experimental data confirm the well known fact that these ions precipitate at low pH, lower for Zr (pH $1-3$) than for Th (pH $3-5$).

The authors did not determine equilibrium constants from their experimental data, but they show a solubility curve in Figure 2 of [1966BIL/BRA]. This curve is based on the pH values measured in the suspensions after 24 hours with a glass electrode calibrated against pH buffers (activity scale) and measurement of the total thorium concentration in the solution. As pH values might shift upon ageing of the suspensions (*cf.*, [1959HIG]) and the equilibrium thorium concentration after filtration or ultracentrifugation is certainly lower than $\mathrm{Th_{tot}}$; the solubility curve neither represents the correct pH at the onset of precipitation/colloid formation nor the classical solubility data from oversaturation. Nevertheless, using the hydrolysis constants and ion interaction coefficients selected in this review and $\log_{10} \gamma_{\mathrm{H^+}} = -0.12$ in 0.31 m NaCl as calculated with the SIT, re-evaluation of the data in [1966BIL/BRA] yields lower and upper limits for the solubility constant of thorium hydroxide ($8.0 \le \log_{10} {}^{*}K^{\circ}_{s,0} \le 9.4$). The mean value, $\log_{10} {}^{*}K^{\circ}_{s,0} = (8.7 \pm 0.7)$, is in reasonable agreement with the solubility constants recalculated by this review from numerous other studies. The constant level of $[\mathrm{Th}] = 1.6 \times 10^{-5}$ M at pH > 5 has no chemical significance, it simply reflects the detection limit of light scattering caused by solid particles, which was at $[\mathrm{Th}]_{\mathrm{tot}} = 3 \times 10^{-5}$ M for the equipment used by [1966BIL/BRA]. In an earlier study of Bilinski *et al.* [1963BIL/FUR], analogous experiments were performed in $\mathrm{Th(NO_3)_4}$-KOH "self media" without background electrolyte to keep ionic strength constant. For comparison they are also shown in Figure A-16.

Figure A-16: Solubility of thorium hydroxide determined by the tyndallometric method in 50% seawater [1966BIL/BRA] and $Th(NO_3)_4$-KOH solutions of variable ionic strength [1963BIL/FUR] at 20°C. The dashed lines are calculated for $I = 0.31$ mol·kg^{-1} (in aqueous NaCl) with $\log_{10} {}^{*}K^{o}_{s,0} = 8.0$ (lower limit) and 9.4 (upper limit) and the hydrolysis constants and ion interaction coefficients selected by this review.



[1966CHI/GAR]

The enthalpies of transformation and fusion of $ThCl_4$ (and several elements and alloys) were measured with an adiabatic calorimeter. Adequate adiabatic conditions were obtained by using a small external power source to compensate for a lack of temperature uniformity on the surface of the platinum radiation shield.

At fusion or transformation points, the thermal effect was determined by measuring, at constant power input to the sample, the time required to raise its temperature by 2 K.

The $ThCl_4$(cr) used, whose actual preparation was not described, was described as being *ca.* 99.8% pure, despite having as much as 1.5 mol% (1050 ppm) oxygen (possibly as $ThOCl_2$) and 0.1 mol% of each C and N and smaller amounts of Fe, Cr and Ni. Samples were sealed in tantalum containers, and premelted before the determinations. This will of course have removed much of the oxygen from the sample. There is also the possibility of the formation of lower chlorides, whose status is far from clear (see Section VIII.2.1). A solid-solid transition of unknown origin was observed at (679 ± 2) K, with an enthalpy of transition of (5.0 ± 1.0) $kJ \cdot mol^{-1}$ (three determinations). The melting point was found to be (1042 ± 2) K, and the enthalpy of fusion (61.5 ± 2.6) $kJ \cdot mol^{-1}$ (four determinations).

The enthalpies of fusion of ten other metals and alloys (plus $CaCl_2$) were also determined, and were within 5% of the literature values for these materials, except for Bi and Mg, where the deviations were 6.0 and 8.6%.

[1966GAN/KNA]

This is Knudsen-effusion study of the decomposition pressures of lead over the compounds in the Th-Pb system from 910 to 1263 K, depending on the phase field. The vapour pressure of pure lead was also determined from 908 to 1178 K. The mass losses of the cell during heating were measured by an automatically registering thermobalance. The decomposition pressures of the diphasic phase fields containing ThPb, $ThPb_2$, $ThPb_3$, and $ThPb_4$. The last compound was not previously recognised in the Th-Pb system. The measured vapour pressure of pure lead is in good agreement with the values derived from [1989COX/WAG]. The decomposition pressures in the various phase fields were combined with the vapour pressure of pure lead to provide Gibbs energies of formation of ThPb(cr), $ThPb_2$(cr), $ThPb_3$(cr), and $ThPb_4$(cr) from *ca.* 900 to 1300 K. As discussed in Section XI.5, Chiotti *et al.* [1981CHI/AKH] have reassessed these data, making small corrections to the derived equations for the decomposition pressures to obtain better agreement with the phase diagram.

[1966GIN/ARO]

Measurements on solid-state electrochemical cells with a CaF_2(cr) electrolyte were used to obtain thermodynamic data on thorium phosphides at 1073 to 1223 K. Two cells were studied: (I) Th, $ThF_4|CaF_2|ThF_4$, Th, $ThP_{0.55}$ and (II) Th, $ThF_4|CaF_2|ThF_4$, ThP, Th_3P_4. The emf of the first cell relates to the activity of thorium in the P-saturated metal, and is of no immediate interest to the review.

Th_3P_4(cr) was prepared from thorium and red phosphorus, and ThP by thermal decomposition of Th_3P_4(cr); their mixtures with ThF_4(cr) for the emf samples were annealed in tungsten or silica. Oxygen analyses by vacuum-fusion generally showed 600 − 800 ppm oxygen, but with one samples of $ThP_{0.96}$ as high as 1400 ppm; nitrogen and hydrogen levels were less than 100 ppm. Although appreciable (up to 2 mole%), such oxygen contamination should not be too important in the experiments with the second cell, since the overall P/Th should in general not be critical to the results.

The time required for stable emf values is not stated, except for a few values which were left for 7 − 15 h before measurement. Measurements made after both increasing and decreasing the temperature differed by of 2−3 mV in general, and the mean emf was adopted. However, the standard deviation of the emf cell (II) at the mid temperature was estimated to be as high as 11.4 mV, since there were noticeable differences in the emf for mixtures with P/Th ratios of 1.21, 1.15 and 1.01, particularly the last. This may be due to non-stoichiometry in 'ThP', or the greater effect of oxygen contamination near the stoichiometric composition of the monophosphide, or to slow attainment of equilibrium.

The detailed results are not reported, but for cell (II), the authors calculated the Gibbs energy of the cell reaction:

$$4\mathrm{ThP(cr)} \rightleftharpoons \mathrm{Th_3P_4(cr)} + \mathrm{Th(cr)} \qquad \text{(A.52)}$$

to be:

$$[\Delta_\mathrm{f} G_\mathrm{m}]^{1223\,\mathrm{K}}_{1073\,\mathrm{K}}\,((\mathrm{A.52}), T) = -\,(224700 \pm 23400) + (38.9 \pm 31.0)\,T\ \mathrm{J{\cdot}mol^{-1}}$$

where the uncertainties are twice those quoted by the authors.

Of course, these results correspond to the oxygen saturated phosphides, which may not be exactly stoichiometric either.

The authors combined these data with the partial pressures of P_2(g) in the same diphasic region ThP(cr) + Th_3P_4(cr), over a much higher temperature range, to calculate the Gibbs energies of these phases. As noted in the Appendix A entry for [1963GIN/EFI], this review does not consider their results to be reliable enough, especially at the lower temperatures relevant to the combined analysis, for this to be a dependable procedure.

[1966HEN/JOH]

This paper of Hentz and Johnson is discussed together with [1965HEN/TYR], a related paper of the same group.

[1966HEU/EGA]

The Gibbs energy of formation of ThF_4(cr) was determined at 873 K with emf cells using a CaF_2 solid electrolyte and Mg/MgF_2(cr), Al/AlF_3, and Ni/NiF_2 counter electrodes. A silica cell was used for experiments with Mg/MgF_2 and Al/AlF_3 electrodes, but an all-nickel container was required for the cell with Ni/NiF_2. Separate experiments demonstrated that there was no electronic conduction in the CaF_2 solid electrolyte. Equilibrium was achieved only slowly, in 2−3 days. Measurements were made only at 873 K. The data are analysed by the third-law in Section VIII.1.1.2.3.

[1966LEV]

The enthalpy of Th(cr) and Th(l) relative to 310 K was measured in a drop calorimeter from 1269 to 1650 K for α-Th, from 1667 to 1991 K for β-Th and from 2069 to 2100 K for Th(l).

Analysis of the crystal-bar thorium used showed only trace amounts of some metallic elements and 50 ppm C and 90 ppm O. The calorimetric sample, a cylinder *ca*. 2.5 cm in diameter and 2.5 cm long, was sealed in a tungsten container. Tungsten appeared to be inert to Th(l) for a period of 2 h at 2100 K, the highest temperature reached. Temperatures were measured pyrometrically in a black-body hole bored in the tungsten container.

The data were consistent with the transition temperatures of 1653 and 2033 K reported earlier by Eash and Carlson [1960EAS/CAR], and these were used to calculate the enthalpies of transition and fusion, which were estimated to be (3590 ± 120) and (13800 ± 1250) $\text{J}\cdot\text{mol}^{-1}$ respectively. The enthalpy data were fitted to the equations:

$$H_{\text{m}}(T) - H_{\text{m}}(310) = -17140 + 36.510\,T\ (\text{J}\cdot\text{mol}^{-1}) \text{ for } \alpha\text{-Th and}$$

$$H_{\text{m}}(T) - H_{\text{m}}(310) = 4515 + 15.702\,T + 5.795\times10^{-3}\,T^{2}\ \text{J}\cdot\text{mol}^{-1} \text{ for } \beta\text{-Th.}$$

The temperature range in the liquid region was too small to derive a meaningful heat capacity.

The uncertainty in the derived heat capacities was estimated by the author to be 1.5%.

[1966SU/NOV]

This paper deals mainly with the pressure and composition of the vapour in the KCl-$ThCl_4$ system, but does include six measurements of the vapour pressure of pure $ThCl_4$(cr) from 933 to 1043 K, by the boiling point method.

$ThCl_4$ was prepared by chlorination of thorium oxalate with a stream of chlorine saturated with CCl_4(g) at 923 to 973 K. It is described (in the English translation) as melting “at 669°C, very close to the 770°C given in tables”, (the melting point selected by the review is 769°C), and unspecified analyses showed the Cl/Th ratio to be (3.98 ± 0.02).

The data, which are included in the discussion in Section VIII.2.1.4.1, are in excellent agreement with the corpus of other vapour pressure determinations for $ThCl_4$(cr).

[1966TAK/HON]

The phase diagram between Th and ThC was studied by metallographic and X-ray techniques and by measurements of the electrical resistivity in quenched and slowly-cooled Th-C alloys. The α-β transformation temperature of thorium increased gradually with carbon content up to 2.3 at% C, and rapidly thereafter. Extrapolation to zero carbon content gave T_{trs}(Th, cr) = (1633 ± 10) K.

[1967ARO]

Thermodynamic information on the various diphasic fields in the Th-S system was obtained from emf measurements on solid state cells, using CaF_2 as the electrolyte, at 1100 to 1200 K. The cells employed were:

$$Th(cr), ThF_4(cr) \mid CaF_2 \mid Th(cr), ThS(cr), ThF_4(cr)$$

$$Th(cr), ThF_4(cr) \mid CaF_2 \mid ThS(cr), Th_2S_3(cr), ThF_4(cr)$$

$$Th(cr), ThF_4(cr) \mid CaF_2 \mid Th_2S_3(cr), Th_7S_{12}(cr), ThF_4(cr)$$

$$Th(cr), ThF_4(cr) \mid CaF_2 \mid Th_7S_{12}(cr), ThS_2(cr), ThF_4(cr)$$

Steady emf values were attained only very slowly, especially for the two cells containing Th_7S_{12}(cr); moreover, the emf values varied appreciably (± 10mV) for different compositions in the same phase field, indications perhaps that equilibrium was not completely attained. This is often the case for solid-state emf reactions involving non-fluorides. For this reason we have quoted only the Gibbs energy values given by Aronson, rather then the enthalpies and entropies derived over a short temperature range.

The Gibbs energy obtained from the first cell relates to the activity of thorium in Th(cr) saturated with sulphur, and is of no importance for the review. The other cells involve the reactions listed below, with the corresponding Gibbs energy change at 1173 K.

$$Th(cr) + Th_2S_3(cr) \rightleftharpoons 3\,ThS(cr) \qquad (A.53)$$

$$\Delta_r G_m\,((A.53), 1173\text{ K}) = -(82.8 \pm 8.2)\text{ kJ·mol}^{-1}$$

$$Th(cr) + Th_7S_{12}(cr) \rightleftharpoons 4Th_2S_3cr) \qquad (A.54)$$

$$\Delta_r G_m\,((A.54), 1173\text{ K}) = -(166.1 \pm 8.2)\text{ kJ·mol}^{-1}$$

$$Th(cr) + 6ThS_2(cr) \rightleftharpoons Th_7S_{12}(cr) \qquad (A.55)$$

$$\Delta_r G_m\,((A.55), 1173\text{ K}) = -(398.3 \pm 16.7)\text{ kJ·mol}^{-1}.$$

In the absence of any entropy or heat capacity data for the higher sulphides, no reliable data can be derived for Th_7S_{12}(cr) or ThS_2(cr), but since we have reasonably precise enthalpies of formation for ThS(cr) and Th_2S_3(cr), $\Delta_r G_m$ ((A.53), 1173 K) can be used to derive an approximate value for the entropy of Th_2S_3(cr). With the reasonable assumption that $\Delta_r C_{p,m}$ (A.54) is zero, the derived value is S°_{m} (Th_2S_3, cr, 298.15 K) = (179.9 ± 18.0) J·K^{-1}·mol^{-1} where the uncertainty excludes that from $\Delta_r C_{p,m}$ (A.54).

[1967BEN/HOF]

Parts of the Th-N phase diagram were determined by X-ray, microscopic, chemical, and thermal analyses of phases equilibrated with nitrogen (up to 3 bar) at temperatures up to 3093 K. The Th-ThN portion of the phase diagram is a peritectoid-peritectic system wherein, upon heating, the face centred cubic Th phase with a N:Th ratio (0.08 ± 0.02) decomposes peritectoidally at (1878 ± 20) K to body centred cubic Th and ThN. The body centred cubic Th phase with a N:Th ratio (0.09 ± 0.02) decomposes peritectically at (2073 ± 25) K to liquid Th and ThN. The Th-rich boundary of the ThN phase extends from the N:Th ratio (0.97 ± 0.03) at 1849 K to 0.87 at 2273 K, while the N-rich boundary extends from the N:Th ratio (1.03 ± 0.03) at 1888 K to 1.08 at 2338 K. The mononitride phase melts congruently at (3093 ± 30) K with the N:Th ratio (0.995 ± 0.005) under 2 atm $N_2(g)$, in agreement with the data of Olsen and Mulford [1965OLS/MUL]. The Th-rich boundary of the rhombohedral Th_3N_4 phase changes with increasing temperature from the N:Th ratio 1.33 at 1873 K to (1.29 ± 0.03) at 2233 K.

[1967BER]

Beran [1967BER] investigated the formation of mononuclear Th(IV) hydroxide complexes at 25°C by means of sorption onto two cation exchange materials (Katex S–4 and S–15) which differ only in their swelling properties. The experiments were performed at $I = 0.5$ M ($HClO_4$-$NaClO_4$) and low total thorium concentrations of 10^{-6} M, spiked with trace amounts of ^{234}Th for radiometric analysis. The author used glass and calomel reference electrodes for pH measurements. Details on electrode calibration and the transformation of the measured values into $-\log_{10}[OH^-]$ values used for data evaluation are not given in the paper. According to the ion product of water calculated with NEA-TDB auxiliary data ($\log_{10} K_w^\circ = -13.75$ in 0.5 M $NaClO_4$), the studies were performed in the range $-\log_{10}[H^+] = 1.0 - 3.5$.

In Figure 1 of [1967BER], the distribution coefficients $\log_{10} K_{S-4}$ and $\log_{10} K_{S-15}$

$$K = ([Th]_{sorbed} / [Th]_{aq}) (V_{sln} / m_{CE}) \tag{A.56}$$

with V_{sln} = volume of solution and m_{CE} = mass of cation exchange material, are shown as function of pOH = $-\log_{10}[OH^-]$. It is evident that both the distribution coefficients $\log_{10} K_{S-4}$ and $\log_{10} K_{S-15}$ and also their dependence on pH are different. The two curves are not shifted in parallel but cross each other at $\log_{10}[OH^-] \approx -10.3$. This means that the differences between the distribution coefficients of the Th^{4+} ion (predominant at pH < 2, where $\log_{10} K_{S-4}$ and $\log_{10} K_{S-15}$ are approximately constant) and the hydroxide complexes are not the same in the two ion exchangers, as expected.

The authors calculated the average charge ($\bar{Z}$) of the dissolved thorium species $Th(OH)_n^{4-n}(aq)$, from the different values of K_{S-15} and K_{S-4} at given pH according to:

$$\bar{Z} = \{\log_{10}(K_{S-15}/K_{S-4}) / \log_{10}(V_{S-4}/V_{S-15})\} + 1 \tag{A.57}$$

where V_{S-4}/V_{S-15} is a constant value (V = specific volume (mL) of swollen cation exchange materials S−4 and S−15 (mL) per gram of dry substance). The Th(IV) species are expected to be mononuclear at the low aqueous Th concentrations of about 5×10^{-7} M and pH < 3.5; however there seems to be no justification for Eq.(A.57). At a given pH the ratio between the overall distribution coefficients reflects differences in the individual distribution coefficients of the sorbed species and these values are known to vary with the cross-linking of the ion-exchanger. The calculated ratio will thus reflect the average charge of sorbed Th and not the average charge in solution. The stepwise equilibrium constants $\log_{10} K_n$ ($n = 1-4$) for the reactions:

$$\mathrm{Th(OH)}_{n-1}^{4-n+1} + \mathrm{OH}^- \rightleftharpoons \mathrm{Th(OH)}_n^{4-n}$$

calculated by Beran from the plot of $\overline{Z}$ *vs.* pOH (Figure 2 in [1967BER]) are not reliable. The corresponding overall formation constants $\log_{10} {}^*\beta^{\circ}_{n,1}$, extrapolated to zero ionic strength with the SIT, are orders of magnitude higher than values from other studies accepted by this review.

Table A-27: Equilibrium constants $\log_{10} K_n$ and $\log_{10} \beta_{n,1}$ at $I = 0.5$ M ($HClO_4$-$NaClO_4$) and 25°C reported by Beran [1967BER]; $\log_{10} \beta^{\circ}_{n,1}$ and $\log_{10} {}^*\beta^{\circ}_{n,1}$ are extrapolated to $I = 0$ with the SIT by this review.

Complex	$\log_{10} K_n$	$\log_{10} \beta_{n,1}$	$\log_{10} \beta^{\circ}_{n,1}$	$\log_{10} {}^*\beta^{\circ}_{n,1}$
$Th(OH)^{3+}$	11.64 ± 0.07	11.64 ± 0.07	12.9 ± 0.1	– 1.1 ± 0.1
$Th(OH)_2^{2+}$	10.80 ± 0.07	22.44 ± 0.10	24.6 ± 0.2	– 3.4 ± 0.2
$Th(OH)_3^{+}$	10.62 ± 0.05	33.06 ± 0.11	35.8 ± 0.2	– 6.2 ± 0.2
$Th(OH)_4$(aq)	10.45 ± 0.07	43.51 ± 0.13	46.5 ± 0.2	– 9.5 ± 0.2

Nevertheless this paper is helpful to judge hydrolysis constants derived by cation exchange methods. The different pH-dependence of the sorption behaviour of Th(IV) onto different cation exchange materials shows that the evaluation of pH-dependent distribution (sorption) coefficients requires not only the fitting of the formation constants $\log_{10} \beta_{n,m}$ (or $\log_{10} {}^*\beta_{n,m}$) of the hydroxide complexes formed in solution but also of their equilibrium constants $\log_{10} {}^{\mathrm{CE}}K_{n,m}$ for the sorption onto the cation exchange material (CE):

$$\mathrm{Th}_m\mathrm{(OH)}_n^{4m-n}\mathrm{(aq)} + \mathrm{CE} \rightleftharpoons \mathrm{CE{-}Th}_m\mathrm{(OH)}_n^{4m-n}\mathrm{(sorbed)}.$$

This is further corroborated by the cation exchange study of Davydov and Toropov [1986DAV/TOR2] at pH 1 – 4 ($I = 0.1$ M), where the distribution coefficients remain constant up to pH 3, whereas for the two cation exchange materials used by Beran [1967BER], Katex S–4 and S–15, the distribution coefficients begin to decrease already at pH > 2.5 and pH > 2.2, respectively.

[1967BIL/ING2]

Bilinski and Ingri [1967BIL/ING2] investigated the precipitation of thorium from aqueous solutions of thorium nitrate (1.25 mM) and ammonium oxalate (2.5 – 80 mM) at pH 1 to 10 and a temperature of 20°C. Ionic strength was kept constant at $I = 1.0$ M ($NaClO_4$). The H^+ concentration in the perchlorate solutions was decreased coulometrically and measured with a glass and a Ag/AgCl reference electrode. The precipitates formed, fluffy $Th(OH)_4(s)$ at pH 6 − 8 and $Th(C_2O_4)_2{\cdot}6H_2O(cr)$ at pH 1 − 2, were characterised by chemical analyses. The solubility of $Th(OH)_4(s)$ in the presence of oxalate and the potentiometric data in excess of oxalate were evaluated assuming simply the formation of one binary thorium oxalate complex:

$$Th(OH)_4(s) + 4\,C_2O_4^{2-} + 4H^+ \rightleftharpoons Th(C_2O_4)_4^{4-} + 4H_2O(l) \qquad (A.58)$$

$$Th^{4+} + 4\,C_2O_4^{2-} \rightleftharpoons Th(C_2O_4)_4^{4-} \qquad (A.59)$$

The calculated equilibrium constants, $\log_{10} {}^*K_{s,4}$ (A.58) = 34.8 and $\log_{10} \beta_4$ (A.59) = 24.2, respectively, are given without uncertainties. The difference between the two equilibrium constants yields a solubility constant of $\log_{10} {}^*K_{s,0}$ ($Th(OH)_4$, s, 1 M $NaClO_4$) = 10.6. However, as the simple aqueous speciation assumed for the investigated ternary solutions is not well ascertained, this solubility constant is not included in the final data selection. Data on the hydrolysis of Th(IV), as indicated by the title of the paper, are not given in [1967BIL/ING2], but in an earlier paper of Bilinski *et al.* [1963BIL/FUR].

[1967CHI/DOO]

The electrical resistivity of thorium rods containing 80 − 200 ppm of carbon, by weight, (plus 8 − 50 ppm N and 50 − 190 ppm O) were measured from room temperature to 1973 K, and the α-β transformation temperatures inferred from discontinuities in the resulting curves. Extrapolation of the measurements to zero carbon content indicates T_{trs} = (1623 ± 10) K for pure thorium. These results, showing that carbon raises the transformation temperature, are consistent with the phase boundaries established at much higher carbon contents.

[1967MER/SKO]

The solubility of $ThP_2O_7(s)$ was determined at 25°C in a 0.1 M $(Na,H)ClO_4$ ionic medium. The solid phase was characterised using elemental analysis before the experiments, but not after equilibrium had been attained. The concentration of H^+ in the various test solutions, as determined by the pH, varied between 100 and 5 mM and the corresponding solubility between 12.26×10^{-6} and 0.25×10^{-6} M. It is not clear how the solubility product and the formation of the equilibrium constant for the complex $ThP_2O_7(aq)$ have been determined; the authors point out that the concentration of $[ThP_2O_7(aq)]$ is constant in the presence of the solid phase of the same composition. They report the following equilibrium constants:

$$\log_{10} K_{s,0} = -(24.25 \pm 0.02) \text{ and } \log_{10} \beta_1 = (18.0 \pm 0.2),$$

for the reactions:

$$ThP_2O_7(s) \rightleftharpoons Th^{4+} + P_2O_7^{4-}$$

and

$$\mathrm{Th^{4+} + P_2O_7^{4-} \rightleftharpoons ThP_2O_7(aq)}$$

where the uncertainties are those given by the authors. The equilibrium constants depend on the auxiliary data used and the dissociation constants of pyrophosphoric acid used differ substantially from those selected in the present review. In addition the authors have not tested other equilibrium models than the one proposed; in particular they have not considered the possible formation of ternary complexes $\mathrm{ThH}_p(\mathrm{P_2O_7})_q$ (charge omitted for simplicity). For these reasons this review has not accepted the proposed equilibrium constants.

[1967MOS/ESS]

The authors have measured the solubility of $\mathrm{Th(HPO_4)_2{\cdot}4H_2O(s)}$ and $\mathrm{U(HPO_4)_2{\cdot}4H_2O(s)}$ in $\mathrm{HClO_4}$ solutions by varying the total concentration of phosphoric acid from 0.1 mM to 1.5 M at a constant hydrogen ion concentration of 0.35 M. There is no information about the temperature used and this review assumes that these data refer to “room temperature” around 20°C; there is no information about the characterisation of the solid phase, but this is well known and the present review has therefore accepted the procedures used. The experimental solubility for $\mathrm{U(HPO_4)_2{\cdot}4H_2O(s)}$ fits well to a smooth solubility curve (Figure 1 in [1967MOS/ESS]) indicating that the experimental procedures used are satisfactory. As the experimental data have been made at constant $[\mathrm{H^+}]$ it is not possible to determine the stoichiometry of the complexes with respect to $\mathrm{H^+}$. The reported conditional constants are valid at $[\mathrm{H^+}] = 0.35$ M. The reported equilibrium constants, $\log_{10}\beta_n$, for the reactions:

$$\mathrm{Th^{4+}} + n\,\mathrm{HPO_4^{2-}} \rightleftharpoons \mathrm{Th(HPO_4)}_n^{4-2n} \qquad n = 1-3$$

are $\log_{10}\beta_1 = 10.6$, $\log_{10}\beta_2 = 22.6$ and $\log_{10}\beta_3 = 31.3$, respectively. The value of $\log_{10}\beta_2$ is doubtful according to the present review as it would imply that the bonding strength of the second ligand is larger than that of the first and this is a very unusual situation that is not encountered in the other actinide(IV) complexes discussed in [1967MOS/ESS]. The solubility product for $\mathrm{Th(HPO_4)_2{\cdot}4H_2O(s)}$ is $\log_{10} K_{s,0} = -26.89$, considerably smaller than the value $\log_{10} K_{s,0} = -21.0$ (-19.9 for the experiments using a Th tracer) proposed in [1956CHU/STE] in sulphuric acid, but the agreement is better with their reported value in nitric acid, $\log_{10} K^{\circ}_{\mathrm{s},0} = -(26.6 \pm 0.2)$. In the latter study the effects of phosphate (and sulphate) complexation on the solubility were not taken into account. The experimental data in [1967MOS/ESS] are satisfactory, but as the stoichiometry with respect to $\mathrm{H^+}$ is not known, the reported equilibrium constants are not accepted by this review.

[1968DAN/MAG]

This potentiometric study uses the methodology and data analysis as described in [1954HIE] and [1964HIE/SIL] but the experimental concentration range is extended to higher thorium concentrations, up to 0.5 M Th(IV). The authors have chosen to change the proton concentration in the test solutions by adding 2 M NaOH. This is unfortunate due to the risk of local precipitation of hydrous oxides; they also note that the reproducibility of the experimental data is poor at $\bar{n}_{\mathrm{OH}} > 1$. Nevertheless the data analysis has been made using all the experimental information. The experiments have been made at 25.0°C using 4 M $NaNO_3$ and 4 M $NaClO_4$ as ionic media. In the $NaNO_3$ medium the Th_{tot} concentrations vary between 0.01 and 0.5 M, the $-\log_{10}[H^+]$ range between 2 and 3.5 and $\bar{n}_{\mathrm{OH}}$ from 0.05 to 1.4; in the $NaClO_4$ medium $[Th]_{tot}$ varies between 0.05 and 0.5 M, the $-\log_{10}[H^+]$ range between 2 and 3.5 and $\bar{n}_{\mathrm{OH}}$ between 0.05 and 1.9. The ionic medium composition changes significantly at the highest thorium concentrations. The highest $\bar{n}_{\mathrm{OH}}$ values are obtained in the $NaClO_4$ ionic medium. The graphical analysis using the "core and links" model is not consistent with the least-squares model as previously found by Hietanen and Sillén [1964HIE/SIL] and only the least-squares equilibrium constants are therefore listed in Table A-28.

Table A-28: Equilibrium constants $\log_{10}{}^{*}\beta_{n,m}$ ($Th_m(OH)_n^{4m-n}$) for the formation of Th(IV) hydroxide complexes for each ionic medium at 25°C.

Complex $Th_m(OH)_n^{4m-n}$	$\log_{10}{}^{*}\beta_{n,m}$ (4 M NO_3^-)	$\log_{10}{}^{*}\beta_{n,m}$ (4 M ClO_4^-)
$Th_2(OH)^{7+}$	-	-2.72 ± 0.09
$Th_2(OH)_2^{6+}$	-5.49 ± 0.04	-
$Th_3(OH)_5^{7+}$	-	-12.42 ± 0.05
$Th_2(OH)_4^{4+}$	-	-10.49 ± 0.02
$Th_3(OH)_6^{6+}$	-17.92 ± 0.07	-
$Th_4(OH)_8^{8+}$	-	-19.23 ± 0.11
$Th_6(OH)_{14}^{10+}$	-	-36.23 ± 0.13
$Th_4(OH)_{12}^{4+}$	-37.21 ± 0.06	-

The equilibrium constants in perchlorate media proposed by Danesi *et al.* are in poor agreement with those of other authors, even though they describe their own experimental data well. This is another example of the difficulty in assigning a unique chemical model for the Th(IV) hydrolysis using potentiometric data alone. As the primary experimental data are only given as graphs of $\bar{n}_{\mathrm{OH}}$ *vs.* $-\log_{10}[H^+]$ it has not been possible to test them against the models suggested in [1964HIE/SIL] and [1965BAE/MEY]. In the 4 M nitrate medium, the equilibrium constant for the (2,2) species is in good agreement with the measurements in [1982MIL/SUR2] in 0.5−3.0 M $NaNO_3$ and the equilibrium constant for the (8,4) species is consistent with the value from [1991GRE/LAG2] in 3.0 M $NaClO_4$. The value for the (12,4) complex in 4 M $NaNO_3$ is compatible with the values reported in 0.1 M KNO_3 [1983BRO/ELL] and 3.0 M $NaClO_4$ [1991GRE/LAG2], *cf.*, Section VII.3.4.1.

[1968GIN]

Mass-spectrometric measurements were made on a nitrogen-containing Th-B-P alloy, contained in a tungsten crucible, but at two temperatures only, 2702 and 2745 K. The alloy was formed from a mixture of ThP and BN, but most of the nitrogen had been lost during earlier experimentation. Ion currents were converted to pressures using a silver calibration.

The authors combine the above reaction enthalpies with published thermodynamic data to give the dissociation energy D° (298.15 K) and the enthalpy of formation, $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\circ}$ (298.15 K) of ThN(g) of (577.4 ± 33.5) and (470.7 ± 31.4) $\mathrm{kJ \cdot mol^{-1}}$ respectively. The required thermal functions for ThP(g) and ThN(g) were estimated from those of US(g) and ThO(g) respectively. The only values quoted are of $((G_{\mathrm{m}} - H_{\mathrm{m}}(298.15\ \mathrm{K}))/T$ at 2500 and 3000 K.

These data have been recalculated by the review in Section X.1.1.2, but because of the paucity of the experimental data, and the various assumptions in the derivation, no data have been selected for ThN(g).

[1968GOL/KAL]

The complex formation in the Th(IV)-nitrite system was investigated using conductometry, spectrophotometry and polarography in methanol. The composition and equilibrium constants for ternary complexes $\mathrm{Th(OMe)_2(NO_2)^+}$, $\mathrm{Th(OMe)_2(NO_2)_2}$ and $\mathrm{Th(OMe)_2(NO_2)_3^-}$ were determined. These data are not relevant for estimates of nitrite complexes in aqueous solution.

[1968HIE/SIL]

This study of Th(IV) hydrolysis has been made in a 3.00 M (Na)Cl medium and a temperature of 25°C. The paper also includes a reinterpretation of experimental data from [1954HIE], [1954KRA/HOL] and [1965BAE/MEY]. The experimental method is the same as in [1954HIE] but with special care to reduce the amount of protolytic impurities, mainly iron, in the ionic medium. This is essential in order to increase the accuracy at the lowest values of $\mathrm{Th_{tot}}$, *cf.* p. 267 in [1968HIE/SIL]. The authors also used coulometric methods in order to avoid impurities and local $\mathrm{OH^-}$ excess in the titrations. The authors checked the reversibility of the system and that the potentials remained stable over time periods up to two weeks. The authors tested both glass- and hydrogen-electrodes and found the latter to be superior; all experimental data given in the paper refer to this electrode. The interpretation of the data and the testing of different chemical models were made using the least-squares method, LETAGROP developed by Sillén and his co-workers. Experimentally this study still represents the state of the art in potentiometric studies. The study covers a wide range of $\mathrm{Th_{tot}}$ concentrations, ten different concentrations from 0.10 to 100 mM, and a $-\log_{10}[\mathrm{H^+}]$ range from 2 to 4; $\bar{n}_{\mathrm{OH}}$ varied from 0 to about 1.7. The authors noticed that the potentials were not constant at the highest values of $\bar{n}_{\mathrm{OH}}$ and these data were left out in the analysis. At $\bar{n}_{\mathrm{OH}}$ around 1.5 the potential did not vary more than 0.2 mV over a two week period corresponding to a change in $-\log_{10}[\mathrm{H}^+]$ of about 0.003. The chemical models tested are given in Table A-29.

The "best" set of equilibrium constants is provided by Model III, but the difference between the different models is not large. In order to test the relative concentrations of the complexes in Model III, we have calculated the species distribution in two of the titrations and also explored possible structural models. From the distribution diagrams it is obvious that the predominant species are binuclear complexes $\mathrm{Th_2(OH)_2^{6+}}$, $\mathrm{Th_2(OH)_3^{5+}}$ and the hexanuclear complex $\mathrm{Th_6(OH)_{14}^{10+}}$. The trinuclear complex $\mathrm{Th_3(OH)_3^{9+}}$ is only present to a few percent in the test solutions, except at the highest total concentration of Th, where it amounts to about ten percent. Of the minor species suggested, the complex $\mathrm{Th_3OH^{11+}}$ seems unlikely on chemical grounds. Binuclear Th complexes have been identified both in solution and in the solid state [1968JOH], [1968JOH2], [1991JOH/MAG]; the hexanuclear complex may well have an octahedral $\mathrm{Th_6}$-core similar to that found in the uranium(IV) basic salt $\mathrm{U_6O_4(OH)_4(SO_4)_6}$, [1952LUN]; this review has not found any solid-state structures containing trinuclear hydroxide units. The other species found in the least-squares analysis may well be artefacts due to undetected systematic errors such as the formation of small amounts of larger polymers or colloids [2002NEC/MUL], [2003BIT/MUL], activity factor variations, *etc*.

The "best" chemical model is the one that gives the smallest least-squares residuals. The different models are shown in Table A-29. and the "best" speciation diagrams in Figure A-17. It is worth noting that the main difference between the models is found among the minor complexes, species that constitute only a few percent of the total concentration of Th(IV); this is shown in the speciation diagrams for some of the other models shown in Figure A-18, Figure A-19 and Figure A-20. It is instructive to compare the results given in Table A-29. In Model I we can note that the minor species (2,3) and (8,4) disappear when introducing a systematic error in $\bar{n}_{\mathrm{OH}}$, but that the effect on the major species is very small. Similar effects are also noticed in Models II-IV. Based on the least-squares analysis alone, Model III-B is the "best" one. The major species (1,1), (2,2) are present in all models, while several other combinations of complexes result in similar fit to the experimental data. It is obviously not straightforward to select the "best" chemical model and one must if possible use other criteria, such as the compatibility of the proposed stoichiometry with the known coordination chemistry of Th(IV). In our analysis we will remove minor species from consideration, as they are very strongly correlated with experimental artefacts.

Table A-29: The “best” combinations of equilibrium constants for Th(IV) hydrolysis in 3 M (Na)Cl as identified by a LETAGROP least-squares analysis. Model I has $m \le 4$; Model II has $m \le 5$; Model 3 $m \le 6$ and Model IV no restrictions on m, where m is the the number of OH groups in the complex. In Models A no systematic errors are taken into account; in Models B the least-squares refinements have been made by assuming a systematic error in $\bar{n}_{\mathrm{OH}}$. The standard deviation $\sigma(\bar{n}_{\mathrm{OH}})$ is small but systematically smaller for the models with $m \le 6$; these accordingly represent the “best” set of those investigated. Complexes that are poorly defined in the least-squares analysis have no estimated standard deviation in $\log_{10} {}^*\beta_{n,m}$. The typical systematic error in $\bar{n}_{\mathrm{OH}}$ is about 0.005 in Model III.

(*n*,*m*)		Model I-A	Model I-B
1,1	$\mathrm{ThOH^{3+}}$	-4.60 ± 0.20	-4.52 ± 0.13
1,2	$\mathrm{Th_2(OH)^{7+}}$	–	–
2,2	$\mathrm{Th_2(OH)_2^{6+}}$	-4.83 ± 0.08	-4.90 ± 0.06
3,2	$\mathrm{Th_2(OH)_3^{5+}}$	–	–
5,2	$\mathrm{Th_2(OH)_5^{3+}}$	–	–
1,3	$\mathrm{Th_3(OH)^{11+}}$	–	–
2,3	$\mathrm{Th_3(OH)_2^{10+}}$	-4.05	–
3,3	$\mathrm{Th_3(OH)_3^{9+}}$	–	–
8,4	$\mathrm{Th_4(OH)_8^{8+}}$	-20.97	–
9,4	$\mathrm{Th_4(OH)_9^{7+}}$	-24.26 ± 0.11	-24.22 ± 0.08
11,5	$\mathrm{Th_5(OH)_{11}^{9+}}$	–	–
12,5	$\mathrm{Th_5(OH)_{12}^{8+}}$	–	–
14,6	$\mathrm{Th_6(OH)_{14}^{10+}}$	–	–
25,10	$\mathrm{Th_{10}(OH)_{25}^{15+}}$	–	–
$\sigma\,\bar{n}_{\mathrm{OH}}$		0.044	0.030

(*n*,*m*)		Model II-A	Model II-B
1,1	$\mathrm{ThOH^{3+}}$	-4.77 ± 0.18	-4.57 ± 0.13
1,2	$\mathrm{Th_2(OH)^{7+}}$	–	–
2,2	$\mathrm{Th_2(OH)_2^{6+}}$	-4.74 ± 0.06	-4.90 ± 0.08
3,2	$\mathrm{Th_2(OH)_3^{5+}}$	-9.14	-8.68 ± 0.12
5,2	$\mathrm{Th_2(OH)_5^{3+}}$	–	–
1,3	$\mathrm{Th_3(OH)^{11+}}$	–	–
2,3	$\mathrm{Th_3(OH)_2^{10+}}$	-3.92 ± 0.24	-4.53
3,3	$\mathrm{Th_3(OH)_3^{9+}}$	–	–
8,4	$\mathrm{Th_4(OH)_8^{8+}}$	–	–
9,4	$\mathrm{Th_4(OH)_9^{7+}}$	–	–
11,5	$\mathrm{Th_5(OH)_{11}^{9+}}$	-28.56 ± 0.10	-29.61
12,5	$\mathrm{Th_5(OH)_{12}^{8+}}$	-32.56 ± 0.13	-32.24 ± 0.10
14,6	$\mathrm{Th_6(OH)_{14}^{10+}}$	–	–
25,10	$\mathrm{Th_{10}(OH)_{25}^{15+}}$	–	–
$\sigma\,\bar{n}_{\mathrm{OH}}$		0.023	0.014

Table A-29 (continued)

(n,m)		Model III-A	Model III-B	Model III'-A
1,1	$ThOH^{3+}$	– 5.23	– 5.14 ± 0.22	– 5.28
1,2	$Th_2(OH)^{7+}$	–	–	– 2.64
2,2	$Th_2(OH)_2^{6+}$	– 4.75 ± 0.05	– 4.78 ± 0.04	– 4.78 ± 0.06
3,2	$Th_2(OH)_3^{5+}$	– 8.71 ± 0.10	– 8.72 ± 0.08	– 8.67 ± 0.10
5,2	$Th_2(OH)_5^{3+}$	– 17.32	– 17.16 ± 0.14	– 17.39
1,3	$Th_3(OH)^{11+}$	– 1.35 ± 0.23	– 1.50 ± 0.23	–
2,3	$Th_3(OH)_2^{10+}$	–	–	–
3,3	$Th_3(OH)_3^{9+}$	– 6.90 ± 0.20	– 6.86 ± 0.14	– 6.92 ± 0.23
8,4	$Th_4(OH)_8^{8+}$	–	–	–
9,4	$Th_4(OH)_9^{7+}$	–	–	–
11,5	$Th_5(OH)_{11}^{9+}$	–	–	–
12,5	$Th_5(OH)_{12}^{8+}$	–	–	–
14,6	$Th_6(OH)_{14}^{10+}$	– 36.38 ± 0.04	– 36.42 ± 0.03	– 36.38 ± 0.04
25,10	$Th_{10}(OH)_{25}^{15+}$	–	–	–
$\sigma\,\bar{n}_{OH}$		0.015	0.011	0.016

(n,m)		Model IV-A	Model IV-B
1,1	$ThOH^{3+}$	– 5.04 ± 0.25	– 4.97 ± 0.16
1,2	$Th_2(OH)^{7+}$	–	–
2,2	$Th_2(OH)_2^{6+}$	– 4.74±0.05	– 4.76 ± 0.04
3,2	$Th_2(OH)_3^{5+}$	– 8.93	– 8.94 ± 0.20
5,2	$Th_2(OH)_5^{3+}$	– 17.09 ± 0.18	– 16.99 ± 0.11
1,3	$Th_3(OH)^{11+}$	– 1.19 ± 0.19	– 1.36 ± 0.18
2,3	$Th_3(OH)_2^{10+}$	–	–
3,3	$Th_3(OH)_3^{9+}$	– 6.86 ± 0.19	– 6.83 ± 0.13
8,4	$Th_4(OH)_8^{8+}$	– 21.06	– 21.11 ± 0.22
9,4	$Th_4(OH)_9^{7+}$	–	–
11,5	$Th_5(OH)_{11}^{9+}$	–	–
12,5	$Th_5(OH)_{12}^{8+}$	–	–
14,6	$Th_6(OH)_{14}^{10+}$	– 36.56 ± 0.13	– 36.58 ± 0.10
25,10	$Th_{10}(OH)_{25}^{15+}$	– 65.29	– 65.35 ± 0.21
$\sigma\,\bar{n}_{OH}$		0.013	0.010

Figure A-17: Distribution diagram for the Th(IV)-hydroxide system in 3 M (Na)Cl, using the "best" set of equilibrium constants from Model III-B (Table A-29). Note that many of the complexes suggested there occur in such low concentrations that they are not seen in the figures.

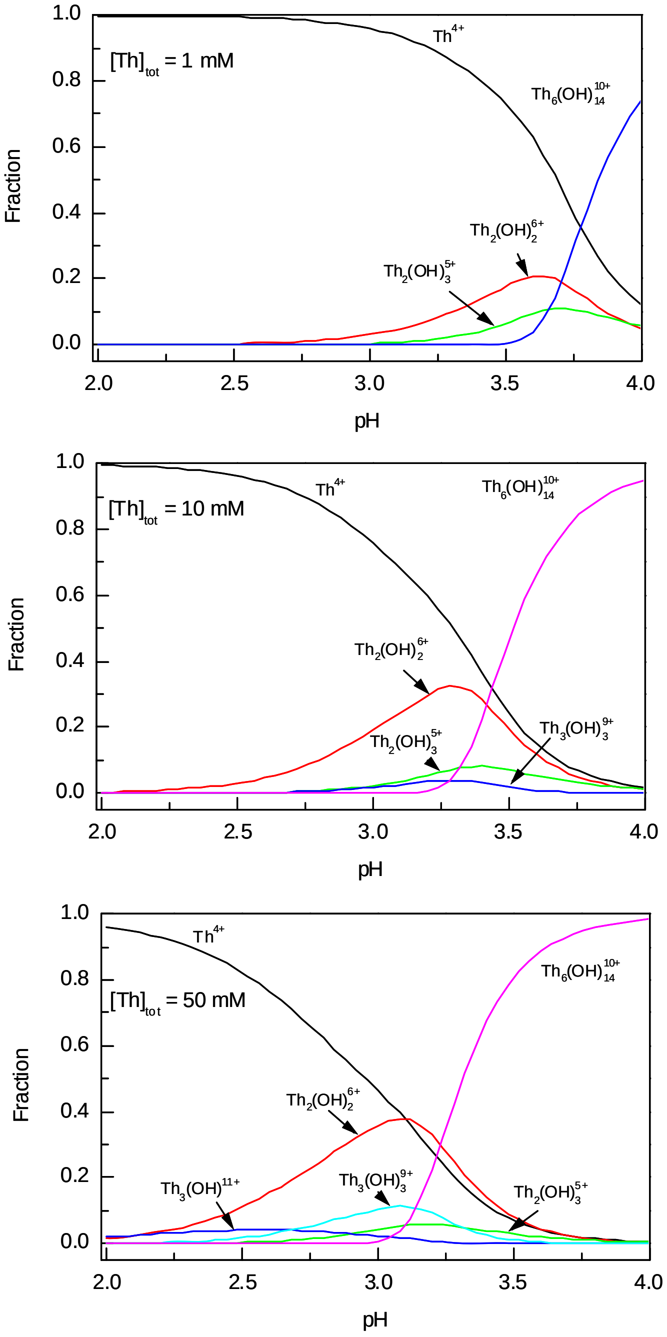


Figure A-18: Th(IV) speciation using Model I-A. The concentrations of species (1,1) and (2,3) are too low to be seen in the figure. The highest pH where precise data are obtained is around 3.2.

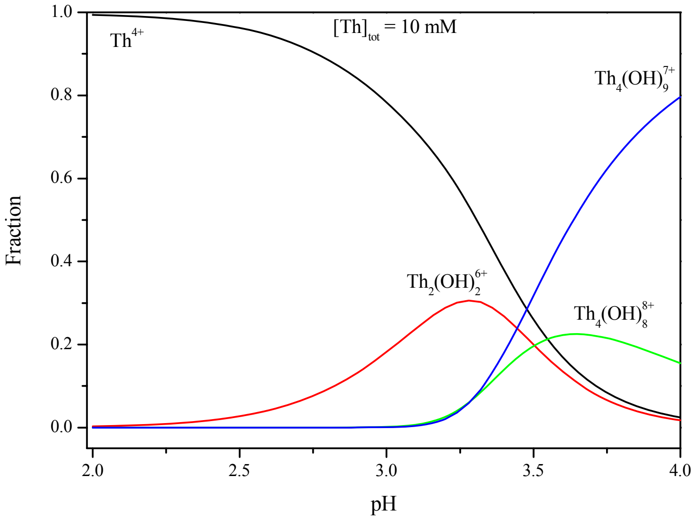


Figure A-19: Th(IV) speciation using Model II-A. The concentrations of species (1,1) and (2,3) are too low to be seen in the figure; the concentration of (3,2) is also low and its existence can hardly be considered established. The highest pH where precise data are obtained is around 3.2.

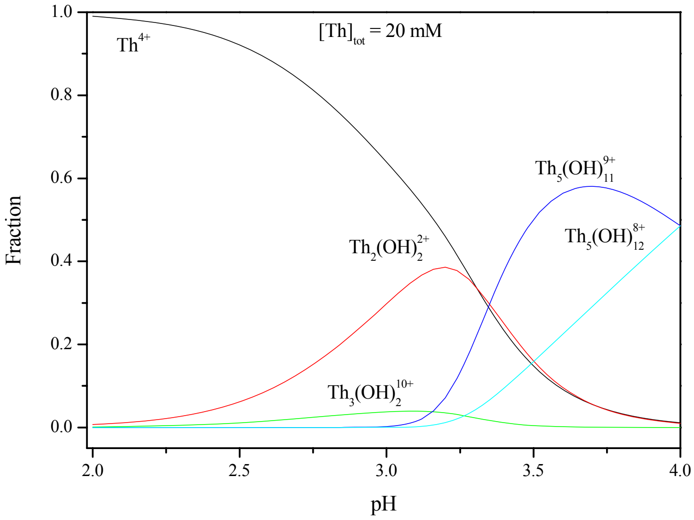
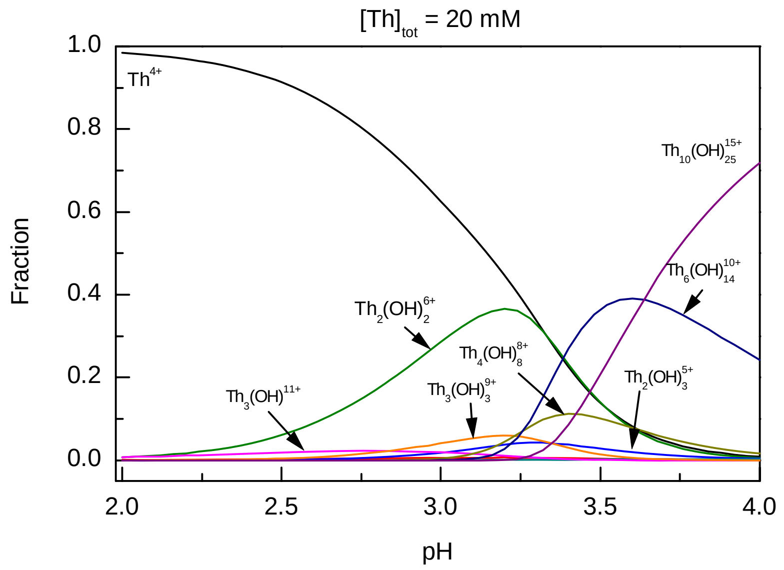


Figure A-20: Th(IV) speciation using Model IV-A; this model is very different from Models I and II. The highest pH where precise data are obtained is around 3.2.



This paper also contains a discussion and reinterpretation of experimental data in 1 M (Na)ClO$_4$ using the data from Hietanen [1954HIE], Kraus and Holmberg [1954KRA/HOL] and Baes *et al.* [1965BAE/MEY]. The comparison has been made using two different least-squares programs, LETAGROP and the Rush program from Oak Ridge. The data refer to a 1 M (Na)ClO$_4$ ionic medium and temperature 0, 25 and 95°C and the various equilibrium constants are given in Table A-30. The agreement between the different experiments is excellent, as indicated by the values of $\sigma(\bar{n}_{OH})$, despite the fact that they have been made in different laboratories and with slightly different potentiometric titration methods. It is also clear that the speciation model is very different from that found in 3 M NaCl. Another important difference is the $\bar{n}_{OH}$ range available before precipitation occurs; this is much larger in the perchlorate medium. This observation is important for the discussion of colloid/polymer formation [2002NEC/MUL], [2003BIT/MUL].

Distribution diagrams for Th(IV) in 1 M (Na)ClO$_4$ are shown in Figure A-21 using the data from [1954HIE] and Model B (Figure a) and the data from [1954KRA/HOL] with LETAGROP, Model B (Figure b). There is only a slight difference between the two least-squares programs, and no significant difference in the speciation. There is an error in Table 5 of [1968HIE/SIL], the entry for $Th_2(OH)_2^{6+}$ is placed in the column for the (2,1) complex. The equilibrium constant for $Th(OH)_2^{2+}$ from [1954KRA/HOL] and [1965BAE/MEY] is so small that no significant amount of this complex is present in the test solutions. This review has therefore not included this equilibrium constant when selecting the “best” set of equilibrium constants. The major species in both data sets are $\text{Th}_2(\text{OH})_2^{6+}$, $\text{Th}_4(\text{OH})_8^{8+}$ and $\text{Th}_6(\text{OH})_{15}^{9+}$. A comparison of the least-squares refinement of the same data using two different least-squares methods indicate that the standard deviations in the equilibrium constants is seriously underestimated.

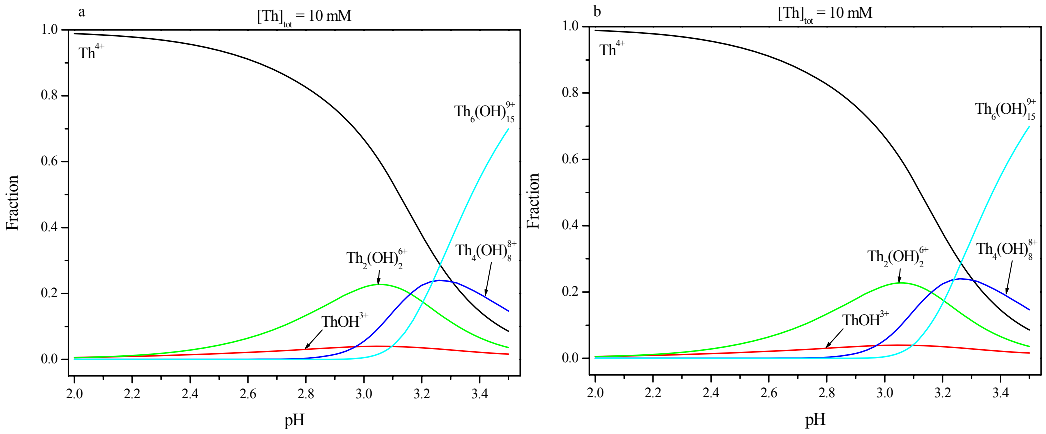
Additional discussion is given in the comments to [1954KRA/HOL] and [1965BAE/MEY].

Table A-30: Reinterpretation by [1968HIE/SIL] of the hydrolysis data and the corresponding equilibrium constants ($\log_{10} {}^*\beta_{n,m}(\text{Th}_m(\text{OH})_n^{4m-n})$) for Th(IV) in 1 M (Na)ClO$_4$ from [1954HIE], [1954KRA/HOL] and [1965BAE/MEY]. In Model A the data have been used without assumptions of a systematic error in $\bar{n}_{OH}$; in Model B such an error has been refined using the least-squares program LETAGROP; Oak Ridge denotes the least-squares program developed by Rush at Oak Ridge.

(1,1)	(2,1)	(2,2)	(8,4)	(15,6)	σ($\bar{n}_{\text{OH}}$)	Data from Ref.	*t*
Th(OH)^{3+}	Th(OH)_2^{2+}	$\text{Th}_2(\text{OH})_2^{6+}$	$\text{Th}_4(\text{OH})_8^{8+}$	$\text{Th}_6(\text{OH})_{15}^{9+}$		Model	(°C)
– 4.33±0.07	– 8.48±0.10	– 5.60±0.06	– 22.79±0.05	– 43.84±0.06	0.012	[1965BAE/MEY] A	0
– 4.31±0.06	– 8.46±0.09	– 5.59±0.06	– 22.80±0.05	– 43.81±0.05	0.010	[1965BAE/MEY] B	0
– 4.32±0.02	– 8.48±0.03	– 5.60±0.02	– 22.79±0.02	– 43.84±0.02	0.012	[1965BAE/MEY] Oak Ridge	0
– 2.28±0.06	– 4.50±0.02	– 2.56±0.12	– 10.49±0.09	– 20.63±0.07	0.015	[1965BAE/MEY] A	95
– 2.25±0.03	– 4.51±0.02	– 2.59±0.08	– 10.44±0.05	– 20.61±0.05	0.009	[1965BAE/MEY] B	95
– 2.29±0.02	– 4.50±0.01	– 2.55±0.03	– 10.49±0.03	– 20.63±0.02	0.015	[1965BAE/MEY] Oak Ridge	95
– 4.21±0.13	– 7.72±0.07	– 4.61±0.06	– 19.15±0.01	– 37.02±0.06	0.015	[1954KRA/HOL] A	25
– 4.23±0.11	– 7.69±0.06	– 4.61±0.05	– 19.16±0.05	– 37.02±0.05	0.012	[1954KRA/HOL] B	25
– 4.15±0.04	– 7.70±0.03	– 4.61±0.02	– 19.01±0.02	– 36.76±0.02	0.015	[1954KRA/HOL] Oak Ridge	25
– 3.69±0.01	a	– 4.43±0.01	– 18.75±0.01	– 36.37±0.12	0.042	[1954HIE] A	25
– 3.71±0.08	a	– 4.44±0.07	– 18.78±0.08	– 36.42±0.08	0.028	[1954HIE] B	25

a: There is an error in Table 5 of [1968HIE/SIL] the equilibrium constant for the (2,2) species is erroneously given in the column for the (2,1) species.

Figure A-21: Speciation diagram using a) the data from [1954HIE] as reanalysed in [1968HIE/SIL] and b) the data from [1954KRA/HOL] as reanalysed by the chemical model from [1965BAE/MEY] using the LETAGROP least-squares program as described in [1968HIE/SIL].



[1968HUB/HOL2]

The enthalpies of formation of analysed samples of thorium carbides were obtained from combustion calorimetry in 25 atm oxygen at 298.15 K.

Samples of various stoichiometries were prepared by reacting in an arc furnace fully analysed thorium metal rods (99.7% purity) with spectrographic quality graphite rods, followed by remelting processes. From the full analysis of the samples given in Table A-31 hereunder their molecular composition could be calculated.

Table A-31: Analyses of the thorium carbide samples.

C/Th	0.75	0.81	0.91	1.00	1.91	1.91
wt%(Th)	96.00	95.8	97.82	98.54	99.22	99.77
wt%(C)combined	3.61	3.99	4.38	4.86	8.93	8.97
wt%(C)free	—	—	—	0.055	0.14	0.04
wt%(O)	0.37	0.18	0.24	0.161	0.066	0.016
wt%(N)	0.012	0.013	0.018	0.009	0.008	0.012
wt%(Si)	0.004	0.004	0.005	0.005	0.002	0.005

The main impurities were oxygen and nitrogen, which were assumed to be combined as ThO_2 (plus some SiO_2, and small amounts of metallic oxides) and Th_3N_4, respectively. The authors estimated that there is an uncertainty of ± 0.01 C/Th ratio in the formula of each compound.

Eight to ten combustion experiments were performed for each sample. Analytical results showed that the combustion of the samples averaged 97.8%.

After conversion to constant pressure and correction for impurities, the reported enthalpies of formation at 298.15 K are given in Table A-32.

Table A-32: Enthalpies of formation of ThC_x(cr).

x = C/Th	0.75	0.81	0.91	1.00	1.91	1.91
$-\Delta_f H^o_m$ (ThC_x, cr, 298.15 K) ($kJ\cdot mol^{-1}$)	69.4 ± 6.7	98.3 ± 3.8	118.8 ± 7.9	123.8 ± 4.6	124.3 ± 7.5	125.1 ± 5.4

[1968JOH], [1968JOH2]

The first of these studies is a single crystal X-ray investigation of the structure of $Th_2(OH)_2(NO_3)_6(H_2O)_8$(s), a compound that contains discrete binuclear complexes $Th_2(OH)_2(NO_3)_6(H_2O)_4$ containing double hydroxide bridges, resulting in a Th–Th distance of 3.99 Å, linking the Th atoms.

The nitrate ligands are coordinated through two oxygen atoms resulting in a first sphere coordination number of 11. This unusual coordination geometry is a result of the small ligand bite in the nitrate ligand. The structure provides important geometry information for the interpretation of large angle X-ray diffraction (LAXS) data from solutions containing hydrolysed Th(IV) complexes, the topic of the second study.

In [1968JOH2] Johansson studies the structure of Th test solutions with different ratio $OH^-_{tot}/Th_{tot} = \bar{n}_{OH}$ varying between 0 and 3 and at a total concentration Th_{tot} = 1.95 M. It is remarkable that these solutions remain clear (with the exception of a slight Tyndall effect at $\bar{n}_{OH} = 3$; the test solutions eventually solidify to form a glassy transparent substance. The experimental LAXS data were treated using standard methods that involve deconvolution to obtain a radial distribution curve, followed by least-squares fitting of different test models using the reduced intensity function to deduce the best model. It is not straightforward to obtain a structural model in this way as the structure has to be determined from one-dimensional data, that is the distances between pairs of atoms and number of such distances in the test solutions. The testing is facilitated by the fact that interactions involving Th are large in comparison with pair distances involving light atoms.

The test solutions used by Johansson contains several different hydroxide complexes and he has estimated the speciation using the equilibrium constants of Hietanen and Sillén [1964HIE/SIL]; this is obviously not correct due to the very large difference in composition and total concentration of Th(IV); however the information on the Th–Th and the Th–O distances in the first coordination sphere as a function of $\bar{n}_{OH}$ is certainly correct. Johansson reports values of the different pair distances and their frequency based on least squares fitting of the reduced intensity function, rather than using the radial distribution function. The data indicate that polynuclear complexes are formed, that the complexes contain coordinated nitrate and that the coordination number of Th(IV) is high and possibly decreases with increasing $\bar{n}_{\mathrm{OH}}$. The Th–Th distance at $\bar{n}_{\mathrm{OH}} = 0.69$ is 3.99 Å in good agreement with the data from solid $Th_2(OH)_2(NO_3)_6(H_2O)_8$(cr); the distance decreases gradually and is 3.925 Å at $\bar{n}_{\mathrm{OH}} = 2.44$. There is no significant variation in the Th–O distance as $\bar{n}_{\mathrm{OH}}$ varies.

This study does not provide any thermodynamic data but it confirms the formation of polynuclear complexes and that hydroxide bridging is an important structural element both in solution and the solid state.

[1968JUZ/GER]

A new modification of Th_3N_4 was obtained by thermal degradation of $Th_2N_2(NH)$ or by quenching samples prepared by heating Th_3N_4 and ThO_2. β-Th_3N_4 has a monoclinically distorted La_2O_3 lattice with $a = 6.952$, $b = 3.830$, $c = 6.206$ Å, $\beta = 90.71°$. It transforms monotropically to α-Th_3N_4.

[1968OHA/MOR]

The reviewers have only been able to read the English abstract of this paper. The authors report equilibrium constants for chloride and nitrate complexes that have been determined using a potentiometric method. There are no details in the abstract and the experimental approach can therefore not be evaluated. However, potentiometric determination of the free ligand concentrations using a chloride sensitive electrode as used here is not very accurate for systems where weak complexes are formed. The nitrate system seems to have been investigated using the same method and measuring the competition between chloride and nitrate. This method is even less likely to provide accurate results. The experiments have been made at three different temperatures, 15, 25 and 35°C and in KNO_3, $NaClO_4$ and $NaNO_3$ - $NaClO_4$ media with concentrations ranging from 0.05 to 1.6 M. It is not clear from the abstract if the ionic strength has been kept constant, although the figures indicate that this might be the case. The authors find a significant ionic strength dependence of the equilibrium constants. For $ThCl^{3+}$ the equilibrium constant decreases from 6 M^{-1} at $I = 0.5$ M, to 2.8 M^{-1} at $I = 1.0$ M; extrapolation to zero ionic strength gave an equilibrium constant of 37 M^{-1}. The extrapolation to zero ionic strength seems to have been made without use of theory. In view of the limited information on experimental details, this review has not accepted the data provided by Ohashi and Morozumi.

[1968TED/RUM]

The authors have determined the equilibrium constants in the Th(IV)- NO_3^- system in a 2.0 M $H(NO_3,ClO_4)$ ionic medium and a temperature of 25ºC, using cation exchange based on a method developed by Fronaeus [1951FRO] and adapted to Pu^{4+} by Grenthe and Norén; the latter study has been evaluated under [1960GRE/NOR] by Lemire *et al.* [2001LEM/FUG]. The reviewers in [2001LEM/FUG] pointed out that the large variation in the ionic medium composition necessary to study the weak Pu(IV) nitrate complexes in [1960GRE/NOR] made it impossible to decide if the experimental observations were due to activity factor variations or complex formation and they accepted only the equilibrium constant for the formation of $Pu(NO_3)^{3+}$. The equilibrium constants of Tedesco *et al.* are:

$$Th^{4+} + NO_3^- \rightleftharpoons ThNO_3^{3+} \qquad \log_{10} \beta_1 = (1.22 \pm 0.03)$$

$$Th^{4+} + 2NO_3^- \rightleftharpoons Th(NO_3)_2^{2+} \qquad \log_{10} \beta_2 = (1.53 \pm 0.15)$$

$$Th^{4+} + 3NO_3^- \rightleftharpoons Th(NO_3)_3^{+} \qquad \log_{10} \beta_3 = (1.10 \pm 0.28).$$

The equilibrium constants in [1968TED/RUM], which refer to an ionic strength of $I = 2.0$ M $H(NO_3, ClO_4)$ and a temperature of 25°C, have been determined in test solutions where $[NO_3^-] < 0.5$ M. Extrapolation from $I = 2.2$ m to zero ionic strength using the ion-interaction constants in Table B-4 ($\Delta\varepsilon = -(0.21 \pm 0.17)$, $-(0.41 \pm 0.21)$ and $-(0.66 \pm 0.19)$ $kg\cdot mol^{-1}$ for n = 1, 2 and 3, respectively) yields $\log_{10} \beta_1^{\circ}$ = (2.59 ± 0.37), $\log_{10} \beta_2^{\circ} = (3.83 \pm 0.49)$ and $\log_{10} \beta_3^{\circ} = (3.74 \pm 0.50)$.

This review has followed the evaluation of [1960GRE/NOR] in [2001LEM/FUG] on the analogous Pu^{4+}- NO_3^- system that only the equilibrium constant for the formation of the first nitrate complex can be determined. The value of $\log_{10} \beta_1^{\circ}$ = (2.59 ± 0.37) is significantly larger than the values for the corresponding complexes in the U(IV), Np(IV) and Pu(IV) systems, (1.47 ± 0.13), (1.90 ± 0.15) and (1.95 ± 0.15), respectively. The value of $\log_{10} \beta_2^{\circ}$ = (3.83 ± 0.49) is also considerably larger than the value for U(IV) ($\log_{10} \beta_2^{\circ}$ = (2.30 ± 0.05) [1992GRE/FUG]). As the stability of complexes of complexes with a given ligand usually increases in the order Th(IV) < U(IV) < Np(IV) ≤ Pu(IV), this review does not accept the equilibrium constants given in [1968TED/RUM].

[1969BAC/BRO]

This is a large angle X-ray diffraction study of the structure of the Th^{4+} ion and of the structure of an hydroxide complex in test solutions formally described as containing $ThO(ClO_4)_2$. The experimental data are analysed using the radial distribution function and estimating the agreement of the experimental curve with that calculated using different structure models. The fitting has not used the least-squares approached used by Johansson [1968JOH2] and no quantitative comparison of different models has been made. The structure of Th^{4+} was made in test solutions containing 2.79 M $Th(ClO_4)_4$ and a large excess of $HClO_4$ to ensure that no hydrolytic species are present. The authors report pair interactions at 1.50 Å, due to Cl–O distances in the perchlorate ion, and one distance at 2.50 Å, presumably due to $Th–OH_2$ and O–O distances in the perchlorate ion, the latter equal to 2.40 Å. It is very difficult to deconvolute the radial distribution peaks, but the authors suggest a coordination number of 11 for the aquo ion. The uncertainty in the coordination number is large and the data are also compatible with coordination numbers nine and ten.

The experiments in the hydrolysed test solutions were made at a total concentration of Th(IV) equal to 3.95 M, with an average number of two coordinated hydroxide ions per Th. The radial distribution curve contains a large narrow peak at 4.00 Å in addition to those in the test solution containing Th^{4+}. The integral of the 4.00 Å peak indicates pair interactions in a tetrahedral Th_4-unit and the authors suggest that this has the stoichiometry $Th_4(OH)_6^{10+}$, with the hydroxide bridges along the six edges in a tetrahedron. Another possibility that has not been discussed is a "cubane" core "$Th_4(OH)_4$" with one additional hydroxide coordinated to each Th, resulting in a $Th_4(OH)_8^{8+}$ stoichiometry as suggested in some potentiometric studies. A planar structure as in the "$Zr_4(OH)_8$"-core [1960MUH/VAU] has two different metal-metal distances and can therefore be excluded.

[1969BAS]

Finely divided thorium was treated with PH_3(g) at 823 K to give Th_3P_4(cr), which was mixed with further Th(cr) and heated *in vacuo* at 1473 – 1573 K to give $ThP_{0.99}$(cr), with a lattice parameter of 5.833 Å. The apparent melting point under a helium atmosphere was 3173 K, but the author was unable to determine whether this was the true melting point, or the temperature of a eutectic with the tungsten container.

[1969DAH/GAN]

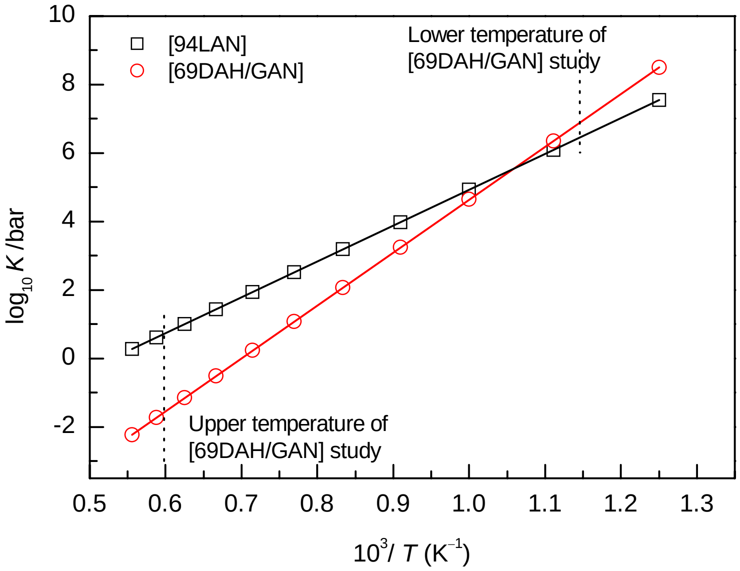
The dissociation pressure of bismuth in the system bismuth-thorium was determined using weight-loss Knudsen effusion between 884 and 1759 K. Isothermal dissociation curves and X-ray diagrams confirmed the stoichiometric compounds $ThBi_2$(cr) and Th_3Bi_4(cr). A homogeneity range from *ca.* $ThBi_{0.80}$ and $ThBi_{1.08}$ is indicated for the ThBi(cr) phase. The pressure measurements gave no indication of the compound Th_5Bi_3, although this is a well-established compound in the system. Equations are given for the values of $\log_{10}(p_{Bi} + p_{Bi_2})$ for the vaporisation of pure Bi and the dissociation pressures of bismuth in the univariant regions: liquid + $ThBi_2$, $ThBi_2$ + Th_3Bi_4, Th_3Bi_4 + $ThBi_{1.08}$, $ThBi_{0.8}$ + Th_3Bi and Th_3Bi + liquid.

The Th-Bi alloys were prepared from 99.999% Bi and nuclear grade Th (< 70 ppm impurities) in CaF_2 crucibles at 1073 K and annealed.

Lattice constant measurements obtained from X-ray data are given for $ThBi_2$(cr) and Th_3Bi_4(cr); these agree well with earlier values. Expressions for $\log_{10}(p_{Bi} + p_{Bi_2})$, $\log_{10}p_{Bi}$ and $\log_{10}a_{Bi}$ for the various Th-Bi phase fields are given.

However, there are a number of problems with this study. Since the vapour contains both Bi_2(g) and Bi(g), it is necessary to know the relative proportions of each before the measured mass loss can be converted to the individual Bi(g) and Bi_2(g) pressures. The authors used an expression for the dimerisation equilibrium constant they derived from the assessment by [1959GRO/LEV] and the torsion effusion study by [1963ALD/PRA]. These are reliable studies for the equilibrium constant but only for the temperature range around 1000 K, but the authors extrapolated the derived equation to 1673 K without change. The dimerisation constant calculated from the thermodynamic data for Bi(cr, l), Bi(g) and Bi_2(g) given in the Landolt-Bornstein tables [1994LAN]**,** is compared with that used by [1969DAH/GAN] in Figure A-22. From this it is seen that although the dimerisation constant used by the authors is reasonably accurate around 1000 K, it markedly underestimates the fraction of Bi_2(g) in the vapour at higher temperatures – indeed by a factor as high as 150 at the highest temperatures used. Thus their calculated pressures of Bi(g) over pure Bi(l) will be appreciably too high at the higher temperatures. As a consequence, since the bismuth activities are calculated from the ratio of the derived p_{Bi} in a given phase field to that for pure Bi(l), their calculated activities will be too low at the higher temperatures. However, the compositions of the residual solid, which were calculated from the mass of bismuth lost from the initial samples, should not be affected.

Figure A-22: Dimerisation constant for 2Bi(g) $\rightleftharpoons$ Bi_2(g)



It should be noted that, although at higher temperatures, there are appreciable amounts of Bi_3(g) and Bi_4(g) in the vapour over pure Bi(l), in the study under discussion, the activities of bismuth in the system at the higher temperatures are so low that these species are no longer important.

Another problem with this study is that the experimental bismuth pressures are not consistent with the phase diagram in some areas. In particular there is no appreciable change in activity as the composition of the effusing solid passing through the Th_5Bi_3 composition, where there is well-established compound. Moreover, the authors found evidence for the formation of a thorium-rich phase with a composition around Th_3Bi(cr), but this phase has not been observed in any other studies. Dahlke *et al.* [1969DAH/GAN] also found that the monobismuthide phase has a considerable range of homogeneity, from $ThBi_{0.8}$ to $ThBi_{1.08}$, but again, there is no independent evidence for this. A further difficulty in processing the data from this study is that neither the solubility nor the activity of thorium in the melt in equilibrium with the most Bi-poor region was measured by the authors, so individual Gibbs energies of the Th-Bi compounds cannot be derived from this work alone (but see below).

Because of the inappropriate equation for the dimerisation reaction, all the results of Dahlke *et al.* have been completely re-evaluated from their raw data, using the data for the dimerisation constant calculated from the data given in [1994LAN], but from the total vapour pressures of pure Bi(l) measured by [1969DAH/GAN]. This helps to cancel any related experimental errors in the pressure measurements in the Th-Bi phase fields. The resulting bismuth activities in the various diphasic fields are shown in Figure A-23, which also includes the original values reported by [1969DAH/GAN]. It will be seen that at the higher temperatures, the recalculated bismuth activities are substantially lower than those given by the original authors, due, as noted above, to their overestimating the partial pressure of Bi(g) in the vaporisation of pure Bi(l).

The corresponding partial Gibbs energy of bismuth in these phase fields are given in Table A-33.

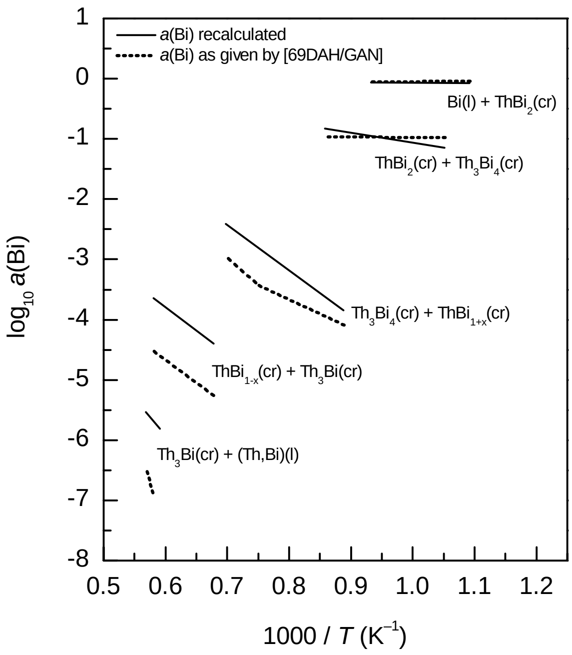
Table A-33: Bismuth potentials in the diphasic field in the Th-Bi system.

Phase field	$\Delta_{\text{sln}}G_{\text{m}}$ (Bi) ($\text{J·K}^{-1}\text{·mol}^{-1}$)	Temperature range (K)
(Th,Bi)(l) + Th_3Bi(cr)	$-237850 + 29.30\,T$	1691 − 1759
Th_3Bi(cr) + $ThBi_{1-x}$(cr)	$-147218 + 15.60\,T$	1474 − 1723
$ThBi_{1+x}$(cr) + Th_3Bi_4(cr)	$-144119 + 54.35\,T$	1126 − 1433
Th_3Bi_4(cr) + $ThBi_2$(cr)	$-31631 + 11.233\,T$	951 − 1165
$ThBi_2$(cr) + (Bi,Th)(l)	$-188 + 0.636\,T$	916 − 1073

The recalculated activities in the diphasic field Th_3Bi_4(cr) + $ThBi_2$(cr) from 950 to 1150 K can be combined with the Gibbs energy of formation of $ThBi_2$(cr) in a similar temperature range measured by Poyarkov *et al.* [1974POY/LEB] to give an estimate of $\Delta_{\text{f}}G_{\text{m}}$ (Th_3Bi_4, cr), as discussed in Section X.5. In principle, this could be extended to the remaining phase fields, but owing to uncertain phase boundaries of

ThBi(cr), and discrepancies with the phase diagram, this is not thought to be a meaningful proposition.

Figure A-23: Bismuth activities from [1969DAH/GAN], recalculated.



[1969GIN2]

Mass-spectrometric measurements were made on a Th-B-P alloy, contained in a tungsten crucible, but at only two temperatures, 2705 and 2804 K. Ion currents were converted to pressures by comparison with the $P_2(g) \rightleftharpoons 2P(g)$ equilibrium, using early JANAF data for these species.

The authors combine the third-law enthalpies of various reactions involving Th, Th_2, ThB, ThP, B, P, P_2 gaseous species with published thermodynamic data to calculate the dissociation energy D° (0 K) and the enthalpies of formation, $\Delta_{f}H^{\circ}_{m}$ (298.15 K), using estimated thermal functions for ThP(g) and ThB(g) from quoted estimated molecular parameters.

In view of the paucity of the experimental data, and the various assumptions in the derivations, no data have been selected for ThP(g), ThB(g) or $Th_2(g)$, but the relevant data have been re-evaluated in the relevant sections of the review for information only.

[1969KHA/MOL2]

The IR spectra of the solid phases: 1. $Na_6[Th(CO_3)_5]\cdot 12H_2O$; 2. $Na_6[Th(CO_3)_5]\cdot 20H_2O$; 3. $Th(OH)_2(CO_3)\cdot 2H_2O$; 4. $[C(NH_2)_3)_6][Th(CO_3)_5]\cdot 4H_2O$ and 5. $[Co(NH_3)_6]_2[Th(CO_3)_5]\cdot 4H_2O$ have been used to suggest the mode of coordination of the coordinated carbonate ligand. The first compound was suggested to have only bidentate coordination, which is in agreement with the solid-state structure. However, 2, 4 and 5 were suggested to have both mono- and bidentate carbonato ligands; this assignment is incorrect for compound 4 for which an X-ray structure is available. This review concludes that the assignment of ligand bonding mode based on IR data should be made with caution.

[1969NOR]

The author has used liquid-liquid extraction with thenoyltrifluoroacetone (TTA) and potentiometry using a fluoride selective electrode to determine the stoichiometry and equilibrium constants of the fluoride complexes of Th(IV) and U(IV); only the Th(IV) data will be discussed here as the U(IV) data have been reviewed previously in [1992GRE/FUG]. The experiments have been made in a 4 M $HClO_4$ ionic medium at 20°C. The experimental data are described in detail and this study provides very useful information on the quality of the two experimental approaches used. The same author has previously studied the Zr(IV) and Hf(IV) systems using the same experimental approach. The slope of the ion selective electrode was determined experimentally and equilibrium was assumed to be attained when the emf changed by less than 0.1 mV/h. The experiments were made at three different total concentrations of Th(IV), 0.90, 1.79 and 4.48 mM and with the total concentration of HF varying from 0.406 to 225 mM. This corresponds to a concentration of free fluoride, $8\times10^{-8} < [F^-] < 5\times10^{-3}$ M. The analysis of the experimental emf data is straightforward and the conditional equilibrium constants for the two reactions:

$$Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+$$
$$({}^*K_1 = (1.19 \pm 0.01)\times10^4\ M^{-1} \quad {}^*\beta_1 = (4.76 \pm 0.04)\times10^4)$$

$$Th^{4+} + 2HF(aq) \rightleftharpoons ThF_2^{2+} + 2H^+$$
$$({}^*K_2 = (2.8 \pm 0.1)\times10^6\ M^{-2} \quad {}^*\beta_2 = (4.48 \pm 0.16)\times10^7)$$

are accepted by this review, but the uncertainty of ${}^*K_1$ has been increased by a factor of 5. The conditional constants ${}^*K_n$ include the factor $[H^+]^n$, *i.e.:*

$${}^*K_n = [ThF_n^{4-n}]/([Th^{4+}][HF(aq)]^n) \text{ and hence } {}^*K_n\,[H^+]^n = {}^*\beta_n$$

where ${}^*\beta_n$ are the true equilibrium constants for the reactions above. Note that Norén has used the opposite notation.

The liquid-liquid extraction study has been made using a total concentration of Th(IV) equal to 0.1 mM and with the total concentration of HF varying from 0 to 0.961 mM, so that only the equilibrium constant for the formation of ThF^{3+} can be determined from these data. The reason is the low extraction of Th(IV) at the very high hydrogen concentration used, even at the very high concentration of TTA = 1.98 M in the benzene phase. The equilibrium constant thus determined, $^{*}K_1 = (1.1 \pm 0.1)\times 10^4$ M^{-1}, and $^{*}\beta_1 = (4.4 \pm 0.1)\times 10^4$, is in fair agreement with the potentiometric value, but less precise.

The true equilibrium constants for the reactions above, $^{*}\beta_1 = (4.76 \pm 0.20)\times 10^4$ and $^{*}\beta_2 = (4.48 \pm 0.16)\times 10^7$, are accepted by this review and included in the evaluation of the selected values.

[1969SMI/THA]

The following enthalpies of solution of Th(cr), $ThCl_4$ (cr), U(cr), UCl_4(cr) in HCl were obtained at 298.15 K: Th(cr): $-(761.1 \pm 0.8)$ kJ·mol^{-1} and $ThCl_4$(cr): $-(186.8 \pm 0.8)$ kJ·mol^{-1}, in 6.06 M HCl - 0.005 M Na_2SiF_6; U(cr): $-(605.8 \pm 5.2)$ kJ·mol^{-1} and UCl_4(cr): $-(168.9 \pm 3.0)$ kJ·mol^{-1} in 6.03 M HCl - 0.005M Na_2SiF_6. The concentrations of thorium and uranium in the solutions were in the 1 to 3 millimolar range.

The results reported by these authors for the enthalpy of solution of Th(cr) and $ThCl_4$(cr) agree well with other literature values. Although little information is given in this paper on the characterisation of the compounds, these data are used, in conjunction with the enthalpy of solution of the metal and of the tetrachloride in 6.00 M HCl - 0.005 M Na_2SiF_6 [1950EYR/WES], and of the tetrachloride in 6.00 M HCl [1973FUG/BRO], to evaluate $\Delta_f H_m^\circ(Th^{4+})$ and $\Delta_f H_m^\circ(ThCl_4, \beta)$.

[1969ZMB]

This paper reports a mass-spectrometric study of the reactions between Ca(g) and ThF_4(g) over the temperature range 1308 to 1336 K. In addition to these species, CaF^+, ThF_2^{2+} and ThF_3^+ were observed in the mass spectrum arising from a mixture of CaF_2(cr) and Th(cr) heated in a molybdenum effusion cell. “Equilibrium” constants were calculated for the two reactions $Ca(g) + n ThF_4(g) \rightleftharpoons ThF_{4-n}(g) + n CaF(g)$, $n = 1, 2$, assuming the required corrections for ionisation cross-sections and instrumental sensitivities cancel for such reactions. Third-law enthalpies of reactions were calculated assuming constant values of $\Delta_r(G_m(T) - H_m(298.15\text{ K}))$ over the short temperature range, based on values for the similar reactions involving zirconium. No second-law values were reported, owing to the very short temperature range of the study.

These data are a subset of those reported in [1970ZMB] and it should be noted that the headings of Table 3 in [1969ZMB] are incorrect – the equilibrium constants reported as K_1 and K_2 are in fact values of $10^3 \cdot K_1$ and $10^4 \cdot K_2$, as in [1970ZMB]. This is clear from the reported values of $\Delta_r(G_m(T) - H_m(298.15\text{ K}))$ and $\Delta_r H_m(298.15\text{ K})$.

These data are discussed in Section VIII.1.1.1.2.

[1970BAU]

A lanthanum fluoride membrane electrode was used to measure free fluoride concentrations in test solutions that contain mixtures of NaF, HF or HNO_3 and $Th(NO_3)_4$ in

0.01 M NH_4NO_3 with the total ionic strength maintained at (0.01 ± 0.001) M. The experiments are described in detail, and the response of the fluoride electrode in different solutions and at different temperatures is discussed. Thorium fluoride equilibrium data (free fluoride molar concentrations and total molar concentrations of fluoride, hydrogen, and thorium) at 5, 25, and 45°C are presented in tabular form.

The experimental data are interpreted through the average number of fluorides per thorium atom. The concentration-dependent stability constants thus calculated were converted to constants at zero ionic strength through the modified Debye-Hückel relationship for the experimental temperatures. These constants were then used to calculate other thermodynamic parameters through the use of van't Hoff relationship assuming that $\Delta_r H_m^\circ$ (A.60) is independent of temperature. The $\log_{10} K_n$ (A.60) values for:

$$\mathrm{ThF}_{n-1}^{(5-n)+} + \mathrm{F}^- \rightleftharpoons \mathrm{ThF}_n^{(4-n)+} \tag{A.60}$$

at different temperatures, 0.01 M ionic strength, and at zero ionic strength reported by the authors are shown in Table A-34.

Table A-34: Equilibrium constants for the stepwise Reactions (A.60).

Equilibrium constant	Experimental temperatures		
	5°C	25°C	45°C
	0.01 M NH_4NO_3		
$\log_{10} K_1$	8.11	8.08	7.95
$\log_{10} K_2$	6.29	6.36	6.20
$\log_{10} K_3$	4.64	4.57	4.55
$\log_{10} K_4$	3.33	3.28	3.71[a]
	Zero ionic strength		
$\log_{10} K_1^\circ$	8.46	8.44	8.32
$\log_{10} K_2^\circ$	6.55	6.62	6.48
$\log_{10} K_3^\circ$	4.81	4.75	4.73
$\log_{10} K_4^\circ$	3.41	3.36	3.80[a]

a: The author considers these value as dubious.

The values of equilibrium constants for ThF_n^{4-n}, with n varying from 1 to 4, at zero ionic strength reported by [1970BAU] are in all cases lower than the values reported by many other authors (*e.g.*, [1951ZEB/ALT], [1950DAY/STO], [1949DOD/ROL], [1990SAW/CHA2], see Table VIII-6 for details), indicating a systematic error in the data reported by [1970BAU]. The equilibrium constant for the formation of ThF_4(aq) reported by [1970BAU] is unreliable due to suspected precipitation of ThF_4(cr, hyd) at the higher fluoride concentrations used in the experiments. Therefore, this review has not accepted the values reported by [1970BAU]. This review has also not accepted the enthalpies and entropies of the reaction proposed by [1970BAU] because of uncertainties in the quality of equilibrium data and the limited temperature range used to determine the enthalpies of reaction. Although the equilibrium data reported by [1970BAU] are not accepted in this review, it is of interest to determine how well the NONLINT-SIT predicted concentrations based on the equilibrium data recommended in this review (Tables VIII-6 and VIII-7) compare with the experimental data reported by [1970BAU]. The experimental and predicted F^- activities are compared in Figure A-24 and the distribution of different predicted species is listed in Table A-35. These comparisons (Figure A-24 and Table A-35) between the predicted and experimental F^- activities show a close agreement (but systematically too low) at relatively high fluoride concentrations ($\log_{10}[F^-] > -6.5$) and up to about 0.5 log-units lower experimental activities than the predicted at relatively low fluoride concentrations ($\log_{10}[F^-] < -6.5$).

Figure A-24: Observed ([1970BAU]) and predicted F^- activities at 25°C for fluoride-selective electrode studies in 0.01 M NH_4NO_3 solutions. Predictions based on NONLINT-SIT calculations using the thermodynamic data summarised in Tables VIII-8 and VIII-9.

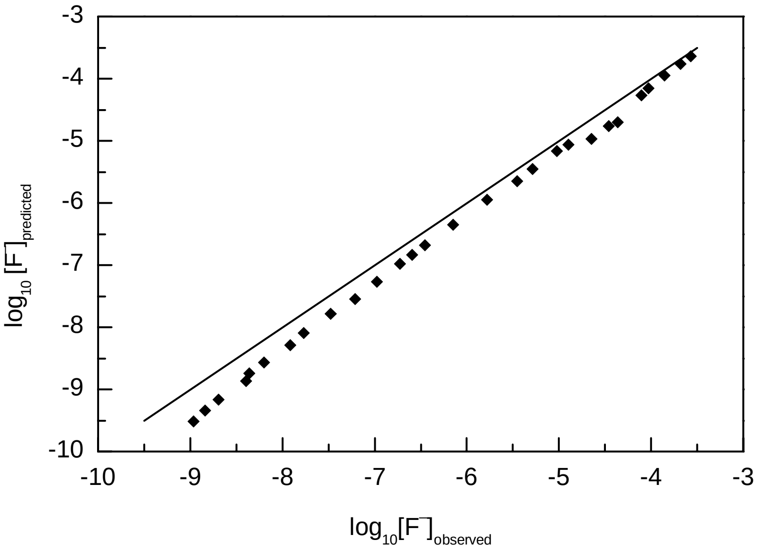


Table A-35: Experimental [1970BAU] and predicted concentrations at 25°C for fluoride-selective electrode data.

Experimental concentrations (m)						Predicted concentrations (m)[a]						
H_{Total}	NH_4	NO_3	Th_{Total}	F_{Total}	$F^-_{activity}$	$F^-_{activity}$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	$ThF_4(aq)$	ThF_6^{2-}
8.038E-04	5.438E-03	7.707E-03	3.758E-04	3.778E-05	1.090E-09	3.055E-10	3.381E-04	3.770E-05	3.997E-08	9.899E-13	7.000E-14	7.000E-14
8.426E-04	6.400E-03	8.306E-03	2.757E-04	3.960E-05	1.450E-09	4.571E-10	2.362E-04	3.947E-05	6.272E-08	2.328E-12	7.000E-14	7.000E-14
8.705E-04	7.059E-03	8.738E-03	2.035E-04	4.092E-05	2.030E-09	6.839E-10	1.627E-04	4.072E-05	9.690E-08	5.386E-12	7.000E-14	7.000E-14
9.004E-04	7.837E-03	9.200E-03	1.263E-04	4.232E-05	4.020E-09	1.361E-09	8.418E-05	4.192E-05	1.984E-07	2.195E-11	7.000E-14	7.000E-14
9.082E-04	8.030E-03	9.320E-03	1.062E-04	4.269E-05	4.400E-09	1.807E-09	6.378E-05	4.216E-05	2.649E-07	3.889E-11	7.000E-14	7.000E-14
9.162E-04	8.227E-03	9.443E-03	8.566E-05	4.306E-05	6.300E-09	2.685E-09	4.300E-05	4.226E-05	3.949E-07	8.620E-11	7.000E-14	7.000E-14
9.242E-04	8.428E-03	9.568E-03	6.481E-05	4.344E-05	1.220E-08	5.176E-09	2.214E-05	4.192E-05	7.545E-07	3.173E-10	1.217E-13	7.000E-14
9.275E-04	8.509E-03	9.618E-03	5.637E-05	4.359E-05	1.700E-08	8.091E-09	1.396E-05	4.125E-05	1.159E-06	7.606E-10	4.553E-13	7.000E-14
9.308E-04	8.591E-03	9.669E-03	4.787E-05	4.374E-05	3.340E-08	1.663E-08	6.440E-06	3.916E-05	2.264E-06	3.058E-09	3.768E-12	7.000E-14
9.324E-04	8.632E-03	9.695E-03	4.359E-05	4.383E-05	6.090E-08	2.864E-08	3.479E-06	3.647E-05	3.634E-06	8.460E-09	1.797E-11	7.000E-14
9.341E-04	8.673E-03	9.720E-03	3.930E-05	4.390E-05	1.050E-07	5.458E-08	1.589E-06	3.168E-05	6.005E-06	2.660E-08	1.074E-10	7.000E-14
9.358E-04	8.714E-03	9.746E-03	3.500E-05	4.398E-05	1.875E-07	1.059E-07	6.478E-07	2.506E-05	9.215E-06	7.918E-08	6.206E-10	7.000E-14
9.366E-04	8.735E-03	9.759E-03	3.284E-05	4.402E-05	2.560E-07	1.476E-07	3.958E-07	2.136E-05	1.096E-05	1.313E-07	1.436E-09	7.000E-14
9.374E-04	8.756E-03	9.772E-03	3.068E-05	4.406E-05	3.510E-07	2.080E-07	2.311E-07	1.755E-05	1.268E-05	2.139E-07	3.292E-09	7.000E-14
9.391E-04	8.798E-03	9.798E-03	2.634E-05	4.414E-05	7.100E-07	4.457E-07	6.194E-08	1.008E-05	1.561E-05	5.647E-07	1.863E-08	7.000E-14
9.408E-04	8.839E-03	9.824E-03	2.199E-05	4.421E-05	1.666E-06	1.122E-06	1.015E-08	4.160E-06	1.622E-05	1.478E-06	1.229E-07	7.000E-14
5.000E-04	9.377E-03	9.896E-03	1.235E-05	2.984E-05	3.502E-06	2.265E-06	1.417E-09	1.171E-06	9.203E-06	1.692E-06	2.838E-07	7.000E-14
2.007E-05	9.907E-03	9.937E-03	7.220E-06	2.018E-05	5.200E-06	3.516E-06	3.214E-10	4.114E-07	5.010E-06	1.427E-06	3.712E-07	7.000E-14
2.080E-05	9.931E-03	9.951E-03	4.820E-06	2.020E-05	9.500E-06	6.871E-06	4.303E-11	1.076E-07	2.561E-06	1.426E-06	7.250E-07	2.266E-13
5.030E-04	9.374E-03	9.877E-03	1.230E-05	4.921E-05	1.260E-05	8.770E-06	5.722E-11	1.831E-07	5.574E-06	3.967E-06	2.576E-06	1.311E-12
1.465E-04	9.532E-03	9.701E-03	3.217E-05	1.062E-04	2.260E-05	1.079E-05	8.319E-11	3.290E-07	1.236E-05	1.083E-05	8.654E-06	6.635E-12
1.649E-04	9.514E-03	9.682E-03	3.211E-05	1.249E-04	3.450E-05	1.722E-05	2.017E-11	1.274E-07	7.641E-06	1.070E-05	1.364E-05	2.665E-11
1.805E-04	9.350E-03	9.538E-03	4.697E-05	1.805E-04	4.350E-05	1.991E-05	1.823E-11	1.339E-07	9.324E-06	1.514E-05	2.237E-05	5.842E-11
1.582E-04	9.608E-03	9.701E-03	2.340E-05	1.582E-04	7.799E-05	5.433E-05	2.671E-13	5.322E-09	1.007E-06	4.452E-06	1.794E-05	3.501E-10
1.823E-04	9.581E-03	9.675E-03	2.372E-05	1.823E-04	9.380E-05	6.934E-05	1.084E-13	2.756E-09	6.657E-07	3.754E-06	1.930E-05	6.129E-10
4.754E-04	9.291E-03	9.580E-03	2.334E-05	2.801E-04	1.400E-04	1.138E-04	7.000E-14	6.687E-10	2.649E-07	2.449E-06	2.062E-05	1.756E-09
4.361E-04	9.252E-03	9.416E-03	3.122E-05	3.970E-04	2.100E-04	1.730E-04	7.000E-14	2.641E-10	1.595E-07	2.247E-06	2.881E-05	5.670E-09
9.886E-05	9.406E-03	9.498E-03	2.291E-05	3.649E-04	2.672E-04	2.275E-04	7.000E-14	8.697E-11	6.906E-08	1.279E-06	2.155E-05	7.335E-09

a: All 7.000E-14 numbers are model limiting values, the actual value is lower than this.

[1970DEV/RUD]

The energy of formation of ThF_4(cr) was measured by combination of the elements in a bomb calorimeter. Five samples (*ca.* 2 g*)* of thorium foil, in which the principal impurities were 520 ppm O, 225 ppm C and 200 ppm Fe, were combusted in 25 atm fluorine. The small residues (0.7 to 1.8%) of unburnt thorium were determined by dissolution of the product in 50% HCl containing 5% H_2SiF_6 and measuring the hydrogen evolved. The product was identified to be ThF_4(cr) from its monoclinic X-ray pattern. The derived enthalpy of formation was $\Delta_f H_m$ (ThF_4, cr, 298.15 K) = – (2110.8 ± 5.0) $kJ\cdot mol^{-1}$.

[1970NOV/COS]

This paper deals principally with the electronic structure of $UC_{1-x}N_x$ solid solutions, but for comparative purposes, de Novion and Costa measured the magnetic susceptibility of ThN(cr) from 3.5 to 8.9 K, from which the coefficient γ of the electronic contribution to the heat capacity $C_v(\text{electronic}) = \gamma T$ was found to be 3.12 $mJ\cdot K^{-2}\cdot mol^{-1}$. This value was used by Adachi *et al.* [2005ADA/KUR] as supplementary information in their calculations of the heat capacity of ThN(cr).

[1970SER/ALM]

This is a potentiometric study made at 25°C and an ionic strength of 0.50 M. The total concentration of thorium varied from 5 to 0.25 mM and the value of $\bar{n}_{OH}$ from 0.01 to 2.58. The authors demonstrate the formation of polynuclear complex but they have preferred to analyse their data using the “core and link” model described in [1964HIE/SIL]. The experimental data are consistent with this model, but as this does not provide a proper chemical description of the constitution of the complexes, as discussed in the present review, these data are not accepted by this review.

[1970ZMB]

This journal paper reports briefly the ‘equilibrium’ constants for the reactions between Ca(g) and ThF_4(g), many of which were also reported in the conference paper [1969ZMB], *q.v.* However, [1970ZMB] reports additional measurements, extending the temperature range of the study from 1288 to 1341 K, and also reports the correct orders of magnitude of the calculated constants for the two reactions $Ca(g) + nThF_4(g) \rightleftharpoons ThF_{4-n}(g) + nCaF(g)$, $n = 1, 2$.

These data are discussed in Section VIII.1.1.1.2.

[1971BRE]

The thermodynamic data for the lanthanide and actinide metals were combined with spectroscopic data to develop a method of estimating the energies of the electronic configurations of the neutral gaseous atoms. Energies are tabulated for the lowest spectroscopic level of each configuration. In particular for Th(g), there are seven such levels not identified in the current (1992) listing [1992BLA/WYA] These are estimated to lie at 20000, 23000, 28000, 31000, 39000(2) and 42000 cm^{-1}, so they will not contribute to the thermal functions of Th(g) to any significant extent at temperatures relevant for the review, but they have nevertheless been included in the calculations for completeness.

[1971HEI/DJE]

This is a study of the reduction of thoria by carbon from 2156 to 2410 K. The results indicated that 1.96, rather than 2, mole of CO(g) were formed per mole of thorium, suggesting the probable dissolution of some oxygen in the dicarbide. The equilibrium pressure of CO(g) was given by the expression $\log_{10} p_{\text{CO}} / \text{bar} = 9.57 - 2.335 \times 10^4 T^{-1}$ in the temperature range studies. These data are included in the discussion of $\Delta_{\text{f}} G^{\circ}_{\text{m}}$ (ThC_2, cr) in Section XI.1.1.3.

[1971KIC/STE]

Kiciak and Stefanowicz performed potentiometric measurements at an approximately constant low thorium concentration of $[\text{Th}]_{\text{tot}}$ = 0.68 – 0.76 mM and low ionic strength (I = 0.01 – 0.04 M) at 20°C. The titrant was 0.100 M NaOH, no ionic medium was used. The ionic strength is given by the sum of the initial $\text{Th(NO}_3)_4$ and acid concentrations (HNO_3, HCl or HClO_4) and varied throughout the titrations up to pH 4.5, typically from 0.016 to 0.011 M and 0.023 to 0.016 M.

A precision pH-meter (accuracy of 0.005 pH units) and a glass and calomel reference electrode calibrated against pH standards were used to measure pH values (activity units) which were converted into $-\log_{10}[\text{H}^+]$ using the Debye-Hückel equation. However, the absolute accuracy that can be achieved with the applied electrode calibration is at best ±0.02 pH-units, which is not sufficient for the determination of accurate results from potentiometric titration data. This problem becomes evident from the results shown in Table 1 of [1971KIC/STE]. The value of $\bar{n}_{\text{OH}}$ = 0.5 was reached at pH = (3.00 ± 0.05) in titrations starting at initial acid concentrations below 0.01 M (I = 0.013 − 0.016 M) and at pH = (3.40 ± 0.05) in titrations starting at initial acid concentrations of about 0.03 M (I = 0.037 M).

The authors assumed that polynuclear complexes can be neglected under their experimental conditions and calculated the following equilibrium constants $\log_{10} {}^*\beta_{n,1}(\text{Th(OH)}_n^{4-n})$, (mean values at I = 0.01 − 0.04 M), for the mononuclear Th(IV) hydroxide complexes:

$$\log_{10} {}^*\beta_{1,1} = -(3.61 \pm 0.20)$$

$$\log_{10} {}^*\beta_{2,1} = -(7.62 \pm 0.20)$$

$$\log_{10} {}^*\beta_{3,1} = -(11.17 \pm 0.20)$$

$$\log_{10} {}^*\beta_{4,1} = -(14.43 \pm 0.20).$$

In the review of Baes and Mesmer [1976BAE/MES], the equilibrium constants for Th(OH)^{3+} and Th(OH)_2^{2+} were designated as “useful estimates” but it was remarked that the equilibrium constant for $Th(OH)_2^{2+}$ might possibly be affected by the interference of the dinuclear species $Th_2(OH)_2^{6+}$. The slight variation of ionic strength has no dramatic effect on the extrapolation to zero ionic strength: $\log_{10} {}^*\beta^o_{1,1} = -3.2$ and $\log_{10} {}^*\beta^o_{2,1} = -7.0$. However, for the experimental reasons discussed above, these equilibrium constants should also be used with caution. The equilibrium constants for $Th(OH)_3^+$ and particularly for $Th(OH)_4(aq)$, which is calculated to be the predominant complex at pH 3.5−4.5 according to Figure 3 in [1971KIC/STE], are not reliable. It is well known from other potentiometric titration studies that polynuclear complexes with high positive charge are predominant under these conditions (pH range, thorium concentration), also at low ionic strength (*cf.* [1983BRO/ELL]).

It is obvious from the introduction that the authors were not aware of the current literature at the time, a fact that might explain both their neglect of polynuclear complexes and the far from adequate calculation method used to calculate the equilibrium constants from the experimental $\bar{n}_{OH}$ *vs.* pH data. The reported equilibrium constants are not reliable because of an erroneous chemical model, the neglect of polynuclear species that are totally dominating the speciation under the experimental conditions used.

[1971KLO/MUK]

In this study of thorium fluoride complexes, the experimental method is the same as used in [1969NOR] but the experiments have been made at 25°C and two different constant total concentrations of H^+, 0.100 and 1.00 M. The ionic strength was 3.00 M using $(Na,H)ClO_4$ as the ionic medium. Titrations were made at three different total concentrations of Th(IV), 3, 10 and 30 mM. Precipitation of $ThF_4(s)$ took place when $\bar{n}_F$ was slightly below 2, but the titrations were continued in the presence of the solid. These experiments indicated that the initial solid phase was transformed to $NaThF_5(s)$. Analysis of the experimental resulted in the following equilibrium constants: $\log_{10} {}^*\beta_1 = (4.52 \pm 0.05)$; $\log_{10} {}^*\beta_2 = (7.26 \pm 0.14)$; $\log_{10} {}^*\beta_3 = (8.9 \pm 0.3)$. The solubility constant for the reaction:

$$ThF_4(s) + 4H^+ \rightleftharpoons Th^{4+} + 4HF(aq); \qquad \log_{10} {}^*K_{s,0} = -(15.17 \pm 0.15).$$

By using the dissociation constant for HF(aq) with $\log_{10} K_{HF} = 3.28$, valid in 3.00 M $NaClO_4$ they obtain: $\log_{10} \beta_1 = (7.80 \pm 0.05)$; $\log_{10} \beta_2 = (13.82 \pm 0.14)$; $\log_{10} \beta_3 = (18.8 \pm 0.3)$ and $\log_{10} K_{s,0} = -(28.29 \pm 0.15)$.

This is a precise study with all necessary information required to assess the methodology used and the equilibrium constants and their estimated uncertainty are accepted by this review.

[1971KOR/DRO]

The equilibrium constant for the reaction $ThCl_4(cr) + 0.5O_2(g) \rightleftharpoons ThOCl_2(cr) + Cl_2(g)$ at six temperatures from 743 to 895 K is given by $\log_{10} K_p / \text{bar}^{0.5} = -636/T - 0.458$, corresponding to an enthalpy of reaction of (12.1 ± 4.2) kJ·mol^{-1} at 820 K. The equilibrium was approached from the oxygen-rich side, since the reaction between $ThOCl_2$(cr) and chlorine was extremely slow.

As noted in Section VIII.2.1.6.1, these data are discounted, since the derived enthalpy of formation of $ThOCl_2$(cr) does not agree with other consistent determinations, and the calculated entropy of reaction is negative, which is unlikely for a reaction in which a net 0.5 mole of gas is formed. It seems likely that equilibrium was not reached in these experiments, or the presence of adventitious water affected the results.

[1971KUS/IMO]

Th_3N_4(cr) and Th_2N_2O(cr) were thermally decomposed at 1473 − 1623 K in vacuum. In both cases, the lattice parameter of ThN(cr) produced by the decomposition varied from 5.156 to 5.161 Å, in good agreement with those previously reported, when the decomposition was nearly completed; but, when the product contained a large amount of the undecomposed Th_3N_4 or Th_2N_2O phase, a value as high as 5.180 Å was observed. The equilibrium nitrogen pressures for the reactions:

$$2Th_3N_4(cr) \rightleftharpoons 6ThN(cr) + N_2(g)$$

$$4Th_2N_2O\ (cr) \rightleftharpoons 6ThN(cr) + 2ThO_2(cr) + N_2(g)$$

(the reaction assumed by this review) were determined by heating the specimen in a disk form on a W strip heater up to 2258 K under predetermined N_2 pressures and measuring the decomposition temperature from the change of the specific emissivity at that point. The results are: $\log_{10} p_{N_2}/\text{bar} = 6.215 - 1.399\times10^4/T$ for $Th_3N_4(cr) \rightleftharpoons ThN(cr)$, $\log_{10} p_{N_2}/\text{bar} = 13.550 - 3.095\times10^4/T$ for $Th_2N_2O(cr) \rightleftharpoons ThN(cr) + ThO_2(cr)$. These data are discussed in Sections X.1.1.1 and X.1.1.4.

[1971LAU/FOU]

Laubscher and Fouché studied the formation of Zr(IV), Hf(IV) and Th(IV) thiocyanate complexes by liquid-liquid extraction.

Only the Th(IV) data will be discussed here. The equilibrium constants have been determined in a 3.00 M $(Na^+,H^+)ClO_4^-$ ionic medium with a constant hydrogen ion concentration of 0.500 M. There is no information about the temperature and this review has assumed that they refer to 25°C. The equilibrium analysis was based on measurements of the distribution of trace amounts of Th(IV) between an aqueous phase containing different concentrations of thiocyanate and a benzene phase containing the extracting ligand, thenoyltrifluoroacetone (TTA) or dinonyl naphthalene sulphonic acid (DNNS). The hydrogen ion concentration was sufficiently high to prevent significant amounts of hydroxide complexes to be formed. The experimental distribution data cover the concentration range 0.00 M < [SCN$^-$] < 1.00 M in the TTA system and 0.00 M < [SCN$^-$] < 2.50 M in the DNNS system, respectively. The equilibrium constants deduced from these data are given in Table A-36; this table also includes data from [1950WAG/STO].

Table A-36: Equilibrium constants determined in a 3.00 and 1.00 M $(Na^+,H^+)ClO_4^-$ ionic medium reported in [1971LAU/FOU] and [1950WAG/STO], respectively.

Method	Ionic medium $[H^+]$ = 0.50 M	β_1 (M^{-1})	β_2 (M^{-2})	β_3 (M^{-3})	β_4 (M^{-4})	Reference
DNNS	I = 3.00	7.12 ± 1.11	33.9 ± 5.3	14.3 ± 7.3	32.4 ± 2.7	[1971LAU/FOU]
TTA	I = 3.00	9.01 ± 0.62	25.1 ± 2.7	5.8 ± 2.6	-	[1971LAU/FOU]
TTA	I = 1.00	12.1	60	-	-	[1950WAG/STO]

The results reported by Waggener and Stoughton [1950WAG/STO] were given without any details in an ORNL quarterly report. The values of β_1 and β_2 are in fair agreement in the two extraction systems, while the discrepancy is larger for β_3 and β_4; the authors suggest that this might be due to the formation of mixed Th(IV)-SCN^--TTA complexes in the aqueous phase, but this is an *ad hoc* assumption. A large part of the ClO_4^- in the ionic medium has been replaced by SCN^- in the range where β_3 and β_4 are determined; the equilibrium constants might then be artefacts due to the activity factor variations resulting from the changes in the ionic medium. This review has only accepted the values of β_1 and β_2 and selected their average and an uncertainty range that covers their respective uncertainties, β_1 = (8.0 ± 1.5) M^{-1}, β_2 = (30 ± 10) M^{-2}, $\log_{10}\beta_1$ = (0.90 ± 0.08) and $\log_{10}\beta_2$ = (1.48 ± 0.14). These values differ significantly from those proposed in the Raman study of Manouvrier and Devaure [1978MAN/DEV].

[1971LOR/DIE]

These authors measured the enthalpies of combustion of thorium and plutonium carbides by oxygen bomb combustion calorimetry.

Samples of various stoichiometries were prepared by sintering mixtures of the hydrides and graphite in the appropriate ratios under vacuum (*ca.* 10^{-8} bar) at 1673 K. Determination of carbon (combustion), oxygen and nitrogen (reducing fusion under He), as well as phase analysis (X-ray diffraction and metallography) are mentioned, but no details were given. Elementary analysis indicated metallic impurities in amounts smaller than 300 parts per million.

In the case of the thorium carbides, three to eight combustion experiments were carried out for each sample. The reported combustion yields ranged between 90 and 100%.

The reported enthalpies of formation in $kJ \cdot mol^{-1}$ at 298.15 K are given in Table A-37.

Table A-37: Enthalpy of formation of ThC_x(cr).

x = C/Th	$-\Delta_f H^o_m$ (ThC_x, cr) ($kJ \cdot mol^{-1}$)	Number of measurements
0.76	36.0 ± 7.1	6
0.80	59.4 ± 7.9	3
0.84	69.3 ± 12.6	5
0.85	69.5 ± 5.0	4
0.95	118.4 ± 6.3	6
0.96	97.5 ± 14.6	8
1.01	126.4 ± 10.5	7
1.20	141.4 ± 8.4	5
1.91	159.0 ± 16.7	5

[1971MIL2]

Milić and other members of the Sillén group have made extensive studies of the hydrolysis of Th(IV) in a number of different ionic media. The experimental methods are the same in all of these studies and will not be commented upon; it is sufficient to note that they represent the state of the art in potentiometric investigations. The present study includes a large number of titrations and all experimental data are reported in the paper. The study covers a $[Th]_{tot}$ range from about 1 mM to 120 mM and a $-\log_{10}[H^+]$ range from 2 to about 3.5. The values of $\bar{n}_{OH}$ are at most 0.6 in these studies and the concentration of the (15,6) complex is therefore not as large as in the perchlorate ionic media. This may also be the reason why the (8,4) complex was not identified. The analysis of the data was made using the least-squares method LETAGROP, often with additional analysis of systematic errors. The initial analysis of the average number of hydroxide per thorium and the nuclearity was made using the graphical methods of Sillén and the final analysis using least-squares fitting. The selected set of "best-fitting" complexes and their equilibrium constants are given in Table A-38.

The agreement between calculated and experimental data is excellent with these constants. From the SIT we expect that the equilibrium constant for a certain cationic complex will not depend strongly on the cation in the ionic medium; this is also the case with the exception of the constant for the (15,6) complex. In view of the small amounts of this complex in the test solutions we suggest that the estimated uncertainty in the equilibrium constant is too small. The species $Th_3(OH)_5^{7+}$ is present in large amounts in the test solutions and represents a species not found in perchlorate media. As shown by Baes and Mesmer [1976BAE/MES], these data can as well be described with the model appropriate for $NaClO_4$ solutions, including the species (2,2), (8,4) and (15,6). Accordingly, the equilibrium constant for the (5,3) complex from [1971MIL2] has not been selected by this review. The complex $Th_2(OH)_3^{5+}$ is present in small amounts and we do not consider this species as definitively identified.

Table A-38: Equilibrium constants of Th(IV) hydroxide complexes formed in 3 M Li, K and Mg nitrate ionic media at a temperature of 25°C. The reported uncertainty is equal to 3σ. Constants without uncertainty estimates are not well determined and correspond to species that are present in small amounts in the test solutions, *cf.* Figs. 9 and 10 in [1971MIL2].

Ionic medium	Complex	$\log_{10} {}^{*}\beta_{n,m}$
3 M (Li)NO_3	$Th_2(OH)_2^{6+}$	– 5.14 ± 0.01
	$Th_3(OH)_5^{7+}$	– 14.23 ± 0.06
	$Th_3(OH)_3^{9+}$	max – 7.33
3 M (K)NO_3	$Th_2(OH)_2^{6+}$	– 5.10 ± 0.03
	$Th_2(OH)_3^{5+}$	– 8.98 ± 0.08
	$Th(OH)_2^{2+}$	– 9.67 max – 8.90
	$Th_6(OH)_{15}^{9+}$	– 40.95 ± 0.07
3 M (Mg)NO_3 (= 1.5 M $Mg(NO_3)_2$)	$Th_2(OH)_2^{6+}$	– 5.17 ± 0.01
	$Th_3(OH)_5^{7+}$	– 14.29 ± 0.07
	$Th_6(OH)_{15}^{9+}$	– 43.20 ± 0.08

[1971SAS/KUB]

The Langmuir vaporisation and the surface ionisation of solid ThC_2 + C (and also LaC_2, CeC_2, PrC_2, NdC_2, and UC_2) from a heated graphite filament were studied mass spectrometrically from *ca.* 2545 to 2780 K (for ThC_2). Small amounts of neutral and ionic metal dicarbide were present in addition to neutral and ionic metal atoms in all the MC_2-C systems except for NdC_2-C. The enthalpy of the reaction Th(g) + 2C(cr) $\rightleftharpoons$ ThC_2(g) was calculated by the authors to be $\Delta_r H_m$(2662 K) = (108.0 ± 19.7) kJ·mol^{-1} from the slope of the neutral MC_2/M ratio, the uncertainty not including those relating to the detector efficiency and ionisation cross-sections of Th(g) and ThC_2(g).

[1971TAN/YAM]

The Gibbs energy of formation of ThF_4(cr) was determined at 873 K with emf cells using a CaF_2 solid electrolyte and Al/AlF_3, UF_3/UF_4 and U/UF_3 counter electrodes.

ThF_4 was prepared from a mixture of ThO_2(cr) and 20% excess NH_4HF_2 maintained at 433 K, followed by heating to 623 − 673 K in purified argon and removal of volatile material at 973 K. Reaction between ThF_4 and CaF_2 was minimised by using a single crystal of CaF_2 as the electrolyte.

Steady emf values were obtained, but no details are given in the translation available to the reviewers. Measurements were made only at 873 K. The data are analysed by the third-law in Section VIII.1.1.2.3.

[1971USH/SKO]

In this paper on the formation of acetate complexes of scandium and thorium in water and aqueous ethanol mixtures at I = 0.05 M and 25°C, Usherenko and Skorik [1971USH/SKO] used preliminary hydrolysis constants of $\log_{10}{}^{*}\beta_{1,1}$ ($\mathrm{Th(OH)^{3+}}$) = −3.15 (water, I = 0.05 M), −2.77 (25 vol.%/19.8 mass.% ethanol) and −2.17 (50 vol.%/40.3 mass% ethanol). The experimental determination of the hydrolysis constants is reported in a later paper of these authors [1972USH/SKO].

[1972ACK/RAU]

The vapour pressure of Th(l) was determined by a combination of target mass-effusion (2380 to 2494 K) and mass-spectrometric (2010 to 2460 K) techniques, using single crystal tungsten cup inside a tungsten effusion cell. Crystal-bar thorium of high (99.95%) purity was used, but no detailed analyses are given. Prior to the measurements of a given sample, it was placed in the mass-spectrometer source and heated until the ThO(g) intensities were less than 2% of the total metal intensity. This treatment was repeated after transfer to the effusion cell. The mass of thorium on the targets (*ca.* 1 µg) was determined by activation analysis. In the mass-spectrometric experiments the initial $\mathrm{ThO^+}$ intensity was *ca.* five times that of $\mathrm{Th^+}$, but fell by a factor of 250 after 6 h treatment at 2400 K.

The melting point of Th was measured to be 2020 K, and the eutectic temperature with tungsten 1968 K. The solubility of W in Th(l) was found to be small, varying linearly from 1.5 mol% at 2000 K to 3.0 mol% at 2500 K. No correction was made for the small solubility of tungsten in Th(l). The absolute mass-loss effusion measurements were used to normalise the mass-spectrometric data, to give the vapour pressure equation for Th(l), $\log_{10} p_{\mathrm{Th}}/\mathrm{bar} = -(29770 \pm 220)/T + (6.030 \pm 0.098)$ from 2010 to 2460 K. The uncertainties are the authors' 1−σ values.

The vapour pressures of Hf(cr), Hf(l) and Zr(l) were also measured by the same techniques. For all three elements, the measured vapour pressures are consistent with the thermodynamic properties of the vapour and condensed phases.

[1972DAN/NOV]

The specific heat of ThN(cr) was measured at 7 to 300 K in an adiabatic calorimeter, with a claimed accuracy of 1% at low temperatures and 2.5% at 300 K. The ThN sample had a lattice parameter of (5.1591 ± 0.0003) Å and contained about 2000 ppm oxygen, which X-ray analysis indicated was present as 1.5 wt% $\mathrm{ThO_2}$. It is not clear whether the authors corrected their heat capacities for this. Only heat capacity values at round temperatures from 10 to 300 K are reported, together with S°_{m} (ThN, cr, 298.15 K) = (56.0 ± 1.5) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. The value of $C^{\circ}_{p,\mathrm{m}}$ (ThN, cr, 298.15 K) interpolated from the reported values at 280 and 300 K is (45.0 ± 1.1) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

[1972KNA/MUL]

Mass-loss Knudsen effusion was used to determine pressures of $ThCl_4(g)$ in the thermal decomposition reaction, $2ThOCl_2(cr) \rightleftharpoons ThO_2(cr) + ThCl_4(g)$, from 819 to 1006 K:

$$\log_{10} p_{ThCl_4}/\text{bar} = -14573/T - 3.27\log_{10}T + 21.36.$$

The results were processed by the review (Section VIII.2.1.6) by the second-law method to give the enthalpy of formation and standard entropy of the oxychloride. The oxychloride is appreciably more stable with respect to $ThO_2(cr)$ and $ThCl_4(cr)$ than is $ThOF_2(cr)$ with respect to the similar reaction.

[1972KNA/MUL2]

The Knudsen effusion method was used to determine the vapour pressure of tetragonal $ThCl_4$ at 671 to 882 K. The melting point of $ThCl_4$ was also determined by DTA to be 1042.7 K.

$ThCl_4$ was prepared by chlorinating the residue from heating hydrated $Th(NO_3)_4$ in a graphite crucible with a mixture of Cl_2, CCl_4 and Ar at 1033 − 1059 K, and collecting the product in a quartz condenser at 573 − 673 K, to avoid organic contaminants. The product was stated to contain 99.6 − 100% $ThCl_4$, and left a residue of 0.1 − 0.5% ThO_2 after sublimation from the Knudsen cell.

The X-ray examination showed a tetragonal structure and the material was presumably the tetragonal β-modification normally found in such preparations. Mass-loss effusion measurements were made from a platinum Knudsen cell from 671 to 982 K, with good reproducibility. It was observed that a sample of $ThCl_4$ contaminated with water gave appreciably lower vapour pressures, between those for the anhydrous $ThCl_4$ and the decomposition pressure of $ThOCl_2$ (see [1972KNA/MUL]).

The vapour pressures were well represented by the equation:

$$\log_{10} p/\text{bar} = -11740/T - 3.273\log_{10}T + 20.165.$$

The entropy and enthalpy of sublimation were extrapolated by the authors to 298.15 K, but these values will depend on the values taken for the heat capacities of the solid and gas.

[1972KUS/IMO]

This is an English language version of [1971KUS/IMO].

[1972PAT/RAM]

An organic phase containing 0.05 M dinonyl naphthalene sulphonic acid in benzene was used to extract thorium from 2.0 M perchloric and sulphuric acid solutions at 10, 25, or 40°C. The data on K_d values as a function of temperature and molarity of HSO_4^- are presented. The authors report the values of equilibrium constants as a function of temperature and based on these values at 25°C, they have also reported values for heats and entropies of different reactions (listed in Table A-39).

Table A-39: Equilibrium constants (molal scale) as a function of temperature and enthalpies and entropies of reaction at 25°C; all values at $I_m = 2.204$ m.

Reaction	$\log_{10} {}^*\beta_n$ (at $I_m = 2.204$ m)		
	10°C	25°C	40°C
$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+$	2.34 ± 0.07	2.26 ± 0.03	2.24 ± 0.13
$Th^{4+} + 2\,HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + 2H^+$	3.59 ± 0.01	3.56 ± 0.06	3.51 ± 0.03
	$\Delta_r H_m$ (kJ·mol^{-1})		$\Delta_r S_m$ (J·K^{-1}·mol^{-1})
$Th^{4+} + HSO_4^- \rightleftharpoons ThSO_4^{2+} + H^+$	– 3.8		31.0
$ThSO_4^{2+} + HSO_4^- \rightleftharpoons Th(SO_4)_2(aq) + H^+$	0		24.7

This review calculated the values of $\log_{10} {}^*\beta_n^o$ from the $\log_{10} {}^*\beta_n$ reported by [1972PAT/RAM] at different temperatures form the relationship:

$$\log_{10} {}^*\beta_n^o = (\log_{10} {}^*\beta_n - \Delta z^2 D + \Delta\varepsilon I_m) \pm (\sigma\Delta\varepsilon I_m)$$

using the SIT model. An appropriate temperature dependent value of D, the Debye-Hückel term, and ion interaction parameters ($\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)$, $\varepsilon(H^+, ClO_4^-) \approx \varepsilon(H^+, HSO_4^-) = (0.14 \pm 0.02)$, and $\varepsilon(ThSO_4^{2+}, ClO_4^-) = (0.3 \pm 0.1)$ kg·mol^{-1}) were used in these calculations (for details about the selection of these parameters see Section IX.1.3.2). The $\log_{10} {}^*\beta_1^o$ and $\log_{10} {}^*\beta_2^o$ values thus determined are (4.21 ± 0.32) and (5.71 ± 0.25) at 10°C, (4.19 ± 0.32) and (5.76 ± 0.25) at 25°C, and (4.26 ± 0.32) and (5.82 ± 0.25) at 40°C. The values at 25°C are very similar to the values calculated from several other sources (*e.g.*, [1958MAI/FOM], [1951ZEB/ALT], [1959ZIE]) and were used in deriving the final value selected in this review for these reactions. Table A-40 shows that there is close agreement between the experimental aqueous thorium concentrations at different sulphate concentrations and the concentrations predicted by the aqueous phase model selected in this review (Tables IX-2 and IX-5). The aqueous thorium concentrations are not reported in this paper but were calculated from the reported K_d values assuming that the concentration $[Th_{org}]$ is constant at 10^{-6} m. Graphical comparisons are presented in Figure IX-4 (See Section IX.1.3.2).

[1972PER]

The author has studied the hydrolysis of Th(IV) by dilution of 3.56 mM thorium nitrate solutions at pH 3.1−3.8 with dilute HNO_3 solutions of the same pH and of 0.393 M thorium nitrate solutions at pH 2.92 with solutions of pH 2.0−2.7 and measuring the resulting change in pH. The method will in principle provide some information on hydrolysis, but data of this type require much more experimental work than the “standard” titration methods. Quantitative evaluation requires that the ionic medium is constant and this is not the case here. There is no quantitative evaluation of the experimental data and the conclusions are only qualitative and provide no thermodynamic information.

Table A-40: Observed [1972PAT/RAM] and predicted aqueous thorium concentrations at 25°C for solvent extraction studies from 2.2 m $HClO_4$-H_2SO_4 (data are plotted in Figure IX-4).

Experimental concentrations (m)		Predicted concentrations (m)				
Total sulphate	Total Th(aq)	Total Th(aq)	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2(aq)$	$Th(SO_4)_3^{2-}$
5.289×10^{-3}	9.901×10^{-8}	1.045×10^{-7}	7.266×10^{-8}	3.053×10^{-8}	1.284×10^{-9}	3.667×10^{-12}
1.058×10^{-2}	1.364×10^{-7}	1.392×10^{-7}	7.271×10^{-8}	6.129×10^{-8}	5.135×10^{-9}	2.935×10^{-11}
2.116×10^{-2}	2.155×10^{-7}	2.171×10^{-7}	7.280×10^{-8}	1.235×10^{-7}	2.055×10^{-8}	2.350×10^{-10}
3.173×10^{-2}	3.040×10^{-7}	3.065×10^{-7}	7.289×10^{-8}	1.866×10^{-7}	4.622×10^{-8}	7.924×10^{-10}
4.231×10^{-2}	4.082×10^{-7}	4.077×10^{-7}	7.299×10^{-8}	2.507×10^{-7}	8.217×10^{-8}	1.879×10^{-9}
5.289×10^{-2}	5.208×10^{-7}	5.211×10^{-7}	7.307×10^{-8}	3.159×10^{-7}	1.285×10^{-7}	3.673×10^{-9}
6.347×10^{-2}	6.369×10^{-7}	6.464×10^{-7}	7.317×10^{-8}	3.819×10^{-7}	1.850×10^{-7}	6.349×10^{-9}
7.405×10^{-2}	7.752×10^{-7}	7.844×10^{-7}	7.326×10^{-8}	4.490×10^{-7}	2.520×10^{-7}	1.009×10^{-8}
8.463×10^{-2}	9.259×10^{-7}	9.345×10^{-7}	7.336×10^{-8}	5.170×10^{-7}	3.291×10^{-7}	1.506×10^{-8}
9.520×10^{-2}	1.089×10^{-6}	1.098×10^{-6}	7.344×10^{-8}	5.862×10^{-7}	4.167×10^{-7}	2.145×10^{-8}
1.058×10^{-1}	1.261×10^{-6}	1.274×10^{-6}	7.354×10^{-8}	6.563×10^{-7}	5.147×10^{-7}	2.946×10^{-8}

[1972SAT]

This letter to the editor provides no thermodynamic information. The author has used experimental determination of the molar compressibility to calculate hydration numbers of different metal ions, including Th^{4+}. Data of this type give no information on the number of water molecules in the first coordination sphere, only an "operational" coordination number, in this case 14 for Th^{4+}. Operational coordination numbers of this type are always dependent on the method used and are therefore of limited chemical interest.

[1972USH/SKO]

The authors determined mononuclear hydrolysis constants $\log_{10} {}^*\beta_{1,1}$ ($Th(OH)^{3+}$) and $\log_{10} {}^*\beta_{2,1}$ ($Th(OH)_2^{2+}$) in water and in aqueous ethanol mixtures containing 19.8 and 40.3 mass% ethanol at $I = 0.05$ M and 25°C. Similar measurements were made for the trivalent lanthanide, yttrium, and scandium ions, which do not concern this review. Usherenko and Skorik [1972USH/SKO] observed a linear relationship between $\log_{10} \beta^{\circ}_{1,1}$ ($Th(OH)^{3+}$) and the reciprocal of the dielectric constant of the solvent.

The present review considers only the hydrolysis constants for Th^{4+} in aqueous solution reported in [1972USH/SKO]:

$$\log_{10} {}^{*}\beta_{1,1}\,(\mathrm{Th(OH)}^{3+}, I = 0.05\ \mathrm{M}) = -(3.15 \pm 0.07) \qquad \log_{10} {}^{*}\beta^{\circ}_{1,1} = -\,2.63,$$

$$\log_{10} \beta^{\circ}_{1,1} = 11.36$$

$$\log_{10} {}^{*}\beta_{2,1}\,(\mathrm{Th(OH)}_2^{2+}, I = 0.05\ \mathrm{M}) = -(6.56 \pm 0.16) \qquad \log_{10} {}^{*}\beta^{\circ}_{2,1} = -\,5.70,$$

$$\log_{10} \beta^{\circ}_{2,1} = 22.28.$$

The conditional equilibrium constants were determined by potentiometric titration at a single thorium concentration of 5 mM using 0.01 M CO_2-free NaOH. Titrations were performed under Ar atmosphere; ionic strength was kept constant at I = 0.05 M with NaCl and $NaClO_4$. The H^+ concentration was measured with glass and Ag/AgCl reference electrodes calibrated by titrating HCl standard solutions. The acid concentration of the initial thorium perchlorate solutions was determined by titration in the presence of sodium oxalate. The primary experimental data, the number of titrations and the pH range investigated are not given in [1972USH/SKO]. The reported equilibrium constants at zero ionic strength were calculated using Davies equation and $\log_{10} K^{\circ}_{\mathrm{w}} = -\,13.99$ for the ion product of water.

The results reported by Usherenko and Skorik [1972USH/SKO] are of a reasonable order of magnitude. However, the possible formation of polynuclear thorium hydroxide complexes is not taken into account by the authors. This would have required additional studies at different total thorium concentrations. Therefore the reported results are not considered by the present review in the selection of data for thorium hydroxide complexes.

[1973ACK/RAU2]

The Th-O system was studied by investigating the vaporisation behaviour of the dioxide phase and the univariant system, Th(1) + ThO_2(cr). A combination of mass effusion and time-of-flight mass-spectrometric techniques was employed to yield an internally consistent set of thermodynamic data. The thorium used was crystal-bar material with fewer than 200 ppm total impurities, which was also used for the preparation of ThO_2(cr).

Th(l) was contained inside a ThO_2 cup inside the tungsten effusion cell. The ionisation currents of ThO^+(g) and Th^+(g) were measured over the univariant diphasic system were determined from 1780 to 2420 K, thus including ranges where the thorium is both solid and liquid. The total effusion rate of thorium-bearing species from the same sample was measured (in a different apparatus) from 2080 to 2214 K by the collection of a known fraction of the effusate on quartz targets and subsequent determination of the thorium by activation analysis. From the mass-spectrometric results, it is clear that ThO(g) is the only species which contributes significantly to the mass effusion rate. The mass-spectrometric results were then normalised to the mass-effusion results to give the equation for the partial pressure of ThO(g) over the system Th(l)-ThO_2(cr): $\log_{10} p_{\mathrm{ThO}}/\mathrm{bar} = -\,28630/T + 7.585$. The normalised pressure of Th(l) is identical to that over pure Th(cr or l) within experimental error and since the solubility of Th in

$ThO_2(cr)$ is insignificant in this temperature range, the activities of the coexisting liquid metal and dioxide phases below 2400 K are essentially unity.

Measurements of the ion intensities of the species in the isomolecular exchange reaction $YO(g) + Th(g) \rightleftharpoons ThO(g) + Y(g)$ were carried out using a mixture Y_2O_3 and Th held in a single-crystal Ta cup inside a tungsten effusion cell from 1930 to 2280 K. With the reasonable assumption that the instrumental sensitivities cancel for such a simple isomolecular reaction, the equilibrium constant was equated to the corresponding intensity ratio $\log_{10} K = -9020/T - 0.496$ (1930 − 2280 K).

The congruently vaporising composition of thoria was measured from both the O and Th-rich sides by analysing the residues from samples heated in a tungsten cell for 3 − 6h, followed by measurement of the weight gain on combustion in air at 1673 K. At 2820 K, the congruently vaporising composition was shown to be $ThO_{(1.994 \pm 0.002)}$.

These results were combined by the authors with thermal functions for the species involved to evaluate the standard Gibbs energy of formation of ThO(g) from 1600 to 3000 K. The authors then re-evaluated the measurements of Ackermann *et al.* [1963ACK/RAU] on the total effusion rate of the vaporisation of $ThO_2(cr)$, to calculate the individual partial pressures of $ThO_2(g)$, ThO(g), and O(g) over the congruently evaporating dioxide phase and thus standard Gibbs energy of formation of the gaseous dioxide.

This is a high quality study, whose results are included in the analysis of the data for ThO(g) and $ThO_2(g)$ in Section VII.1.

[1973ACK/RAU3]

This study is centred on the identification of the thermal decomposition products of the residue formed upon dissolution of thorium and uranium metals in hydrochloric acid. The authors first confirmed earlier studies [1962KAT/KAP] which showed that such residues correspond to an oxide hydride containing chloride and hydroxide ions. They showed, that, in the case of thorium, the ultimate decomposition product upon heating in air at 1173 K was $ThO_2(cr)$ and that HCl was evolved in this reaction. They also studied by X-ray diffraction samples of the decomposition products of both (thorium and uranium) residues heated *in vacuo* at 1073 K for 4 hours in tungsten crucibles. In the case of thorium, they identified two sets of diffraction lines, the most intense set corresponding to $ThO_2(cr)$ and the other set, about 10% as intense as that of $ThO_2(cr)$, was consistent with a cubic face centred structure with $a = (5.302 \pm 0.003)$ Å which they tentatively ascribed to ThO(cr). The authors suggested that given the quantity of this phase and the purity of the original metal samples the amounts of carbon and nitrogen in this phase would be very low. Some support for the existence of a ThO(cr)-based phase was obtained from high temperature diffractometer data, in which the decomposition of the thorium residue began to show, at 973 K, the simultaneous presence of $ThO_2(cr)$ and, as a very minor constituent, ThO(cr). This minor constituent persisted up to 1273 to 1473 K, at which point the intensity of the lines of face centred cubic thorium metal began to increase. One line attributed to ThO(cr), in the presence of lines due to Th(cr) and ThO_2(cr), was also shown on a low angle diffractometer trace of a sample heated at about 1373 K for half an hour and then cooled to room temperature. These results are consistent with the high temperature decomposition of a ThO(cr)-based phase into, essentially, the metal and the dioxide, although, in spite of the confidence expressed by the authors, the presence of light element impurities (carbon, nitrogen…) and possibly tungsten, could have played a role in stabilising the ThO(cr) phase. In any case, it seems clear that pure ThO(cr) is not a stable phase in the binary Th-O phase diagram.

In the case of the uranium residue the results were indicative of an analogous decomposition process upon heating.

[1973DER/FAU]

This is a preparative study where the authors have identified a number of different carbonate phases and determined their analytical composition and unit cells. The following Th(IV) phases have been identified: $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot 4H_2O$; $[C(NH_2)_3]_4[Th(CO_3)_4]\cdot 6H_2O$; $[C(NH_2)_3]_2[Th(CO_3)_3]\cdot 4H_2O$; $Na_6[Th(CO_3)_5]\cdot 12H_2O$; $Na_4[Th(CO_3)_4]\cdot 7H_2O$. Only the penta-carbonates were obtained in crystalline form.

[1973DER/FAU2]

The authors have used four different methods, potentiometry (measurement of the hydrogen ion concentration), cryoscopy (measurement of freezing point depression), conductometry and ion exchange, to determine the stoichiometry of the complexes formed in the Th(IV)-carbonate system. The experiments have not been made at constant ionic strength and no equilibrium constants have been proposed. However, the authors proposed the formation of three different complexes $Th(CO_3)_4^{4-}$, $Th(CO_3)_5^{6-}$, and $Th(CO_3)_6^{8-}$. In two previous studies [1962FAU/DER], [1962FAU/DER2] they specifically stated that both the cryoscopic and the potentiometric data were only consistent with the penta-carbonato complex as the limiting species. This complex was confirmed in the potentiometric study presented and identified using the inflexion point in the titration and this qualitative observation is accepted by this review. The conductometric titration data also show slope changes that Dervin and Faucherre interpret as a result of changes in the speciation. However, in order to validate this suggestion it is necessary to compare the experimental data with calculated data obtained using different speciation models, this has not been done and accordingly even the qualitative observations are not accepted by this review. The distribution coefficient of Th(IV) between an aqueous phase and an anion exchange phase (Dowex 1X8) was measured as a function of the carbonate concentration. Analysis of the slope of $\log_{10} D$ *vs.* $\log_{10}[CO_3^{2-}]$ was interpreted qualitatively and the authors suggested the formation of the complexes $Th(CO_3)_5^{6-}$, and $Th(CO_3)_6^{8-}$. This review does not accept this interpretation. The latter complex is an artefact arising from activity coefficient variations due to changes of the solution composition (*cf.* the discussion in Section XI.1.3.3).

[1973DER/FAU3]

The solubility of the previously identified [1973DER/FAU] solid thorium(IV) pentacarbonato phases $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s)$ and $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ has been measured as a function of the bicarbonate and carbonate concentration in nitrate media of constant concentration of the corresponding cation, $[C(NH_2)_3^+]$ = 2.0 M and $[Na^+]$ = 2.0 M, respectively. The experimental data refer to the reaction:

$$M_6[Th(CO_3)_5]\cdot xH_2O(s) \rightleftharpoons 6M^+ + Th(CO_3)_n^{4-2n} + (5-n)\,CO_3^{2-} \tag{A.61}$$

where the value of n can be determined from a slope analysis and the solubility constant from the measured solubility.

In the first set of data the solid phase was $[C(NH_2)_3]_6[Th(CO_3)_5](s)$ and the solubility was measured using a guanidinium nitrate ionic medium:

1) 2.0 M $C(NH_2)_3(HCO_3\text{-}NO_3)$ solutions with $[HCO_3^-]$ = 0.2 − 1.0 M and I = 2.0 M
2) $(C(NH_2)_3)_2CO_3\text{-}C(NH_2)_3NO_3$ solutions with $[C(NH_2)_3^+]$ = 2.0 M, $[CO_3^{2-}]$ = 0.25 − 1.0 M and I = 2.25 − 3.0 M

The solubility of $[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s)$ in 2.0 M $C(NH_2)_3(HCO_3\text{-}NO_3)$ solution had a constant value: $[Th(CO_3)_5^{6-}] = 1.57\times 10^{-3}$ M. From these data we obtain the equilibrium constant $K_{s,5} = [C(NH_2)_3^+]^6[Th(CO_3)_5^{6-}] = 0.10\ M^7$ ($\log_{10} K_{s,5} = -1.00$) for the reaction:

$$[C(NH_2)_3]_6[Th(CO_3)_5]\cdot xH_2O(s) \rightleftharpoons 6C(NH_2)_3^+ + Th(CO_3)_5^{6-} + xH_2O(l) \tag{A.62}$$

The solubility in the $C(NH_2)_3)_2CO_3\text{-}C(NH_2)_3NO_3$ solutions remained constant at 1.7×10^{-3} M, in the range 0.25 M < $[CO_3^{2-}]$ < 0.35 M, indicating the predominance of $Th(CO_3)_5^{6-}$ in solution and $K_{s,5} = [C(NH_2)_3^+]^6[Th(CO_3)_5^{6-}] = 0.109\ M^7$ ($\log_{10} K_{s,5} = -0.98$), consistent with the value in the bicarbonate solutions. At higher carbonate concentrations the solubility increases with the slope +1 apparently indicating an equilibrium between $Th(CO_3)_5^{6-}$ and $Th(CO_3)_6^{8-}$. The authors propose the reaction:

$$Th(CO_3)_5^{6-} + CO_3^{2-} \rightleftharpoons Th(CO_3)_6^{8-} \tag{A.63}$$

As shown below for the analogous results with $Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$ it is clear that the activity coefficients do not remain constant at these high and varying carbonate concentrations and this review therefore does not accept the interpretation given by Dervin and Faucherre. It is not possible to extrapolate the conditional solubility constant $\log_{10} K_{s,5}$ (I = 2 M) to zero ionic strength, because the ion interaction coefficients between $C(NH_2)_3^+$ and NO_3^-, HCO_3^-, CO_3^{2-}, and $Th(CO_3)_5^{6-}$ are not known.

In a second set of solubility experiments the solid phase was

$Na_6[Th(CO_3)_5]\cdot12H_2O(s)$; this is about 10 times more soluble than the guanidinium phase and accordingly the variation in ionic strength is larger. The solubility was measured in following media:

1) 2.0 M $Na(HCO_3\text{-}NO_3)$ solution ($I = 2.14\ mol\cdot kg^{-1}$); $[HCO_3^-] = 0.2 - 1.0$ M

2) $Na_2CO_3\text{-}NaNO_3$ solutions with $[Na^+] = 2.0$ M, $[CO_3^{2-}] = 0.15 - 1.0$ M and $I = 2.15 - 3.0$ M.

Dervin and Faucherre noted that the solubility remained constant (0.021 M) in the bicarbonate solutions and at carbonate concentrations below 0.40 M where the predominant complex is $[Th(CO_3)_5^{6-}]$ and calculated the corresponding solubility constant, $K_{s,5} = [Na^+]^6[Th(CO_3)_5^{6-}] = 1.34\ M^7$ ($\log_{10} K_{s,5} = 0.13$). In both sets of experiments the ratio carbonate to bicarbonate was varied and the results indicated that no ternary hydroxide-carbonate complexes were formed.

This review uses equation (A.64) for the calculation of the solubility constant $\log_{10} K^{\circ}_{s,5}$ at zero ionic strength from the conditional equilibrium constant $\log_{10} K_{s,5}$ in 2.0 M $Na(HCO_3\text{-}NO_3)$:

$$\begin{aligned}\log_{10} K^{\circ}_{s,5} = {} & \log_{10} K_{s,5} - 42D + 6\,\{\varepsilon(Na^+, HCO_3^-)\cdot m_{HCO_3^-} + \varepsilon(Na^+, NO_3^-)\cdot m_{NO_3^-}\} \\ & + \varepsilon(Th(CO_3)_5^{6-}, Na^+)\cdot m_{Na^+} + 12\log_{10} a_w \qquad (A.64)\end{aligned}$$

The increase of the Na^+ concentration and ionic strength caused by the dissolution of $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ has to be taken into account and the data have to be converted to the molal scale. With $\log_{10} K_{s,5} = 0.49$ (molal scale) and $I = 2.61\ mol\cdot kg^{-1}$ ($D = 0.240$), $\varepsilon(Na^+, HCO_3^-) = (0.00 \pm 0.02)\ kg\cdot mol^{-1}$, $\varepsilon(Na^+, NO_3^-) = -(0.04 \pm 0.03)\ kg\cdot mol^{-1}$, $\varepsilon(Th(CO_3)_5^{6-}, Na^+) = -(0.30 \pm 0.15)\ kg\cdot mol^{-1}$, and the water activity a_w = 0.9385 we obtain: $\log_{10} K^{\circ}_{s,5} = -(11.0 \pm 0.5)$.

A mean value of $\log_{10} K^{\circ}_{s,5} = -(11.2 \pm 0.4)$, is obtained from the solubility data in $Na_2CO_3\text{-}NaNO_3$ solutions according to equation (A.65):

$$\begin{aligned}\log_{10} K^{\circ}_{s,5} = {} & 6\log_{10}[Na^+] + \log_{10}[Th(CO_3)_5^{6-}] - 42D + 6\,\varepsilon(Na^+, CO_3^{2-})\cdot m_{CO_3^{2-}} + \\ & + \varepsilon(Th(CO_3)_5^{6-}, Na^+)\cdot m_{Na^+} + 12\log_{10} a_w \qquad (A.65)\end{aligned}$$

with $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03)\ kg\cdot mol^{-1}$ and $\varepsilon(Th(CO_3)_5^{6-}, Na^+) = -(0.30 \pm 0.15)\ kg\cdot mol^{-1}$. This mean value is close to that calculated from the data reported in [1961LUZ/KOV], $\log_{10} K^{\circ}_{s,5} = -(11.3 \pm 0.3)$. The $\log_{10} K^{\circ}_{s,5}$ values calculated from the solubility experiments with $Na_6[Th(CO_3)_5]\cdot12H_2O(s)$ in bicarbonate [1973DER/FAU3] and carbonate solutions [1961LUZ/KOV2], [1973DER/FAU3] are accepted by this review and used to select thermodynamic data for this solid phase.

The consistency of the $\log_{10} K^{\circ}_{s,5}$ values obtained from all experimental data over the whole carbonate concentration range (Table A-41) shows that the observed increase of the solubility at $[CO_3^{2-}] > 0.3$ M, is not caused by the formation of $Th(CO_3)_6^{8-}$ as assumed by Dervin and Faucherre [1973DER/FAU3] but by the variation of the activity coefficients as a consequence of the composition of the medium and the very large Debye-Hückel term (−42 *D*).

Table A-41: Evaluation of $\log_{10} K^{o}_{s,5}$ ($Na_6[Th(CO_3)_5]\cdot 12H_2O(s)$) from the solubility data of [1973DER/FAU3] in Na_2CO_3-$NaNO_3$ solution.

Molar concentrations ($mol\cdot L^{-1}$)			m_i/c_i	I_m	a_w	$\log_{10} K_{s,5}$	$\log_{10} K^{o}_{s,5}$ [a]
$[Na_2CO_3]$	$[NaNO_3]$	[Th]	($L\cdot kg^{-1}$)	($mol\cdot kg^{-1}$)			
	2.00		1.0692		0.939		
0.15	1.70	0.0215	1.0602	2.76	0.942	0.48	– 11.19 ± 0.46
0.20	1.60	0.0215	1.0572	2.80	0.944	0.47	– 11.21 ± 0.44
0.25	1.50	0.0215	1.0543	2.85	0.945	0.46	– 11.23 ± 0.43
0.30	1.40	0.0215	1.0513	2.89	0.946	0.45	– 11.25 ± 0.42
0.40	1.20	0.025	1.0453	3.07	0.949	0.54	– 11.24 ± 0.39
0.50	1.00	0.029	1.0393	3.24	0.951	0.61	– 11.23 ± 0.38
0.60	0.80	0.033	1.0333	3.40	0.954	0.67	– 11.22 ± 0.36
0.70	0.60	0.036	1.0273	3.56	0.956	0.72	– 11.22 ± 0.35
0.80	0.40	0.040	1.0214	3.71	0.959	0.76	– 11.22 ± 0.35
0.90	0.20	0.043	1.0154	3.86	0.961	0.80	– 11.22 ± 0.35
1.00	0.00	0.046	1.0094	4.00	0.964	0.83	– 11.22 ± 0.35

a: The large uncertainties arise from the ionic strength corrections (error propagation accounting for the uncertainties of the SIT coefficients)

[1973FUG/BRO]

The enthalpies of solution of the following halides in 1 and 6 M HCl were measured at (298.15 ± 0.05) K:

Table A-42: Enthalpy of solution ($kJ\cdot mol^{-1}$) of β-$ThCl_4$, β-$ThBr_4$, $ThI_4(cr)$, $UBr_4(cr)$, $UI_4(cr)$ and $NpBr_4(cr)$ in 1 and 6 M HCl.

	1 M HCl	6 M HCl		1 M HCl	6 M HCl
$ThCl_4(\beta)$	– 241.8 ± 0.7	– 188.3 ± 0.4	$ThBr_4(\beta)$	– 283.2 ± 1.3	– 233.9 ± 0.8
ThI_4 (cr)	– 322.0 ± 0.6	– 276.0 ± 1.2	$UBr_4(cr)$	– 264.6 ± 0.5	– 205.7 ± 0.9
$UI_4(cr)$	– 289.9 ± 1.3	– 240.2 ± 1.3	$NpBr_4(cr)$	– 258.8 ± 0.5	– 199.2 ± 0.4

The concentrations of the various actinide halides in the solutions were in the 1 to 3 millimolar range.

The results reported in this study are for very pure samples prepared in duplicate and characterised by X-ray data and gravimetric/titrimetric techniques. Uncertainty limits are reported for the 95% confidence interval.

In conjunction with results from [1949WES/ROB3], [1950EYR/WES], and [1969SMI/THA], and of $\Delta_f H_m^o$ ($ThCl_4$, β, 298.15 K), these data are used for the determination of $\Delta_f H_m^o$ (Th^{4+}, 298.15 K). They serve also as basis for the selection of the enthalpies of formation of β-$ThBr_4$ and ThI_4(cr).

[1973ONO/KAN]

Ono *et al.* have measured the heat capacity of ThN(cr) and Th_3N_4(cr) *in vacuo* from 450 to 850 K, using a high temperature double-adiabatic calorimeter, with synthetic sapphire and 'reactor grade' ThO_2(cr) as standards. The samples were prepared from Th(cr) by hydrogenation and reaction with N_2(g), and were analysed for Th and N, the derived compositions being $ThN_{0.95}$ and $Th_3N_{3.93}$. The ThO_2 content of the final samples was indicated to be < 2%; no corrections were made for this.

Individual experimental data are not reported, but the results are presented as small diagrams and as fitted equations for the range 298.15 K < T < 850 K. As noted in Section X.1, their derived heat capacity equations give somewhat lower values of $C_{p,m}^o$ at 298.15 K than those derived from low-temperature measurements [1972DAN/NOV], [1973DEL], so the authors' data have been refitted with constraints of $C_{p,m}^o$ (298.15 K) equal to these values. The equations have been extrapolated to 2000 K in order to process the Th_3N_4 dissociation pressure data to derive a value for the enthalpy of formation of ThN(cr).

[1973SAT/KOT]

The authors have studied the distribution of Th(IV) between an aqueous phase containing hydrochloric acid, potassium thiocyanate and tricaprylmethylammonium chloride (TCA-Cl) into benzene. TCA acts as a liquid ion exchanger according to:

$$SCN^-(aq) + TCA\text{-}Cl(org) \rightleftharpoons TCA\text{-}SCN(org) + Cl^-(aq) \qquad (A.66)$$

This equilibrium was studied in a first set of experiments without Th(IV). In a second set of experiments the distribution coefficient of Th(IV) between an aqueous phase and benzene was measured at different concentrations of KSCN (0.2 − 2 M). The total concentration of Th(IV) was 0.0026 M, of TCA-Cl 0.094 M and HCl between 0.05 and 0.4 M. The stoichiometry of the extracted Th(IV) complex was determined in test solutions where the KSCN concentration was 1 M and the extraction reaction was:

$$Th(SCN)_6^{2-}(aq) + 2TCA\text{-}SCN(org) \rightleftharpoons (TCA)_2\,Th(SCN)_6^{2-}(org) + 2SCN^-(aq) \qquad (A.67)$$

The absorption and IR spectra in both the aqueous and the organic phase were consistent with the extraction equilibrium (A.67). There is no quantitative information on the equilibrium constant for Reaction (A.67) or for the complex formation reactions in the aqueous phase.

[1973SKE/PAT]

The Gibbs energy of formation of ThF_4 was determined from 961 to 1076 K with emf cells using a CaF_2 solid electrolyte and Ni/NiF_2 as the counter electrode. The ThF_4 used contained up to 500 ppm Ca and 100 − 120 ppm Mg and Si. Reaction between ThF_4 and CaF_2 was minimised by using a single crystal of CaF_2 as the electrolyte. Symmetrical double cells provided a continuous check on the absence of thermal gradients and data reproducibility. Initial stable emfs were obtained within a few hours, and in 0.5 − 1 h after a change in temperature.

The results are presented only in the form of graphs and equation of the emf as a linear function of the temperature. The data are analysed by the third-law in Section VIII.1.1.2.3.

[1974BIN/SCH2]

The vapour pressure of $ThCl_4$(cr) was measured from 559 to 702 K by mass-spectrometric Knudsen effusion. No details whatever are given of the $ThCl_4$ sample used. No absolute measurements were made but approximate pressures were determined by calibration with a zinc standard. However for these pressures, the plot of $\log_{10}p$ *vs.* $1/T$ has a noticeable curvature, attributed to unspecified experimental errors. The authors therefore preferred to combine their experimental pressure $\log_{10}p/\text{bar} = -7.2597$ at 636.4 K, the weighted mean temperature of their measurements, with an extrapolation of the measurements of [1939FIS/GEW2] (at the appreciably higher temperatures of 974 to 1036 K) by assuming $\Delta_{\text{sub}}C_{p,\text{m}} = (-17.41 - 13.8\times10^{-3}\,T)\ \text{J·K}^{-1}\text{·mol}^{-1}$, based on the data for the sublimation of $ZrCl_4$ from the 1971 JANAF tables. The sublimation enthalpy and entropy at 298.15 K were calculated.

Given the lack of information on the sample, the difficulties of mass-spectrometric pressure calibrations, and the admitted unknown experimental errors, these data have been given low weight in the assessment of the sublimation data. The pressures calculated by calibration with zinc are included on Figure VIII-6 for comparison with the more precise data.

[1974GAB/REE]

This is a comprehensive study of the infra-red spectra of ThO_2(g) (and some lanthanide oxides), vaporised from iridium or tungsten cells and condensed into argon matrices. Oxides substituted with ^{18}O were also studied, so that the observed frequency shifts for the isotopomers could be compared with those calculated from a normal co-ordinate analysis. The observed frequencies of ν_1 and ν_3 of 787.4 and 735.3 cm^{-1} for $Th^{16}O_2$ were consistent with a bent molecule with a O–Th–O angle of (122.5 ± 2.0)°. The frequencies are essentially the same as those found by Linevsky [1963LIN], using a lower resolution spectrometer, although he inferred an interbond angle of (106 ± 10)°.

For ThO(g), the values obtained for ω_e and $\omega_e x_e$ of (883.8 ± 1.8) and (1.9 ± 0.9) cm^{-1} are reasonably close to those found from the detailed analysis of the vapour (895.77 and 2.39 cm^{-1}) [1985EDV/LAG2] and references quoted therein.

[1974HIL/MUR]

High temperature mass spectrometric measurements were made on the equilibria $0.5\text{Th(cr)} + 0.5\text{ThO}_2\text{(cr)} \rightleftharpoons \text{ThO(g)}$ from 1782 to 1940 K and $\text{ThO(g)} + \text{Si(g)} \rightleftharpoons \text{Th(g)} + \text{SiO(g)}$ (2064 to 2212 K).

In both reactions, a molybdenum Knudsen cell was used, inside which a rough thoria cell was made by firm tamping of ThO_2 powder. Additional material (Th(cr) for the first reaction, and $MoSi_2$, Th and ThO_2, with or without Mo powder, for the second reaction) were then added to this crude ThO_2 crucible.

For the first reaction, the pressures of ThO(g) (ten data points) were estimated by assuming the ionisation cross-sections for Th(g) and ThO(g) are equal, and the activity of Th(cr) was unity. With these assumptions, which the authors suggest lead to an uncertainty of ± 20% in $\log_{10} p_{\text{ThO}}$, this was given by the expression:

$$\log_{10} p_{\text{ThO}} / \text{bar} = 8.392 - 30480/T \qquad (1782-1940\ \text{K}).$$

For the second (isomolecular) reaction, the instrumental efficiencies are likely to cancel out and the equilibrium constants will be little different from those for the corresponding ionic reaction, and thus $\log_{10} K = -2.7216 + 1001.9/T$ (fitted by this review). All these experimental values have been included in the assessment of the data for $\Delta_f H^\circ_m$ (ThO, g, 298.15 K) in Section VII.1.1.2.

The authors also describe the difficulties in interpreting the threshold voltage for ThO ionisation.

[1974KOH/STE]

The high temperature vaporisation of the thorium-carbon systems was studied by the Knudsen effusion-mass spectrometric method. (Similar studies were carried out on the Ti-C, Zr-C and Hf-C systems, which do not concern the present review). The samples used were prepared *in situ* in the mass-spectrometer by heating a mixture of thorium powder with excess graphite powder in tungsten or tantalum effusion cells. Formation of the (carbon-saturated) dicarbide was verified by X-ray diffraction. Thorium dicarbide and tetracarbide species were identified in the gas phase and second- and third-law methods were used to determine the standard enthalpies for the reactions $\text{Th(g)} + 2\text{C(cr)} \rightleftharpoons \text{ThC}_2\text{(g)}$ and $\text{Th(g)} + 4\text{C(cr)} \rightleftharpoons \text{ThC}_4\text{(g)}$. The thermal functions for the gaseous carbides used in the calculations are discussed in terms of assumed molecular structures and electronic contributions to the partition functions. In addition, a maximum value was established for the dissociation energy of ThC(g).

The results from this paper, which agree within their uncertainties with the similar studies by [1980GUP/GIN] (according to these authors) and [1964JAC/BAR], are analysed in more detail in Sections XI.1.2.1 and XI.1.2.2. It is noted in these sections that recent calculations by Kovács and Konings [2008KOV/KON] indicate that ThC_2(g) and ThC_4(g) are not linear, as assumed by [1974KOH/STE], but have L-shaped and fan-shaped structures respectively. This results in considerable differences in the calculated and experimental entropies of the relevant reactions and no data are selected for ThC_2(g) or ThC_4(g) for this review.

[1974MAG/ROM]

Complex formation in the Th(IV)-azide system was studied at 25ºC using potentiometric methods, *i.e.* the determination of $-\log_{10}[\mathrm{H}^+]$ in a 3.00 M $NaClO_4$ ionic medium. Data from three series of titrations with a total concentration of Th(IV) equal to 10.00, 20.00 and 50.00 mM were used to deduce the equilibrium constants for the species $\mathrm{Th(N_3)}_n^{4-n}$, $n = 1-2$. The hydrogen ion concentration in all experiments was larger than 1.2 mM and hydrolysis can therefore be neglected. The experimental methods used and the analysis of the data are excellent and the equilibrium constants $\log_{10}\beta_1$ = (3.09 ± 0.11) and $\log_{10}\beta_2$ = (6.37 ± 0.08) are accepted by this review. These equilibrium constants have been obtained by a least-squares fitting to the experimental data and the estimated uncertainty has been assumed by this review to be 3σ. The protonation constant for the azide ion, necessary for the analysis of the experimental data, $\log_{10}K = 4.78$ is taken from Maggio *et al.* [1967MAG/ROM].

[1974MAS/JHA]

Thorium tetrachloride has been shown to possess two polymorphic forms. The crystal structure or the β form, stable above 678 K, has been well established to be tetragonal with space group $I4_1/amd$ and lattice parameters a = 8.486 and c = 7.465 Å. The low-temperature α form, which can only be obtained if extreme care is taken in cooling the sample, has been shown to be tetragonal with space group $I4_1/a$ with a = (6.408 ± 0.001) and $c = (12.924 \pm 0.003)$ Å. The β form is isomorphous with the other actinide tetrachlorides [1968BRO]. As this is the form normally obtained at room temperature, the values for this polymorph are considered to be the standard thermodynamic data for $ThCl_4$(cr).

[1974MAS/JHA2]

Using single crystal X-ray diffraction, these authors confirmed the existence of the β tetragonal form (space group $I4_1/amd$) of $ThBr_4$(cr), and reported the lattice parameters as $a = (8.934 \pm 0.003)$ Å and $c = (7.964 \pm 0.001)$ Å. They also showed that this phase is metastable below (699 ± 5) K and identified the low temperature α form, which they obtained by careful cooling the β phase or annealing the untransformed salt for several hours in the temperature range 623 to 673 K. This α form was shown to be tetragonal, space group $I4_1/a$, with $a = (6.737 \pm 0.001)$ Å and $c = (13.601 \pm 0.003)$ Å. The two crystalline forms of $ThBr_4$ are isomorphous with the two corresponding $ThCl_4$ forms. From their DTA observations, the authors estimated that the melting point of $ThBr_4$ to be (951 ± 5) K.

[1974NEU/ZMB]

The reaction $ThO(g) + La(g) \rightleftharpoons Th(g) + LaO(g)$ was studied from 1759 to 1961 K (18 data points) in a double-focusing mass spectrometer, by heating a mixture of Th(cr) and La_2O_3(cr) in a tungsten Knudsen cell with a tantalum liner.

For the above isomolecular reaction, the instrumental efficiencies are likely to cancel out and the equilibrium constants will be little different from those for the corresponding ionic reaction, and thus $\log_{10} K = -0.78 - 14161/T$. These experimental values have been included in the assessment of the data for $\Delta_f H^\circ_m$ (ThO, g, 298.15 K) in Section VII.1.1.2. The third law enthalpy of formation of ThO(g), calculated by the review, is $-(13.0 \pm 12.9)$ kJ·mol^{-1} where the uncertainty is the statistical value only. Inclusion of the experimental uncertainties, mainly the ion efficiencies, is estimated to increase this to 15.0 kJ·mol^{-1}.

[1974POY/LEB]

The emf of the cell Th(cr)| KCl-NaCl +$ThCl_{4-x}$| KCl-NaCl +$ThCl_4$|Th-Bi(l, saturated), with molybdenum conductors, was used to determine the thorium activity in Th-saturated liquid bismuth from 953 to 1093 K. The Th-Bi alloys were prepared by melting thorium chips (99.8% pure) with bismuth (99.9% pure) in BeO crucibles directly in the cell. The emf was given by $E(T) = (589 - 0.191\,T)$ mV, with a reproducibility of 5 mV. Poyarkov *et al.* suggested that the phase in equilibrium with the saturated solution was Th_3Bi_4(cr), but the more recent work by [1982BOR/BOR2] indicate that $ThBi_2$(cr) is stable up to *ca.* 1500 K and the data of [1974POY/LEB] have been assumed to refer to the partial Gibbs energy of thorium in the {Bi(l) + $ThBi_2$(cr)} phase field: $\Delta_{sln} G_m$ (Th) = $(-224220 + 67.78\,T)$ J·mol^{-1}. These data can be therefore be used to calculate the Gibbs energy of formation of $ThBi_2$(cr) around 1000 K. With the low solubility of thorium, the chemical potential of bismuth will be close to the ideal value and $\Delta_f G_m$ ($ThBi_2$, cr) (from Bi(l)) in the temperature range of the study by [1974POY/LEB] is calculated to be:

$$[\Delta_f G^\circ_m]^{1100\text{K}}_{950\text{K}} (\text{ThBi}_2, \text{cr}, T) = -222900 + 66.3\,T\ (\text{J·mol}^{-1}).$$

As noted in Section X.5, this value is reasonably consistent with the enthalpy of formation measurements of [1982BOR/BOR2] at 300 K.

Poyarkov *et al.* [1974POY/LEB] also made measurements of the cell

Th-Zn(l, saturated)| KCl-NaCl +$ThCl_4$ |Th-Bi(l, saturated), but the analysis of these requires a knowledge of the thermodynamics of the Th-Zn system. In the light of the more direct measurements using the cell with a pure Th electrode, these data have not been utilised by the review.

The solubility of thorium in bismuth was also determined in this study. These measurements were in good accord with other data and were included in the assessment of all the solubility data by [1981CHI/AKH], mentioned in Section X.5.

[1975DAN]

The specific heat of thorium monocarbide was measured between 2 and 300 K. A sintered sample was prepared from thorium obtained by the van Arkel process and reported to contain less than 200 ppm impurities. According to chemical analyses (no details given), the overall composition of the carbide sample corresponded to $ThC_{0.965}N_{0.015}O_{0.020.}$ The lattice parameter was reported to be $a = (5.3444 \pm 0.0002)$ Å. This sample was measured over the whole temperature range 2 to 300 K.

Another ThC sample reported as "containing a larger quantity of oxygen", without more details, was measured in the temperature range 2 to 10 K; it is not clear whether any measurements were made at higher temperatures with this sample.

Up to 7 K, the specific heat data were fitted to the classical relation $C_{p,\mathrm{m}}/T = \gamma + \alpha T^2$ and a value of $\gamma = (2.12 \pm 0.04)$ mJ·K^{-2}·mol^{-1} was obtained with a derived Debye temperature θ_D of (262 ± 2) K. These results are in disagreement with those reported by [1964HAR/MAT], who give $\gamma = (2.9 \pm 0.2)$ mJ·K^{-2}·mol^{-1} and $\theta_D = 280$ K, which the author attributed to possible differences in the stoichiometry of the samples. (A subsequent study [1979MAU/BOU] gives $\gamma = 3.38$ mJ·K^{-2}·mol^{-1} and $\theta_D = 238$ K for $ThC_{0.75}$(cr)).

Danan makes no mention of correction for the impurities in either sample, but merely attributes his given heat capacity and derived thermal functions to ThC(cr), thus: $C^{\circ}_{p,\mathrm{m}}$ (ThC, cr, 298.15 K) = (45.1 ± 0.5) J·K^{-1}·mol^{-1} and S°_{m} (ThC, cr, 298.15 K) = (58.0 ± 0.8) J·K^{-1}·mol^{-1}. These uncertainties, although consistent with the scatter of the data presented graphically, are smaller than those suggested by the claimed precision of the calorimeter, 2−3% from 100 to 300 K.

These results are discussed further in Section XI.1.1.

[1975OHA/ADE]

This paper reports standard enthalpies of formation at 298.15 K, based on solution reaction or fluorine bomb calorimetry, on a series of alkali metal uranates, molybdates, chromates, Li_3N, Li_2O, $MoC_{0.502}$, $MoC_{0.651}$, U_3Si, β-US_2, and $ThS_{1.029}$.

The only compound of immediate interest for this review is the thorium monosulphide, which was studied by solution calorimetry in 6.000 M HCl.

The sample was the same as that used by Flotow *et al.* [1971FLO/OSB] for heat capacity measurements. More analytical details on the sample were given in this solution calorimetry study. It had a S/Th ratio of (1.043 ± 0.005) and was reported to contain 3.77 mass% Th_2S_3, 1.47 mass% ThOS, 88 ppm C, and 15 ppm N. The S/Th ratio of the monosulphide phase in the sample was calculated to be (1.029 ± 0.019) and the reported calorimetric results are given for $ThS_{1.029}$(cr). We therefore assume that these results refer to a measured value which has been adjusted for the presence of the impurities, although no mention is made in the paper as to the value assumed for $\Delta_f H_m^o$ (ThOS, cr, 298.15 K), which is not known experimentally.

Thus, for Reaction (A.68)

$$\begin{aligned} ThS_{1.029}(cr) + 4H^+ \text{ (in 6.00 M HCl)} \rightarrow \{Th^{4+} + 1.029H_2S\} \text{ (in 6.00 M HCl)} \\ + 0.971\,H_2(g) \qquad \text{(A.68)} \end{aligned}$$

the authors obtained $\Delta_r H_m^o$ ((A.68), 298.15 K) = −(394.05 ± 1.84) $kJ\cdot mol^{-1}$. The thorium concentration in the resulting solution was *ca.* 1.6×10^{-2} M.

Combination of this value with $\Delta_f H_m$ (Th^{4+}, 6.00 M HCl) = – (758.957 ± 1.600) $kJ\cdot mol^{-1}$ (see Section VI.1) –neglecting small dilution effects– and with $\Delta_f H_m$ (H_2S, 6.00 M HCl, 298.15 K) ≈ $\Delta_f H_m^o$ (H_2S, aq, 298.15 K) = – (38.6 ± 1.5) $kJ\cdot mol^{-1}$, from the auxiliary values selected in this review, leads to:

$$\Delta_f H_m (ThS_{1.029}, \text{cr}, 298.15\text{ K}) = -(404.63 \pm 2.88)\ kJ\cdot mol^{-1}.$$

[1975PAL/CIR]

These authors report the enthalpies of formation of RX_3 compounds (R = Y, Th or U; X = Ga, In, Tl, Sn or Pb) as determined by dynamic differential calorimetry (integration of DTA peaks, with a calibration from elements and compounds of known heats of fusion). These studies follow previous studies by the same group on rare earth intermetallic compounds having the same general formula. The calorimetric method used is described in one of these earlier publications [1973PAL].

In the case of thorium the compounds with In, Tl, Sn, and Pb were studied. Purities of 99.95% for the thorium metal and 99.999% for the other elements used are given without further details. Samples (1 to 2 g) were obtained by mixing and pressing the powdered metals into the calorimetric molybdenum reaction chamber. Use of a dry box under ultra pure argon atmosphere was mentioned for the handling of oxidisable substances. Only results from compounds showing a single phase ($AuCu_3$ type), as verified by micrographic and X-ray analyses, were considered. Micrography could not be carried out on $ThPb_3$ and $ThTl_3$, owing to the high reactivity of these compounds. The authors indicate that several samples were prepared to test the reproducibility of the results.

The reaction temperatures were 773 K for $ThIn_3$, 843 K for $ThTl_3$, and 793 K for $ThSn_3$ and $ThPb_3$. At these temperatures, In, Tl, Sn and Pb are liquid. After correcting for the enthalpy of fusion of these elements the authors report $\Delta_f H_m^o$ (ThIn$_3$, cr, 298.15 K) = −(150.6 ± 15.1) kJ·mol^{-1}, $\Delta_f H_m^o$ (ThTl$_3$, cr) = −(103.8 ± 10.4) kJ·mol^{-1}, $\Delta_f H_m^o$ (ThSn$_3$, cr) = −(162.3 ± 16.2) kJ·mol^{-1} and $\Delta_f H_m^o$ (ThPb$_3$, cr) = −(117.2 ± 11.7) kJ·mol^{-1} to be valid at 298.15 K. The values are in fact those at the temperatures stated, and are assumed by the authors to be the same at 298.15 K. We have made the same assumption, but, in the values quoted above, have doubled the authors' uncertainty to ± 10%.

Finally, they correlate their results, together with the various literature data for the enthalpies of formation of MX$_3$ intermetallic compounds, with the atomic radii of the involved elements.

These values of the enthalpies of formation were those selected by [1982WAG/EVA].

[1975PAT/RAM]

The equilibrium constants of chloride and fluoride complexes of Th(IV) and Np(IV) have been determined using liquid-liquid extraction with the liquid ion-exchanger dinonyl naphthalene sulphonic acid as the extractant. The experiments have been made at 25°C in 2.00 M HClO$_4$ ionic medium. The liquid ion-exchanger allows efficient extraction even at high hydrogen ion concentrations. The chloride concentration was varied from 0.1 to 1.0 M, so there are large changes in composition of the ionic medium. The extraction data were described using two equilibrium constants:

$$\mathrm{Th^{4+} + Cl^- \rightleftharpoons ThCl^{3+}}; \qquad \beta_1 = (1.3 \pm 0.1)\ \mathrm{M^{-1}}$$

$$\mathrm{Th^{4+} + 2Cl^- \rightleftharpoons ThCl_2^{2+}}; \qquad \beta_2 = (0.5 \pm 0.1)\ \mathrm{M^{-2}}.$$

These equilibrium constants describe the experimental data, but the variations in the distribution coefficients can also be a result of activity factor variations in the aqueous phase.

The fluoride system was investigated by varying the total concentration of HF between 0.5 and 100 mM. In order to describe the distribution equilibria only one equilibrium constant is required:

$$\mathrm{Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+} \qquad {}^*\beta_1 = (2.7 \pm 0.14) \times 10^4.$$

This value is in good agreement with previous investigations and is accepted by this review.

[1975RAG/RAM]

The complex formation between Th(IV) and Cl$^-$, Br$^-$ and HF has been studied using liquid-liquid extraction using dinonyl naphtalene sulphonic acid (HDNNS), a liquid-cation exchanger soluble in organic solvents but not in water. The experiments have been made at 25°C and an ionic strength/ionic medium given in Table A-43. The experimental data consist of the distribution coefficient of ^{234}Th at trace concentrations as a function of the ligand concentration in test solutions where the hydrogen ion concentration was constant at values given in Table A-43. The fluoride complexes of Th(IV) are strong and therefore it was not necessary to make large changes in the composition of the ionic medium. The total concentration of HF varied from 0.05 to 1.00 mM. The situation is very different in the studies of chloride and bromide complexation; the chloride concentration varied from 0.1 to 1.0 M and the bromide concentration from 0.1 to 1.2 M. Accordingly there are large changes in the ionic medium and it is difficult or impossible to decide if the observed variation in the distribution coefficient of Th(IV) is a result of complex formation or the variation of the activity coefficients of Th^{4+} and H^+ in the distribution equilibrium (A.69). The authors have interpreted the data as being due to the distribution equilibrium:

$$Th^{4+}(aq) + 4\,HDNNS(org) \rightleftharpoons Th(DNNS)_4(org) + 4H^+(aq) \qquad (A.69)$$

where (aq) and (org) denote the aqueous and organic phases, respectively. The concentration of Th^{4+}(aq) depends on the formation of complexes with Cl^- and Br^-.

The equilibrium constants are given in Table A-43; they are obtained using a graphical (Cl^-) or a least-squares method (Br^-).

Table A-43: Equilibrium constants of Th(IV) complexes with Cl^- and Br^-.

Reaction	Experimental conditions	β
$Th^{4+} + Cl^- \rightleftharpoons ThCl^{3+}$	25°C, 2.00 M H^+, I = 2.00 M	$(1.3 \pm 0.1)\ M^{-1}$
$Th^{4+} + 2Cl^- \rightleftharpoons ThCl_2^{2+}$		$(0.25 \pm 0.1)\ M^{-2}$
$Th^{4+} + Br^- \rightleftharpoons ThBr^{3+}$	25°C, 0.6 M H^+, I = 1.00 M	$(0.81 \pm 0.05)\ M^{-1}$
$Th^{4+} + 2Br^- \rightleftharpoons ThBr_2^{2+}$	–”–	$(0.20 \pm 0.04)\ M^{-2}$

The question is now if one should describe the observed variation in the distribution equilibrium (A.69) as a result of complex formation or activity coefficient variations. This review has calculated the change in activity coefficients for Th^{4+} and H^+ in two test solutions, 2.00 M $HClO_4$ and 1.50 M $HClO_4$ + 0.50 M HCl using the SIT and interaction coefficients selected by this review, $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)$; $\varepsilon(Th^{4+}, Cl^-) = (0.25 \pm 0.03)$; $\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)$; $\varepsilon(H^+, Cl^-) = (0.12 \pm 0.01)$ $kg\cdot mol^{-1}$, with:

$$D = \frac{[Th(DNNS)_4][H^+]^4}{[Th^{4+}][HDNNS]^4} \qquad (A.70)$$

We can safely assume that the activity coefficients of the species in the organic phase are constant as they are uncharged and have concentrations that are not changing significantly. Hence only the activity coefficients of the aqueous species are expected to vary with the change in composition of the aqueous phase. The activity coefficients:

$$\log_{10}\gamma\,(\mathrm{Th}^{4+}) = -\,16D + \varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4^-)\, m_{\mathrm{ClO}_4^-} + \varepsilon(\mathrm{Th}^{4+}, \mathrm{Cl}^-)\, m_{\mathrm{Cl}^-}$$

$$\log_{10}\gamma\,(\mathrm{H}^{+}) = -D + \varepsilon(\mathrm{H}^{+}, \mathrm{ClO}_4^-)\, m_{\mathrm{ClO}_4^-} + \varepsilon(\mathrm{H}^{+}, \mathrm{Cl}^-)\, m_{\mathrm{Cl}^-}$$

in the two test solutions are then:

$\log_{10}\gamma(\mathrm{Th}^{4+}, 2.13\text{ m HClO}_4) = -\,3.727 + 1.491 = -2.236$

$\log_{10}\gamma(\mathrm{H}^{+}, 2.13\text{ m HClO}_4) = -\,0.233 + 0.298 = 0.065$

$\log_{10}\gamma(\mathrm{Th}^{4+}, 1.60\text{ m HClO}_4, 0.53\text{ m HCl}) = -\,3.727 + 1.120 + 0.133 = -2.474$

$\log_{10}\gamma(\mathrm{H}^{+}, 1.60\text{ m HClO}_4, 0.53\text{ m HCl}) = -\,0.233 + 0.224 + 0.064 = 0.055.$

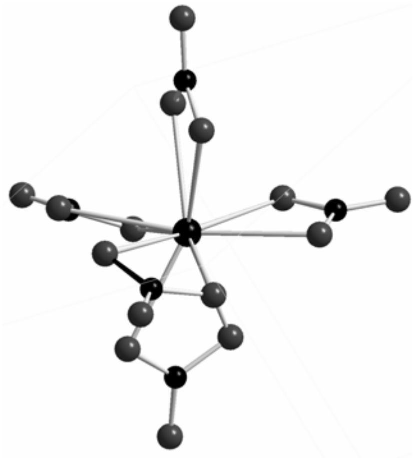
We find that, as a result of changes in activity coefficients, the value of $\log_{10} D$ should decrease by 0.198, corresponding to a decrease in D by a factor of 1.58. The experimental decrease for the chloride system from Table 1 in [1975RAG/RAM] by a factor of 1.76 is in reasonable agreement with the changes due to activity coefficient variations. However, we cannot exclude the formation of chloride (and bromide) complexes, but they are certainly smaller than the values obtained without taking ionic medium variations into account.

[1975VOL/RIM3]

This paper is discussed together with [1975VOL/RIM2].

Both these studies [1975VOL/RIM2], [1975VOL/RIM3] are single-crystal X-ray structure determinations of ternary carbonates. The structures contain isolated complexes of the complex $\mathrm{Th(CO_3)_5^{6-}}$ providing structural support of the formation of this species. The structure of the complex shown in Figure A-25 indicates that there is no space for the addition of a sixth carbonate.

Figure A-25: Structure of $\mathrm{Th(CO_3)_5^{6-}}$



The carbonate ligands form a trigonal bipyramid arrangement around Th, a geometry that is different from the more common bicapped square antiprism. The compound $Na_6[Th(CO_3)_5]\cdot 12H_2O$ has previously been described as a double-salt with the composition $Na_4[Th(CO_3)_5]\cdot Na_2CO_3\cdot 12H_2O$, [1962KAR/VOL], a proposal based on the IR spectrum of the compound. The structure is unequivocally determined by the X-ray data and the proposal by [1962KAR/VOL] demonstrates the very common fallacies of using qualitative IR data as a tool for structure assignment.

[1976BAE/MES]

Baes and Mesmer's [1976BAE/MES] comprehensive survey and critical review of the hydrolysis of cations is the most frequently cited standard book on metal ion hydrolysis and widely accepted to represent the state of the art for long time after its publication. The authors have in most cases made their own analysis of previously published data and tested a number of different equilibrium models. The choice of models is based on the standard deviation of the experimental average number of coordinated hydroxide ions $\bar{n}_{\mathrm{OH}}$. However, one should complement this method by a calculation of the speciation in the various test solutions as done in the present review. Species that occur in low concentrations should be looked upon with suspicion as gradual changes in diffusion potentials and changes in the ionic medium may be erroneously interpreted as minor complexes. The discussion of the hydrolytic behaviour of thorium(IV) is based on the following potentiometric titration studies which are also included in the data evaluation of the present review:

- [1965BAE/MEY] (including the reinterpretation of [1954KRA/HOL] data in 1 M $NaClO_4$)
- [1968HIE/SIL] (data in 3 M NaCl)
- [1968DAN/MAG] (data in 4 M $NaNO_3$ and 4 M $NaClO_4$)
- [1971MIL2] (data in 3 M $LiNO_3$, 3 M KNO_3 and 1.5 M $Mg(NO_3)_2$)
- [1971KIC/STE] (data in dilute HNO_3, HCl and $NaClO_4$, $I = 0.01 - 0.04$ M)

The selection of data is further based on solubility studies with ThO_2(cr) at 95°C [1965BAE/MEY] and with ThO_2(am, hyd) at 17°C [1964NAB/KUD]. The qualitative results reported in [1966HEN/JOH], [1968JOH], [1968JOH2] are also discussed.

- *Ionic strength corrections and selected values at zero ionic strength*

Baes and Mesmer used the Guggenheim equation for ionic strength corrections:

$$\log_{10} {}^*\beta_{n,m} = \log_{10} {}^*\beta^{\circ}_{n,m} + \mathrm{a}\cdot\sqrt{I} / (1 + \sqrt{I}) + \mathrm{b}I,$$

with $\mathrm{a} = \Delta z^2 A$ ($A = 0.509\ \mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$ at 298.15 K).

The Debye-Hückel term $A\cdot\sqrt{I} / (1 + \sqrt{I})$, differs from the corresponding term in the SIT, $A\cdot\sqrt{I} / (1 + 1.5\sqrt{I})$ which leads to different values at $I = 0$ (*cf.* Table A-44).

The specific interaction parameter b is also different from the corresponding Δε value because of the different Debye-Hückel terms. Up to the review of Baes and Mesmer [1976BAE/MES], there were no data available to model the ionic strength dependence of the equilibrium constants for polynuclear species in one of the ionic media. The common method to estimate equilibrium constants at zero ionic strength was to use an experimental value at finite ionic strength and then to use only the Debye-Hückel term to estimate the value at zero ionic strength.

The selected enthalpy and entropy values for hydrolysis reactions, based on potentiometric data at 0, 25 and 95°C in 1 m $NaClO_4$, were adopted from [1965BAE/MEY].

Table A-44: Equilibrium constants $\log_{10} {}^*\beta^{\circ}_{n,m}$ ($Th_m(OH)_n^{4m-n}$) at I = 0 and 25°C selected by Baes and Mesmer [1976BAE/MES] and the present review.

	[1976BAE/MES]		present review
$Th(OH)^{3+}$	– 3.20 [a]		– 2.5 ± 0.5
$Th(OH)_2^{2+}$	– 6.93 [a]		– 6.2 ± 0.5
$Th(OH)_3^{+}$	≤ –11.7 [b]		No selection
$Th(OH)_4(aq)$	– 15.9 [b]		– 17.4 ± 0.7
$Th_2(OH)_2^{6+}$	– 6.14 [c]	(–5.7) [d]	– 5.9 ± 0.5
$Th_4(OH)_8^{8+}$	– 21.1 [c]	(–20.5) [d]	– 20.4 ± 0.4
$Th_6(OH)_{15}^{9+}$	–36.76 [c]	(–36.8) [d]	– 36.8 ± 1.5

a: Calculated from the equilibrium constant of [1971KIC/STE] in dilute solutions.

b: Calculated from solubility data of [1964NAB/KUD], see text.

c: Calculated from the equilibrium constant of [1965BAE/MEY] in 1 m $NaClO_4$ with b = 0.

d: Equilibrium constant of [1965BAE/MEY] in 1 m $NaClO_4$ extrapolated to I = 0 with the SIT.

- *Polynuclear hydroxide complexes*

The models proposed in the literature to describe the potentiometric data in perchlorate (1 M $NaClO_4$ [1954KRA/HOL], [1965BAE/MEY]), chloride (3 M NaCl [1968HIE/SIL]) and nitrate media (3 M $LiNO_3$, 3 M KNO_3 and 1.5 M $Mg(NO_3)_2$ [1971MIL2]) were discussed and test calculations with different sets of species were performed. The conclusions for perchlorate media are consistent with similar calculations performed in [1968HIE/SIL] and accepted in the present review. Baes and Mesmer [1976BAE/MES] selected the model including the polynuclear complexes (2,2) = $Th_2(OH)_2^{6+}$, (8,4) = $Th_4(OH)_8^{8+}$ and (15,6) = $Th_6(OH)_{15}^{9+}$. An attempt to fit the potentiometric data in 3 M NaCl [1968HIE/SIL] with the same model demonstrated that the standard deviation $\sigma(\bar{n}_{OH})$ increased to 0.033 compared to 0.014 if the species (2,2), (3,2) and (16,4) are used as proposed in [1968HIE/SIL].

On the other hand, calculations for nitrate media showed that the model selected for perchlorate media could also be applied to potentiometric data in 3 M $LiNO_3$, 3 M KNO_3 and 1.5 M $Mg(NO_3)_2$ [1971MIL2]. The resulting standard deviations $\sigma(\overline{n}_{OH})$ were found to be very small (0.0051, 0.0084 and 0.0029, respectively). Therefore Baes and Mesmer selected the model including the species (2,2), (8,4) and (15,6) as well for nitrate media. The equilibrium constants are shown in Table A-45. It is to be noted that the calculated equilibrium constants for the complexes (2,2) and (15,6), which are the same as in the models originally proposed by Milić [1971MIL2], differ only slightly from the $\log_{10}{}^*\beta_{2,2}$ and $\log_{10}{}^*\beta_{15,6}$ values calculated in [1971MIL2] in combination with the species (5,3) and (3,3) in 3 M $LiNO_3$, (3,2) in 3 M KNO_3 and (5,3) in 1.5 M $Mg(NO_3)_2$. The present review therefore also considers the proposed equilibrium constants $\log_{10}{}^*\beta_{8,4}$ as reasonable estimates.

Table A-45: Equilibrium constants $\log_{10}{}^*\beta_{n,m}(Th_m(OH)_n^{4m-n})$ in nitrate media calculated by Baes and Mesmer [1976BAE/MES] from the potentiometric data of Milić [1971MIL2] at 25°C.

	3 M KNO_3	3 M $LiNO_3$	1.5 M $Mg(NO_3)_2$
$Th_2(OH)_2^{6+}$	– 5.00	– 5.12	– 5.14
	– 5.10 [a]	– 5.14 [a]	– 5.17 [a]
$Th_4(OH)_8^{8+}$	– 21.71	– 22.59	– 22.58
$Th_6(OH)_{15}^{9+}$	– 40.92	–	– 43.45
	– 40.95 [a]	–	– 43.20 [a]

a: Equilibrium constants reported in [1971MIL2].

- *Mononuclear hydroxide complexes*

Baes and Mesmer [1976BAE/MES] selected the equilibrium constants and the specific interaction parameters b for the first two mononuclear Th(IV) hydroxide complexes, $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$, $\log_{10}{}^*\beta^{o}_{1,1} = -(3.20 \pm 0.2)$ and $\log_{10}{}^*\beta^{o}_{2,1} = -(6.93 \pm 0.2)$, from potentiometric data in dilute solutions [1971KIC/STE] and 1 m $NaClO_4$ [1954KRA/HOL], [1965BAE/MEY]. Combining these values with the solubility data of Nabivanets and Kudritskaya [1964NAB/KUD] in 0.1 M $NaClO_4$, they calculated an upper limit of $\log_{10}{}^*\beta^{o}_{3,1}$ ($Th(OH)_3^{+}$) ≤ -11.7 and $\log_{10}{}^*\beta^{o}_{4,1}$ ($Th(OH)_4$, aq) = – (15.9 ± 0.3). The two latter values are not reliable. As shown later by potentiometry [1983BRO/ELL] and ultracentrifugation [2004ALT/NEC], polynuclear and colloidal Th(IV) hydroxide species are predominant at pH and Th concentrations of the saturated solutions in [1964NAB/KUD] (*cf.*, Appendix A review of [1964NAB/KUD]). Accordingly, the solubility constant derived from the experimental data in [1964NAB/KUD], $\log_{10}{}^*K^{o}_{s,0}$ (ThO_2, am, hyd) ≈ 9.4, is somewhat higher than the value calculated in the present review.

- *$ThO_2(cr)$*

For crystalline ThO_2(cr), Baes and Mesmer [1976BAE/MES] propose a value of $\log_{10} {}^*K^\circ_{s,0}$ (ThO_2, cr, 25°C) ≈ 6.6 ($\log_{10} K^\circ_{s,0}$ (ThO_2, cr, 25°C) ≈ −49.4) which is calculated from thermochemical data with reference to NBS, private communication. They also claim that this value is consistent with the experimental value determined by [1965BAE/MEY] at 95°C ($\log_{10} {}^*K_{s,0}$ (ThO_2, cr, 1 m $NaClO_4$, 95°C) = 4.26) which, extrapolated to $I = 0$ ($\log_{10} {}^*K_{s,0}$ (ThO_2, cr, 95°C) = (2.5 ± 0.3)) and to 25°C by estimating entropy changes, leads to $\log_{10} {}^*K^\circ_{s,0}$ (ThO_2, cr, 25°C) = (6.3 ± 0.5).

The equilibrium constant selected in [1976BAE/MES] differs considerably from the values based on the data selected in this review: $\log_{10} {}^*K^\circ_{s,0}$ (ThO_2, cr, 298.15 K) = (1.77 ± 1.11) or $\log_{10} K^\circ_{s,0}$ (ThO_2, cr, 298.15 K) = −(54.24 ± 1.11).

[1976CHE/WES]

The heat capacity $Th(NO)_3 \cdot 5H_2O$(cr) has been measured in an adiabatic calorimeter between 5 and 350 K. The compound was analysed for thorium by gravimetry and for water by the Karl Fischer method, with results agreeing with theoretical values within narrow uncertainty limits. The values reported for 298.15 K are $C^\circ_{p,\mathrm{m}} = (480.74 \pm 0.42)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, $S^\circ_\mathrm{m} = (543.08 \pm 0.42)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ and $-(G^\circ_\mathrm{m}(298.15\,\mathrm{K}) - H^\circ(0)) = (267.23 \pm 0.25)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

No anomalies in the heat capacity curve were detected.

The entropy value obtained in this study is used in the determination of S°_m (Th^{4+}, 298.15 K).

[1976CHO/UNR]

This paper describes a study of the aqueous actinide fluoride complexes. Only the Th(IV) data will be discussed. The experiments have been made at 25°C in a 1.00 M $HClO_4$ ionic medium. For the Th(IV)-fluoride system two experimental methods were used at different temperatures: (1) potentiometry using a fluoride sensitive electrode (at 3, 25 and 47°C) and (2) liquid-liquid extraction with dinonyl naphthalene sulphonic acid (at 10, 25 and 55°C). The experimental methods are briefly described, with no information on primary experimental data. However, the work was done in a specialist laboratory and this review therefore accepts the equilibrium constants proposed as listed in Table A-47. The authors have used the temperature variation of the equilibrium constants to deduce the enthalpy and entropy of reaction, but these quantities are very uncertain due to the experimental errors. These quantities for the reaction between Th^{4+} and F^- calculated using the dissociation constant of HF are given in Table A-46.

Table A-46: Thermodynamic parameters for the reaction $Th^{4+} + F^- \rightleftharpoons ThF^{3+}$ at 25°C and 1.00 M $HClO_4$.

$-\Delta_r G_m^o$ (kcal·mol^{-1})	$\Delta_r H_m^o$ (kcal·mol^{-1})	$\Delta_r S_m^o$ (cal·K^{-1}·mol^{-1})	Method
10.12 ± 0.05	0.26 ± 0.32	34.8 ± 1.2	extraction
10.16 ± 0.06	0.56 ± 0.44	36.05 ± 1.5	potentiometry

The estimated uncertainty is too small according to this review.

However it is quite clear that the equilibrium constants vary little with the temperature as often found for reactions between hard acids and hard bases. The authors propose an electrostatic model to correlate the experimental data for the elements studied. This review accepts the equilibrium constants proposed in [1976CHO/UNR], but not the values proposed for the enthalpy and entropy of reaction.

Table A-47: $\log_{10}{}^*\beta_1$ for the reaction $Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+$ studied using liquid-liquid extraction, and emf methods.

	$\log_{10}{}^*\beta_1$ (liquid-liquid extraction)		
Ionic medium	t (°C)		
1.00 M $HClO_4$	10	25	55
	4.65 ± 0.02	4.49 ± 0.03	4.33 ± 0.02
	$\log_{10}{}^*\beta_1$ (emf)		
Ionic medium	t (°C)		
1.00 M $HClO_4$	3	25	47
	4.73 ± 0.02	4.51 ± 0.02	4.45 ± 0.05

[1976MOR/MCC]

The enthalpy of solution of high purity $Th(NO_3)_4{\cdot}5H_2O(cr)$ was measured in 0.01 M $HClO_4$ at 293.15, 298.15, and 308.15 K. At infinite dilution, and after correction for hydrolysis, the value $\Delta_{sln}H_m^o$ ($Th(NO_3)_4{\cdot}5H_2O$, cr, 298.15 K) = – 19.807 kJ·mol^{-1}, was reported. From this result, S_m^o (Th^{4+}, 298.15 K) was calculated, based on S_m^o ($Th(NO_3)_4{\cdot}5H_2O$, cr, 298.15 K) = (543.1 ± 0.8) J·K^{-1}·mol^{-1} from [1976CHE/WES], $\Delta_f H_m^o$ (Th^{4+}), a solubility of 3.7 mol·kg^{-1}, and activity coefficients calculated by Wagman (personal communication to the authors of the paper) based on the vapour pressure measurements of [1947ROB/LEV].

The solubility of $Th(NO_3)_4{\cdot}5H_2O(cr)$ at 298.15 K adopted by the authors was an average of earlier measurements by [1973APE/AZO] 3.74 mol·kg^{-1} and their own determination which yielded (3.66 ± 0.02) mol·kg^{-1}.

Based on the temperature dependence measurements, a value of $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}$, 298.15 K) was also reported.

These results are the basis for the selected data on $S^{\circ}_{\mathrm{m}}(\mathrm{Th}^{4+}$, 298.15 K) and $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{Th(NO_3)_4{\cdot}5H_2O}$, cr, 298.15 K). The values for activity coefficient and solubility of $\mathrm{Th(NO_3)_4{\cdot}5H_2O(cr)}$ taken by the authors are adopted in the present review.

For $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}$, 298.15 K), as discussed in [2003GUI/FAN], the more recent results of [1997HOV] are preferred, as they are obtained using differential measurements, instead of integral enthalpies of solution, under conditions minimising complexation and hydrolysis.

[1976PIA/ZAU]

This is an excellent study of the range of homogeneity of "$\mathrm{ThC_2}$(cr)", prepared from $\mathrm{ThO_2}$(cr) and C(cr) at high temperatures. Compressed samples of various initial mixtures of the two solids were heated in a high-temperature diffractometer operating between 1273 and 1473 K, in a vacuum or a low pressure of CO(g) and the lattice parameters of $\mathrm{ThO_2}$(cr) and the dicarbide monitored. In addition, the equilibrium pressure of CO(g) in the three-phase field $\mathrm{ThO_2}$(cr), C(cr) and "$\mathrm{ThC_2}$(cr)" was measured from 1738 to 2283 K, although the uncertainty in the temperature of the samples was estimated to be ± 30 K. The results are included in the discussion of $\Delta_{\mathrm{f}}G^{\circ}_{\mathrm{m}}(\mathrm{ThC_2}$, cr) in Section XI.1.1.3.

[1976POY/LEB]

The emf of the cell

$$\mathrm{Th(cr)}\,|\,\mathrm{KCl\text{-}NaCl + ThCl_{4-x}}\,\vdots\,\mathrm{KCl\text{-}NaCl + ThCl_4}\,|\,\mathrm{Pb\text{-}Th(l)} + \text{compound}$$

with molybdenum conductors, was used to determine the thorium activity in Th-saturated liquid lead from 949 to 1043 K. The Th-Pb alloys were prepared by melting Th (99.6% pure) with lead (99.9% pure) in BeO crucibles. The emf was given by $E(T) = 393.5 - 0.139\ T$ (mV), with a reproducibility of 2 mV. The actual compound present in the saturated solution was not identified, but was assumed to be $\mathrm{ThPb_4}$(cr), as indicated by Gans *et al.* [1966GAN/KNA] for this temperature range.

These data have thus been assumed to refer to the partial Gibbs energy of Th in the {Pb(l) + $\mathrm{ThPb_4}$ (cr)} phase field: $\Delta_{\mathrm{sol}}G_{\mathrm{m}} = -151870 + 56.646\,T$ ($\mathrm{J{\cdot}mol^{-1}}$). With the low solubility of thorium in Pb(l), (see below), the activity of lead in the melt will be very close to one and $\Delta_{\mathrm{f}}G_{\mathrm{m}}(\mathrm{ThPb_4}$, cr) (from Pb(l)) in the temperature range of the study by [1976POY/LEB] is given by the same expression:

$$[\Delta_{\mathrm{f}}G_{\mathrm{m}}]^{1050\mathrm{K}}_{950\mathrm{K}}(\mathrm{ThPb_4}, \mathrm{cr}, T) = -151870 + 56.646\,T \quad (\mathrm{J{\cdot}mol^{-1}})$$

The solubility of thorium in lead was also determined in this study:

$$\log x_{\mathrm{Th}} = -4310/T + 1.667.$$

Thus x_{Th} (1000 K) = 0.227 at%. This value is quoted (presumably in error) in the paper to be the solubility at 1000°C, rather than 1000 K.

[1976SCH/VER]

The authors carried a series of compatibility experiments to obtain limiting values for the Gibbs energies of thorite ($ThSiO_4$), zircon ($ZrSiO_4$) and phenacite (Be_2SiO_4). All experiments were carried out at 1000 K and 1 kbar pressure. For $ThSiO_4$, approximately 100 mg of mixtures of the compounds of both the left-hand and right-hand sides of the two reactions below were heated (in separate experiments). The samples (together with *ca.* 10 mg of water) were contained in welded gold capsules and heated to *ca.* 1000 K and 1 kbar pressure for 2 to 12 weeks. After the runs, the samples were quenched and the products analysed by XRD. Although none of the reactions had gone to completion, in all cases the direction of reaction could be established unambiguously.

The results indicated that the two reactions:

$$\mathrm{CaTiO_3(perovskite) + ThSiO_4(thorite) \rightleftharpoons ThO_2(cr) + CaTiSiO_5(sphene)}$$

$$\mathrm{ThO_2(cr) + 0.5\,NaAlSi_3O_8(albite) \rightleftharpoons 0.5\,NaAlSiO_4(nepheline) + ThSiO_4(thorite)}$$

both have $\Delta_r G_m < 0$ at 1000 K and 1 kbar, and hence for the following reactions:

$$\mathrm{ThO_2(cr) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons ThSiO_4(thorite)} \quad (A.71)$$

$$\mathrm{CaTiO_3(perovskite) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons CaTiSiO_5(sphene)} \quad (A.72)$$

$$\mathrm{0.5\,NaAlSiO_4(nepheline) + SiO_2(\alpha\text{-quartz}) \rightleftharpoons 0.5\,NaAlSi_3O_8(albite)} \quad (A.73)$$

$\Delta_r G_m$ (A.72) < $\Delta_r G_m$ (A.71) < $\Delta_r G_m$ (A.73) at 1000 K and 1 kbar.

The authors used data from Robie and Waldbaum [1968ROB/WAL] for Reactions (A.72) and (A.73), adjusted to 1000 K and 1 kbar. This review has repeated these calculations using the most recent data from the same laboratory, Robie and Hemingway [1995ROB/HEM] to give the values in Table A-48.

Table A-48: Limiting Gibbs energies of reaction.

Reaction	$\Delta_r G_m$ (1000 K, 1 bar) (kJ·mol^{-1})	$\Delta_r G_m$ (1000 K, 1 kbar) (kJ·mol^{-1})
(A.72)	-15.90 ± 3.70	-15.96 ± 3.70
(A.73)	-9.70 ± 2.60	-9.67 ± 2.60

This study would thus suggest that the $\Delta_r G_m$ ((A.71), 1000 K, 1 bar) is $-(12.8 \pm 7.0)$ kJ·mol^{-1}.

The authors reduce their data to 298.15 K assuming $\Delta_r C_{p,m}$ (A.71) to be zero, and further calculated $\Delta_r H_m$ ((A.71), 298.15 K) by estimating $\Delta_r S_m$ ((A.71), 298.15 K) to be the same as that for the corresponding reaction involving zirconium. Schuiling *et al.* [1976SCH/VER] do not quote the values used, but those from NEA data [2005BRO/CUR] would give $\Delta_r S_m$ (298.15 K) = −7.5 J·K^{-1}·mol^{-1}; $\Delta_r H_m$ (298.15 K) = − 22.9 kJ·mol^{-1} However, comparison with the enthalpy of Reaction (A.71) by [2005MAZ/USH] discussed in Section XI.2.2, suggests that the enthalpy and entropy of the two reactions are probably appreciably different, and this review has not attempted to estimate $\Delta_r H_m$((A.71), 298.15 K) from the data of [1976SCH/VER].

[1976SOU/SHA]

This is a study at 25°C of the adsorption of various actinides, including thorium, on to zirconium phosphate from HNO_3 solutions (0.1 to 6 M) and NH_4NO_3 solutions (0.1 to 6 M). The authors have not used a constant ionic medium and they have not taken the sorption of charged complexes into account when calculating the equilibrium constants. For this reason the equilibrium constant reported by them and given in Table A-49 are not considered reliable by this review.

The experimental data given in Table A-49 for nitrate and chloride indicate that the function Φ_1 (for notation see [1976SOU/SHA]) in both cases increases strongly with increasing ligand concentration. With the method used by the authors the slope of Φ_1 *vs*. [ligand] is equal to β_2 and the corresponding values for the nitrate and chloride systems calculated by this review are approximately 14 M^{-2} and 65 M^{-2}. These constants are much larger than those found by other authors using phase equilibrium methods in electrolyte media of constant ionic strength. This is another indication that the equilibrium constants in [1976SOU/SHA] are not reliable.

Table A-49: Equilibrium constants for Th(IV) nitrate and chloride complexes at 25°C.

Reaction	β_1
$Th^{4+} + NO_3^- \rightleftharpoons Th(NO_3)^{3+}$	2.5 M^{-1}
$Th^{4+} + Cl^- \rightleftharpoons ThCl^{3+}$	2.8 M^{-1}

[1977CAT/SAT]

Samples of Th_4H_{15}(cr) and Th_4D_{15}(cr) of good crystallinity were prepared at pressures of H_2(g) or D_2(g) from 600 to 800 bar and temperatures from 1073 to 1173 K, and the composition, structure and superconducting properties of the material produced were examined. Values for the pressures at which Th_4H_{15}(cr) was formed are given as a function of temperature, but, as the authors state, because of hysteresis, these are undoubtedly not the true equilibrium pressures. Moreover, at the high temperatures involved, both the di- and higher hydride show substantial non-stoichiometry. These measurements are therefore of limited use for a reliable determination of the enthalpy of formation of Th_4H_{15}(cr).

[1977KAD/LEB]

The emf of the cell

$$\text{Th(cr)}\,|\,\text{KCl-NaCl-3 wt\% ThCl}_{4-x}\,\vdots\,\text{KCl-NaCl-3 wt\% ThCl}_4\,|\,\text{Sn-Th(l)} + \text{compound}$$

was used to determine the thorium activity in Th-saturated liquid tin from 952 to 1130 K. The emf was given by $E(T) = (535.1 - 0.1339\,T)$ mV, with a reproducibility of 2 mV. The actual compound present in the saturated solution was not identified by the authors. The thorium activity in the saturated solution is thus $\Delta_{\text{sol}}G_{\text{m}} = -206517 + 51.677\,T$ J·mol^{-1} in this temperature range.

With the low solubility of thorium in Sn(l), (see below), the chemical potential of tin in the melt will be close to the ideal value and if ThSn_3(cr) is the phase in equilibrium with the saturated liquid, its Gibbs energy of formation (from Sn(l)) in the temperature range of the study by [1977KAD/LEB] is then calculated to be

$$[\Delta_{\text{f}}G^{\text{o}}_{\text{m}}]^{1130\,\text{K}}_{952\,\text{K}}\ (\text{ThSn}_3,\ \text{cr},\ T) = -203377 + 48.762\,T \quad \text{J·mol}^{-1}$$

Kadochnikov *et al.* estimated the uncertainties in the thorium potential to be only ±400 J·mol^{-1}, but the uncertainty in the enthalpy values is much higher, ±6300 J·mol^{-1}, as quoted by the authors.

The solubility of thorium in liquid tin from 950 to 1130 K was also determined in this study to be:

$$\log x(\text{Th}) = -4330/T + 2.2360.$$

[1977MIL2]

This review concerns the two papers [1973MIL] and [1977MIL2]. The first paper [1973MIL] is an attempt to correlate the ionic strength/ionic medium dependence of the equilibrium constants for hydrolysis reactions with physico-chemical parameters; hydrolysis constants for Th^{4+}, UO_2^{2+}, Ni^{2+} and Pb^{2+} are used as examples. In [1977MIL2] the correlations were extended to enthalpy and entropy values for hydrolysis reactions of thorium derived from calorimetric measurements. Experimental data and numerical results are not given in this short report but in the following [1981MIL2].

The ionic medium dependence of the equilibrium constants for a metal ion, M, is calculated from the equation $Z_{\text{M}}(m) = Z_{\text{M}}(w)\text{e}^{-F(m)}$, where $Z_{\text{M}}(m)$ and $Z_{\text{M}}(w)$ denote the average number of coordinated hydroxide groups per metal-ion in the ionic medium (m) and pure water (w), respectively, $F(m) = \text{c(c)}E_{\text{h}}(\text{c})E_{\text{h}}(\text{a})z(\text{a})/z(\text{c})$, where z(a) and z(c) are the charges and c(a) and c(c) the concentrations of the anion and cation in the ionic medium and E_{h}, finally, is the solvation energy. There is no theoretical foundation for these equations; the main factor describing the medium dependence of equilibrium constants are the electrostatic interactions between the reactants and products and the medium ions, which is not considered at all in the model proposed here. It is very difficult to see why the hydration energy should be a major factor for the medium dependence as this depends mainly on interactions between the metal ions and the solvent in the first coordination sphere. The fact that Milić observes a linear correlation is no proof of the validity of the approach. Correlations should only be made when there is a theoretical basis for a functional relationship between two (or more) quantities and as indicated above this is not the case here. The application of this linear correlation to the extrapolation of conditional equilibrium constants of the thorium hydroxide complexes $\mathrm{Th_2(OH)_2^{6+}}$ and $\mathrm{Th_2(OH)_3^{5+}}$ in 0.5−3 M chloride media to zero ionic strength leads to $\log_{10}{}^{*}\beta^{\circ}_{m,n}$ values which differ by about one $\log_{10}$ unit from those obtained in this review using the SIT (*cf.* discussion of [1981MIL2]).

To conclude, this paper does not provide a useful method to estimate the ionic medium / ionic strength dependence of equilibrium constants and all equilibrium constants at zero ionic strength deduced by the approach in [1973MIL] are rejected by the present review.

[1978FLO/OSB]

The heat capacities of $\mathrm{ThH_{1.996}}$(cr) and $\mathrm{ThH_{3.746}}$(cr) were measured from 5.6 to 347 K. The samples were prepared from high purity Th(cr) whose main impurities were 85 ppm O and 23 ppm C. The heat capacities were represented by a sum of terms each of which could be extrapolated to higher temperatures (up to 1000 K). Values of $C_{p,\mathrm{m}}$ and the derived thermal functions are tabulated at round values from 5 to 350 K. The values of $C^{\circ}_{p,\mathrm{m}}$ and S°_{m} at 298.15 K are: $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{ThH_2}$, cr, 298.15 K) = (36.71 ± 0.07) and S°_{m} ($\mathrm{ThH_2}$, cr, 298.15 K) = (50.73 ± 0.10) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$; $C^{\circ}_{p,\mathrm{m}}$ ($\mathrm{ThH_{3.75}}$, cr, 298.15 K) = (51.32 ± 0.10) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and S°_{m} ($\mathrm{ThH_{3.75}}$, cr, 298.15 K) = (54.42 ± 0.11) $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

These results were combined with thermochemical data derived from hydrogen dissociation pressure measurements to calculate the standard enthalpies and entropies of formation of $\mathrm{ThH_2}$(cr) and $\mathrm{ThH_{3.75}}$(cr) at temperatures from 298.15 to 1000 K.

[1978GIN]

This short paper mainly concerns the stability of $\mathrm{ThC_3}$(g), which is present in very small amounts in the vaporisation of carbon-saturated $\mathrm{ThC_2}$(cr), studied by mass-spectroscopic Knudsen effusion from 2542 to 2710 K. The study also measured the intensities from the $\mathrm{ThC_2}$(g) molecule, but there is insufficient detail given for them to be included in the analysis in Section XI.1.2.

[1978KNA/MUN]

The authors studied the thermal dissociation of thorium iodide mass-spectrometrically, and suggested that substantial decomposition to lower iodides and iodine vapour occurs when both the solid and liquid are heated. Coarse crystals of $\mathrm{ThI_4}$(cr), prepared from the elements, were used to minimise the oxygen and water contents of the samples used in the (unspecified) Knudsen cell. The variation of the intensities of the $\mathrm{ThI_4}$, $\mathrm{ThI_3}$, $\mathrm{ThI_2}$, $\mathrm{I_2}$ and I ions observed in the mass-spectrometer was studied from *ca.* 625 to 800 K.

Details of the method by which the intensities were converted to pressure are far from clear. It is indicated that p_{ThI_4} was obtained by calibration against the pressures (from an unspecified source) of pure liquid ThI_4, despite the fact that the authors themselves suggest that both solid and liquid ThI_4 decompose strongly on heating (although in fact this is probably not so, see below). The iodine pressures were established from a gravimetric determination of p_{I_2} over the two monovariant equilibria involving ThI_4(cr) + ThI_3(cr) and Th(cr) + ThI(cr). However, absolutely no details are given of these calibration data. The pressures of I_2(g) over ThI_4(cr) and ThI_4(l) given in the paper are much higher than those of ThI_4(g), especially at low temperatures.

The authors interpret the various plateaux obtained as corresponding to equilibria involving successively ThI_3(cr) + ThI_2(cr), ThI_2(cr) + ThI(cr), and ThI(cr) + Th(cr). The authors suggest from the small temperature range of stability of ThI_2(cr) that this phase disappears at higher temperature, and relate this to some small peaks observed by Scaife and Wylie [1964SCA/WYL] at 803 K, which they attribute to the reaction $2\text{ThI}_2(\text{cr}) \rightleftharpoons \text{ThI}_3(\text{cr}) + \text{ThI}(\text{cr})$, but there is no further confirmation of this. In particular, there was no unambiguous characterisation of ThI(cr), and the fact that [1964SCA/WYL] not only found, but prepared, ThI_2(cr, β) well above 803 K seem to have been ignored. The authors also used their pressure data to calculate the enthalpies and entropies of all the iodides, but these data are much different from those that trends in the actinide series would suggest, and have not been accepted by the review

It must also be noted that a later mass-spectrometric and gravimetric study of this system at the same laboratory [1986FLE/KNA] indicates that the mass-spectrometry in the study by [1978KNA/MUN] may be flawed due to the use of bare metal heating elements. Flesch *et al.* [1986FLE/KNA] found that the iodine pressure from the decomposition of ThI_4 was, in fact, less than 10% of that of ThI_4(g). In view of this, and the reservations in the derivation of the results noted above, no data from this study has been accepted by the review.

[1978MAN/DEV]

The formation of thiocyanate complexes of Zn^{2+}, Mn^{2+}, Al^{3+}, In^{3+}, Th^{4+} and Hg^{2+} at different pressures have been investigated using Raman spectroscopy. The method requires large metal ion and SCN^- concentrations and the experiments have been made at a total concentration of M^{n+}-SCN^- of about 2.7 M by varying the ratio $[\text{SCN}^-]/[\text{M}^{n+}]$ between 0.5 and 8 and measuring the intensity of the CN stretch vibration in SCN^-; this changes significantly between free and coordinated ligand and the intensity can be used to determine the corresponding concentrations. Only the results for the Th(IV)-SCN^- system will be discussed. The authors report equilibrium constants for the formation of Th(SCN)^{3+} and Th(SCN)_3^+ equal to $\log_{10}\beta_1 = (1.40 \pm 0.15)$ and $\log_{10}\beta_3 = (2.27 \pm 0.09)$ at 20°C and 1 atm. The data show conclusively that the thiocyanate ligand is coordinated at the nitrogen end. The fact that the authors were not able to identify the complex Th(SCN)_2^{2+} is surprising and indicates that there might be some flaws in the quantitative evaluation of the experimental data. This review has therefore not used the reported equilibrium constants in the selection, but note that $\log_{10}\beta_1$ is in fair agreement with the value obtained by liquid-liquid extraction in the study of [1973SAT/KOT].

[1979BEL/SEM]

The authors have studied the vaporisation of thoria by mass-spectrometric measurements. There are very few experimental details in the paper, except that the ionising electron energy was 70 eV, much higher than that used by other workers. Both ThO(g) and ThO_2(g) were observed, but it proved very difficult to obtain stable and reliable ion currents for ThO^+(g). However, the ratio of the ion currents due to ThO^+ and ThO_2^+, after correction for fragmentation, was 0.60 at 2610 K and 0.73 at 2785 K. No absolute pressures are given for ThO_2(g), but the variation of ion current with temperature in the range 2480 to 2860 K corresponded to an enthalpy of sublimation of (684.9 ± 20.0) $\text{kJ}\cdot\text{mol}^{-1}$ at the congruently vaporising composition. This is negligibly different from ThO_2 in the temperature range used, so these results can be regarded as applying to the simple reaction $ThO_2(cr) \rightleftharpoons ThO_2(g)$. The value given is the average of seven runs carried out over a period of time, using two different mass spectrometers.

This enthalpy of sublimation has been converted to give $\Delta_{\text{sub}}H_{\text{m}}^{\circ}$ (ThO_2, cr, 298.15 K) = (746 ± 21) $\text{kJ}\cdot\text{mol}^{-1}$. However it is noted in Section VII.1.3.2 that there is an appreciable difference between the enthalpies of sublimation of thoria obtained using the second-law and third-law methods, so it is not surprising that this value differs noticeably from the consensus of third-law values given in Section VII.1.3.2.

[1979MAU/BOU]

The specific heats of $ThC_{0.75}$(cr), $ThC_{0.6}N_{0.4}$(cr) and ThP(cr) were measured from 2 to 15 K and the results used to calculate the Debye temperature and the density of states at the Fermi level of the three compounds.

[1979SIN/PRA]

Vapour pressures of solid and liquid thorium tetrachloride were measured at 880 − 1024, 1055 − 1126 K by the transpiration technique and from 923 − 1043, 1045 − 1161 K by the boiling point method. The $ThCl_4$ used was prepared from thorium hydride and chlorine gas at 500 K, and purified by vacuum distillation at 1000 K. The analysed Th/Cl ratio was reported to be 1/4. The container for both techniques was silica, which could perhaps have reacted with $ThCl_4$ to form $ThOCl_2$. However, the results from the two techniques are self-consistent and agree well with those by [1939FIS/GEW2] and [1989LAU/HIL]. The melting temperature and enthalpy of fusion of $ThCl_4$ were evaluated from the vapour pressure curves to be 1043 K, and (62.1 ± 3.7) $\text{kJ}\cdot\text{mol}^{-1}$, respectively.

[1979SIN/PRA2]

This is a short progress report describing measurements of the vapour pressure of ThI_4(cr) and ThI_4(l). The work was presented in a Conference paper [1980PRA/NAG] on the vaporisation of all the thorium halides, but no details are given; it has not been published elsewhere.

The measurements were made using both the transpiration and boiling temperature techniques in the temperature ranges 730 to 849 K for solid and 855 to 1044 K for liquid. The ThI_4 used for the study was prepared by the reaction of iodine gas with thorium hydride and purified by distillation; no analyses are given.

The vapour pressures obtained by the two techniques agreed within 6 − 7% over the whole temperature range. The constants A and B in the equation $\log_{10}(p/\text{atm}) = A / T + B$ are given in Table A-50.

Table A-50: Vapour pressure equations for ThI_4(cr) and ThI_4(l).

Phase	Transpiration		Boiling Temperature	
	A	B	A	B
ThI_4(cr)	− 10697	10.589	− 10316	10.122
ThI_4(l)	− 7917	7.309	− 7948	7.363

The melting temperature and enthalpy of fusion derived from the combined measurements were 853 K and 44.7 $kJ \cdot mol^{-1}$; no uncertainties are given.

[1980ACK/TET]

This paper deals principally with the thermodynamic properties of slightly hypostoichiometric thoria (with O/Th ratios down to 1.96). In particular, it treats very thoroughly the oxygen potentials and total pressure of thorium-bearing species over these oxides, together with the variation of the congruently vaporising composition and the lower phase boundary with temperature. The details of such studies are beyond the scope of the present review, but the paper does include additional measurements of the total vapour pressure over essentially stoichiometric thoria, measured by a transpiration technique. Although only the results of three measurements at 2400, 2500 and 2655 K are reported graphically, it is important to include these results, since they were obtained by a technique different from all the other studies. The authors do in fact state that their results agree with the total vapour pressures measured by Ackermann *et al.* [1963ACK/RAU] to within 10% (although the values read from the graph deviate a little more than that).

The transpiration experiments were carried out using a flow gas of hydrogen containing varying amounts of water vapour, to set up an appropriately low oxygen pressure in the system. The sintered granules of initially stoichiometric thoria were held in a tungsten crucible with a perforated base, held in a tungsten tube. The total vapour pressure was calculated from the weight-loss of the sample under investigation.

The pressures of thorium-bearing species increased by a factor of several hundred across the range of composition at temperatures from 2400 to 2655 K, due to a sharp increase of the ThO(g) contribution, consistent with the higher pressures in the presence of the strongly reducing tantalum, measured by Hoch and Johnston [1954HOC/JOH].

[1980BLA/LAG]

The heat capacities of Th_3As_4(cr) and U_3As_4(cr) were measured from 5 to 300 K. Th_3As_4(cr) was prepared by heating in a silica tube, *in vacuo* at 873 K, a mixture of the elements in a As/Th ratio of 2, to form $ThAs_2$(cr), which was decomposed to form Th_3As_4(cr) by further very slow heating up to 1273 K. X-ray investigation showed that the material was single-phase with a lattice parameter of (8.945 ± 0.005) Å, but no other analytical details were given.

Th_3As_4(cr) is non-magnetic with a smooth specific heat curve, while the uranium compound has a sharp λ-peak at 195.8 K, due to a ferromagnetic transition. The thermodynamic functions are derived and tabulated. Interpolation of the given values gives $C^{\circ}_{p,\mathrm{m}}$ (Th_3As_4, cr, 298.15 K) = 183.31 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and S°_{m} (Th_3As_4, cr, 298.15 K) = 274.56 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. The various contributions to the specific heat of U_3As_4(cr) are discussed.

[1980BLA/TRO]

The heat capacities of UAs(cr) and ThAs(cr) were measured from 5 to 300 K, using the same equipment as in the related paper [1980BLA/LAG] by the same group. ThAs(cr) was prepared by thermal decomposition of Th_3As_4(cr) at 1673 K under a dynamic vacuum. The compound was reported as single phase with a lattice parameter of (5.976 ± 0.001) Å, but no analytical details were given. ThAs(cr) is non-magnetic with a smooth specific heat curve, while the uranium compound displays two sharp anomalies. The first, around 64 K, is ascribed to the transition from type IA to type I antiferromagnetic structure. The second anomaly, at 122.8 K, corresponds to the Néel temperature. The thermodynamic functions of the two compounds are tabulated. The values at 298.15 K are:

$$C^{\circ}_{p,\mathrm{m}}\,(\mathrm{ThAs, cr, 298.15\ K}) = 50.52\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}\ \text{and}$$

$$S^{\circ}_{\mathrm{m}}\,(\mathrm{ThAs, cr, 298.15\ K}) = 79.79\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

The experimental result on the specific heat of UAs(cr) as a function of temperature is discussed in detail.

[1980CAE/CAS]

The authors measured the partial pressures of gaseous species over the oxides La_2O_3(cr), Y_2O_3(cr), and ThO_2(cr) contained in tantalum effusion cells, in order to investigate the gettering ability of tantalum at high temperatures. For the study of ThO_2(cr), the temperature range was 2057 to 2421 K. There are no experimental details whatever in the paper, only a one sentence reference to a previous publication (by different authors, Trevisan and Depaus [1973TRE/DEP]), which indicates that the pressures were determined by mass-spectrometry, with conversion from ion intensities *via* a silver calibration. The major species in the vapour was ThO(g), the total pressure being appreciably higher than that over stoichiometric ThO_2(cr) measured in tungsten, in agreement with the work of Hoch and Johnston [1954HOC/JOH]. As expected, TaO(g) was also an present in appreciable amounts. The following equations are given for the pressures of ThO(g) and ThO_2(g) over the hypostoichiometric ThO_{2-x}(cr) formed in the tantalum cell:

$$\log_{10} p_{\mathrm{ThO(g)}} / \mathrm{bar} = -36490/T + 9.839 \qquad 2573-2973 \text{ K}$$

$$\log_{10} p_{\mathrm{ThO_2(g)}} / \mathrm{bar} = -40310/T + 10.427 \qquad 2573-2773 \text{ K}$$

Since the activity of thorium is undefined, the pressures of ThO(g) cannot be utilised to calculate the stability of this species; for ThO_2(g), third law calculations again cannot be used, since the activity of ThO_2 in the ThO_{2-x}(cr) formed is not known. However, this activity is unlikely to change appreciably with temperature, so a second law calculation can be employed, and is included in the analysis in Section VII.1.3.2.

[1980GUP/GIN]

Six gaseous carbides of thorium, ThC_n ($n = 1-6$), were identified in a Knudsen effusion mass spectrometric investigation of the vapour phase above a Th-U-Rh-graphite system at high temperatures. The ion intensities of the thorium-containing species effusing from a mixture of ThC_2, UC_2, Rh and an excess of graphite in a graphite-lined tantalum effusion cell were measured as functions of temperature at 2300−2700 K. The corresponding partial pressures were then calculated, using the $2Au(g) \rightleftharpoons Au_2(g)$ equilibrium as a standard. No individual pressures are reported, only the atomisation energies at 298.15 K and the standard enthalpies at 298.15 K for the all the reactions Th(g) + nC(graphite) $\rightleftharpoons$ ThC_n(g) (by the second and third laws), using thermal functions for the ThC_n(g) species calculated from quoted estimated parameters. The thermal functions for ThC_2(g) given by [1980GUP/GIN] are appreciably greater than those suggested by [1974KOH/STE], due to a different assumed electronic contribution, based on that for the Th^{2+} gaseous ion. It is now known that such a comparison appreciably overestimates the electronic contribution to the thermal functions of molecular ions. As noted in Section XI.1.2, recent calculations by Kovács and Konings [2008KOV/KON] indicate that ThC_2(g) and ThC_4(g) are not linear, as assumed by [1980GUP/GIN] but have L-shaped and fan-shaped structures respectively.

In the absence of detailed experimental results, no further analysis of this study is possible. However, there is an implication in the paper that their results for the Th(g) + 2C(cr) $\rightleftharpoons$ $ThC_2(g)$ equilibrium are very similar to those of Kohl and Stearns [1974KOH/STE], although the derived third-law enthalpies of formation of $ThC_2(g)$ are appreciably different owing to the use of different thermal functions.

[1980NAG/BHU2]

The vapour pressure of solid $ThF_4(cr)$ was measured by the transpiration technique and that of $ThF_4(l)$ by both transpiration and the boiling point method, with self-consistent results.

The sample of ThF_4 used in these studies was prepared from active ThO_2 and anhydrous HF at 750 − 800 K; the only analytical details are that it was shown to be more than 99.5% pure by analysis. The containers were nickel in all the studies. For the transpiration studies, it was found to be difficult to saturate the vapour using a horizontally disposed apparatus, so a vertical assembly was used. The vapour pressure of the solid was measured by the transpiration technique from 1293 to 1375 K and that of the liquid by transpiration from 1394 to 1510 K and by the boiling point method from 1395 to 1554 K, with good self-consistency. The measured pressures are *ca.* 30 − 40% higher than those obtained by [1958DAR/KEN] and [1989LAU/BRI], which agree to within a few percent.

[1980NAK/TAK]

The heat capacities of metallic uranium and thorium were determined from at 84 to 991 K by laser-flash calorimetry.

The sample of thorium used was a disk. 11 mm in diameter, weighing 2.4 g. The main impurities were 155 ppm C and 190 ppm O. Eleven series of experiments, with a total of 206 data points, were carried out.

The heat-capacity values for thorium are several percent lower than those of Griffel and Skochdopole [1953GRI/SKO] below 298.15 K and of Wallace [1960WAL] above this temperature. However, the enthalpy data at high temperature (including those published after 1980) are in good agreement with the results of [1980NAK/TAK]. A revised table of thermodynamic functions of thorium from 80 to 1000 K is given. The standard values are $C^{\circ}_{p,\mathrm{m}}$ (Th, cr, 298.15 K) = 26.24 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ and S°_{m} (Th, cr, 298.15 K) = 52.64 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. These results, using very pure metal, and extending both below and above 298.15 K, are the basis for the values for the thermal functions of α-Th up to 1000 K selected by this review.

The results of [1980NAK/TAK] indicate that the excess heat capacity of thorium is not appreciable below 1000 K, in contrast with a large excess heat capacity for uranium above 300 K.

The results on uranium agree well with those in the literature.

[1980PIC/KLE]

The partial enthalpies $\Delta_{\mathrm{sln}}H_{\mathrm{m}}$ of solution of hydrogen in solid thorium hydrides with H/Th ratios from 0 to 2.003 were measured calorimetrically at 700 K.

The crystal bar thorium used was from the same source as that used by Flotow and Osborne [1978FLO/OSB] and contained 500 ppm total metallic impurities, 14 ppm nitrogen and 50 ppm oxygen. The authors found a sharp change in $\Delta_{\mathrm{sln}}H_{\mathrm{m}}$ at H/Th ≈ 0.03, associated with the formation of the dihydride. In the diphasic region $\Delta_{\mathrm{sln}}H_{\mathrm{m}}$ was relatively constant at *ca.* $-(75 \pm 2)$ kJ·mol^{-1} to H/Th ≈ 1.0, and then decreased slowly to *ca.* -94 kJ·mol^{-1} at the lower phase boundary of $ThH_{1.987}$(cr). In the $ThH_{2\pm x}$ single phase region, the enthalpy of solution increased rapidly to *ca.* -12 kJ·mol^{-1} at $ThH_{2.003}$(cr).

By the integration of all these data the enthalpy of formation of ThH_2(cr) at 700 K was calculated to be $-(145.6 \pm 0.8)$ kJ·mol^{-1}. The equilibrium pressures of hydrogen also were determined for compositions from $1.988 < \mathrm{H/Th} < 2.003$ within the $ThH_{2\pm x}$ single phase field. Combination of the partial Gibbs energies and enthalpies of hydrogen provides information on the entropy of solution. The partial enthalpy and entropy both change dramatically with composition from H/Th = 1.990 to 2.003.

[1980PRA/NAG]

This is a conference paper which collects information on vaporisation studies, all of which have been published in detail elsewhere, so this review is correspondingly brief. The vaporisation behaviour of thorium (and uranium) halides was investigated in the solid and liquid regions by the boiling-temperature and transpiration techniques. Both techniques were used for studies on $ThCl_4$, at 880 − 1161 K. The data derived from the two techniques agree excellently. Boiling-temperature studies were completed for ThF_4(cr), ($ThBr_4$(cr) and $ThBr_4$(l)) and (ThI_4(cr) and ThI_4(l)) at 1395 − 1554 K, 842 − 1089 K and 790 − 1044 K, respectively. All the vapour pressure data are expressed by the equation $\log_{10} p/\mathrm{bar} = \mathrm{A}/T - \mathrm{B}$, with constants given in Table A-51. For convenience this includes also the reference to the fuller papers.

Table A-51: Vapour pressure of thorium halides, $\log_{10} p/\mathrm{bar} = \mathrm{A}/T + \mathrm{B}$.

Species	Temperature range (K)	A	B	Primary reference
ThF_4(l)	1395 – 1554	– 14154	7.376	[1980NAG/BHU2]
$ThCl_4$(cr)	880 – 1043	– 11775	10.106	[1979SIN/PRA]
$ThCl_4$(l)	1045 – 1161	– 8023	6.656	[1979SIN/PRA]
$ThBr_4$(cr)	842 – 971	– 11411	10.656	[1980SIN/PRA]
$ThBr_4$(l)	971 – 1089	– 7813	6.946	[1980SIN/PRA]
ThI_4(cr)	790 – 853	– 10316	10.126	[1979SIN/PRA2]
ThI_4(l)	853 – 1044	– 7915	7.336	[1979SIN/PRA2]

[1980ZHI/KOL]

Only the original Russian paper with an English abstract was available to the reviewers and some details in the study may therefore have escaped our attention. The authors have studied the solubility of thorianite $ThO_2(s)$ in 0.1 M $NaClO_4$ as a function of pH at 17 − 25°C and at 50°C. Their experimental solubility data fall on a smooth curve with a constant solubility of $\log_{10}[Th] = -6.7$ at $pH > 4$; this experimental value is in the range found in many other studies, *cf.* review of [1954GAY/LEI].

The solubility measured by [1980ZHI/KOL] at $pH < 2$ with $ThO_2(s)$ is much lower than literature data for $Th(OH)_4(am)$; with increasing pH the two curves approach each other and at $pH > 5$ they are practically the same (Figure 1 in [1980ZHI/KOL]). There are only two experimental points where the equilibrium constants for the complexes $Th(OH)_n^{4-n}$, $n = 1-3$, can be obtained. The authors propose the solubility constants for the following reactions:

$$ThO_2(s) + H^+ + H_2O(l) \rightleftharpoons Th(OH)_3^+ \qquad \log_{10}{}^*K_{s,3} = -(3.30 \pm 0.07)$$

$$ThO_2(s) + 2H_2O(l) \rightleftharpoons Th(OH)_4(aq) \qquad \log_{10} K_{s,4} = -(6.66 \pm 0.06).$$

It is assumed that there are misprints on p.286 of [1980ZHI/KOL] and the $\log_{10} K_s$ values are negative, as above, and not positive as given there. Combining the equilibrium constants $\log_{10}{}^*K_{s,3} = -(3.30 \pm 0.07)$ and $\log_{10} K_{s,4} = -(6.66 \pm 0.06)$ yields the stepwise equilibrium constant $\log_{10}{}^*K_4$ for the reaction:

$$Th(OH)_3^+ + H_2O(l) \rightleftharpoons Th(OH)_4(aq) + H^+: \qquad \log_{10}{}^*K_4 = -(3.36 \pm 0.09).$$

In view of the limited experimental data in the region where these complexes are formed this review does not accept these values. The authors also discuss the standard Gibbs energy and enthalpy of formation of $ThO_2(s)$ and conclude that new experimental determinations of the standard enthalpy of formation of $ThO_2(s)$ and the hydrolysis constants of Th(IV) are necessary.

[1981BUR/KIJ2]

Enthalpies of solution of the following are reported: $GaCl_3$ and GaI_3 in water (or dilute HCl), methanol, and dimethylsulphoxide; $InCl_3$ and InI_3 in water and in several non-aqueous solvents; $ThCl_4$, ThI_4 and UCl_4 in 1 M HCl, methanol, ethanol, and dimethylsulphoxide. The main purpose of this study is the comparison of the enthalpy of solution of various halides in aqueous and non-aqueous solvents, but it also provides useful data on the enthalpy of solution of $ThCl_4(cr)$ and $ThI_4(cr)$ in 1 M HCl solution.

Commercial anhydrous thorium tetrachloride was used as received, “after purity checks”. It is assumed to have been the most common β-form. Thorium tetraiodide was prepared by reaction between the metal and an excess of iodine which was removed by sublimation. The product was purified by sublimation. No analytical results were given.

The enthalpy of solution of $ThCl_4$ and ThI_4 in 1 M HCl were given as − (242.4 ± 1.9) and − (330.1 ± 2.1) $kJ\cdot mol^{-1}$, respectively, without any detail.

[1981FIS/FIN]

The enthalpy of ThO_2, sealed in tungsten, was measured from 2415 to 3400 K, using a modified high-temperature drop calorimeter. Enthalpies of a sample of molybdenum (NBS reference material) agreed within 1% of the NBS data. No details are given of the ThO_2 sample used.

These data agreed well with other experimental data where they overlapped. The enthalpy results showed there was a phase transition around 3000 K, which was attributed to an order-disorder transition, similar to those found in UO_2 and CaF_2 and other materials with the fluorite structure. The enthalpy data were combined with literature values and fitted to an expression representing the sum of an Einstein lattice contribution and a term proportional to T^2, representing the anharmonic and expansion contributions. This fitting is described in more detail by Finke [1982FIN] (see the review in this Appendix) and agrees very well with the selected values for the thermal functions of $ThO_2(cr)$ selected in this review, at least up to 2900 K.

[1981MIL2]

In three papers of Milić [1981MIL2] and Šuranji and Milić [1981SUR/MIL], [1982SUR/MIL], the hydrolytic behaviour of thorium(IV) is investigated in various chloride media at 25°C by potentiometry and in [1981MIL2] also by calorimetry.

The experimental procedures of the potentiometric studies (coulometry, pH measurements, *etc.*) and evaluation methods are well described. All titrations are performed at a single thorium concentration of 10 mM in the pH range 2.2−3.0 [1981MIL2] or 2.2−3.2 [1981SUR/MIL], [1982SUR/MIL] in following media: 0.5−3 M NaCl and 3 M LiCl, 3 M KCl [1981MIL2], 0.5−3 M LiCl, 0.5−3 M LiCl, [1981SUR/MIL], 0.25−1.5 M MCl_2 (denoted as 0.5−3 M (M)Cl) with M = Mg, Ca, Sr and Ba [1982SUR/MIL].

The potentiometric data were interpreted with the formation of only two dinuclear species, (2,2) = $Th_2(OH)_2^{6+}$ and (3,2) = $Th_2(OH)_3^{5+}$. Other models were not tested; however, the speciation model used is consistent with that of Hietanen and Sillén [1968HIE/SIL] in 3 M NaCl, which has been confirmed by test calculations in the review of Baes and Mesmer [1976BAE/MES] and selected in the present review. The complex (14,6) = $Th_6(OH)_{14}^{10+}$ which is also included in the selected model for chloride media is not relevant under the experimental conditions in [1981MIL2], [1981SUR/MIL], [1982SUR/MIL] (pH < 3.2), *cf.* speciation calculations in Appendix A review of [1968HIE/SIL]. The reported conditional equilibrium constants, with the statistical uncertainties given as 3σ are summarised in Table A-52.

Table A-52: Equilibrium constants $\log_{10} {}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ at 25°C reported in [1981MIL2], [1981SUR/MIL], [1982SUR/MIL].

Reference	Medium	$\log_{10} {}^{*}\beta_{2,2}(\mathrm{Th}_2(\mathrm{OH})_2^{6+})$	$\log_{10} {}^{*}\beta_{3,2}(\mathrm{Th}_2(\mathrm{OH})_3^{5+})$
[1981MIL2]	0.5 M NaCl	– 4.90 ± 0.16	– 7.72 ± 0.05
	1.0 M NaCl	– 4.88 ± 0.03	– 7.93 ± 0.13
	1.5 M NaCl	– 4.95 ± 0.15	– 8.01 ± 0.10
	2.0 M NaCl	– 5.02 ± 0.16	– 8.11 ± 0.12
	2.5 M NaCl	– 5.06 ± 0.12	– 8.12 ± 0.15
	3.0 M NaCl	– 5.08 ± 0.20	– 8.23 ± 0.18
[1981SUR/MIL]	0.5 M LiCl	–	– 7.54 ± 0.01
	1.0 M LiCl	– 5.07 ± 0.13	– 7.85 ± 0.05
	1.5 M LiCl	– 5.01 ± 0.14	– 8.01 ± 0.07
	2.0 M LiCl	– 4.99 ± 0.15	– 8.17 ± 0.10
	3.0 M LiCl	– 4.89 ± 0.07	– 8.49 ± 0.13
[1981MIL2]	3.0 M LiCl	– 5.23 ± 0.15	– 8.28 ± 0.12
[1981SUR/MIL]	0.5 M KCl	–5.84 ± 5.40 [a]	– 7.59 ± 0.03
	1.0 M KCl	– 5.14 ± 0.07	– 7.80 ± 0.11
	1.5 M KCl	– 4.92 ± 0.07	– 8.00 ± 0.04
	2.0 M KCl	– 4.97 ± 0.08	– 8.09 ± 0.05
	2.5 M KCl	– 4.89 ± 0.05	– 8.29 ± 0.05
	3.0 M KCl	– 4.92 ± 0.04	– 8.38 ± 0.06
[1981MIL2]	3.0 M KCl	– 5.04 ± 0.11	– 8.16 ± 0.17
[1982SUR/MIL]	0.25 M $\mathrm{MgCl_2}$	–	– 7.62 ± 0.01
	0.50 M $\mathrm{MgCl_2}$	– 5.12 ± 0.13	– 7.91 ± 0.05
	0.75 M $\mathrm{MgCl_2}$	– 5.01 ± 0.07	– 8.09 ± 0.04
	1.00 M $\mathrm{MgCl_2}$	– 4.93 ± 0.06	– 8.29 ± 0.07
	1.25 M $\mathrm{MgCl_2}$	– 4.90 ± 0.05	– 8.47 ± 0.09
	1.50 M $\mathrm{MgCl_2}$	– 4.90 ± 0.05	– 8.56 ± 0.09
[1982SUR/MIL]	0.25 M $\mathrm{CaCl_2}$	–	– 7.59 ± 0.01
	0.50 M $\mathrm{CaCl_2}$	– 4.96 ± 0.06	– 7.97 ± 0.05
	0.75 M $\mathrm{CaCl_2}$	– 4.95 ± 0.06	– 8.13 ± 0.05
	1.00 M $\mathrm{CaCl_2}$	– 4.97 ± 0.06	– 8.23 ± 0.05
	1.25 M $\mathrm{CaCl_2}$	– 4.92 ± 0.05	– 8.37 ± 0.07
	1.50 M $\mathrm{CaCl_2}$	– 4.92 ± 0.05	– 8.53 ± 0.11
[1982SUR/MIL]	0.25 M $\mathrm{SrCl_2}$	–5.53 max: –5.24 [a]	– 7.66 ± 0.03
	0.50 M $\mathrm{SrCl_2}$	– 5.29 ± 0.19	– 7.95 ± 0.04
	0.75 M $\mathrm{SrCl_2}$	– 5.06 ± 0.10	– 8.09 ± 0.05
	1.00 M $\mathrm{SrCl_2}$	– 4.95 ± 0.07	– 8.25 ± 0.08
	1.25 M $\mathrm{SrCl_2}$	– 4.93 ± 0.05	– 8.41 ± 0.06
	1.50 M $\mathrm{SrCl_2}$	– 4.97 ± 0.05	– 8.52 ± 0.07

(Continued on next page)

Table A-52: (Continued)

Reference	Medium	$\log_{10} {}^*\beta_{2,2}(\mathrm{Th_2(OH)_2^{6+}})$	$\log_{10} {}^*\beta_{3,2}(\mathrm{Th_2(OH)_3^{5+}})$
[1982SUR/MIL]	0.25 M $BaCl_2$	–5.56 max: –5.21 [a]	– 7.62 ± 0.04
	0.50 M $BaCl_2$	– 5.12 ± 0.15	– 7.92 ± 0.05
	0.75 M $BaCl_2$	– 5.02 ± 0.10	– 8.10 ± 0.07
	1.00 M $BaCl_2$	– 4.91 ± 0.04	– 8.29 ± 0.05
	1.25 M $BaCl_2$	– 4.90 ± 0.04	– 8.39 ± 0.07
	1.50 M $BaCl_2$	– 4.96 ± 0.04	– 8.50 ± 0.07

a Equilibrium constants are uncertain and not used in the present review.

- *Ionic strength corrections and equilibrium constants at zero ionic strength*

Šuranji and Milić [1982SUR/MIL] described the ionic strength dependence of the conditional equilibrium constants and the reaction enthalpies in all chloride media by an empirical linear correlation between $\log_{10} {}^*\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ and a "medium factor" (defined in [1981MIL2]) that depends on the ionic medium concentration and the hydration energy of its ions. Correlations that have no theoretical foundation such as this can at best be used for interpolations, but never for extrapolations as in [1981MIL2]; the ionic strength dependence should be described by models based on the existing electrolyte theories. The model used by Milić does not even contain a Debye-Hückel terms and it is not surprising that the extrapolation to infinite dilution in Figure 6 of [1982SUR/MIL] leads to values ($\log_{10} {}^*\beta^\circ_{2,2}(\mathrm{Th_2(OH)_2^{6+}}) = -5.1$, $\log_{10} {}^*\beta_{3,2}(\mathrm{Th_2(OH)_3^{5+}}) = -7.5$) which differ by about one $\log_{10}$ unit from those evaluated in this review using the SIT. In Figure A-26 and Figure A-27 the terms ($\log_{10} {}^*\beta_{n,2} - n\log_{10}a_\mathrm{w} - z^2D$) are plotted against ionic strength I. The evaluated equilibrium constants $\log_{10} {}^*\beta^\circ_{n,2}$ and $\Delta\varepsilon(n,2)_\mathrm{Cl}$ derived from the slopes, $-\Delta\varepsilon(n,2)_\mathrm{Cl}$ for MCl media ($I = m_\mathrm{Cl}$) and $-\Delta\varepsilon(n,2)_\mathrm{Cl}/1.5$ for MCl_2 media ($I = 1.5\ m_\mathrm{Cl}$), are summarised in Table A-53.

Table A-53: Equilibrium constants $\log_{10} {}^*\beta^\circ_{n,2}$ and $\Delta\varepsilon(n,2)_\mathrm{Cl}$ ($\mathrm{kg\cdot mol^{-1}}$) evaluated with the SIT from the data of [1981MIL2], [1981SUR/MIL] and [1982SUR/MIL] at 25°C.

	$\mathrm{Th_2(OH)_2^{6+}}$		$\mathrm{Th_2(OH)_3^{5+}}$	
Data from (Ionic media)	$\log_{10} {}^*\beta^\circ_{2,2}$	$\Delta\varepsilon(2,2)_\mathrm{Cl}$	$\log_{10} {}^*\beta^\circ_{3,2}$	$\Delta\varepsilon(3,2)_\mathrm{Cl}$
[1981MIL2],[1981SUR/MIL] (NaCl, LiCl, KCl)	– 6.06 ± 0.17	0.10 ± 0.08	– 6.86 ± 0.12	0.09 ± 0.07
[1982SUR/MIL] ($MgCl_2$, $CaCl_2$, $SrCl_2$, $BaCl_2$)	– 6.41 ± 0.22	0.00 ± 0.06	– 6.79 ± 0.08	0.18 ± 0.03
This review:	– 5.9 ± 0.5 [a]	0.14 ± 0.15 [a]	– 6.8 ± 0.2 [b]	0.15 ± 0.06 [b]

a: Evaluated in Section VII.3.4.1.1 using simultaneously the selected data in perchlorate, nitrate and chloride media.

b: Mean value considering also the value of [1968HIE/SIL] in 3 M NaCl.

The data of Milić [1981MIL2] are in reasonable agreement with those of Hietanen and Sillén [1968HIE/SIL] in 3 M NaCl, the $\log_{10} {}^*\beta_{2,2}$ value of [1968HIE/SIL] is about 0.3 $\log_{10}$-units higher, while $\log_{10} {}^*\beta_{3,2}$ is about 0.4 $\log_{10}$-units lower. The equilibrium constants $\log_{10} {}^*\beta_{2,2}$ in NaCl, LiCl and KCl media are included in the selection of data in Section VII.3.4.1.1. The $\log_{10} {}^*\beta_{2,2}$ values at [MCl_2] < 1.0 M and hence the extrapolation to $I = 0$ are uncertain. The equilibrium constant $\log_{10} {}^*\beta^{\circ}_{2,2}$ is consistent with that derived in the present review from the data of [1971MIL2] in 0.5 − 3 M $NaNO_3$ media.

Figure A-26: Extrapolation of $\log_{10} {}^*\beta_{2,2}(Th_2(OH)_2^{6+})$ and $\log_{10} {}^*\beta_{3,2}(Th_2(OH)_3^{5+})$ in NaCl, LiCl and KCl media at 25°C [1981MIL2], [1981SUR/MIL] to zero ionic strength with the SIT. The data from [1968HIE/SIL] in 3 M NaCl are shown for comparison.

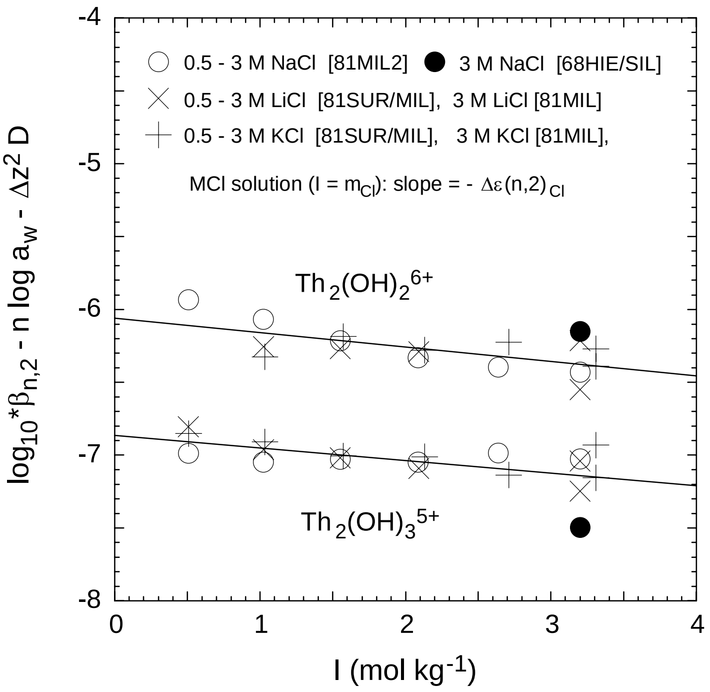
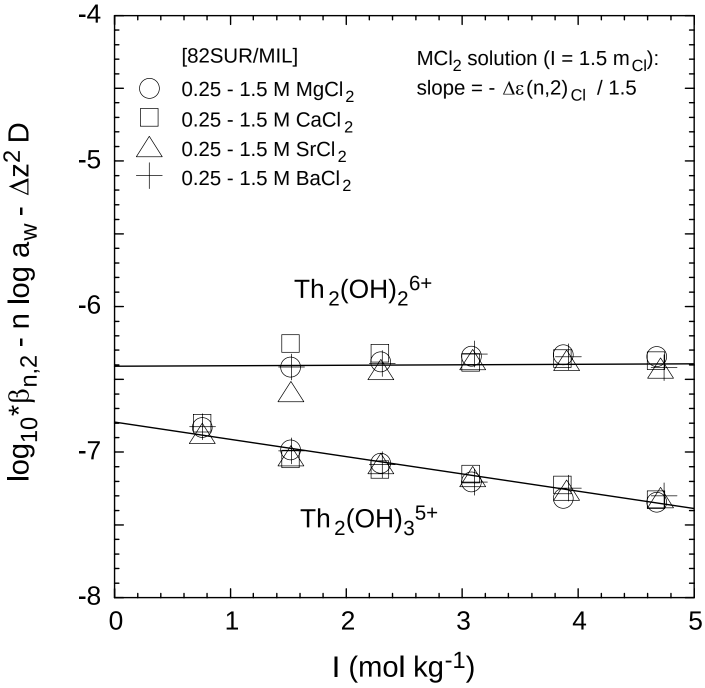


Figure A-27: Extrapolation of $\log_{10}{}^{*}\beta_{2,2}$ ($Th_2(OH)_2^{6+}$) and $\log_{10}{}^{*}\beta_{3,2}$ ($Th_2(OH)_3^{5+}$) in MCl_2 (M = Mg, Ca, Sr, Ba) media at 25°C [1982SUR/MIL] to zero ionic strength with the SIT.



The equilibrium constant $\log_{10}{}^{*}\beta^{\circ}_{3,2}$ and $\Delta\varepsilon(3,2)_{Cl}$ calculated from the data in MCl media [1981MIL2], [1981SUR/MIL] and MCl_2 media [1982SUR/MIL] are in good agreement. They are used in the present review, together with the data of [1968HIE/SIL] in 3 M NaCl, for the selection of data for the complex $Th_2(OH)_3^{5+}$.

- *Calorimetric measurements in [1981MIL2]*

Calorimetric measurements were performed as back-titrations of hydrolysed Th(IV) equilibrium solutions in 0.5−3 M NaCl, 3 M LiCl and 3 M KCl with HCl standard solutions [1981MIL2]. No details are reported, which is unfortunate as it makes it impossible to estimate the accuracy of the results obtained. The following information is missing: the concentration of the HCl titrant and its enthalpy of dilution; the relative amounts of $Th_2(OH)_3^{5+}$ and $Th_2(OH)_2^{6+}$, where the first complex is a minor species, a fact that will strongly affect the accuracy of the corresponding molar enthalpy of reaction. It is not clear from the information given if the full-drawn curves in Figures 4 and 5 of [1981MIL2] have been calculated using the data in Table A-53, or not. The results

([1981MIL2], Table A-53) are given without uncertainties and the number of digits given is no indication of the accuracy; the error in $\Delta_r H_m$(2,2) is at least 2−3% and much larger in $\Delta_r H_m$(3,2). The enthalpy of reaction is large and for the (2,2) complex of the same order of magnitude as the enthalpy of protonation of OH^-; in view of this it is not surprising that the enthalpy of reaction at a given ionic strength of 3 M varies significantly with the ionic medium (NaCl, LiCl and KCl). The enthalpy of protonation of OH^- is −57.5 kJ·mol^{-1} in 1 m NaCl and −56.1 kJ·mol^{-1} in 1 m $NaClO_4$ ([1997GRE/PLY2], p. 418, 420). The ionic strength dependence of this reaction is also significant and varies from −58.5 kJ·mol^{-1} to −57.2 kJ·mol^{-1} between 3 m and 0.5 m NaCl. However, the ionic strength dependence in [1981MIL2] is much larger than expected; a discussion of the ionic strength dependence of reaction enthalpies is given in [1997GRE/PLY2] (see Chapter IX). From the strong dependence of the reaction enthalpies on the chloride concentration, one would expect a larger variation of $\log_{10} {}^*\beta_{n,2}$ than observed, suggesting that the experimental observations may be due to another effect. As indicated above, part of the differences may be artefacts due to the neglect of the medium-dependent enthalpy of dilution of HCl.

Table A-54: Gibbs energies, enthalpies and entropies of hydrolysis reactions reported in [1981MIL2].

Medium	$\Delta_r G_m$ (kJ·mol^{-1})	$\Delta_r H_m$ (kJ·mol^{-1})	$\Delta_r S_m$ (J·K^{-1}·mol^{-1})
$2Th^{4+} + 2H_2O(l) \rightleftharpoons Th_2(OH)_2^{6+} + 2H^+$			
0.5 M NaCl	27.9	86.7	197.3
1.0 M NaCl	27.8	87.0	198.7
1.5 M NaCl	28.2	98.3	235.2
2.0 M NaCl	28.6	109.8	272.5
2.5 M NaCl	28.8	110.3	273.5
3.0 M NaCl	28.9	119.0	302.3
3.0 M LiCl	29.8	133.6	348.3
3.0 M KCl	28.7	101.9	245.6
$2Th^{4+} + 3H_2O(l) \rightleftharpoons Th_2(OH)_3^{5+} + 3H^+$			
0.5 M NaCl	44.4	90.7	155.4
1.0 M NaCl	45.2	76.8	106.0
1.5 M NaCl	45.7	60.1	48.3
2.0 M NaCl	46.2	45.3	−3.0
2.5 M NaCl	46.3	33.3	−43.6
3.0 M NaCl	46.9	21.2	−86.2
3.0 M LiCl	47.2	23.1	−80.9
3.0 M KCl	46.5	38.1	−28.2

In 1 M NaCl, the enthalpy of reaction for the formation of $\mathrm{Th_2(OH)_2^{6+}}$ is in fair agreement with the value in 1 M $\mathrm{NaClO_4}$ given in [1965BAE/MEY], although the entropy of reaction differs significantly. In general, data obtained by calorimetry are more precise than those from the temperature variation of equilibrium constants [1965BAE/MEY], [1976BAE/MES], [2000EKB/ALB], but in view of the criticism given above this review does not accept the reported enthalpy and entropy values.

[1981SMI/MES]

The solubility of $\mathrm{ThF_4(s)}$ has been measured as a function of temperature and the concentration of HF in 4, 8 and 13 M nitric acid. The experimental data have been used to determine equilibrium constants for the complexes ThF_n^{4-n}, $n = 1-4$, and the solubility product of $\mathrm{ThF_4(s)}$. The experimental method is described in detail and the primary experimental data are included. The composition of solid phase has been determined using elemental analysis and the solid has also been characterised using X-ray diffraction. However, the authors were not able to determine the state of hydration for the freshly formed $\mathrm{ThF_4(s)}$ that was amorphous and gave a poor X-ray powder pattern; the solid may thus be any of the known stable hydrates, $\mathrm{ThF_4{\cdot}2.5\text{-}3.0\,H_2O}$, $\mathrm{ThF_4{\cdot}0.5\text{-}2.5\,H_2O}$ and $\mathrm{ThF_4{\cdot}0.25\,H_2O}$. The analysis of the experimental data is satisfactory, but the authors point out that the least-squares analysis is complicated by the large number of parameters, in combination with the scattering of the solubility data. The key problem is that the concentration of free HF has not been measured directly and therefore has to be determined from the mass balance. Therefore, there is a strong correlation between [HF] and the equilibrium constants. However, the agreement between the deduced equilibrium constants obtained in [1981SMI/MES] and previous studies using different experimental methods is good and this review therefore accepts the proposed constants given in Table A-55.

The stepwise equilibrium constants, $\log_{10}{}^{*}K_n$, for the reactions:

$$\mathrm{ThF}_{n-1}^{5-n} + \mathrm{HF(aq)} \rightleftharpoons \mathrm{ThF}_n^{4-n} + \mathrm{H}^+ \qquad n = 1-4$$

are obtained from the data given in Table A-55 and are listed below for the data at 25°C in 4 M and 8 M $\mathrm{HNO_3}$ that are the most accurate; the errors are estimated by this review.

4 M $\mathrm{HNO_3}$: $\log_{10}{}^{*}K_1 = (3.8 \pm 0.4)$; $\log_{10}{}^{*}K_2 = (3.0 \pm 0.4)$
$\log_{10}{}^{*}K_3 = (2.2 \pm 0.4)$; $\log_{10}{}^{*}K_4 = (1.4 \pm 0.4)$;

8 M $\mathrm{HNO_3}$: $\log_{10}{}^{*}K_1 = (3.2 \pm 0.4)$; $\log_{10}{}^{*}K_2 = (2.7 \pm 0.4)$
$\log_{10}{}^{*}K_3 = (2.3 \pm 0.4)$; $\log_{10}{}^{*}K_4 = (1.9 \pm 0.4)$.

For complexes of the type discussed here one often finds a regular decrease in the stepwise equilibrium constants. In this respect the data (based on the least-squares method) look satisfactory. However, the data in 8 M and 13 M $\mathrm{HNO_3}$ have not been used in the selection of equilibrium constants because of the high ionic strength.

Table A-55: Concentration equilibrium constants[a] reported in [1981SMI/MES].

	Reaction	$\log_{10}{}^{*}K$	$\log_{10}{}^{*}K$	$\log_{10}{}^{*}K$
t (°C)		4 M HNO_3	8 M HNO_3	13 M HNO_3
	$ThF_4(s) + 4H^+ \rightleftharpoons Th^{4+} + 4HF(aq)$			
25		-16.25 ± 0.4	-15.60 ± 0.4	-15.9 ± 0.7
50		-15.06 ± 0.3	-14.00 ± 0.3	-16.7 ± 0.1
100		-14.3 ± 0.7	-14.36 ± 0.55	-16.15 ± 0.6
	$Th^{4+} + HF(aq) \rightleftharpoons ThF^{3+} + H^+$			
25		3.8	3.2	2.7
50		3.7	2.9	2.8
100		3.3	2.9	2.7
	$ThF^{3+} + HF(aq) \rightleftharpoons ThF_2^{2+} + H^+$			
25		3.0	2.7	2.7
50		2.9	2.5	3.0
100		2.7	2.6	2.8
	$ThF_2^{2+} + HF(aq) \rightleftharpoons ThF_3^{+} + H^+$			
25		2.2	2.3	2.8
50		2.0	2.1	3.3
100		2.2	2.4	3.0
	$ThF_3^{+} + HF(aq) \rightleftharpoons ThF_4(aq) + H^+$			
25		1.4	1.9	2.8
50		1.2	1.7	3.5
100		1.6	2.2	3.1

a: Values of the solubility products are based on least-squares analyses and the other constants on the constant step-decrement model reported in their Tables 4 and 7, respectively.

Smith *et al.* have also interpreted their data using models with a smaller number of parameters, one parameter relating the complex formation constant in solution to the solubility product of the solid phase, one parameter describing the ratio between two consecutive stepwise equilibrium constants and one parameter describing an assumed regular decrease in this ratio between the stepwise equilibrium constants (Table A-55). Methods like these have been used in studies where the scattering in the experimental data and the number of parameters cannot provide a unique chemical model. In general, Smith *et al.* report a reasonable agreement between the constants calculated with least-squares and the step-decrement methods. The scatter of the experimental data and the uncertainty of the equilibrium constants are so large that the data at different temperature cannot be used to deduce the enthalpy and entropy of reaction.

Because of the very high ionic strengths and the large degree of scatter in the data, it is not possible to precisely determine simultaneously the values of formation constants and the solubility product for ThF_4(cr, hyd) from these data. This review has developed an aqueous phase model in the fluoride system (Table VIII-7) independent of the data in [1981SMI/MES]. These aqueous phase data were used to calculate the solubility products for ThF_4(cr, hyd) with the NONLINT-SIT code and to verify the reliability of the aqueous phase model. Only the data for 4 and 8 M (4.557 and 10.75 m) nitric acid at 25°C and 50°C were reanalysed. In order to do so, the molarities of different elements reported by the authors were converted to molalities. The SIT ion-interaction parameters $\varepsilon(\mathrm{Th}^{4+},\mathrm{NO}_3^-)$, $\varepsilon(\mathrm{ThF}^{3+},\mathrm{NO}_3^-)$, $\varepsilon(\mathrm{ThF}_2^{2+},\mathrm{NO}_3^-)$, and $\varepsilon(\mathrm{ThF}_3^{+},\mathrm{NO}_3^-)$ used in these analyses are listed in Table VIII-8. Reanalyses of [1981SMI/MES] data provided $\Delta_f G_m^o / RT$ values for ThF_4(cr, hyd) of $-(811.372 \pm 2.46)$ at 25°C and $-(811.146 \pm 2.32)$ at 50°C for 4.557 m ionic strength data and of $-(813.058 \pm 4.16)$ at 25°C and $-(813.447 \pm 4.90)$ at 50°C for 10.75 m ionic strength data. The $\Delta_f G_m^o / RT$ values for ThF_4(cr, hyd) thus determined from the data at I = 4.557 m are very similar to the value $-(811.860 \pm 0.915)$ recommended in this review based on solubility studies [1993FEL/RAI] in relatively dilute electrolytes, 0.0001 to 0.01 M. There is some scatter in the data, but the overall agreement between the experimental and predicted thorium concentrations as a function of F^- indicates that the aqueous phase model and $\Delta_f G_m^o / RT$ value for ThF_4(cr, hyd) selected in this review are consistent with the data at I = 4.557 m (Figure VIII-2, Table A-56 and Table A-57). Although the standard deviation in $\Delta_f G_m^o / RT$ value for ThF_4(cr, hyd) based on the data at I = 10.57 m is larger than the standard deviation based on the data at I = 4.557 m and that it is questionable whether the SIT model is applicable to these high ionic strength (10.57 m) solutions, the $\Delta_f G_m^o / RT$ values for ThF_4(cr, hyd) calculated from these data are still within the range of values recommended in this review and thus lends further credence to the values selected here. The experimental and predicted concentrations for different species are presented in Table A-58 and Table A-59 and are compared in Figure A-28 and Figure A-29.

Table A-56: Experimental ([1981SMI/MES]) and predicted concentrations for $\mathrm{ThF_4}$(cr, hyd) at 25°C in 4.557 m $\mathrm{HNO_3}$ solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\mathrm{o}} / \mathrm{R}T$ value for $\mathrm{ThF_4}$(cr, hyd) of $-(811.372 \pm 2.460)$. Predicted values are identical whether the species $\mathrm{ThF_6^{2-}}$ is included or excluded from modelling, since this species is not significant in this chemical system.

Experimental concentrations (m)			Predicted concentrations (m)						
$\mathrm{F_{Total}}$	$\mathrm{F^-}$	$\mathrm{Th_{Total}}$	$\mathrm{Th_{Total}}$	$\mathrm{Th^{4+}}$	$\mathrm{ThF^{3+}}$	$\mathrm{ThF_2^{2+}}$	$\mathrm{ThF_3^+}$	$\mathrm{ThF_4(aq)}$	$\mathrm{F^-}$
3.315E-01	8.127E-05	4.101E-06	1.482E-06	2.992E-12	2.948E-09	1.122E-07	4.503E-07	9.163E-07	8.127E-05
3.885E-01	9.644E-05	5.184E-06	1.377E-06	1.495E-12	1.754E-09	7.944E-08	3.791E-07	9.163E-07	9.644E-05
3.965E-01	9.860E-05	5.480E-06	1.365E-06	1.366E-12	1.640E-09	7.597E-08	3.707E-07	9.163E-07	9.860E-05
1.025E-01	2.393E-05	1.124E-05	3.879E-06	4.133E-10	1.181E-07	1.309E-06	1.535E-06	9.163E-07	2.392E-05
6.801E-02	1.576E-05	1.196E-05	6.687E-06	2.208E-09	4.146E-07	3.022E-06	2.332E-06	9.163E-07	1.576E-05
6.186E-02	1.432E-05	1.208E-05	7.703E-06	3.245E-09	5.535E-07	3.663E-06	2.567E-06	9.163E-07	1.431E-05
5.491E-02	1.269E-05	1.230E-05	9.278E-06	5.264E-09	7.954E-07	4.664E-06	2.897E-06	9.163E-07	1.269E-05
2.461E-02	5.634E-06	4.637E-05	4.042E-05	1.363E-07	9.124E-06	2.371E-05	6.530E-06	9.163E-07	5.631E-06
1.139E-02	2.566E-06	1.196E-04	2.184E-04	2.918E-06	9.078E-05	1.097E-04	1.404E-05	9.163E-07	2.619E-06
1.138E-02	2.418E-06	5.195E-04	2.991E-04	4.934E-06	1.346E-04	1.426E-04	1.601E-05	9.163E-07	2.297E-06
1.151E-02	2.194E-06	1.242E-03	5.396E-04	1.283E-05	2.756E-04	2.299E-04	2.033E-05	9.163E-07	1.809E-06
1.151E-02	1.177E-06	4.808E-03	4.096E-03	2.720E-04	2.721E-03	1.058E-03	4.359E-05	9.163E-07	8.443E-07
1.185E-02	5.735E-07	8.556E-03	8.774E-03	8.000E-04	6.105E-03	1.811E-03	5.703E-05	9.163E-07	6.458E-07
1.219E-02	3.343E-07	1.151E-02	1.249E-02	1.306E-03	8.811E-03	2.312E-03	6.441E-05	9.163E-07	5.720E-07
3.144E-02	5.000E-07	2.791E-02	2.747E-02	3.818E-03	1.963E-02	3.935E-03	8.395E-05	9.163E-07	4.399E-07
3.395E-02	2.095E-07	4.181E-02	4.442E-02	7.259E-03	3.166E-02	5.399E-03	9.820E-05	9.163E-07	3.770E-07
7.223E-02	3.580E-07	7.495E-02	7.414E-02	1.428E-02	5.224E-02	7.505E-03	1.155E-04	9.163E-07	3.219E-07
7.941E-02	3.804E-07	8.100E-02	7.947E-02	1.564E-02	5.587E-02	7.842E-03	1.180E-04	9.163E-07	3.152E-07
1.151E-01	4.193E-07	1.151E-01	1.108E-01	2.414E-02	7.684E-02	9.655E-03	1.307E-04	9.163E-07	2.861E-07
1.173E-01	3.839E-07	1.208E-01	1.171E-01	2.596E-02	8.104E-02	9.995E-03	1.329E-04	9.163E-07	2.815E-07
1.208E-01	3.869E-07	1.242E-01	1.203E-01	2.687E-02	8.309E-02	1.016E-02	1.340E-04	9.163E-07	2.795E-07
1.219E-01	9.866E-08	2.279E-01	2.463E-01	6.797E-02	1.625E-01	1.562E-02	1.647E-04	9.163E-07	2.312E-07
2.370E-01	1.651E-07	3.520E-01	3.603E-01	1.109E-01	2.298E-01	1.940E-02	1.823E-04	9.163E-07	2.118E-07
2.746E-01	1.720E-07	4.044E-01	4.112E-01	1.314E-01	2.587E-01	2.088E-02	1.886E-04	9.163E-07	2.059E-07
3.008E-01	1.958E-07	4.192E-01	4.210E-01	1.354E-01	2.642E-01	2.116E-02	1.897E-04	9.163E-07	2.049E-07
2.165E-01	7.923E-08	4.979E-01	5.384E-01	1.855E-01	3.285E-01	2.417E-02	2.016E-04	9.163E-07	1.952E-07
3.976E-01	1.662E-07	6.175E-01	6.252E-01	2.244E-01	3.744E-01	2.616E-02	2.088E-04	9.163E-07	1.899E-07
4.272E-01	1.353E-07	7.542E-01	7.751E-01	2.948E-01	4.508E-01	2.923E-02	2.194E-04	9.163E-07	1.831E-07

Table A-57: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 50°C in 4.557 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G^o_m / RT$ value for ThF_4(cr, hyd) of $-(811.146 \pm 2.320)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.

Experimental concentrations (m)			Predicted concentrations (m)						
F_{Total}	F^-	Th_{Total}	Th_{Total}	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	F^-
7.063×10^{-2}	1.637×10^{-5}	2.165×10^{-5}	7.939×10^{-6}	2.377×10^{-9}	4.638×10^{-7}	3.511×10^{-6}	2.814×10^{-6}	1.148×10^{-6}	1.637×10^{-5}
2.051×10^{-2}	4.664×10^{-6}	1.048×10^{-4}	7.537×10^{-5}	3.679×10^{-7}	2.033×10^{-5}	4.361×10^{-5}	9.913×10^{-6}	1.148×10^{-6}	4.649×10^{-6}
1.481×10^{-2}	3.234×10^{-6}	4.101×10^{-4}	1.825×10^{-4}	1.826×10^{-6}	6.759×10^{-5}	9.714×10^{-5}	1.479×10^{-5}	1.148×10^{-6}	3.116×10^{-6}
1.709×10^{-2}	2.008×10^{-6}	5.468×10^{-3}	3.327×10^{-3}	1.818×10^{-4}	2.129×10^{-3}	9.682×10^{-4}	4.670×10^{-5}	1.148×10^{-6}	9.876×10^{-7}
3.646×10^{-2}	4.020×10^{-7}	3.532×10^{-2}	3.565×10^{-2}	5.024×10^{-3}	2.548×10^{-2}	5.042×10^{-3}	1.063×10^{-4}	1.148×10^{-6}	4.358×10^{-7}
5.696×10^{-2}	3.673×10^{-7}	5.810×10^{-2}	5.819×10^{-2}	9.676×10^{-3}	4.144×10^{-2}	6.951×10^{-3}	1.246×10^{-4}	1.148×10^{-6}	3.730×10^{-7}
1.253×10^{-1}	2.606×10^{-7}	1.481×10^{-1}	1.492×10^{-1}	3.346×10^{-2}	1.030×10^{-1}	1.259×10^{-2}	1.667×10^{-4}	1.148×10^{-6}	2.826×10^{-7}
1.253×10^{-1}	1.587×10^{-7}	1.823×10^{-1}	1.913×10^{-1}	4.623×10^{-2}	1.302×10^{-1}	1.464×10^{-2}	1.792×10^{-4}	1.148×10^{-6}	2.644×10^{-7}
2.051×10^{-1}	1.862×10^{-7}	2.848×10^{-1}	2.915×10^{-1}	7.991×10^{-2}	1.926×10^{-1}	1.876×10^{-2}	2.015×10^{-4}	1.148×10^{-6}	2.380×10^{-7}
3.418×10^{-1}	1.329×10^{-7}	5.924×10^{-1}	6.159×10^{-1}	2.098×10^{-1}	3.775×10^{-1}	2.840×10^{-2}	2.438×10^{-4}	1.148×10^{-6}	2.036×10^{-7}

Table A-58: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 25°C in 10.75 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G^\circ_m / RT$ value for ThF_4(cr, hyd) of $-(813.06 \pm 4.160)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.

Experimental concentrations (m)			Predicted concentrations (m)						
F_{Total}	F^-	Th_{Total}	Th_{Total}	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	F^-
5.121×10^{-1}	2.134×10^{-5}	1.357×10^{-5}	5.756×10^{-7}	4.234×10^{-12}	1.656×10^{-9}	4.946×10^{-8}	3.548×10^{-7}	1.697×10^{-7}	2.134×10^{-5}
4.005×10^{-1}	1.652×10^{-5}	1.357×10^{-5}	7.146×10^{-7}	1.186×10^{-11}	3.583×10^{-9}	8.268×10^{-8}	4.586×10^{-7}	1.697×10^{-7}	1.652×10^{-5}
1.212×10^{-1}	4.871×10^{-6}	3.588×10^{-5}	2.826×10^{-6}	1.593×10^{-9}	1.411×10^{-7}	9.554×10^{-7}	1.558×10^{-6}	1.697×10^{-7}	4.869×10^{-6}
7.701×10^{-2}	3.080×10^{-6}	6.061×10^{-5}	5.602×10^{-6}	1.003×10^{-8}	5.603×10^{-7}	2.396×10^{-6}	2.466×10^{-6}	1.697×10^{-7}	3.076×10^{-6}
5.484×10^{-2}	2.182×10^{-6}	1.226×10^{-4}	1.009×10^{-5}	4.024×10^{-8}	1.588×10^{-6}	4.798×10^{-6}	3.490×10^{-6}	1.697×10^{-7}	2.174×10^{-6}
1.344×10^{-2}	4.849×10^{-7}	8.978×10^{-4}	3.696×10^{-4}	2.605×10^{-5}	2.038×10^{-4}	1.220×10^{-4}	1.760×10^{-5}	1.697×10^{-7}	4.312×10^{-7}
1.357×10^{-2}	4.597×10^{-7}	1.465×10^{-3}	5.647×10^{-4}	4.903×10^{-5}	3.275×10^{-4}	1.674×10^{-4}	2.061×10^{-5}	1.697×10^{-7}	3.682×10^{-7}
1.357×10^{-2}	1.614×10^{-7}	1.012×10^{-2}	9.754×10^{-3}	2.423×10^{-3}	6.100×10^{-3}	1.176×10^{-3}	5.462×10^{-5}	1.697×10^{-7}	1.390×10^{-7}
1.384×10^{-2}	1.109×10^{-7}	1.384×10^{-2}	1.412×10^{-2}	3.883×10^{-3}	8.685×10^{-3}	1.488×10^{-3}	6.143×10^{-5}	1.697×10^{-7}	1.237×10^{-7}
1.452×10^{-2}	3.180×10^{-8}	3.521×10^{-2}	3.923×10^{-2}	1.385×10^{-2}	2.249×10^{-2}	2.802×10^{-3}	8.424×10^{-5}	1.697×10^{-7}	9.030×10^{-8}
2.930×10^{-2}	5.918×10^{-8}	4.825×10^{-2}	5.018×10^{-2}	1.870×10^{-2}	2.814×10^{-2}	3.251×10^{-3}	9.071×10^{-5}	1.697×10^{-7}	8.391×10^{-8}
3.521×10^{-2}	7.628×10^{-8}	5.027×10^{-2}	5.081×10^{-2}	1.898×10^{-2}	2.846×10^{-2}	3.275×10^{-3}	9.105×10^{-5}	1.697×10^{-7}	8.360×10^{-8}
3.857×10^{-2}	5.502×10^{-8}	6.747×10^{-2}	6.983×10^{-2}	2.787×10^{-2}	3.790×10^{-2}	3.960×10^{-3}	1.001×10^{-4}	1.697×10^{-7}	7.616×10^{-8}
4.704×10^{-2}	4.407×10^{-8}	9.583×10^{-2}	1.001×10^{-1}	4.287×10^{-2}	5.220×10^{-2}	4.893×10^{-3}	1.111×10^{-4}	1.697×10^{-7}	6.870×10^{-8}
5.578×10^{-2}	3.602×10^{-8}	1.314×10^{-1}	1.382×10^{-1}	6.287×10^{-2}	6.933×10^{-2}	5.899×10^{-3}	1.219×10^{-4}	1.697×10^{-7}	6.278×10^{-8}
7.903×10^{-2}	5.753×10^{-8}	1.384×10^{-1}	1.396×10^{-1}	6.359×10^{-2}	6.992×10^{-2}	5.932×10^{-3}	1.222×10^{-4}	1.697×10^{-7}	6.261×10^{-8}
8.091×10^{-2}	5.708×10^{-8}	1.425×10^{-1}	1.437×10^{-1}	6.582×10^{-2}	7.172×10^{-2}	6.032×10^{-3}	1.232×10^{-4}	1.697×10^{-7}	6.211×10^{-8}
1.371×10^{-1}	2.334×10^{-8}	4.731×10^{-1}	4.966×10^{-1}	2.787×10^{-1}	2.058×10^{-1}	1.195×10^{-2}	1.718×10^{-4}	1.697×10^{-7}	4.539×10^{-8}
1.411×10^{-1}	1.725×10^{-8}	6.371×10^{-1}	6.755×10^{-1}	3.965×10^{-1}	2.648×10^{-1}	1.402×10^{-2}	1.853×10^{-4}	1.697×10^{-7}	4.243×10^{-8}

Table A-59: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 50°C in 10.75 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G_m^o / RT$ value for ThF_4(cr, hyd) of $-(813.45 \pm 4.90)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.

Experimental concentrations (m)			Predicted concentrations (m)						
F_{Total}	F^-	Th_{Total}	Th_{Total}	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	F^-
7.795×10^{-2}	3.115×10^{-6}	8.602×10^{-5}	3.732×10^{-6}	6.505×10^{-9}	3.675×10^{-7}	1.589×10^{-6}	1.654×10^{-6}	1.150×10^{-7}	3.110×10^{-6}
4.435×10^{-2}	1.717×10^{-6}	6.586×10^{-4}	1.120×10^{-5}	7.892×10^{-8}	2.388×10^{-6}	5.531×10^{-6}	3.085×10^{-6}	1.150×10^{-7}	1.667×10^{-6}
1.747×10^{-2}	5.394×10^{-7}	2.688×10^{-3}	5.329×10^{-4}	5.384×10^{-5}	3.188×10^{-4}	1.444×10^{-4}	1.576×10^{-5}	1.150×10^{-7}	3.263×10^{-7}
3.494×10^{-2}	5.021×10^{-8}	6.451×10^{-2}	6.663×10^{-2}	2.839×10^{-2}	3.487×10^{-2}	3.291×10^{-3}	7.509×10^{-5}	1.150×10^{-7}	6.877×10^{-8}
3.763×10^{-2}	4.592×10^{-8}	7.392×10^{-2}	7.663×10^{-2}	3.352×10^{-2}	3.946×10^{-2}	3.571×10^{-3}	7.821×10^{-5}	1.150×10^{-7}	6.607×10^{-8}
6.586×10^{-2}	3.086×10^{-8}	1.747×10^{-1}	1.825×10^{-1}	9.272×10^{-2}	8.384×10^{-2}	5.865×10^{-3}	9.991×10^{-5}	1.150×10^{-7}	5.205×10^{-8}
9.139×10^{-2}	2.938×10^{-8}	2.554×10^{-1}	2.653×10^{-1}	1.429×10^{-1}	1.151×10^{-1}	7.212×10^{-3}	1.105×10^{-4}	1.150×10^{-7}	4.727×10^{-8}
1.089×10^{-1}	2.497×10^{-8}	3.494×10^{-1}	3.644×10^{-1}	2.056×10^{-1}	1.501×10^{-1}	8.559×10^{-3}	1.201×10^{-4}	1.150×10^{-7}	4.374×10^{-8}
1.331×10^{-1}	2.341×10^{-8}	4.570×10^{-1}	4.758×10^{-1}	2.788×10^{-1}	1.870×10^{-1}	9.854×10^{-3}	1.285×10^{-4}	1.150×10^{-7}	4.112×10^{-8}

Figure A-28: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 25°C in 10.75 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G_m^o / RT$ value for ThF_4(cr, hyd) of $-(813.06 \pm 4.16)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.

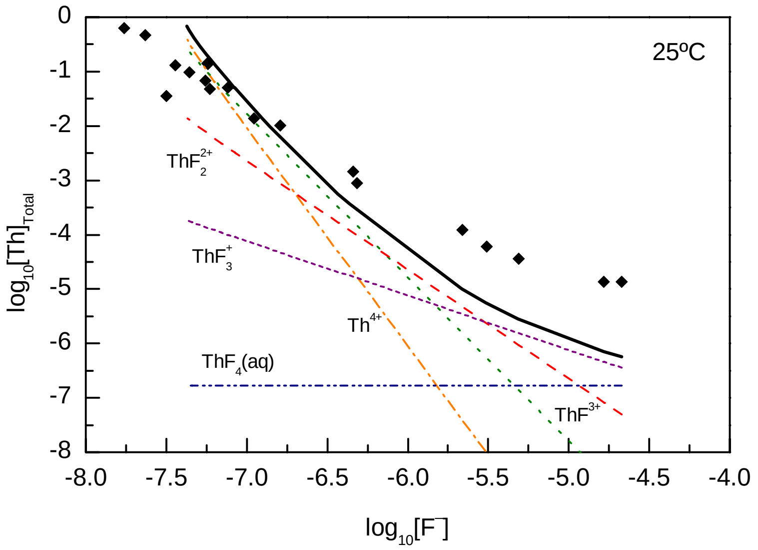
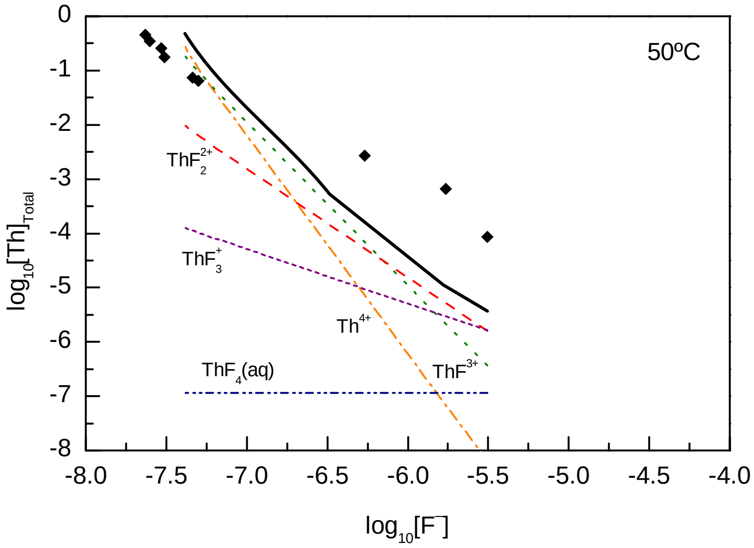


Figure A-29: Experimental ([1981SMI/MES]) and predicted concentrations for ThF_4(cr, hyd) at 50°C in 10.75 m HNO_3 solutions. Predictions based on NONLINT-SIT calculations using thermodynamic model summarised in Tables VIII-8 and VIII-9 with $\Delta_f G^o_m / RT$ value for ThF_4(cr, hyd) of $-(813.45 \pm 4.90)$. Predicted values are identical whether the species ThF_6^{2-} is included or excluded from modelling, since this species is not significant in this chemical system.



[1981SUR/MIL]

Milić [1981MIL2] and Šuranji and Milić [1981SUR/MIL], [1982SUR/MIL] investigated the hydrolytic behaviour of thorium(IV) in various aqueous chloride media at 25°C. These papers are discussed together, *cf.* Appendix A review of [1981MIL2].

[1982BOR/BOR2]

This study was centred on the determination of the enthalpies of formation of the various compounds found in the Th-Bi system. X-ray data and metallographic analyses were also reported.

Thorium metal and bismuth powders of nominal purities 99.8% and 99.999%, respectively, were used and the various alloys were prepared by induction melting the required amounts of thorium and bismuth in tantalum crucibles. Handling the samples and welding of the crucibles were conducted under argon atmosphere.

As shown in Table X-6, Section X.5.1 the reported structures and lattice parameters of the compounds Th_3Bi_4 and $ThBi_2$ confirmed earlier literature results; in addition, new structural data were given for the compounds Th_5Bi_3 and ThBi. However, the authors noted that the ThBi(cr) may be metastable, and that the Th_5Bi_3(cr) phase may be stabilised by minor impurities, like some other phases with this structure.

Use was made of an isoperibol aneroid calorimeter assembly in which the alloys are prepared directly. The instrument had been described previously by the same group [1974CAP/FER]; its performance has been checked with alloy systems of which the enthalpies of formation were already reported in the literature. Results of the measurement at 300 K of the enthalpy of formation of 13 Th-Bi alloys ranging from$Th_{0.2}Bi_{0.8}$ to $Th_{0.75}Bi_{0.25}$ were reported. The reaction was found to be incomplete in the measurements of five further alloys. The following enthalpies of formation, consistent with the formation of the four compounds given above, were derived: $\Delta_f H_m$ (Th_5Bi_3, cr, 298.15 K) = −(532.2 ± 16.7) kJ·mol^{-1}, $\Delta_f H_m$ (ThBi, cr, 298.15 K) = −(162.3 ± 4.2) kJ·mol^{-1}, $\Delta_f H_m$ (Th_3Bi_4, cr, 298.15 K) = −(597.5 ± 14.6) kJ·mol^{-1}, and $\Delta_f H_m$ ($ThBi_2$, cr, 298.15 K) = −(207.1 ± 6.3) kJ·mol^{-1}. The uncertainty limits reported by the authors appear in line with the performances of the calorimetric assembly. Using their results and earlier available data, the authors propose a tentative phase diagram for the Th-Bi system.

[1982FIN]

The author used a three parameter fit of the enthalpy up to the λ-transition, taken to be at 2950 K from the work of [1981FIS/FIN]. This equation is based on lattice (Einstein) and thermal expansion (plus anharmonic) contributions:

$$H_m(T) - H_m^\circ(298.15\,\text{K}) = C_1\theta / (e^{\theta/T} - 1) + C_2 T^2 + \text{constant}$$

with C_1 = 68.654 J·K^{-1}·mol^{-1}, θ = 408.14 K and $C_2 = 4.8174 \times 10^{-3}$ J·K^{-2}·mol^{-1} and the constant (−9988 J·mol^{-1}) is determined from $H_m(T) - H_m^\circ(298.15\,\text{K}) = 0$.

This expression fits the enthalpy and heat capacity data very well, and merges with the low temperature heat capacity data of [1953OSB/WES], since a constraint on $C_{p,m}^\circ$ at 298.15 K was imposed in the fitting. These data agree very well with those selected by this review. The data at higher temperatures (> 2900 K) are not entirely consistent with the enthalpy calculated from the $C_{p,m}^\circ$ measurements of [1996RON/HIE], who showed that the transition is second order, with a peak in the heat capacity at (3090 ± 10) K, as discussed in Section VII.1.2.

[1982JOL/THO]

The authors have used the known structure data and discuss the effect of the bidentate coordination of the carbonate ligand on the splitting of the ν_3(E) vibration frequency. There are no thermodynamic data in this study.

[1982MIL/SUR2]

This potentiometric study of the hydrolysis of Th^{4+} in $NaNO_3$ solutions provides all experimental details and follows the approach of the Sillén school both with regards to experimental technique and data analysis. The experiments have been made at 25.0°C using six different total concentrations of Th, from 2.5 to 100 mM. The $-\log_{10}[\mathrm{H}^+]$ range investigated was 1.5 to 3.5 and the corresponding $\bar{n}_{\mathrm{OH}}$ values vary from 0 to 0.35 − 0.40. The reversibility of the titrations were tested at $[\mathrm{Th}]_{\mathrm{tot}}$ = 2.5 and 10 mM. Three different complexes were proposed, $\mathrm{Th_2(OH)_2^{6+}}$, $\mathrm{Th_3(OH)_5^{7+}}$ and $\mathrm{Th_6(OH)_{15}^{9+}}$; their equilibrium constants, $\log_{10}{}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$, were determined at six different total concentrations of the NaNO$_3$ ionic medium as shown in Table A-60. The large uncertainty in the determination of the equilibrium constant for the (15,6) complex is due to the small maximum value of $\bar{n}_{\mathrm{OH}}$.

Table A-60: Equilibrium constants $\log_{10}{}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}) \pm 3\sigma$ for the hydrolysis reactions of Th^{4+} in (Na)NO$_3$ ionic media. For some of the values of $\log_{10}{}^{*}\beta_{15,6}$ only a range of values could be given; the uncertainty of these values is estimated to 0.5 by this review.

(Na)NO$_3$ medium (M)	$-\log_{10}{}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}) \pm 3\,\sigma$		
	$\mathrm{Th_2(OH)_2^{6+}}$	$\mathrm{Th_3(OH)_5^{7+}}$	$\mathrm{Th_6(OH)_{15}^{9+}}$
0.5	5.06 ± 0.07	12.59 ± 0.12	38.06 ± 0.23
1.0	5.08 ± 0.06	13.04 ± 0.15	39.56 − 39.41
1.5	5.14 ± 0.05	13.30 ± 0.16	40.47 − 40.13
2.0	5.16 ± 0.04	13.61 ± 0.16	41.10 − 40.83
2.5	5.18 ± 0.03	13.79 ± 0.15	41.77 − 41.42
3.0	5.19 ± 0.02	14.23 ± 0.17	42.32 ± 0.23

The authors have described the variation of the equilibrium constants in the different ionic media using a linear correlation between $-\log_{10}{}^{*}\beta_{n,m}$ and a "medium factor" that is not defined but that depends on the ionic medium concentration and the hydration energy of its ions. They have used the same method to compare them with the data in 3 M (Li)NO$_3$, (Na)NO$_3$, (K)NO$_3$ and 4 M (Na)NO$_3$. This review prefers to analyse the data using the specific ion interaction theory. Use of solely of the results of [1982MIL/SUR2] in 0.5 − 3.0 M NaNO$_3$ gives the following values:

$$\log_{10}{}^{*}\beta^{\mathrm{o}}_{2,2} = -(6.13 \pm 0.10) \qquad \Delta\varepsilon(2,2) = (0.18 \pm 0.05)\ \mathrm{kg\cdot mol^{-1}},$$

$$\log_{10}{}^{*}\beta^{\mathrm{o}}_{5,3} = -(13.5 \pm 0.2) \qquad \Delta\varepsilon(5,3) = (0.57 \pm 0.07)\ \mathrm{kg\cdot mol^{-1}},$$

$$\log_{10}{}^{*}\beta^{\mathrm{o}}_{15,6} = -(37.4 \pm 0.6) \qquad \Delta\varepsilon(15,6) = (1.37 \pm 0.17)\ \mathrm{kg\cdot mol^{-1}},$$

The value of $\log_{10}{}^{*}\beta^{\mathrm{o}}_{2,2}$ in 4 M (Na)NO$_3$ calculated by assuming that the SIT can be used at this high ionic strength is equal to − 5.56, in good agreement with the experimental value in [1968DAN/MAG].

[1982SUR/MIL]

Milić [1981MIL2] and Šuranji and Milić [1981SUR/MIL], [1982SUR/MIL] investigated the hydrolytic behaviour of thorium(IV) in various chloride media at 25°C. These papers are discussed together, *cf.* Appendix A review of [1981MIL2].

[1982WAG/EVA]

This is a comprehensive compilation of thermodynamic data that has been supplemented by an erratum [1989COX/WAG]. The present comments on this publication pertain only to the thorium sulphate system. Wagman *et al.* [1982WAG/EVA] report $\Delta_f G_m^o$ for the complexes $ThSO_4^{2+}$, $Th(SO_4)_3^{2-}$ and $Th(SO_4)_4^{4-}$ and for $Th(SO_4)_2(cr)$. These data along with other data presented in this compilation provide 5.44, 10.46, 8.44, respectively, for the $\log_{10} \beta^o$ values of equilibrium constants for the following reactions:

$$Th^{4+} + SO_4^{2-} \rightleftharpoons ThSO_4^{2+}$$

$$Th^{4+} + 3SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$$

$$Th^{4+} + 4SO_4^{2-} \rightleftharpoons Th(SO_4)_4^{4-}$$

The reported values also provide a $\log_{10} K^o$ value of -9.89 for the following reaction:

$$Th(SO_4)_2(cr) + SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$$

The exact origin of these data is not known, but the most likely source of the data for $Th(SO_4)_3^{2-}$ and $Th(SO_4)_4^{4-}$ is the solvent extraction study of [1963ALL/MCD] conducted at relatively concentrated Na_2SO_4 solutions of variable molality. It is difficult to extrapolate values for highly charged species from concentrated electrolytes without the use of proper models for concentrated electrolytes; in fact when electrolyte models (Pitzer and SIT, see [1992FEL/RAI] and this review) suited for concentrated solutions are used, the data in [1963ALL/MCD] are very well described if the $Th(SO_4)_4^{4-}$ species is omitted from the model (see Figure IX-2).

Most of the available studies on this system show that the species $Th(SO_4)_2(aq)$ is important (see Sections IX.1.3.2.1 and IX.1.3.3), but this species was apparently not included in the assessment by [1982WAG/EVA].

Felmy and Rai [1992FEL/RAI] point out that the calculated solubility of $Th(SO_4)_2(cr)$ based on the thermodynamic data quoted in [1982WAG/EVA] are many orders of magnitude lower than those based on experimental data they quote, indicating serious errors in the data reported in [1982WAG/EVA]. For these reasons, the thermodynamic data reported in this compilation are not accepted by this review.

[1983BRO/ELL]

This potentiometric study has been made at 25°C in a 0.10 M KNO_3 ionic medium. The experimental procedure is only briefly described, but based on the previous publications of these authors we assume that it is satisfactory. Four different total concentrations of Th(IV) have been used, 0.196, 0.490, 0.980 and 1.960 mM in the $-\log_{10}[H^+]$ range 3.14−4.03 covering $\bar{n}_{OH}$ up to 2.5. The authors have analysed the data using MINIQUAD, a least-squares program that allows independent minimisation of two experimental quantities. The experimental data result in the following species and equilibrium constants:

$$\log_{10} {}^*\beta_{1,1} = -(2.98 \pm 0.01)$$
$$\log_{10} {}^*\beta_{12,4} = -(30.55 \pm 0.03)$$
$$\log_{10} {}^*\beta_{15,6} = -(34.41 \pm 0.03).$$

They have also tested a number of the species proposed by Hietanen and Sillén [1964HIE/SIL], [1968HIE/SIL], and by Baes *et al.* [1965BAE/MEY], [1976BAE/MES] and find that they do not improve the chemical model. There are surprisingly large differences between the chemical model proposed in this study and those in previous investigations and the authors suggest that the low ionic strength may be one possible reason for this. This review accepts this suggestion because there is no evidence for flaws in the experimental procedures and data analysis. We can test this assumption by making a speciation calculation at ionic strength 0.1 M using the SIT and the equilibrium constant for $Th_2(OH)_2^{6+}$ from [1982MIL/SUR2]. The result is that $Th_2(OH)_2^{6+}$ is *not* present in significant amounts in the test solutions used by Brown and Ellis. There is thus no contradiction between their experimental results and those of previous investigations claiming the presence of $Th_2(OH)_2^{6+}$.

Their equilibrium constant $\log_{10} {}^*\beta_{1,1} = -(2.98 \pm 0.01)$ differs considerably from the values proposed by [1954KRA/HOL] and [1965BAE/MEY]; it is also inconsistent with that suggested by [1968HIE/SIL] but compatible with the value in [2000EKB/ALB]. We can recalculate the equilibrium constant for the (15,6) complex in 0.1 M KNO_3 to 3 M $NaNO_3$ by using SIT and the value of $\Delta\varepsilon(15,6) = (1.4 \pm 0.2)$ $kg\cdot mol^{-1}$ from [1982MIL/SUR2]; we obtain $\log_{10} {}^*\beta_{15,6} = -(39.2 \pm 0.7)$, in poor agreement with the value $\log_{10} {}^*\beta_{15,6} = -(42.32 \pm 0.23)$ from [1982MIL/SUR2].

[1984AMO/BLA2]

The heat capacities of the non-magnetic oxychalcogenides ThOS(cr) and ThOSe(cr) and of the isomorphous antiferromagnetic UOS(cr) and UOSe(cr) were measured from *ca.* 5 to *ca.* 300 K. The samples were prepared by mixing stoichiometric amounts of the dioxides and disulphides and annealed *in vacuo* in silica tubes at 1273 K for three days. X-ray diffraction analysis of the thorium compounds showed the expected PbFCl structure. For ThOS, a weak extra line due to ThO_2 was detected, and for ThOSe, several non-identified very weak extra lines were found. For the adiabatic heat capacity measurements, the samples were mixed with silver powder, or held in a silver cage, to improve heat conduction. The thorium compounds showed no peaks in the heat capacity curves. The derived values for the heat capacity and entropy at 298.15 K were $C^{\circ}_{p,\mathrm{m}}$ (ThOS, cr, 298.15 K) = (67.25 ± 1.35) J·K^{-1}·mol^{-1}, S°_{m} (ThOS, cr, 298.15 K) = (76.3 ± 1.5) J·K^{-1}·mol^{-1} and $C^{\circ}_{p,\mathrm{m}}$ (ThOSe, cr, 298.15 K) = (72.65 ± 1.50) J·K^{-1}·mol^{-1} , S°_{m} (ThOSe, cr, 298.15 K) = (93.5 ± 1.9) J·K^{-1}·mol^{-1}. By a comparison of the data for the thorium and uranium compounds, values of the entropy of ordering (close to R·ln 2) and Schottky contributions to the heat capacity were calculated for the uranium compounds.

[1984EDV/LAG]

Detailed spectral analysis gave the molecular constants for two new excited states of ThO(g). A concise table is given of the 16 excited states of ThO(g) known at that time.

[1984NAK/ZIM]

The hydrolysis of Th(IV) has been investigated at 25°C in 0.50 M KNO_3 using liquid-liquid extraction technique over the pH range 1.5 to 3.8. Tri-n-butyl phosphate (30 vol.% TBP in dodecane) is used as the extractant; the total concentration of Th(IV) was 10 mM. Under the experimental conditions of this study, neither the extraction of Th nor the co-extraction of HNO_3 has a significant effect on the free TBP concentration in the organic phase. The experiments appear well conducted, but there are only eight experimental points, of which three have been used to determine the equilibrium constant $\log_{10}{}^{*}\beta_{1,1} = -(3.28 \pm 0.1)$ for the formation of $Th(OH)^{3+}$ in the reaction:

$$\mathrm{Th^{4+} + H_2O(l) \rightleftharpoons Th(OH)^{3+} + H^+}.$$

The authors assume that the concentration of polynuclear complexes can be neglected; the following speciation diagram (Figure A-30) demonstrates that this is a reasonable approximation when the hydrogen ion concentration is higher than 5 mM. The uncertainty in $\log_{10}{}^{*}\beta_{1,1}$ has been estimated by this review.

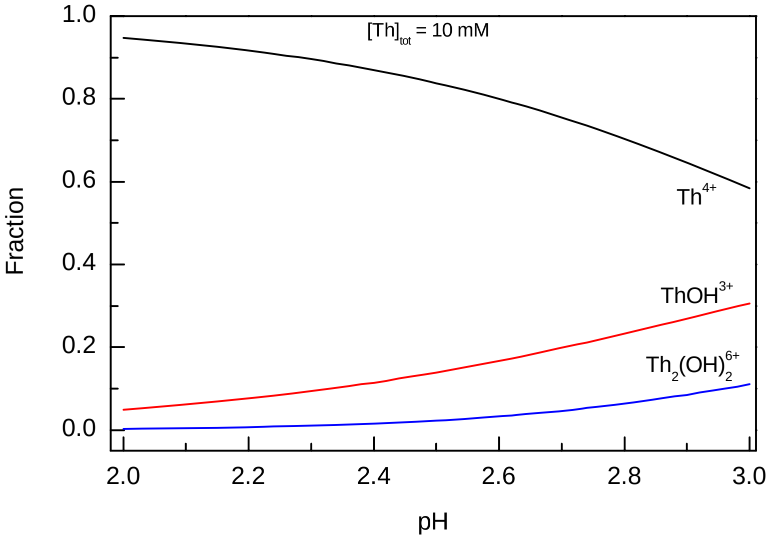
[1985EDV/LAG]

Detailed spectral analysis gave the molecular constants for three new excited states of ThO(g), at 19050, 20062 and 24036 cm^{-1} which have been included in the calculation of the thermal function (*cf.* [1985EDV/LAG2] and subsequent papers by Edvinsson and colleagues).

[1985EDV/LAG2]

A new low-lying excited state designated Q was found in ThO(g). Analyses of transitions from previously known excited states to this Q state have made it possible to accurately relate the G, H, O, and P states to the ground state. A concise table giving the 17 excited states of ThO(g) known at that time, supplemented by later studies, is the basis for the calculation of the thermal functions of ThO(g).

Figure A-30: Speciation diagram for the Th(IV)-water system in 0.5 M KNO_3 and 25°C.



[1985LIV/MUS]

The paper is a careful Raman spectroscopic study of the complex formation in the Th(IV)-thiocyanate system. The experiments have been made in a mixed SCN^-/ClO_4^- ionic medium where the ionic strength varies. The total concentration of Th(IV) is high, the paper referring to spectra with concentrations 0.275 and 0.50 M. It is not clear from the paper how many different SCN^- concentrations were used to determine the four equilibrium constants reported; the highest concentration mentioned in the paper is 1.46 M. The analysis of the data is straightforward due to the fairly large changes in the ν(C−S) frequency, from 751 to 812 cm^{-1}, between free and coordinated SCN^-. As the ionic medium is not constant and the paper does not contain information on the composition of the test solutions used, it is not possible to evaluate the reliability of the concentration constant given in [1985LIV/MUS]. This review notes that the difference between the consecutive equilibrium constants reported is surprisingly small. Because of the paucity of experimental detail this review can only conclude that the Raman data provides independent information of complex formation in the Th(IV)-thiocyanate system and in addition that the thiocyanate ligand is coordinated at the nitrogen end, as expected for a hard acceptor like Th^{4+}.

Complex	Equilibrium constant β_n / M^{-n}
$Th(SCN)^{3+}$	4.0 ± 0.6
$Th(SCN)_2^{2+}$	5.0 ± 0.1
$Th(SCN)_3^{+}$	5.4 ± 0.1
$Th(SCN)_4$	1.4 ± 0.1

[1986DAV/TOR2]

Davydov and Toropov [1986DAV/TOR2] point out that there are large discrepancies between the published equilibrium constants for the first mononuclear Th(IV) hydroxide complex $Th(OH)^{3+}$ from potentiometric and solubility studies. For these reasons they used different experimental methods, cation exchange and colorimetry in the pH range 1.0−4.0, to determine $^*\beta_{1,1}$ ($Th(OH)^{3+}$) at (20 ± 2)°C and $I = 0.1$ M in both nitrate and perchlorate media. To avoid interference of polynuclear species the studies were performed at low total thorium concentrations of 2×10^{-5} to 1×10^{-4} M. Dialysis studies confirmed the absence of large polynuclear Th(IV) complexes and also that there were no artefacts from sorption of Th(IV) on foreign colloids present in the solutions investigated. The formation of thorium colloids at pH > 4.0, shown by dialysis through a cellophane membrane, did not allow them to extend the studies on hydrolysis at $[Th]_{tot} = 2 \times 10^{-5}$ to 1×10^{-4} M to higher pH. The latter observation is in accord with the equilibrium constants selected in the present review, *i.e.*, colloid formation above the solubility limit of ThO_2(am, hyd).

The cation exchange experiments were performed with KU-2 cation exchange resin (equilibration time: 7 days) in HNO_3-$NaNO_3$ solutions, the colorimetric studies with Arsenazo III in both HNO_3-$NaNO_3$ and $HClO_4$-$NaClO_4$ media and with Thoron I in HNO_3-$NaNO_3$ solutions. The pH values were adjusted by dilution of the stock solutions with 0.1 M HNO_3 or 0.1 M $HClO_4$ and addition of NH_3 solution and measured with a glass electrode. Details on the electrode calibration are not reported.

Neither the distribution coefficients K_d nor the optical density (absorption) in the colorimetric studies showed noticeable changes in the pH range 1.0−3.0. The observed changes from pH 3.0 to pH 4.0 were ascribed exclusively to the reaction:

$$Th^{4+} + H_2O(l) \rightleftharpoons Th(OH)^{3+} + H^+$$

Assuming that only Th^{4+} (but not $Th(OH)^{3+}$ or other hydrolysis species) is sorbed onto the cation exchange resin material and that only Th^{4+} forms complexes with the organic reagents used in the colorimetric studies, the following conditional equilibrium constants at (20 ± 2)°C are calculated from the colorimetric studies:

$^*\beta_{1,1} = (3.6 \pm 1.2) \times 10^{-5}$ M^{-1}	Arsenazo III, $I = 0.1$ M (HNO_3-$NaNO_3$ and $HClO_4$-$NaClO_4$)
$^*\beta_{1,1} = (5.2 \pm 1.2) \times 10^{-5}$ M^{-1}	Thoron I, $I = 0.1$ M (HNO_3-$NaNO_3$)

The cation exchange experiment at I = 0.1 M (HNO_3-$NaNO_3$) is not explicitly evaluated; however, it is claimed to confirm the colorimetric results. Further series of cation exchange experiments were performed at constant pH values of 1.0, 2.0 and 3.0 and varying $NaNO_3$ concentration. From the slopes of (3.8 ± 0.4) when $\log_{10}K_d$ is plotted against $\log_{10} a_{Na^+}$ in the range −0.3 to −0.6 the authors concluded that the Th^{4+} ion is the predominant aqueous thorium species up to pH 3. A closer look at Figure 2 in [1986DAV/TOR2] shows that the slopes decrease from pH 1 to pH 3. Moreover, it is by no means ascertained that $Th(OH)^{3+}$ or other hydrolysis species are not sorbed onto the cation exchange resin (*cf.* discussion of [1967BER]) and that they do not form complexes with the organic reagents Arsenazo III or Thoron I. This might explain the very low hydrolysis constant obtained by Davydov and Toropov [1986DAV/TOR2]. The mean value, $\log_{10}{}^*\beta_{1,1}(Th(OH)^{3+}) = -(4.36 \pm 0.14)$ at I = 0.1 M and (20 ± 2)°C, corresponding to $\log_{10}{}^*\beta^{\circ}_{1,1} = -(3.7 \pm 0.2)$ if extrapolated to $I = 0$ with the SIT, is 0.7−1.5 $\log_{10}$ units lower than the values from studies accepted by this review. It is not included in the selection of data for thorium hydroxide complexes.

In a later paper of Davydov and Toropov [1992DAV/TOR], the formation of polynuclear Th(IV) hydroxide complexes is studied at total thorium concentrations of $[Th]_{tot} = 2\times10^{-4}$ to 1×10^{-2} M at pH 3.0−4.5 in 0.1 M HNO_3-NH_4NO_3 and 0.1 M $HClO_4$-NH_4NO_4 media by means of dialysis, centrifugation and spectrophotometry (colorimetry). The authors report the formation of binuclear hydroxide complexes under these conditions. They did not observe an influence of the background medium, either nitrate or perchlorate.

This later paper of Davydov and Toropov [1992DAV/TOR] seems to be an extension of their earlier study [1986DAV/TOR2] at $[Th]_{tot}$ = to 2×10^{-5} to 1×10^{-4} M and pH = 1.0−4.0 to solutions of higher Th concentrations and pH values up to 4.5. Numerical values of equilibrium constants for polynuclear complexes are not given in [1992DAV/TOR]. No evaluation was possible as only the abstract was available to the reviewers.

[1986FLE/KNA]

The sublimation pressure of ThI_4(cr) was measured by mass-loss Knudsen effusion (617 to 760 K) and mass spectrometry, in separate studies. The latter confirmed that the sublimation of ThI_4 is accompanied by a small (5 − 10%) dissociation to a lower iodide and iodine.

In the effusion measurements, there was a significant effect of orifice size, and their pressures were extrapolated to zero orifice size (but without taking into account the presence of the small amount of iodine in the vapour). Although the authors indicate that the reproducibility of the raw measurements was rather poor, the extrapolated results agree well with earlier studies, see Section VIII.4.1.4.

The dissociation pressure for the reaction $2ThOI_2(cr) \rightleftharpoons ThO_2(cr) + ThI_4(g)$ was also determined gravimetrically; again an orifice size effect was observed and the appropriate correction made.

The enthalpy of ThI_4(cr, l), contained in nickel, was also measured in a drop calorimeter from 350 to 1030 K. However, very small samples (*ca*. 0.5 g of both ThI_4 and Ni) were used, so it is not surprising that the results, especially for the liquid, are rather scattered. The enthalpy associated with the nickel capsule was not measured independently, but taken from thermochemical tables [1977BAR/KNA]. The molar heat capacity of ThI_4(cr) was calculated to be 146 $J\cdot K^{-1}\cdot mol^{-1}$ and the enthalpy of fusion to be *ca.* 48 $kJ\cdot mol^{-1}$. The results from the measurements of the liquid were too scattered to allow any reliable value of its heat capacity to be derived, but were consistent with the value of 176 $J\cdot K^{-1}\cdot mol^{-1}$ estimated in [1975RAN]. The melting point of ThI_4(cr) was determined to be (839 ± 2) K, from eight different samples.

[1986WAR/KLE]

This is a summary and assessment of the thermodynamic data of elemental thorium, part of a wider review of all the actinide metals. As noted in Section V.1.2, the values from their assessment are very similar to that of [1982GLU/GUR], except for one notable difference.

Ward *et al*. [1986WAR/KLE] quote S°_{m} (Th, cr, 298.15 K) = 52.64 $J\cdot K^{-1}\cdot mol^{-1}$, from [1980NAK/TAK], whereas the value given by [1982GLU/GUR] (and [1989COX/WAG]) is (51.83 ± 0.50) $J\cdot K^{-1}\cdot mol^{-1}$. As noted in Section V.2.1, this review has investigated this discrepancy in detail and recommends another procedure for estimating the poorly defined heat capacities of Th(cr) between 4 and 20 K, which gives precisely the same value of S°_{m} (Th, cr, 298.15 K), 52.64 $J\cdot K^{-1}\cdot mol^{-1}$, as that of [1986WAR/KLE].

[1987BRU/CAS2]

This paper reports potentiometric measurements in the Th(IV)-H_2O-CO_2(g) system at 25°C in 3.0 M $NaClO_4$ under CO_2(g) partial pressures of 0, 0.29 and 0.97 bar. The experimental procedures and conditions were the same as those reported in an extended later study [1991GRE/LAG2], where the data evaluation was discussed more detailed. Therefore the present review does not further consider the preliminary and brief discussion in [1987BRU/CAS2] but only the more detailed discussion and data evaluation in [1991GRE/LAG2].

[1987EDV/LAG]

Four new systems in the molecular spectrum of ThO(g) were rotationally analysed. The molecular constants for the new states are given. However, two of these, the interrelated Y and W states, cannot as yet be placed in the term scheme.

[1987JOA/BIG2]

The equilibrium constants for the formation of complexes between Th^{4+} and $EDTA^{4-}$ and carbonate were determined using a liquid-liquid extraction technique at 20ºC with benzoylacetone and tributylphosphate (TBP) as the extraction ligands. The experiments were made at two different ionic strengths, 1.0 and 2.5 M (guanidinium carbonate ionic media). The complex formation between Th(IV) and EDTA was also determined and used to estimate the equilibrium constants in the Th(IV)-carbonate system as described in detail by Joâo *et al.* [1987JOA/BIG2]. The binary Th(IV)-EDTA system was studied at a total concentration of EDTA = 2.00 mM and pH varying between 10.49 and 10.55, using ammonia and ammonium nitrate to establish the pH and guanidinium nitrate to make up the ionic strength. TBP was used as a synergistic reagent to increase the distribution coefficient of the uncharged $Th(benzoylacetonate)_4$ complex. The carbonate study was made at one carbonate concentration using a test solution containing $[CO_3^{2-}] = [HCO_3^-] = 0.26$ M (at $I = 1.04$ M) and $[CO_3^{2-}] = [HCO_3^-] = 0.50$ M (at $I = 2.50$ M). The pH in these two sets of experiments was constant at 10.18 and 10.22, respectively, at $I = 1.0$ and 2.5 M. The total concentration of Th(IV) in the experiment was 1.12 mM. Under the conditions used, there is no significant dissociation of the benzoylacetone and it seems reasonable to assume that this ligand does not form ternary Th(IV)-carbonate-benzoylacetonate complexes in aqueous solution. The situation is less obvious for the formation of other ternary complexes, such as Th(IV)-EDTA-hydroxide and Th(IV)-carbonate-hydroxide complexes. The equilibrium constant for the reaction

$$\mathrm{Th(EDTA)(aq) + H_2O(l) \rightleftharpoons Th(EDTA)(OH)^- + H^+} \qquad (A.74)$$

at $I = 0.1$ M is known ($\log_{10} K = -7.2$) [1989SMI/MAR]. Recalculation to $I = 1.0$ gives $\log_{10} K = -7.24$, indicating that $Th(EDTA)(OH)^-$ is the predominant complex at the pH of 10.2 used by Joâo *et al.* Their data have therefore been reanalysed. The experimental data on the U(IV)-carbonate system [1989BRU/GRE] indicates that ternary hydroxide-carbonate complexes are not formed in significant amounts under the conditions used in [1987JOA/BIG2]; this is presumably also the case for the corresponding Th(IV) system as discussed in this review.

Joâo *et al.* [1987JOA/BIG2] analysed the experimental distribution data assuming the following reactions in the aqueous phase

$$\mathrm{Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-}}\ ; \qquad (A.75)$$

and

$$\mathrm{Th^{4+} + EDTA^{4-} \rightleftharpoons Th(EDTA)(aq)};\qquad (A.76)$$

The ratio between the experimental distribution coefficients in the carbonate and EDTA systems, D^C and D^Y (with the same notation as in [1987JOA/BIG2]) is

$$\frac{D^C}{D^Y} = \frac{\beta_1^Y[\mathrm{EDTA}]}{\beta_5^C[\mathrm{CO_3^{2-}}]^5} \times \left([\mathrm{H}_Y^+]/[\mathrm{H}_C^+]\right)^4 \qquad (A.77)$$

where β_5^C and β_1^Y are the equilibrium constants for Eqs. (A.75) and (A.76). Joâo *et al.* [1987JOA/BIG2] report $\log_{10}\beta_5^C$ = (26.2 ± 0.2) and (26.3 ± 0.3) at I = 1.0 and 2.5 M, respectively. However, these values are not accepted by the present review, because, as noted earlier, at the pH used the predominant reaction in the EDTA system is

$$\mathrm{Th^{4+} + EDTA^{4-} + H_2O(l) \rightleftharpoons Th(EDTA)(OH)^- + H^+}; \tag{A.78}$$

The equilibrium constant is

$$\frac{[\mathrm{Th(EDTA)(OH)^-}][\mathrm{H^+}]}{[\mathrm{Th^{4+}}][\mathrm{EDTA}]} = K_{111} \tag{A.79}$$

The known equilibrium constants of Eqs. (A.74) and (A.76) [1989SMI/MAR] then give $\log_{10}K_{111}$ = 22.3 − 7.24 = 15.06. Equation (A.77) must then be modified as follows:

$$\frac{D^C}{D^Y} = \frac{K_{111}^Y[\mathrm{EDTA}]/[\mathrm{H}_Y^+]}{\beta_5^C[\mathrm{CO_3^{2-}}]^5} \times \left([\mathrm{H}_Y^+]/[\mathrm{H}_C^+]\right)^4 \tag{A.80}$$

At the given pH of the experiment at ionic strength 1.0 M, the conditional equilibrium constant to be used in Eq. (A.77) is $\log_{10}K_{111}{}^{\mathrm{cond}} = \log_{10}K_{111}$ + pH = 15.06 + 10.18 = 25.24. Hence, the correct value of $\log_{10}\beta_5$ is 28.3 at I = 1.0 M. This review has accepted the uncertainty of ±0.2 in $\log_{10}\beta_5^C$ proposed in [1987JOA/BIG2]. As the experiments described in [1987JOA/BIG2] were made at constant pH, their slope analysis is not affected by the erroneous composition of the Th(IV) EDTA complex. The recalculated value of $\log_{10}\beta_5{}^{\mathrm{C}}$ differs significantly from that proposed by Joâo *et al.* [1987JOA/BIG2] at I = 1.0 M, $\log_{10}\beta_5^C$ = (26.2 ± 0.2). Östhols *et al.* [1994OST/BRU] have also recalculated the equilibrium constant for the formation of $\mathrm{Th(CO_3)_5^{6-}}$ using the experimental data in [1987JOA/BIG2] and the equilibrium constant for the formation of $\mathrm{Th(EDTA)(OH)^-}$ from [1989SMI/MAR], valid at I = 0.1 M, and found $\log_{10}\beta_5$ = 33.2 at I = 0.5 M. However, it is not clear how this value was obtained and it has therefore not been considered by the present review. The value $\log_{10}\beta_5$ = 28.3 at I = 1.0 M, obtained as described above, is much lower than the selected value of (31.0 ± 0.7) which consistently describes both the EXAFS data in [1997FEL/RAI] and [2006ALT/NEC] and the solubility data involving $\mathrm{Na_6Th(CO_3)_5{\cdot}12H_2O(s)}$ [1961LUZ/KOV2], [1973DER/FAU3] and $\mathrm{ThO_2}$(am, hyd) [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC], [2006ALT/NEC]. With the value of $\log_{10}\beta_5$ = 28.3 from Joâo *et al.* [1987JOA/BIG2] the pentacarbonate complex would not become predominant – see Figures XI-7 and XI-8 in Section XI.1.3.3.

Since the interaction coefficients between $\mathrm{Th^{4+}}$ and $\mathrm{CO_3^{2-}}$ and $\mathrm{HCO_3^-}$ and those between the guanidinium cation and the anions $\mathrm{CO_3^{2-}}$ and $\mathrm{Th(CO_3)_5^{6-}}$ are not known, the recalculated value of $\log_{10}\beta_5$ = 28.3 in guanidinium carbonate solution (I = 1.0 M) cannot be extrapolated to zero ionic strength, but as the Δz^2 term in the SIT equation is equal to zero we may assume that the corresponding $\log_{10} \beta_5^{\circ}$ value differs by less than ± 1.0 from the value at I = 1.0 M.

[1987OET/PET]

Well characterised thorium metal, whose principal impurities were 0.16 at% C, 0.02 at% O and 0.015 at% N, was used in 83 measurements of the enthalpy difference $H_{\mathrm{m}}(T) - H_{\mathrm{m}}^{\circ}(298.15\,\mathrm{K})$ from 302.6 to 694.9 K, with a reproducibility of *ca.* 1% (2σ). The values were adjudged by the authors to be accurate to within 0.2%, based on similar measurements on a sample NBS/NIST standard reference molybdenum. The results were close to the laser flash measurements of [1980NAK/TAK] and thus to the values selected in this review.

[1987RYA/RAI]

Ryan and Rai [1987RYA/RAI] note that there is contradictory information in the literature on the possible formation of anionic complexes $\mathrm{Th(OH)}_5^-$; their own solubility studies on other actinides, reviewed in [2003GUI/FAN] very clearly indicate that the hydrous oxides of tetravalent actinides are not amphoteric. To settle the matter they have performed a solubility study of hydrous thorium oxide over a broad pH range, where the hydroxide concentration extends to 1.38 M. The experiments have been made at 25°C in a 0.1 M $\mathrm{NaClO_4}$ ionic medium, except at pH > 11 where the hydroxide concentration and accordingly the ionic strength, varies by the use of tetraethylammonium hydroxide or lithium hydroxide. The experiments are described in detail and care has been taken to separate the solid phase, part of which is in colloidal form, from the solution. The thorium concentration was measured by neutron activation analysis after centrifugation and ultrafiltration of samples equilibrated for 7 − 27 days. There is no indication of a variation in solubility from pH 6 up to the highest hydroxide concentration. However, the measured solubility $10^{-9} - 10^{-10}$ M is close to the detection limit of the analytical method used. These data support the assumption that anionic hydroxide complexes are not formed in this system.

The authors note that the slope − 5.5 of the initial part of the solubility curve indicates the formation of polynuclear complexes with charge Z > 4, because the species $\mathrm{Th(OH)}^{3+}$ and $\mathrm{Th(OH)}_2^{2+}$ would result in a slope of − 3 to − 2. By using the equilibrium constants proposed by Baes and Mesmer [1976BAE/MES] for $\mathrm{Th(OH)}^{3+}$ and $\mathrm{Th(OH)}_2^{2+}$ and estimating the activity coefficients for the reactants, Ryan and Rai suggest $\log_{10} K_{s,0}^{\circ} = -45.9$ for the reaction:

$$\mathrm{ThO_2(am)} + 2\mathrm{H_2O(l)} \rightleftharpoons \mathrm{Th^{4+}} + 4\mathrm{OH^-}$$

Ryan and Rai emphasise that there is a large difference between the experimental solubility product of $\mathrm{ThO_2(am)}$ and the considerably lower value of $\log_{10} K_{s,0}^{\circ}$ ($\mathrm{ThO_2}$, cr) = − 54.14 which they calculated for crystalline $\mathrm{ThO_2(cr)}$ from thermochemical data. The latter value is close to $\log_{10} K_{s,0}^{\circ}$ ($\mathrm{ThO_2}$, cr) = − (54.24 ± 1.11) calculated in the present review but significantly different from the one proposed by Baes and Mesmer [1976BAE/MES], $\log_{10} K^{\circ}_{s,0}$ (ThO_2, cr) = −49.4.

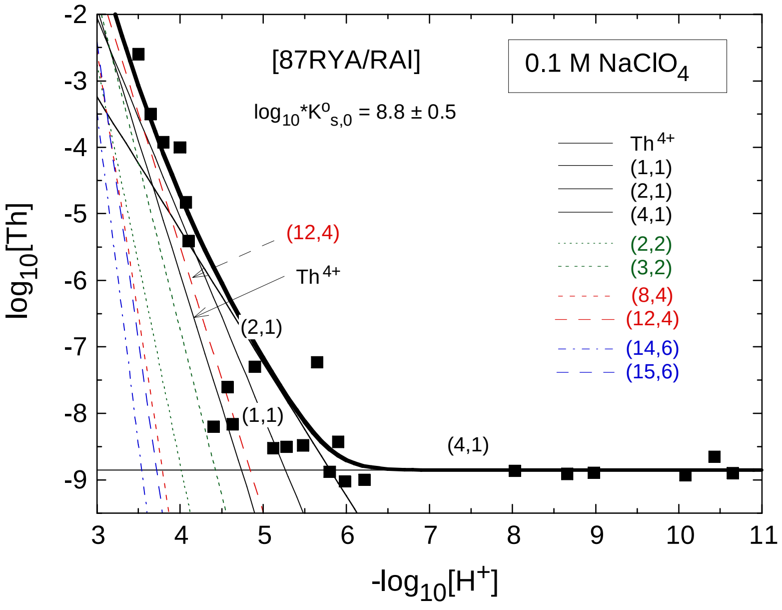
Based on the solubility product $\log_{10} K^{\circ}_{s,0}$ (ThO_2(am, hyd)) = −(45.9 ± 0.5) ($\log_{10} {}^{*}K^{\circ}_{s,0}$ (ThO_2(am, hyd)) = (10.1 ± 0.5)) and the experimental data in neutral and alkaline solutions, Ryan and Rai calculated upper limits of $\log_{10} {}^{*}\beta_4 \leq -19.7$, $\log_{10} {}^{*}\beta_5 \leq -33.1$, and $\log_{10} K_{s,5} < -9$ for the reaction:

$$ThO_2(am) + 2H_2O(l) + OH^- \rightleftharpoons Th(OH)_5^- .$$

Accordingly, the maximum concentration of $Th(OH)_5^-$ is below 10^{-9} M at $[OH^-]$ = 1.0 M which shows that, contrary to results reported in the previous literature, anionic hydroxide complexes are negligible under ordinary chemical conditions.

Using the hydrolysis constants and SIT coefficients selected in the present review, the re-evaluation of Ryan and Rai's solubility data at pH < 6 yields $\log_{10} {}^{*}K^{\circ}_{s,0}$ (ThO_2(am, hyd)) = (8.8 ± 0.5) ($\log_{10} K^{\circ}_{s,0}$ = −(47.2 ± 0.5)). As shown in Figure A-31, the species $Th_4(OH)_{12}^{4+}$, $Th(OH)^{3+}$ and $Th(OH)_2^{2+}$ are predominant in saturated solutions at pH < 5.5. The mean value of the experimental solubility data at pH > 6 in 0.1 M $NaClO_4$ gives $\log_{10} K^{\circ}_{s,4} = -(8.8 \pm 0.4)$ and $\log_{10} {}^{*}\beta^{\circ}_{4,1} = -(17.6 \pm 0.6)$.

Figure A-31: Solubility data for ThO_2(am, hyd) in 0.1 M $NaClO_4$ [1987RYA/RAI]: Recalculation of the solubility constant and aqueous speciation using the hydrolysis constants and SIT coefficients selected in the present review.



[1988EDV/LAG]

Two new systems in the molecular spectrum of ThO(g) were rotationally analysed and the molecular constants for two new excited states designated A' and B' are given.

[1989GRA/KIN]

The enthalpy of reaction for the formation of ThF_n^{4-n}, $n = 1-3$, have been determined calorimetrically at 25°C in a 0.5 M $\mathrm{NaClO_4}$ ionic medium. The experiments were made by titrating a test solution of 20 mM Th^{4+} with an initial pH (presumably $-\log_{10}[\mathrm{H}^+]$) of 1.1 with a solution of 0.1000 M NaF. In addition the authors made a separate experiment to determine the enthalpy of protonation of F^- and the enthalpy of dilution of the NaF titrant. The experiments were carried out until precipitation occurred at $\overline{n}_F \approx 1.7$. The equilibrium constants used to interpret the titration data were taken from [1982MAR/SMI]. The authors have use state of the art equipment and methodology and taken care to minimise systematic errors. This is very important in view of the small reaction enthalpies, corresponding to about 40 mJ for the individual additions of the titrant. This is a very precise experimental study and the conclusions drawn by the authors are accepted by this review.

Table A-61 gives a list of the thermodynamic quantities quoted by [1989GRA/KIN]. The authors have also determined the enthalpy of protonation of F^- using their calorimetric method. This provides an independent method to compare the accuracy of the system using a reaction with a larger enthalpy change. They found an enthalpy of protonation of (12.38 ± 0.38) $\mathrm{kJ \cdot mol^{-1}}$, as compared to literature values 12.2 $\mathrm{kJ \cdot mol^{-1}}$ [1967AHR] and 13.0 $\mathrm{kJ \cdot mol^{-1}}$ [1969AZI/LYL] and the standard value of 12.15 $\mathrm{kJ \cdot mol^{-1}}$ (calculated from Table IV-1).

Table A-61: Thermodynamic quantities for the reactions $\mathrm{Th}^{4+} + n\mathrm{F}^- \rightleftharpoons \mathrm{ThF}_n^{4-n}$ at 25°C and $I_c = 0.5$ M ($\mathrm{NaClO_4}$).

Complex	n	$-\Delta_r G_m$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\Delta_r H_m$ ($\mathrm{kJ \cdot mol^{-1}}$)	$\Delta_r S_m$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)
ThF^{3+}	1	43.3 ± 0.24	1.6 ± 0.03	150 ± 0.8
ThF_2^{2+}	2	76.7 ± 0.12	4.3 ± 0.07	272* ± 0.5
ThF_3^{+}	3	102 ± 0.64	7.8 ± 0.9	370 ± 4

* reported as 270 in [1989GRA/KIN]

The Gibbs energy values and uncertainties in Table A-61 are from [1982MAR/SMI]. The uncertainties in $\Delta_r H_m$ are given at the 1σ level and those in $\Delta_r S_m$ are obtained by combining the uncertainties in the previous quantities.

The reported enthalpies of reaction are positive, in contrast to the values reported by [1990AHR/HEF] in 4.0 M $\mathrm{HClO_4}$, $\Delta_r H_1 = -(2.4 \pm 0.1)$ and $\Delta_r H_2 = -(3.3 \pm 0.4)$ $\mathrm{kJ \cdot mol^{-1}}$ and by Choppin and Unrein [1976CHO/UNR] in 1.0 M $\mathrm{HClO_4}$,

$\Delta_r H_n$ equal to -1.1, -2.2 and -3.0 kJ·mol^{-1} for $n = 1-3$, respectively. The uncertainties in the experimental values are given as one standard deviation from the least-squares method used. The enthalpies of reaction for the formation of the thorium fluoride complexes are small and the numerical values are thus very sensitive to systematic errors such as those resulting from the different ionic media used. A comparison of the calorimetric investigations indicates that the reported experimental uncertainties have not been taken this into account. For the reasons discussed in Section VIII.1.2.2 this review has only selected values for $\Delta_r H^\circ_1$ and $\Delta_r H^\circ_2$, but not for $\Delta_r H^\circ_3$. The selected values are:

$$\Delta_r H^\circ_1 = -(0.4 \pm 2.0) \text{ kJ·mol}^{-1}$$

$$\Delta_r H^\circ_2 = -(3.3 \pm 0.4) \text{ kJ·mol}^{-1}.$$

[1989LAU/BRI]

The gaseous species ThF, ThF_2, ThF_3, and ThF_4 were generated in a heated effusion beam source, and were identified and characterised by mass spectrometry, together with the gaseous oxyfluoride ThOF, arising from an oxygen impurity in the sample. Equilibria involving the reactions of these species with Ba(g) and BaF(g) were studied over considerable temperature ranges. The vapour pressure of ThF_4(cr) was also determined. The thermochemical properties of the Th-F species are derived and the data are compared to those of the corresponding uranium fluorides.

Data are also given for the reaction ThO(g) + BaF(g) $\rightleftharpoons$ ThOF(g) + Ba(g), leading to the enthalpy of formation of ThOF(g).

The sample of ThF_4(cr) used was stated to be 99.9% pure by the suppliers, and was not analysed further. The vapour pressure of the solid was determined by torsion effusion from two graphite cells with diameters differing by a factor of eight, from 1047 to 1201 K. No orifice-size effect was found.

All these data are analysed in Sections VIII.1.1.1.2, VIII.1.1.3.2 and VIII.1.1.4.

[1989LAU/HIL]

The decomposition pressure of $ThOF_2$(cr) was measured by torsion-effusion from 1088 to 1248 K. The solid oxyfluoride vaporises incongruently to give ThF_4(g) and ThO_2(cr). The composition of the vapour was confirmed by mass spectrometry. A small effusion orifice-area dependence indicates, not unexpectedly, a slight kinetic barrier to the incongruent vaporisation process. Although the results with the two cells overlapped only over the range 1133 to 1191 K, the temperature coefficients were very similar and the vapour pressures were therefore extrapolated up or down to cover the range 1100 to 1200 K, and fitted values extrapolated to zero orifice size.

The decomposition pressures were only about a factor of two smaller than the vapour pressure of pure ThF_4(cr) measured by the same authors [1989LAU/BRI], and agree excellently with those of Darnell [1960DAR]. The results were processed by the second-law to give the enthalpy of formation and standard entropy of the solid oxyfluoride. The oxyfluoride is only marginally stable with respect to ThO_2(cr) and ThF_4(cr).

[1989MOO]

Moon has used a combination of solubility experiments and 1 nm-ultrafiltration to determine hydrolysis constants of Th(IV) in 0.1 M and 0.5 M $NaClO_4$ media at 18°C. The solubility of crystalline ThO_2(cr) has been measured at pH 1.5 − 13 in 0.1 M $NaClO_4$ and the solubility of amorphous $Th(OH)_4$(am) at pH 4 − 13 in 0.5 M $NaClO_4$. The ultrafiltration is used to remove particles from the equilibrium solutions, after which the total concentration of Th was determined by neutron activation analysis. The pH values were determined with a Orion Ross electrode and converted into $\log_{10}[OH^-]$. No details are reported in this paper, but the procedures used at that time in this laboratory are described in other papers, *e.g.*, in [1986LIE/KIM] where Moon's results were cited and compared to data for Pu(IV). The resulting solubility curves were analysed using a least-squares method with known equilibrium constants as starting values; the deduced equilibrium constants are shown in Table A-62.

Table A-62: Equilibrium constants for the reactions $m\text{Th}^{4+} + n\text{OH}^- \rightleftharpoons \text{Th}_m(\text{OH})_n^{4m-n}$ in 0.1 M and 0.5 M $NaClO_4$ at 18°C.

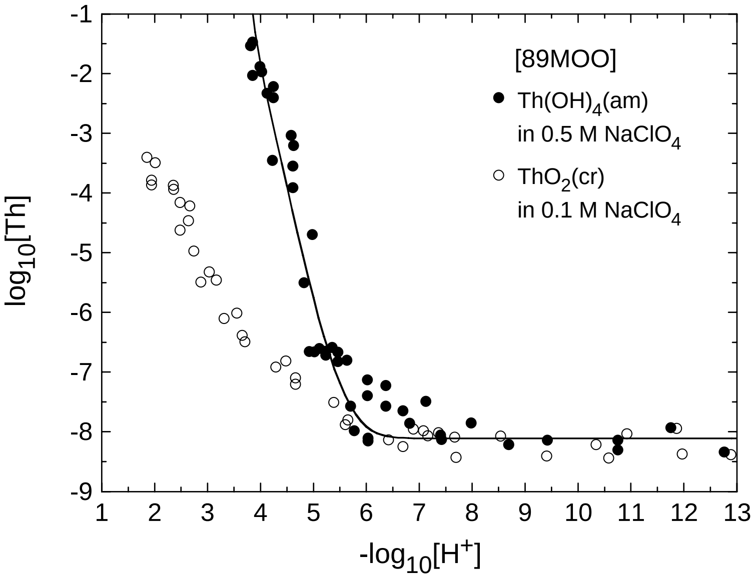
Complex	$\log_{10}\beta_{n,m}$ (0.1 M $NaClO_4$)	$\log_{10}\beta_{n,m}$ (0.5 M $NaClO_4$)
$Th(OH)^{3+}$	12.42 ± 0.02	12.58 ± 0.02
$Th(OH)_2^{2+}$	22.46 ± 0.15	22.33 ± 0.15
$Th(OH)_3^{+}$	34.36 ± 0.07	34.42 ± 0.07
$Th(OH)_4$	42.58 ± 0.08	42.76 ± 0.08
$Th_2(OH)_2^{6+}$	22.11 ± 0.10	30.05 ± 0.04
$Th_2(OH)_3^{5+}$	–	32.21 ± 0.11
$Th_2(OH)_4^{4+}$	–	59.07 ± 0.04
Solid phase	$\log_{10}K_{s,0}$ (0.1 M $NaClO_4$)	$\log_{10}K_{s,0}$ (0.1 M $NaClO_4$)
ThO_2(cr)	– 50.76 ± 0.08	
$Th(OH)_4$(am)		– 50.52 ± 0.08

The experimental data of [1989MOO] are comparable with the results of similar studies [1964NAB/KUD], [1991FEL/RAI], [2000RAI/MOO]; however, the data evaluation shows many shortcomings. To begin with, in the solubility study with $Th(OH)_4$(am) there is no significant concentration of Th^{4+} in the test solutions with the lowest value of pH. Hence it is not possible to determine the solubility product from these data; the reported value is nearly the same as for $ThO_2(cr)$. In addition the concentration of $Th(OH)^{3+}$ is very small, reaching at most a few percent of the total concentration of thorium. It is not possible to determine a precise value of the equilibrium constant under these conditions; the experimental data will most likely be well described also with a model where $Th(OH)^{3+}$ is not included. Nevertheless, the author reports equilibrium constants with surprisingly small uncertainties. Another example of data inconsistency is the large difference in the equilibrium constant for $Th_2(OH)_2^{6+}$ between 0.1 and 0.5 M $NaClO_4$; eight orders of magnitude is not consistent with the expected variation due to activity factor changes. The difference is understandable if the complex is a computational artefact. The author has made the mistake of not comparing different chemical models to see if a unique one can be established, or not. An analysis of this type also gives a much better estimate of the uncertainty in the equilibrium constants. The shortcomings of this study are so large that the equilibrium constants proposed cannot be considered in the final selection of data.

Moon's experimental data for $Th(OH)_4(am)$ in 0.5 M $NaClO_4$, typical for solubility studies of this type, have been re-evaluated using the hydrolysis constants and SIT coefficients selected in the present review. From the data at pH < 6 a solubility constant of $\log_{10} {}^*K^\circ_{s,0}$ = (9.5 ± 0.3) ($\log_{10} K^\circ_{s,0} = -(46.5 \pm 0.3)$) is obtained. The mean value of the experimental solubility data at pH > 6 in 0.1 M $NaClO_4$ gives $\log_{10} K^\circ_{s,4}$ = − (8.1 ± 0.3) and $\log_{10} {}^*\beta^\circ_{4,1} = -(17.6 \pm 0.4)$.

At low pH values Moon's solubility data for $ThO_2(cr)$ are significantly lower than the values for $Th(OH)_4(am)$, but with increasing pH, the solubility of the crystalline oxide continuously approaches the thorium concentration in equilibrium with amorphous thorium hydroxide. At pH > 5 the data measured with $ThO_2(cr)$ and $Th(OH)_4(am)$ are the same (Figure A-32). An interpretation of this unexpected behaviour is presented in Section VII.4.3. Only the data at the lowest pH values actually refer to crystalline $ThO_2(cr)$. With increasing pH, the total solubility is given by smaller particles present in the solid. At pH > 5, the solubility is determined by a small fraction of "$Th(OH)_4(am)$" particles < 5 nm.

Figure A-32: Comparison of solubility data measured by Moon [1989MOO] with $Th(OH)_4(am)$ in 0.5 M $NaClO_4$ and with $ThO_2(cr)$ in 0.1 M $NaClO_4$ at 18°C. The solubility curve for $ThO_2(am, hyd)$ is calculated using the hydrolysis constants and SIT coefficients selected in the present review, in combination with $\log_{10} {}^*K^{\circ}_{s,0} = 9.5$ and $\log_{10} K^{\circ}_{s,4} = -(8.1 \pm 0.3)$.



[1990AHR/HEF]

Ahrland *et al.* report calorimetric studies of mononuclear fluoride complexes of Zr(IV), Hf(IV), U(IV) and Th(IV). Only the experimental data for Th(IV) will be discussed here. The enthalpy of reaction for the formation of ThF^{3+} and ThF_2^{2+} have been determined using calorimetry together with previous information on the equilibrium systems [1969NOR] for the Th(IV) data. This is a precise experimental study and the thermodynamic data are accordingly more precise than those in [1976CHO/UNR]. The experiments are described in detail together with the primary experimental data and these results are accepted by the present review. The reaction values at 298.15 K were: $Th^{4+} + F^- \rightleftharpoons ThF^{3+}$: $\Delta_r G^{\circ}_m(ThF^{3+}) = -46.6$ kJ·mol^{-1}, $\Delta_r H^{\circ}_m(ThF^{3+}) = -(2.4 \pm 0.1)$ kJ·mol^{-1}, $Th^{4+} + 2F^- \rightleftharpoons ThF_2^{2+}$: $\Delta_r G^{\circ}_m(ThF_2^{2+}) = -83.1$ kJ·mol^{-1}, $\Delta_r H^{\circ}_m(ThF_2^{2+}) = -(3.3 \pm 0.4)$ kJ·mol^{-1}.

The thermodynamic quantities used by [1990AHR/HEF] for the protonation of F^-:

$$H^+ + F^- \rightleftharpoons HF(aq) \qquad (A.81)$$

are $-\Delta_r G^o_m$ (A.81) = 20.2 kJ·mol^{-1}, $\Delta_r H^o_m$ (A.81) = 11.9 kJ·mol^{-1} and $\Delta_r S^o_m$ (A.81) = 108 J·K^{-1}·mol^{-1}.

[1990BAZ/EZH]

The authors have studied the structure and vibrational features of $ThCl_4(g)$ using gas electron diffraction. The sample of $ThCl_4(cr)$ contained less than 0.5% impurities (mainly $ThO_2(cr)$), and was vaporised from a molybdenum capsule, which spectroscopic investigations have shown gives essentially only monomeric species.

The results strongly suggested that $ThCl_4(g)$ has tetrahedral T_d symmetry, with a Th–Cl bond distance of 2.567 Å, although a slight distortion of the tetrahedral structure could not be entirely excluded. Assuming the T_d structure, a simple force field analysis with two force constants gave vibration frequencies of (330 ± 30), (80 ± 15), (370 ± 30), and (75 ± 15) cm^{-1}. These are in quite good agreement with those obtained from more recent density functional calculations. The internuclear distance inferred by [1990BAZ/EZH] has been used in the calculations of the thermal functions of $ThCl_4(g)$.

[1990ELY/BRI]

The authors have explored the equilibria in the Th(IV)-H_3PO_4-$LiClO_4$ system using liquid-liquid extraction (with HDEHP in benzene as the extracting ligand). The experiments have been made at a constant ionic strength of 0.2 M at 25°C. There is no information about the temperature; this review assumes that the data refer to 20−25°C. The paper provides details about the experimental methods and the data analysis and the experimental observations can be well described by the proposed chemical model. This consists of the following species:

$$\log_{10} K\,(\mathrm{Th(OH)(H_2PO_4)^{2+}}) = (5.22 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(OH)_2(H_2PO_4)^{+}}) = (3.62 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(H_2PO_4)^{2+}}) = (5.65 \pm 0.05)$$

$$\log_{10} K\,(\mathrm{Th(OH)(H_2PO_4)_2^{+}}) = (4.70 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(OH)(H_2PO_4)_3, aq}) = (2.90 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(H_2PO_4)_4, aq}) = (3.86 \pm 0.04)$$

$$\log_{10} K\,(\mathrm{Th(OH)_2(H_2PO_4)_5^{3-}}\ \text{or}\ \mathrm{Th(H_2PO_3)_3(HPO_4)_2^{3-}}) = -(3.65 \pm 0.13)$$

The stoichiometry of the complexes, which cannot be determined from the equilibrium data because of the proton ambiguity ($\mathrm{Th(OH)(H_2PO_4)_2^{+}} \equiv \mathrm{Th(HPO_4)(H_2PO_4)^{+}}$), has instead been estimated based on partial atomic charges. Despite the care taken both in the experiments and the data analysis, the present review does not accept the stoichiometry and the equilibrium constants proposed; the reasons are: there is a large number of parameters in the model used and only one single model has been tested. In particular one would have liked to see if a model with some of the minor complexes removed could describe the data within the estimated experimental uncertainty. In addition, the reviewers are not confident that the electrostatic considerations are justified to deduce the stoichiometry of the complexes; in particular we notice that hydroxide coordination is assumed to occur even in the pH range where hydrolysis in the binary Th(IV)-hydroxide system is small or negligible; this is in the opinion of the reviewers not likely.

[1990HIL/LAU]

The sublimation of $ThBr_4$(cr) was studied in the temperature range 631 to 768 K by the torsion-effusion method. Supplementary mass-spectrometric measurements indicated that only monomeric $ThBr_4$(g) exists in the vapour at these temperatures, in agreement with the molecular weight derived from the torsion-effusion measurements. The entropy of sublimation was considered to be more consistent with a distorted tetrahedral structure, but later theoretical studies indicate that the $ThBr_4$(g) molecule, in fact has tetrahedral symmetry, as discussed in Section VIII.3.1.4.1.

The gaseous lower-valent species $ThBr_3$, $ThBr_2$, and ThBr were identified in the bromination of Th(cr) at 1500 to 2000 K, and the equilibria involving Th(g), ThBr(g), $ThBr_2$(g) and Br(g) were studied by mass-spectrometry from 1986 to 2455 K. Addition of aluminium to the system allowed the equilibria involving Al(g), AlBr(g), $ThBr_2$(g), $ThBr_3$(g) and $ThBr_4$(g) to be studied from 1696 to 1935 K. Reaction enthalpies, bond dissociation energies, and enthalpies of formation were derived from the results by second law analyses. However, the precise values of the thermal functions used by the authors for correction to 298.15 K are not entirely clear, especially for ThBr(g).

All these data are analysed in detail in Section VIII.3.1.1.

[1990LAU/HIL]

The sublimation of $ThCl_4$(cr) was studied in the temperature range 685 to 775 K by the torsion-effusion method. Supplementary mass-spectrometric measurements indicated that only monomeric $ThCl_4$(g) exists in the vapour at these temperatures, in agreement with the molecular weight derived from the torsion-effusion measurements. The entropy of sublimation was considered to be consistent with a tetrahedral structure, as confirmed by later theoretical studies, as discussed in Section VIII.2.1.4.1

The gaseous lower-valent species $ThCl_3$, $ThCl_2$, and ThCl were identified in the chlorination of Th(cr) with either Cl_2(g) or $CaCl_2$(g) , and the equilibria involving Th(g), ThCl(g), $ThCl_2$(g), $ThCl_3$(g) and Ca(g) and CaCl(g) were studied by mass-spectrometry in various temperature ranges from 2003 to 2478 K. Reaction enthalpies, bond dissociation energies, and enthalpies of formation were derived from the results by second law analyses. However, the precise values of the thermal functions used by the authors for correction to 298.15 K are not entirely clear, especially for ThCl(g).

All these data are analysed in Section VIII.2.1.2.

[1990SAW/CHA2]

There is an extensive review of this paper in [2001LEM/FUG] and we will only make a short summary of the paper and some additional comments. The experimental data were obtained using potentiometric titrations of Th(IV) with HF using a fluoride selective electrode. The ionic medium was 1 M (Na,H)ClO_4 and the measurements were made at (23 ± 2)°C and using a least-squares program (MINIQUAD) for the determination of equilibrium constants and their estimated uncertainty. Primary experimental data for the Th(IV) system are given in Table 3 of [1990SAW/CHA2]; the total concentrations of Th_{tot}, H_{tot} and F_{tot} varied from 20.66 to 10.88 mM, 483.3 to 254.8 mM and 2.11 to 48.4 mM, respectively. The high hydrogen ion concentration results in negligible hydrolysis of Th(IV). The experimental data up to $\bar{n}_F$ around 1.8 seems to be satisfactory, but then the curve increases steeply as previously found in [1949DOD/ROL] and [1971KLO/MUK]; indicating the precipitation of ThF_4(s). However, Sawant *et al.* make no comment about this and describe the experimental data using a set of four complexes, ThF_n^{4-n} and corresponding equilibrium constants. The model is correct but the reported values of equilibrium constants, especially for ThF_4(aq), are questionable and are not accepted by this review. The $\log_{10} \beta_n$ values obtained by the least-squares analysis are reported in [1990SAW/CHA2] as: $\log_{10} \beta_1 = (7.61 \pm 0.01)$; $\log_{10} \beta_2 = (13.42 \pm 0.05)$; $\log_{10} \beta_3 = (17.65 \pm 0.2)$ and $\log_{10} \beta_4 = (23.67 \pm 0.11)$, where this review has estimated the uncertainty of the two first constants to be twice as large as suggested in [1990SAW/CHA2]. Based on the appropriate ion-interaction parameters reported in Table VIII-8 for this system, this review calculated values of $\log_{10} \beta_1^{\circ} = (9.00 \pm 0.14)$; $\log_{10} \beta_2^{\circ} = (15.84 \pm 0.16)$; $\log_{10} \beta_3^{\circ} = (20.66 \pm 0.26)$, which are fairly similar to the values recommended in this review. Since [1990SAW/CHA2] report their raw data, it is of interest to determine how closely the aqueous phase model recommended in this review reproduces the experimental data. For this purpose, the observed fluoride activities reported by [1990SAW/CHA2] are compared with the fluoride activities calculated from the aqueous phase model that included values for β_1° through β_4° (Figure A-33). These comparisons indicate very close agreement between the experimental and the predicted concentrations at low fluoride activities, approximately at $\log_{10}[F^-] < -5.6$. The disagreement at higher fluoride activities, about $\log_{10}[F^-] > -5.6$, is expected as a result of possible complications due to the precipitation of ThF_4(cr, hyd). The distribution of different species is listed in Table A-63.

Figure A-33: Observed ([1990SAW/CHA2]) and predicted F⁻ activities at (23 ± 2)°C for potentiometric titrations using fluoride-selective electrode in 1 M (H, Na)ClO_4 solutions. Predictions based on NONLINT-SIT calculations using the thermodynamic model summarised in Tables VIII-8 and VIII-9.

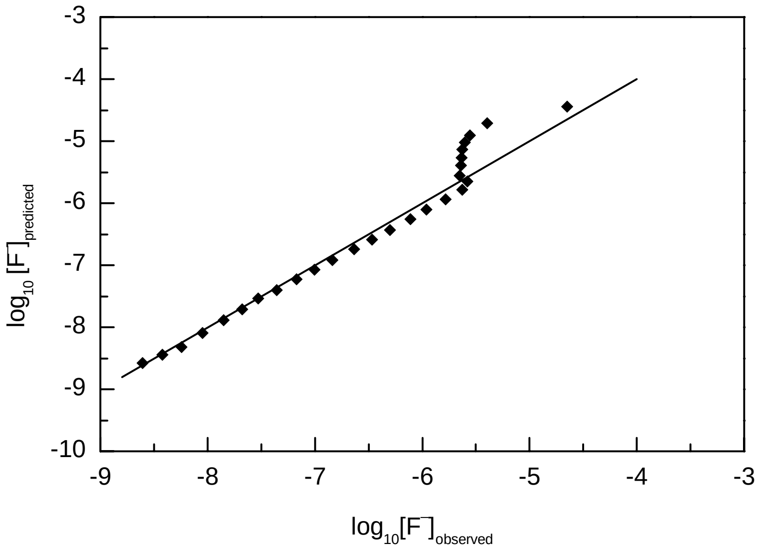


Table A-63: Experimental ([1990SAW/CHA2]) and predicted concentrations of different species at (23 ± 2)°C for potentiometric titrations using fluoride-selective electrode in 1 M (H, Na)ClO_4 solutions. Predictions based on NONLINT-SIT calculations using the thermodynamic model summarised in Tables VIII-8 and VIII-9.

Experimental concentrations (m)						Predicted concentrations (m)[a]						
H_{Total}	Na_{total}	$(ClO_4)_{total}$	Th_{Total}	F_{Total}	$F^-_{activity}$	$F^-_{activity}$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	$ThF_4(aq)$	ThF_6^{2-}
4.833E-01	4.341E-01	9.979E-01	2.066E-02	2.106E-03	2.491E-09	2.630E-09	1.856E-02	2.096E-03	4.365E-06	4.732E-10	7.944E-14	7.000E-14
4.801E-01	4.378E-01	9.973E-01	2.052E-02	2.748E-03	3.792E-09	3.565E-09	1.778E-02	2.730E-03	7.730E-06	1.138E-09	2.594E-13	7.000E-14
4.762E-01	4.424E-01	9.965E-01	2.035E-02	3.544E-03	5.690E-09	4.842E-09	1.682E-02	3.514E-03	1.353E-05	2.706E-09	8.374E-13	7.000E-14
4.679E-01	4.521E-01	9.948E-01	2.000E-02	5.231E-03	9.025E-09	8.054E-09	1.481E-02	5.160E-03	3.309E-05	1.101E-08	5.663E-12	7.000E-14
4.583E-01	4.634E-01	9.928E-01	1.959E-02	7.172E-03	1.412E-08	1.291E-08	1.250E-02	7.019E-03	7.244E-05	3.872E-08	3.194E-11	7.000E-14
4.491E-01	4.741E-01	9.910E-01	1.920E-02	9.023E-03	2.107E-08	1.936E-08	1.032E-02	8.740E-03	1.358E-04	1.090E-07	1.350E-10	7.000E-14
4.414E-01	4.831E-01	9.890E-01	1.887E-02	1.095E-02	2.974E-08	2.904E-08	8.182E-03	1.044E-02	2.443E-04	2.948E-07	5.479E-10	7.000E-14
4.330E-01	4.930E-01	9.877E-01	1.851E-02	1.229E-02	4.384E-08	3.954E-08	6.611E-03	1.153E-02	3.680E-04	6.052E-07	1.531E-09	7.000E-14
4.248E-01	5.026E-01	9.860E-01	1.816E-02	1.396E-02	6.715E-08	5.916E-08	4.845E-03	1.270E-02	6.089E-04	1.502E-06	5.691E-09	7.000E-14
4.182E-01	5.103E-01	9.847E-01	1.787E-02	1.529E-02	9.915E-08	8.472E-08	3.554E-03	1.339E-02	9.212E-04	3.257E-06	1.768E-08	7.000E-14
4.124E-01	5.171E-01	9.835E-01	1.763E-02	1.647E-02	1.457E-07	1.197E-07	2.572E-03	1.372E-02	1.334E-03	6.664E-06	5.105E-08	7.000E-14
4.058E-01	5.248E-01	9.822E-01	1.735E-02	1.780E-02	2.306E-07	1.807E-07	1.686E-03	1.364E-02	2.010E-03	1.519E-05	1.760E-07	7.000E-14
4.002E-01	5.314E-01	9.811E-01	1.710E-02	1.895E-02	3.415E-07	2.594E-07	1.131E-03	1.315E-02	2.784E-03	3.020E-05	5.016E-07	7.000E-14
3.942E-01	5.384E-01	9.799E-01	1.685E-02	2.014E-02	5.010E-07	3.690E-07	7.421E-04	1.233E-02	3.724E-03	5.757E-05	1.363E-06	7.000E-14
3.869E-01	5.470E-01	9.784E-01	1.654E-02	2.164E-02	7.713E-07	5.572E-07	4.367E-04	1.097E-02	5.010E-03	1.169E-04	4.176E-06	7.000E-14
3.802E-01	5.548E-01	9.770E-01	1.625E-02	2.299E-02	1.098E-06	7.852E-07	2.697E-04	9.583E-03	6.183E-03	2.037E-04	1.026E-05	2.667E-13
3.720E-01	5.644E-01	9.753E-01	1.590E-02	2.465E-02	1.654E-06	1.164E-06	1.483E-04	7.839E-03	7.518E-03	3.677E-04	2.747E-05	1.577E-12
3.646E-01	5.731E-01	9.738E-01	1.558E-02	2.616E-02	2.368E-06	1.637E-06	8.475E-05	6.316E-03	8.531E-03	5.870E-04	6.165E-05	7.021E-12
3.576E-01	5.813E-01	9.724E-01	1.528E-02	2.756E-02	2.645E-06	2.218E-06	4.976E-05	5.032E-03	9.217E-03	8.591E-04	1.222E-04	2.559E-11
3.520E-01	5.879E-01	9.713E-01	1.504E-02	2.871E-02	2.224E-06	2.805E-06	3.213E-05	4.119E-03	9.558E-03	1.128E-03	2.029E-04	6.828E-11
3.421E-01	5.994E-01	9.693E-01	1.462E-02	3.070E-02	2.283E-06	4.083E-06	1.522E-05	2.851E-03	9.657E-03	1.661E-03	4.356E-04	3.128E-10
3.337E-01	6.092E-01	9.676E-01	1.426E-02	3.241E-02	2.312E-06	5.433E-06	8.252E-06	2.062E-03	9.311E-03	2.134E-03	7.448E-04	9.529E-10
3.235E-01	6.212E-01	9.655E-01	1.383E-02	3.448E-02	2.348E-06	7.362E-06	4.110E-06	1.394E-03	8.532E-03	2.648E-03	1.252E-03	2.954E-09
3.137E-01	6.327E-01	9.635E-01	1.341E-02	3.646E-02	2.504E-06	9.528E-06	2.167E-06	9.527E-04	7.559E-03	3.038E-03	1.858E-03	7.395E-09
3.032E-01	6.450E-01	9.614E-01	1.296E-02	3.859E-02	2.780E-06	1.227E-05	1.105E-06	6.266E-04	6.407E-03	3.315E-03	2.610E-03	1.733E-08
2.823E-01	6.695E-01	9.572E-01	1.206E-02	4.283E-02	4.013E-06	1.954E-05	2.784E-07	2.525E-04	4.126E-03	3.406E-03	4.275E-03	7.320E-08
2.696E-01	7.378E-01	1.001E+00	1.145E-02	5.088E-02	2.234E-05	3.589E-05	3.610E-08	6.021E-05	1.807E-03	2.734E-03	6.289E-03	3.688E-07

a: All 7.000E-14 numbers are model limiting values, the actual value is lower than this.

[1991FEL/RAI]

This paper is discussed together with [1997RAI/FEL].

These two papers include experimental solubility studies with Th(IV) hydrous oxide in various chloride ionic media: 0.6 M NaCl and KCl, 1.2 and 3.0 M NaCl [1991FEL/RAI], 4.0 and 6.0 m NaCl, 1.82, 1.0 and 3.0 m $MgCl_2$ [1997RAI/FEL]. The solubility experiments were performed at room temperature (*ca.* 22ºC) from undersaturation with amorphous ThO_2(am, hyd) precipitates, purified by washing with water. All experimental details are provided. The results were assumed by this review to be valid for 298.15 K. The operational pH values measured in these chloride solutions with a combined glass-electrode (ROSS type) were converted into H^+ concentrations ($pc_{H^+} = -\log_{10}[H^+]$) using appropriate calibration procedures. The important separation of the test solutions from colloidal hydrous oxide was achieved by centrifugation and using filters with a cutoff limit of 2.5 kDa. The lowest solubilities were measured with ICP-MS ensuring an analytical uncertainty of at most 10%. The measurements were made in the range $3 < -\log_{10}[H^+] < 10.5$ with short (5 − 8 days) and long (51 − 372 days) equilibration times. The experimental data are given as plots of $\log_{10}$ [Th] *vs.* $-\log_{10}[H^+]$ and in an Appendix of [1991FEL/RAI]; they scatter significantly as invariably found in studies of this type. The solubility is approximately constant at $-\log_{10}[H^+] > 6$, indicating that an uncharged complex is predominating here [1991FEL/RAI].

Felmy *et al.* [1991FEL/RAI] interpreted the solubility data at $-\log_{10}[H^+] < 6$ in 0.6 − 3.2 m NaCl and in 0.10 M $NaClO_4$ using the ion interaction approach of Pitzer. The observed solubility in 0.1 M $NaClO_4$ from [1987RYA/RAI] was three to four orders of magnitude lower than in 0.6 M NaCl [1991FEL/RAI]. The specific ion interactions between Th^{4+} and Cl^- and between Th^{4+} and ClO_4^- are very different and must influence the activity coefficient of Th^{4+} significantly. Binary Pitzer parameters for the interaction Th^{4+}-Cl^- and the standard Gibbs energy of formation of Th^{4+} were taken from [1973PIT/MAY] and [1976FUG/OET], respectively. This model was refined in [1997RAI/FEL] including the solubility studies in up to 6.0 m NaCl and 1.0 − 3.0 m $MgCl_2$ solutions. Based on the binary parameters $\beta^{(0)}_{Th^{4+}/Cl^-} = 1.092$, $\beta^{(1)}_{Th^{4+}/Cl^-} = 13.7$, $\beta^{(2)}_{Th^{4+}/Cl^-} = -160$, and $C^{\phi}_{Th^{4+}/Cl^-} = -0.112$ from [1992ROY/VOG], Rai *et al.* [1997RAI/FEL] described the solubility of ThO_2(am, hyd) in NaCl and $MgCl_2$ solutions with the ternary parameters $\theta_{Th^{4+}/Na^+} = 0.42$, $\psi_{Th^{4+}/Na^+/Cl^-} = 0.21$ and $\theta_{Th^{4+}/Mg^{2+}} = 0.60$, $\psi_{Th^{4+}/Mg^{2+}/Cl^-} = 0.21$, respectively. The equilibrium constant for the reaction:

$$ThO_2(am, hyd) + 2H_2O(l) \rightleftharpoons Th^{4+} + 4OH^-$$

evaluated without taking hydrolysis reactions into account is $\log_{10} K^{o}_{s,0} = -45.5$ ($\log_{10} {}^{*}K^{o}_{s,0} = 10.5$), nearly the same as found in [1987RYA/RAI]. The uncertainty has not been estimated. Felmy *et al.* [1991FEL/RAI] tried to fit the solubility data by including also hydrolytic species, but without success. It is very difficult to estimate both equilibrium constants and Pitzer parameters even from very precise experimental data.

The fit between the thermodynamic model used and the experimental data varies; it is good in 0.1 M $NaClO_4$, in 0.6 M NaCl and at the high NaCl and $MgCl_2$ concentrations studied in [1997RAI/FEL]. In 1.2 and 3.0 M NaCl the fitted function deviates significantly and systematically from most experimental data.

As Th(IV) hydroxide complexes are not included in the models proposed in [1991FEL/RAI] and [1997RAI/FEL], the solubility and hydrolysis constants selected in this review must not be combined with the Pitzer parameters used by Rai *et al.* [1997RAI/FEL] for the Th^{4+} ion and vice versa – the solubility constants given in [1997RAI/FEL], [2000RAI/MOO] must not be combined with the SIT coefficients and hydolysis constants evaluated in the present review.

The experimental data of [1991FEL/RAI] and [1997RAI/FEL] have been re-evaluated using the hydrolysis constants and SIT coefficients selected in the present review. The values of $\log_{10} {}^*K^\circ_{s,0}$ and $\log_{10} K^\circ_{s,4}$ obtained from the solubility data are summarised in Table A-64. The corresponding values obtained from the study of [1987RYA/RAI] in 0.1 M $NaClO_4$ and a later study of this group in 0.1 M NaCl [2000RAI/MOO] are included for comparison. The solubility curves calculated with these "best fit" values of $\log_{10} {}^*K^\circ_{s,0}$ and $\log_{10} K^\circ_{s,4}$ are shown as dashed lines in Figure A-34. With the exception of the high $\log_{10} {}^*K^\circ_{s,0}$ value derived from solubility data in 0.1 M NaCl [2000RAI/MOO] and the high $\log_{10} K^\circ_{s,4}$ value derived from the widely scattered data in 3.0 M NaCl, the values recalculated to zero ionic strength are reasonably consistent, even those which were recalculated from the solubility data in 1.8 and 3.0 m $MgCl_2$ solutions, outside the validity range of the SIT. The mean values derived from the studies in 0.6 – 3.2 m NaCl [1991FEL/RAI], $\log_{10} {}^*K^\circ_{s,0} = (9.3 \pm 0.6)$ and $\log_{10} K^\circ_{s,4} = -(7.9 \pm 1.0)$ corresponding to $\log_{10} {}^*\beta^\circ_{4,1} = -(17.2 \pm 1.2)$ and the mean value derived from the data at pH < 6 in 4.0 and 6.0 m NaCl and in 1.0 m $MgCl_2$, $\log_{10} {}^*K^\circ_{s,0} = (8.4 \pm 0.7)$, are in the range of the equilibrium constants derived from other solubility studies with ThO_2(am, hyd), but the origin of the difference between the $\log_{10} {}^*K^\circ_{s,0}$ values from [1991FEL/RAI] and [1997RAI/FEL] is not clear. Both values are considered in the selection of thermodynamic data.

Table A-64: Equilibrium constants $\log_{10}\,{}^{*}K^{\circ}_{s,0}$ and $\log_{10} K^{\circ}_{s,4}$ at zero ionic strength re-evaluated by this review from solubility studies of [1991FEL/RAI], [1997RAI/FEL] with ThO_2(am, hyd) at room temperature. The values derived from [1987RYA/RAI], [2000RAI/MOO] are added for comparison. The results were assumed by this review to be valid for 298.15 K.

Reference	Medium	$\log_{10}\,{}^{*}K^{\circ}_{s,0}$	$\log_{10} K^{\circ}_{s,4}$
[1987RYA/RAI]	0.1 M $NaClO_4$	8.8 ± 0.5	−8.8 ± 0.4
[2000RAI/MOO]	0.1 M NaCl	9.8 ± 0.3	
[1991FEL/RAI]	0.6 M NaCl/KCl	9.4 ± 0.6	−8.3 ± 1.0
	1.2 M NaCl	9.3 ± 0.6	−8.1 ± 0.9
	3.0 M NaCl	9.2 ± 0.7	−7.4 ± 1.0
[1997RAI/FEL]	4.0 m NaCl	8.3 ± 0.7	
	6.0 m NaCl	8.1 ± 0.7	
	1.0 m $MgCl_2$	8.8 ± 0.4	
	1.8 m $MgCl_2$	7.8 ± 0.8 [a]	
	3.0 m $MgCl_2$	8.0 ± 0.7 [a]	

a: Ionic media far outside the validity range of the SIT.

Figure A-34: Solubility data determined by Rai *et al.* with ThO_2(am, hyd) at I = 0.1 M [1987RYA/RAI], [2000RAI/MOO], in 0.6 – 6.0 m NaCl and in 1.0 – 3.0 m $MgCl_2$ [1991FEL/RAI], [1997RAI/FEL]. The solid lines (——) are calculated with the hydrolysis constants and SIT coefficients selected by this review and $\log_{10}\,{}^{*}K^{\circ}_{s,0}$ = (8.5 ± 0.9) selected for ThO_2(am, aged, hyd). Dashed lines (– – –): Best fit at the corresponding ionic strength yielding the $\log_{10}\,{}^{*}K^{\circ}_{s,0}$ and $\log_{10} K^{\circ}_{s,4}$ values given in Table A-64.

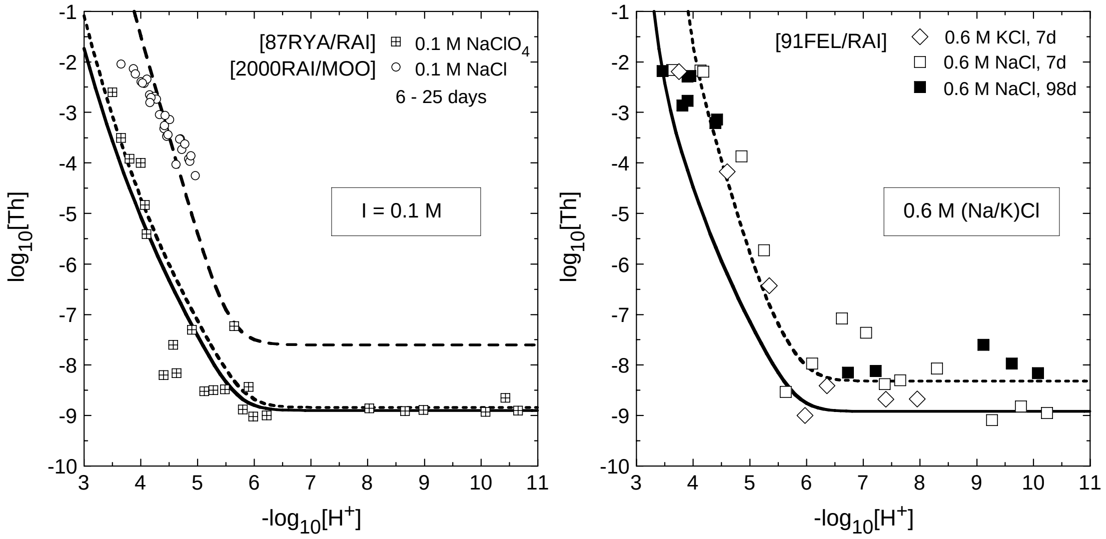


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Figure A-34 (continued)

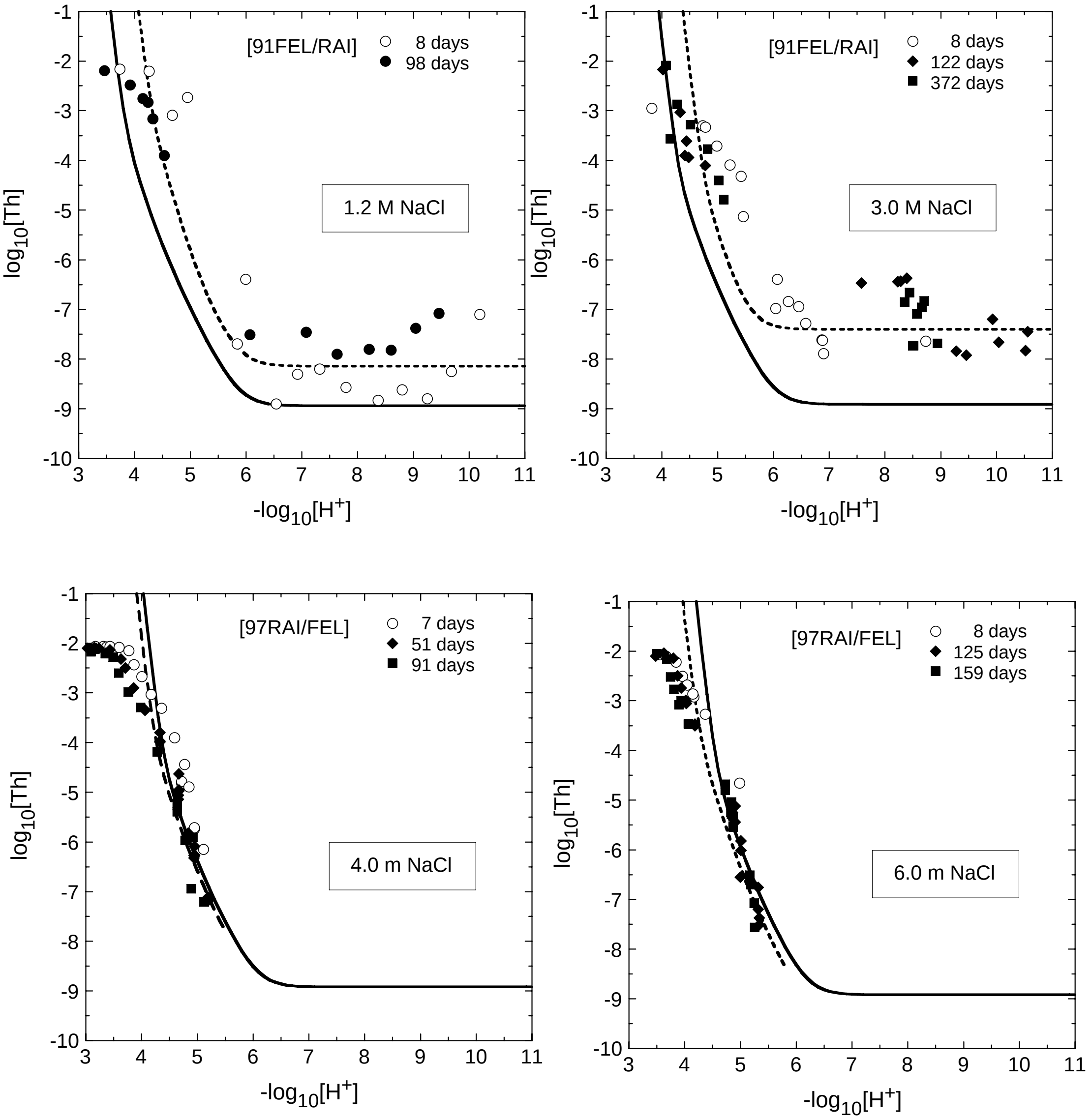

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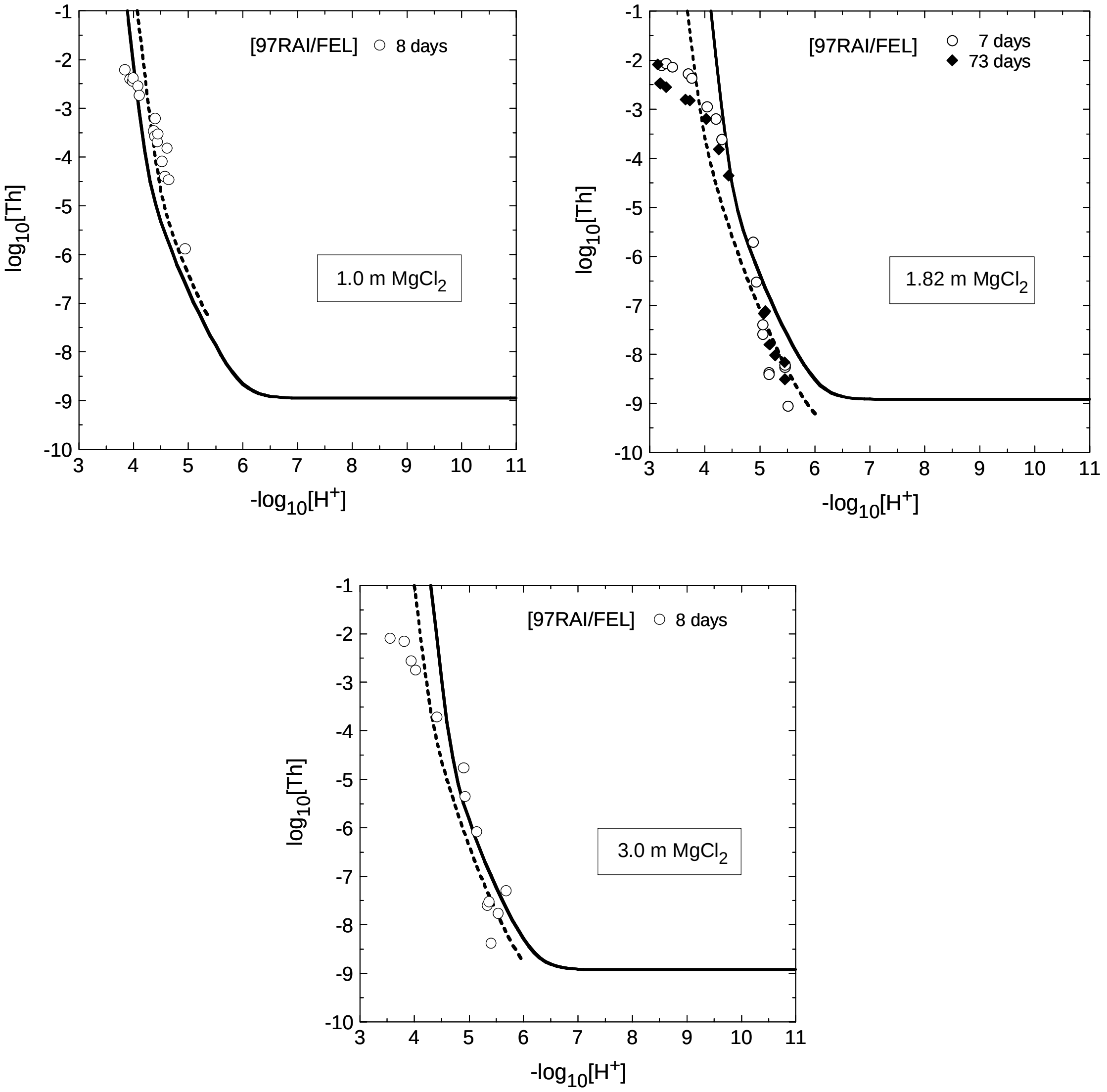
Figure A-34 (continued)



Effect of ageing on the solubility constant

The solubility data determined by [1991FEL/RAI] and [1997RAI/FEL] at pH < 5 in 3 − 6 m NaCl after relatively short equilibration time (< 10 days, open points) and after more than 70 days (filled points) clearly indicate ageing effects. The solubility data for fresh and aged ThO_2(am, hyd) give the solubility constants in Table A-65. The low Th concentrations at pH > 6, show no dependence on equilibration time.

The effect of ageing of ThO_2(am, hyd) precipitates may be interpreted in terms of increasing particle size *via* dissolution-precipitation equilibria, so called Ostwald ripening. This effect is kinetically favoured at higher aqueous Th concentrations, *i.e.*, at low pH.

The mean values of $\log_{10} {}^*K^\circ_{s,0}$ derived from the solubility data measured after equilibration for more than 70 days, $\log_{10} {}^*K^\circ_{s,0} = (9.1 \pm 0.4)$ (from [1991FEL/RAI]), and (8.1 ± 0.6) (from [1997RAI/FEL]), are included in the selection of data for ThO_2(am, aged, hyd). The corresponding solubility curves calculated with the selected solubility constant of $\log_{10} {}^*K^\circ_{s,0}$ (ThO_2(am, aged, hyd) = (8.5 ± 0.9) and the selected hydrolysis constants and SIT coefficients are shown as solid lines in Figure A-34.

Table A-65: Solubility constants $\log_{10} {}^*K^\circ_{s,0}$ at zero ionic strength re-evaluated from solubility studies of [1991FEL/RAI], [1997RAI/FEL] with fresh and aged ThO_2(am, hyd).

Reference	Medium	$\log_{10}{}^*K^\circ_{s,0}(ThO_2$(am, hyd))	
		Fresh (< 10 days)	Aged (> 70 days)
[1991FEL/RAI]	0.6 M NaCl/KCl	(9.5 ± 0.5)	(9.1 ± 0.4)
	1.2 M NaCl	(9.5 ± 0.7)	(9.2 ± 0.4)
	3.0 M NaCl	(9.8 ± 0.4)	(8.9 ± 0.5)
[1997RAI/FEL]	4.0 m NaCl	(8.6 ± 0.5)	(8.2 ± 0.5)
	6.0 m NaCl	(8.4 ± 0.6)	(8.0 ± 0.6)
	1.0 m $MgCl_2$	(8.8 ± 0.4)	

[1991GRE/LAG2]

This is a potentiometric study conducted in a 3.0 M $NaClO_4$ ionic medium at 25°C. The binary Th(IV)-OH^- system was investigated first and the ternary Th(IV)-OH^--CO_3^{2-} system was then studied at two different partial pressures of CO_2(g), 0.29 bar (in N_2(g)) and 0.97 bar. The experiments are described in detail with the primary experimental data listed.

The main part of the study concerns the hydrolysis of Th(IV). The total Th(IV) concentrations used in these studies were 0.275, 0.535, 0.612, 1.066, 2.640 and 6.966 mM and the values of $-\log_{10}[H^+]$ covered a range of 2.5 to 4.1. Six different chemical models were tested against the experimental data using a least-squares program (LETAGROP) where the difference between experimental and calculated emf was minimised. The authors note that all of the solutions contain a large number of complexes, some of which are present in small amounts. All models give a small standard deviation in the error-carrying variable (the measured potential), at most 0.7 mV, corresponding to a standard deviation of 0.01 in $-\log_{10}[\mathrm{H}^+]$. The two best models (Model 1 and Model 2), are given in Table A-66.

Table A-66: Equilibrium constants, $-\log_{10}{}^*\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$ ±3σ in 3 M $\mathrm{NaClO_4}$ and the standard deviation in the error-carrying variable E (in mV) from the least squares analysis of experimental data for the Th(IV)-hydroxide system. U is the error square sum for the different models.

$(n,m) = \mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$	Model 1	Model 2
$(1,1) = \mathrm{ThOH}^{3+}$	4.35 ± 0.09	4.06 ± 0.07
$(3,1) = \mathrm{Th(OH)}_3^+$	12.3 ± 0.2	-
$(4,1) = \mathrm{Th(OH)_4(aq)}$	16.65 ± 0.04	16.58 ± 0.07
$(2,2) = \mathrm{Th_2(OH)}_2^{6+}$	5.10 ± 0.17	5.1 ± 0.2
$(3,2) = \mathrm{Th_2(OH)}_3^{5+}$	7.87 ± 0.05	-
$(8,4) = \mathrm{Th_4(OH)}_8^{8+}$	19.6 ± 0.2	19.17 ± 0.08
$(12,4) = \mathrm{Th_4(OH)}_{12}^{4+}$	34.86 ± 0.05	34.89 ± 0.10
$(14,6) = \mathrm{Th_6(OH)}_{14}^{10+}$	33.67 ± 0.05	-
$(15,6) = \mathrm{Th_6(OH)}_{15}^{9+}$	-	37.57 ± 0.09
$(16,6) = \mathrm{Th_6(OH)}_{16}^{8+}$	42.9 ± 0.4	-
σ(EMF)/mV	0.42	0.70
U(EMF)/(mV)^2	17.27	45.03

The authors selected Model 1, but point out that one can remove species (16,6) and (3,1) without a large changes in the error square sum; this does not change the values of the remaining equilibrium constants within their estimated errors. It is difficult to decide between Models 1 and 2 using even these precise data. Two stoichiometries of the hexanuclear complexes ($\mathrm{Th_6(OH)}_{15}^{9+}$ or $\mathrm{Th_6(OH)}_{14}^{10+}$ with minor amounts of $\mathrm{Th_6(OH)}_{16}^{8+}$) have been suggested in previous studies and the final choice is discussed in the main text (Section VII.3.4.1.4). The present review concludes that there is good evidence for the formation of the following complexes and equilibrium constants:

$\mathrm{Th(OH)}^{3+}$	$\log_{10}{}^*\beta_{1,1} = -(4.2 \pm 0.15)$
$\mathrm{Th_2(OH)}_2^{6+}$	$\log_{10}{}^*\beta_{2,2} = -(5.1 \pm 0.2)$
$\mathrm{Th_4(OH)}_8^{8+}$	$\log_{10}{}^*\beta_{8,4} = -(19.4 \pm 0.2)$
$\mathrm{Th_4(OH)}_{12}^{4+}$	$\log_{10}{}^*\beta_{12,4} = -(34.9 \pm 0.1)$.

These values are accepted by the present review and are included in the evaluation of selected data.

Four of the titrations were made with a total concentration of Th(IV) less than 0.001 M where the formation of a precipitate of hydrous oxide is minimised. However the data at $-\log_{10}[\text{H}^+] > 3.8$ may be influenced by the formation of a precipitate even if none was observed experimentally. The complex $\text{Th(OH)}_4\text{(aq)}$ is formed at the highest values of $-\log_{10}[\text{H}^+]$ and the proposed equilibrium constant is not accepted by this review.

The experimental studies of the carbonate system were made at two different partial pressures of $\text{CO}_2\text{(g)}$ (0.29 and 0.97 atm.). The experimental values of $\bar{Z}\,(\log_{10}[\text{H}^+])$, where $\bar{Z}$ is the average number of protons formed in the reactions, change dramatically from those in the binary Th(IV)-OH$^-$ system, clearly demonstrating that carbonate complexes are formed. However it was not possible to analyse the experimental data in terms of a unique chemical model. Grenthe and Lagerman noticed that the very steep $\bar{Z}\,(\log_{10}[\text{H}^+])$ curves might indicate the formation of complexes with high nuclearity. The proposed complexes are "$\text{Th}_8(\text{OH})_{24}(\text{CO}_2)_2^{8+}$" $\equiv$ $\text{Th}_8(\text{OH})_{20}(\text{CO}_3)_2^{8+}$ and "$\text{Th}_{16}(\text{OH})_{52}(\text{CO}_2)_{16}^{12+}$" $\equiv$ $\text{Th}_{16}(\text{OH})_{20}(\text{CO}_3)_{16}^{12+}$; they might be formed through linking of hydroxide complexes by carbonate bridges. However, this review agrees with [1991GRE/LAG2] that is not possible to deduce a unique chemical model from these data. The formation of large ternary complexes is confirmed by a comparison of the solubility studies of Östhols *et al.* [1994OST/BRU] in 0.5 M NaClO_4 and Altmaier *et al.* [2005ALT/NEC] in 0.5 M NaCl, both studies performed with ThO_2(am, hyd) under CO_2 partial pressures of 1.0 and 0.1 bar. The data of Östhols *et al.* [1994OST/BRU] in the region of minimum solubility at pH 4.5 – 6.5, determined after 300 nm filtration, are considerably higher than those of Altmaier *et al.* [2005ALT/NEC], where large complexes were removed by 1.2 nm ultrafiltration and ultracentrifugation at 5×10^5 g. For the test solutions with the lowest total concentration of Th(IV), the steep rise in the $\bar{Z}$ -curves occurs at $-\log_{10}[\text{H}^+]$ around 3.3, where there should be no precipitation of Th(IV) hydrous oxide and no significant formation of carbonate complexes according to Figure XI-2; the potentiometric and the solubility data are not consistent. A possible explanation suggested by this review might be that hydrous oxides precipitate on the CO_2 gas-bubbles.

[1991JOH/MAG]

The coordination around Th(IV) in aqueous perchlorate, chloride and nitrate solutions has been determined using large angle X-ray scattering (LAXS) data. The total concentration of Th(IV) in the various test solutions range from approximately 1 to 2.5 molal; the concentrations of perchlorate from 5 – 11 m; the concentration chloride from 4 – 7 m and nitrate from 4.4 – 10 m. At these high total concentrations of electrolytes the water activity is significantly different from unity. The hydrogen ion concentration in the test solutions is sufficiently high to prevent hydrolysis.

The data in perchlorate solutions indicates that perchlorate is not coordinated and that the first coordination sphere contains (8.0 ± 0.5) coordinated water ligands with a bond distance Th–OH_2 of 2.48 Å; the perchlorate ions seems to be located in the second coordination sphere, presumably linked by hydrogen bonding and electrostatic interactions to the first sphere. The coordination number in the chloride system is 10.5, with indications of chloride entering the first coordination sphere. One would not expect that coordination of chloride should result in an increase of the coordination number and the difference observed probably indicates the uncertainty in the determination of coordination numbers using LAXS. The LAXS data from nitrate solutions indicate that inner-sphere nitrate complexes are formed and that these are stronger than chloride complexes. The nitrate ligand seems to be bi-dentate coordinated, as in most crystal structures and the coordination number is larger than eight, indicating that several nitrate ligands are coordinated at the high nitrate concentrations used.

[1991MAR2]

This paper describes an empirical electrostatic model for the estimation of the Gibbs energy of hydration of ions. [1987MAR] is a publication with a similar topic but this was not available to the reviewers. We assume that the later study [1991MAR2] is based on the previous one. The key parameters in the model are the charge and "corrected" ionic radii of the ions. The physico-chemical model consists of two parts: the ion with a layer of n water molecules that are considered rigid and subject to electrostriction and a second layer with the same properties as the bulk solvent. The number of water molecules is determined by an empirical fitting using the relationship $n = A|Z|/r$, where A is an empirical parameter. There is no reason to expect that this simplistic expression should give a proper description of the inner coordination sphere of ions. For Th^{4+} the value of n is 14.4, in poor agreement with experimental observations. The correction to the ionic radius, Δr, is a measure of the thickness of the "rigid" layer of water surrounding the hydrated ion; this quantity is also determined by a fitting procedure. The fitted parameters involve a comparison of experimental and calculated Gibbs energy of hydration, $\Delta_{\mathrm{hyd}}G^{\circ}_{\mathrm{m}}$; the result is listed in Table 1 of [1991MAR2]. For thorium the result is $\Delta_{\mathrm{hyd}}G^{\circ}_{\mathrm{m}}$ (calc) = -5395 kJ·mol^{-1} and $\Delta_{\mathrm{hyd}}G^{\circ}_{\mathrm{m}}$ (exp) = -5815 kJ·mol^{-1}. It is of interest to compare these values with the data given by Yang *et al.* [2001YAN/TSU] in their Table 1. They find a difference in binding energy between gas phase and solvent equal to 2663 kJ·mol^{-1} for $Th(H_2O)_9^{4+}$ with slight variations between different geometries (15 kJ·mol^{-1}); the corresponding solvation energy for $Th(H_2O)_{10}^{4+}$ is 2709 kJ·mol^{-1}. These values indicate that the structure of the first coordination sphere affects the hydration energy, an effect that is not taken into account in models of the type used by Marcus. The difference in hydration energy between the empirical and the quantum mechanical model is a factor of about two and it is difficult to judge the reason for this; however one should notice that $\Delta_{\mathrm{hyd}}G^{\circ}_{\mathrm{m}}$ (exp) is not obtained directly but involves a number of extra-thermodynamic assumptions. This review does not consider the Gibbs energy of hydration of Th^{4+} as reliable; however the relative values of the Gibbs energy of solvation listed in Table 1 of [1991MAR2] are probably more reliable than their absolute values.

[1992BIS/KRA]

This paper contains no quantitative information on thorium complexes. The authors note that solubility experiments on hydrous thorium oxide did not reach equilibrium after 2 months and that the only experimental data they have obtained refer to a "quasi-solubility" curve obtained after equilibration for ten days. There is no other useful information for this review.

[1992BLA/WYA]

This report is a comprehensive collection of the energy levels of the gaseous atoms and ions of all the actinide elements. The listing for Th(g) contains 693 energy levels, the highest level being at 46844 cm^{-1}, 2156 cm^{-1} below the ionisation level, (49000 ± 1000) cm^{-1}.

These data have been utilised to calculate S°_{m} (Th, g, 298.15 K) = (190.170 ± 0.010) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $C^{\circ}_{p,\text{m}}$ (Th, g, 298.15 K) = (20.790 ± 0.005) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The calculated heat capacities at higher temperatures have been fitted four-term equations as a function of T.

The uncertainties have been estimated by this review.

[1992ENG/ALB]

The authors have used liquid-liquid extraction to investigate the hydrolysis of Th(IV) and the complex formation with acetylacetone, which transfers Th(IV) from an aqueous to a toluene phase. The experiments have been made at 25°C in a 1 M NaClO_4 ionic medium over the pH range 1 − 11. The pH was measured using a glass-electrode calibrated with standard buffers; hence the reported equilibrium constants are not concentration constants but "mixed" equilibrium constants. The authors mention neither the electrode system used for pH measurements, nor how they converted measured pH values into $\log_{10}[\text{H}^+]$ or $\log_{10}[\text{OH}^-]$. They mention that no corrections were made for different liquid junction potentials during calibration and 1.0 M NaClO_4 test solutions. Depending on the electrode type and junction electrolyte used, this can lead to large errors for up to 0.3 units in $\log_{10}[\text{H}^+]$. With the exception of these shortcomings, the experimental method used is satisfactory; the measured distribution coefficients are not dependent on sorption of Th(IV) on the container walls. The analysis of the data is less satisfactory, the proposed equilibrium constants have large uncertainties and do not describe the experimental data except in certain regions; it is obvious to this review that the chemical model is incomplete.

The measured distribution coefficient, D_{M}, is equal to:

$$D_M = \frac{\lambda_4\,\beta_{140}[\mathrm{L}]^4}{1+\sum_1^n \beta_{1n0}[\mathrm{L}]^n + \sum_1^p \beta_{10p}[\mathrm{OH}]^p} \tag{A.82}$$

where the equilibrium constant for the reaction:

$$m\mathrm{Th}^{4+} + n\mathrm{L}^- + p\mathrm{OH}^- \rightleftharpoons \mathrm{Th}_m\mathrm{L}_n(\mathrm{OH})_p^{4m-n-p}$$

is

$$\beta_{m,n,p} = \frac{[\mathrm{Th}_m\mathrm{L}_n(\mathrm{OH})_p^{4m-n-p}]}{[\mathrm{Th}^{4+}]^m[\mathrm{L}]^n[\mathrm{OH}]^p}\,; \tag{A.83}$$

HL is acetylacetone, and L^- the corresponding anion, the concentration of which can be calculated as shown in Eq. (A.84),

$$[\mathrm{L}^-] = \frac{K_a\left[\mathrm{HL}\right]_{\mathrm{org}}}{\left[\mathrm{H}^+\right](1+K_d+K_a\left[\mathrm{H}^+\right]^{-1})}\,; \tag{A.84}$$

D_M is the measured distribution coefficient for M = Th between the organic and aqueous phases, λ_4 the distribution coefficient of the uncharged complex $\mathrm{ThL_4}$, K_a the dissociation constant of HL and K_d the distribution coefficient for HL between 1 M $\mathrm{NaClO_4}$ and toluene.

The reported equilibrium constants are given in Table A-67.

Table A-67: Equilibrium constants for Th(IV) hydroxide and acetylacetonate complexes at 25°C in 1 M $\mathrm{NaClO_4}$. The distribution coefficient K_d(HL) between toluene and water is 3.23. The value of λ_4 is 427.

Complex	$\log_{10}\beta_{m,n,p}$
$\mathrm{ThL^{3+}}$	$\log_{10}\beta_{1,1,0} = 8.2 \pm 0.6$
$\mathrm{ThL_2^{2+}}$	$\log_{10}\beta_{1,2,0} = 15.4 \pm 0.6$
$\mathrm{ThL_3^{+}}$	$\log_{10}\beta_{1,3,0} = 22.6 \pm 1.9$
$\mathrm{ThL_4}$	$\log_{10}\beta_{1,4,0} = 25.8 \pm 1.2$
$\mathrm{Th(OH)^{3+}}$	$\log_{10}\beta_{1,0,1} = 9.1 \pm 3.1$
$\mathrm{Th(OH)_2^{2+}}$	$\log_{10}\beta_{1,0,2} = 19.0 \pm 2.7$
$\mathrm{Th(OH)_3^{+}}$	$\log_{10}\beta_{1,0,3} = 26.2 \pm 2.9$
$\mathrm{Th(OH)_4(aq)}$	$\log_{10}\beta_{1,0,4} = 33.1 \pm 3.0$
$\mathrm{L^-}$	$\log_{10}K_\mathrm{a} = -9.0$

The total concentration of Th is low, 0.1 mM, indicating that mononuclear complexes are favoured; however, previous potentiometric data indicate that polynuclear complexes still play an important role at this low concentration. From Eq. (A.82) it is apparent that the authors have not taken the possible formation of ternary complexes into account. As the primary experimental data are only given in the rather small figures we have not been able to reanalyse them. However, the large uncertainty in the reported equilibrium constants and the neglect of ternary and polynuclear complexes makes the constants proposed unreliable.

[1992EWA/SMI]

Ewart *et al.* [1992EWA/SMI] studied the solubilities of thorium, protactinium, uranium, neptunium, plutonium, and americium, presumably at room temperature (*ca.* 22°C) under conditions representative of a cementitious near-field environment. The solubility of $Th(OH)_4(s)$ in water pre-equilibrated with 1:3 ordinary Portland cement / blast furnace sludge plus limestone aggregate ($I \approx 0.03$ M) was measured from oversaturation at $[Th]_{tot} = 10^{-4}$ M by adding an aliquot of $ThCl_4$ stock solution and adjusting pH in the range of 8 – 13. The experiments were performed in a nitrogen glove box. The thorium concentrations analysed by ICP-MS after 25000 − 30000 MWCO (Molecular Weight Cut-Off) (*ca.* 2 – 4 nm) ultrafiltration were in the range $(4 \pm 2) \times 10^{-9}$ M, independent of pH. Equilibration time and pH measurement are not reported in this paper, but the results are comparable to those of other authors [1989MOO], [1987RYA/RAI], [1991FEL/RAI], [2002NEC/MUL].

[1992FEL/RAI]

The study was undertaken to develop a reliable thermodynamic model for thorium sulphate systems extending from dilute to concentrated electrolytes (Li_2SO_4, NH_4SO_4, Na_2SO_4, K_2SO_4, H_2SO_4) in order to account for strong ion-interactions or complex formation that can occur for these electrolytes in dilute solution. Extensive use was made of the solvent extraction data reported by [1963ALL/MCD] and of the solubility data summarised in [1965LIN2] to develop a comprehensive thermodynamic model using the Pitzer approach. The model developed in this study included 1) Pitzer ion-interaction parameters for Th^{4+} with sulphate and bisulphate and for $Th(SO_4)_3^{2-}$ with the bulk electrolyte cations, and 2) molar Gibbs energies of formation of aqueous species ($Th(SO_4)_2(aq)$ and $Th(SO_4)_3^{2-}$) and for several $Th(SO_4)_2{\cdot}xH_2O$ (x = 4, 8, or 9) solids and double salts of $Th(SO_4)_2$ with Na_2SO_4, K_2SO_4, and $(NH_4)_2SO_4$. The Pitzer ion-interaction parameters and $\Delta_f G^o_m/RT$ values for all of the species used in the model are listed in the Table A-68 and Table A-69 given below. Temperature-corrected Pitzer ion-interaction parameter values, the chemical potential of water and A^{φ}, a Debye-Hückel term, were used to correct for temperature effects. The predictions by this model provided close agreement with extensive reliable experimental solvent extraction and solubility data [1965LIN2] extending from dilute to concentrated electrolytes. In addition to the values reported for various solids, the authors show that the $\Delta_f G^o_m$ value listed by [1982WAG/EVA] for $Th(SO_4)_2(cr)$ most likely is in error.

Table A-68: Ion interaction (Pitzer) parameters given in [1992FEL/RAI].

Binary interactions

Cation	Anion	$\beta^{(o)}$ (kg·mol^{-1})	$\beta^{(1)}$ (kg·mol^{-1})	$\beta^{(2)}$ (kg·mol^{-1})	C$^{\varphi}$ (kg^2·mol^{-2})
Na^+	SO_4^{2-}	0.01958	1.113	—	0.00497
Na^+	HSO_4^-	0.0454	0.398	—	—
Na^+	OH^-	0.0864	0.253	—	0.0044
Na^+	$Th(SO_4)_3^{2-}$	0.12	—	—	—
K^+	SO_4^{2-}	0.04995	0.7793	—	—
K^+	$Th(SO_4)_3^{2-}$	0.90	—	—	—
Li^+	SO_4^{2-}	0.136	1.27	—	–0.00406
Li^+	$Th(SO_4)_3^{2-}$	0.52	—	—	—
Th^{4+}	SO_4^{2-}	1.56	—	—	—
Th^{4+}	HSO_4^-	1.44	—	—	—
Th^{4+}	Cl^-	1.014	13.3	–200	–0.103
H^+	SO_4^{2-}	0.0298	—	—	0.0438
H^+	HSO_4^-	0.2065	0.5556	—	—
H^+	$Th(SO_4)_3^{2-}$	0.84	—	—	—
NH_4^+	$Th(SO_4)_3^{2-}$	0.26	—	—	—

Neutral species	Anion	λ (kg·mol^{-1})
$Th(SO_4)_2(aq)$	HSO_4^-	0.68
$Th(SO_4)_2(aq)$	Cl^-	0.29

Ternary interactions

Cation	Cation	Anion	θ_{cc} (kg·mol^{-1})	ψ_{cca} (kg^2·mol^{-2})
NH^{4+}	Th^{4+}	SO_4^{2-}	−0.44	0.06
H^+	Th^{4+}	Cl^-	0.60	0.08

Table A-69**:** Dimensionless molar Gibbs energies of formation at 25°C unless otherwise identified (from [1992FEL/RAI]).

Species	Temperature (ºC)	$\Delta_f G_m / RT$
$H_2O(l)$	16	– 96.375
$H_2O(l)$		– 95.6635
$H_2O(l)$	30	– 95.297
SO_4^{2-}		– 300.386
Th^{4+}		– 284.227
$Th(SO_4)_2(aq)$		– 911.69
$Th(SO_4)_3^{2-}$		– 1214
$Th(SO_4)_2\cdot Na_2SO_4\cdot 6H_2O(s)$	16	– 2011.29
$Th(SO_4)_2\cdot (NH_4)_2SO_4\cdot 4H_2O(s)$	16	– 1668.39
$Th(SO_4)_2\cdot 2(NH_4)_2SO_4\cdot 2H_2O(s)$	16	– 1841.41
$Th(SO_4)_2\cdot 3(NH_4)_2SO_4\cdot 3H_2O(s)$	16	– 2303.52
$Th(SO_4)_2\cdot K_2SO_4\cdot 4H_2O(s)$	16	– 1837.57
$Th(SO_4)_2\cdot 2K_2SO_4\cdot 2H_2O(s)$	16	– 2181.81
$Th(SO_4)_2\cdot 3.5K_2SO_4(s)$	16	– 2790.83
$Th(SO_4)_2\cdot 9H_2O(s)$		– 1775.9
$Th(SO_4)_2.\cdot 9H_2O(s)$	16	– 1782.38
$Th(SO_4)_2\cdot 8H_2O(s)$		– 1680
$Th(SO_4)_2\cdot 8H_2O(s)$	30	– 1677.07
$Th(SO_4)_2\cdot 4H_2O(s)$	30	– 1294.13

The $\Delta_f G_m^o / RT$ values of Th species, along with the values for auxiliary species reported by the authors, were used to calculate equilibrium constants for reactions involving thorium sulphate compounds and complexes (Table A-70). The literature data used by [1992FEL/RAI] formed the basis for developing a model based on SIT parameters. For these interpretations the SIT parameters reported in Table IX-2 and the values of β_1^o, β_2^o, and β_3^o selected in this review (Table IX-1) were used in the NONLINT-SIT program to determine the solubility products of various hydrated thorium sulphates. The details of these calculations are discussed in the text sections IX.1.3.3 and IX.1.3.4. The solubility products reported in Table A-70 are on an average about 1.9 $\log_{10}$-units lower than the solubility products calculated by this review with the SIT model (see Table IX-4). This is primarily a result of differences in the $\log_{10} \beta_2^o$ and $\log_{10} \beta_3^o$ values of (9.69 ± 0.27) and (10.748 ± 0.076) with the SIT model and of 11.592 and 12.427 used by [1992FEL/RAI] for $Th^{4+} + n\,SO_4^{2-} \rightleftharpoons Th(SO_4)_n^{4-2n}$. It should be noted that apart from these differences the fits to experimental data are equally good with both models, in the ionic strength range where the SIT model is applicable.

Table A-70: Equilibrium constants of reactions involving thorium sulphate compounds and complexes. The values are based on the Pitzer model and the $\Delta_f G_m^o/RT$ values presented in [1992FEL/RAI].

Reaction	Temperature (ºC)	$\log_{10} K^o$
$Th^{4+} + 2\,SO_4^{2-} \rightleftharpoons Th(SO_4)_2(aq)$		11.592
$Th^{4+} + 3\,SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-}$		12.427
$Th(SO_4)_2 \cdot Na_2SO_4 \cdot 6H_2O(s) \rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2\,Na^+ + 6\,H_2O$	16	– 15.788
$Th(SO_4)_2 \cdot (NH_4)_2SO_4 \cdot 4H_2O(s) \rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2\,NH_4^+ + 4\,H_2O$	16	– 14.535
$Th(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O(s) \rightleftharpoons Th^{4+} + 4\,SO_4^{2-} + 4\,NH_4^+ + 2\,H_2O$	16	– 15.088
$Th(SO_4)_2 \cdot 3(NH_4)_2SO_4 \cdot 3H_2O(s) \rightleftharpoons Th^{4+} + 5\,SO_4^{2-} + 6\,NH_4^+ + 3\,H_2O$	16	– 15.669
$Th(SO_4)_2 \cdot K_2SO_4 \cdot 4H_2O(s) \rightleftharpoons Th^{4+} + 3\,SO_4^{2-} + 2K^+ + 4\,H_2O$	16	– 16.838
$Th(SO_4)_2 \cdot 2K_2SO_4 \cdot 2H_2O(s) \rightleftharpoons Th^{4+} + 4\,SO_4^{2-} + 4\,K^+ + 2\,H_2O$	16	– 20.612
$Th(SO_4)_2 \cdot 3.5K_2SO_4(s) \rightleftharpoons Th^{4+} + 5.5\,SO_4^{2-} + 7\,K^+$	16	– 24.660
$Th(SO_4)_2 \cdot 9H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 9\,H_2O$	25	– 12.998
$Th(SO_4)_2 \cdot 9H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 9\,H_2O$	16	– 13.031
$Th(SO_4)_2 \cdot 8H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 8\,H_2O$	25	– 12.896
$Th(SO_4)_2 \cdot 8H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 8\,H_2O$	30	– 12.896
$Th(SO_4)_2 \cdot 4H_2O(s) \rightleftharpoons Th^{4+} + 2\,SO_4^{2-} + 4\,H_2O$	30	– 12.135

[1992FUG/KHO]

This standard text on the chemical thermodynamics of actinide elements contains information on most of the inorganic complexes of Th(IV) that are discussed in the present critical review. As judged by the Introduction the authors have used the same principles of evaluation as in the present critical review to evaluate the equilibrium constants of aqueous inorganic complexes, with the difference that the Guggenheim equation

$$\log_{10} \beta_n = \log_{10} \beta_n^o + \Delta z^2 \frac{A\sqrt{\mu}}{1+\sqrt{\mu}} + B\mu$$

has been used to calculate the ionic strength dependence of the equilibrium constants. μ is the ionic strength, z the ionic charge, A the Debye-Hückel parameter and B a specific ion interaction parameter that is not identical with the corresponding parameter ε because of the different Debye-Hückel terms; there are no tabulations of the B parameters. The difference between the equilibrium constants at zero ionic strength calculated with the Guggenheim and SIT approaches is usually small. The analysis of the different experimental studies is not as well documented as in the NEA series and accordingly only the final outcome of the analysis can be compared with the ones obtained in the present review. These equilibrium constants are listed in the tables in the main chapter. For the important Th(IV)-hydroxide system the authors of [1992FUG/KHO] have not selected any constants at zero ionic strength. Equilibrium constants have been selected for the complexes ThF^{3+}, ThF_2^{2+}; $ThCl^{3+}$, $ThCl_2^{2+}$; $ThClO_3^{3+}$; $ThBrO_3^{3+}$; $ThIO_3^{3+}$; $ThSO_4^{2+}$; $Th(SO_4)_2(aq)$; $Th(NO_3)_n^{4-n}$, $n = 1-4$; $Th(H_3PO_4)^{4+}$, $Th(H_2PO_4)^{3+}$, $Th(H_2PO_4)_2^{2+}$ $Th(H_3PO_4)(H_2PO_4)^{3+}$; $Th(CrO_4)^{2+}$. In addition there are discussions of complex formation in the following binary Th(IV) systems: N_3^-; HPO_4^{2-}; $P_2O_7^{4-}$ and SCN^-. The corresponding experimental data are also discussed in the present review.

[1993ABE/GLA]

The authors have studied the tetranuclear complex "$Zr_4(OH)_8^{8+}$" in aqueous solution using NMR spectroscopy. Based on these data they suggest that the stoichiometry of the complex is $[Zr_4(OH)_8(OH_2)_8^{I}(OH_2)_8^{II}]^{8+}$, where $(OH_2)^{I}$ and $(OH_2)^{II}$ denote two different sites of the coordinated water that differ by their rate of exchange of protons with the bulk water. The authors also note the extremely slow rates of exchange of both water and hydroxide with the water solvent, a feature that is much more pronounced than in the less hydrolysed Th(IV).

[1993FEL/RAI]

The solubilities of a number of binary and ternary thorium fluorides were studied as a function of the concentrations of NaF and NH_4F. The original precipitate was formed by reacting thorium stock solution in 0.1 M HNO_3 with 0.1 M HF and portions of this precipitate was suspended in NaF and NH_4F solutions ranging in concentrations from 0.0001 M to 1.0 M. The suspensions were equilibrated over a period of about 3 months at room temperature (this review has assumed a temperature of (22 ± 2)°C). All equilibrated solids were found to be crystalline and characterised by XRD and total chemical analyses. The characterised solids in the NaF system included $ThF_4{\cdot}xH_2O(s)$, $ThF_4{\cdot}NaF{\cdot}H_2O(s)$, and $ThF_4{\cdot}3NaF(s)$, and those in the NH_4F system included $ThF_4{\cdot}xH_2O(s)$ and $ThF_4{\cdot}NH_4F(s)$. The aqueous phase concentrations were determined after filtration through ~ 0.0018 µm filters. The measured pH values were > 4.2 indicating that F^-, rather than HF(aq), is the important aqueous fluoride species. The data were interpreted using the Pitzer model. The values of $\Delta_f G_m^o / RT$ for ThF_3^+ and $ThF_4(aq)$ were calculated from the data given by [1982WAG/EVA]; other values, including the $\Delta_f G_m^o / RT$ values for $ThF_4{\cdot}xH_2O(s)$, $ThF_4{\cdot}NaF{\cdot}H_2O(s)$, $ThF_4{\cdot}NH_4F(s)$, ThF_5^-, and ThF_6^{2-} and the associated Pitzer ion-interaction parameters for the important species, were fitted. For reasons given in the discussion of these values in Section VIII.1.3, the proposed equilibrium constants based on the data of [1982WAG/EVA] have not been accepted. Although [1993FEL/RAI] do not list $\Delta_f G_m^o / RT$ values for ThF^{3+} and ThF_2^{2+}, they state that according to the data reported in [1982WAG/EVA], these species do not contribute significantly to the total thorium concentrations at the fluoride concentrations used in the experiments. The values of equilibrium constants determined from the $\Delta_f G_m^o / RT$ values and of the important Pitzer ion interaction parameters they report are given in the following tables.

Table A-71: Ion interaction parameters used by [1993FEL/RAI] in studies with thorium in NaF and NH_4F solutions.

Species	$\beta^{(0)}$ ($kg \cdot mol^{-1}$)	$\beta^{(1)}$ ($kg \cdot mol^{-1}$)	C^{φ} ($kg^2 \cdot mol^{-2}$)
Na^+ -F^-	0.0215	0.2107	0.0
NH_4^+ -F^-	0.08089	0.2021	0.00093
NH_4^+ - ThF_6^{2-}	– 1.3	0.0	0.0

Table A-72: Equilibrium constants for different reactions based on the data in [1993FEL/RAI].

Reaction	$\log_{10} K^{\circ}$
$Th^{4+} + 3F^- \rightleftharpoons ThF_3^+$	18.891 [a]
$Th^{4+} + 4F^- \rightleftharpoons ThF_4(aq)$	22.239[a]
$Th^{4+} + 5F^- \rightleftharpoons ThF_5^-$	24.763 [b]
$Th^{4+} + 6F^- \rightleftharpoons ThF_6^{2-}$	25.562 [b]
$ThF_4 \cdot xH_2O(cr) \rightleftharpoons Th^{4+} + 4F^- + xH_2O(l)$	–28.927 [b]
$ThF_4 \cdot NaF \cdot H_2O(cr) \rightleftharpoons Th^{4+} + 5F^- + Na^+ + H_2O(l)$	–34.028 [b]
$ThF_4 \cdot NH_4F(cr) \rightleftharpoons Th^{4+} + 5F^- + NH_4^+$	–33.888 [b]

a: Values from [1982WAG/EVA].

b: Uncertainty values are not reported by the authors, but they are far less than 0.2 in all cases

The study of [1993FEL/RAI] is the only source of data available for double salts and for the solubility of ThF_4(cr, hyd) in relatively dilute solutions where the fluoride accounts for the major portion of the total fluoride concentrations. This is also the only study conducted at relatively high fluoride concentrations where the anionic thorium fluoride complexes are shown to be important. The aqueous phase model selected in this review is significantly different from the aqueous phase model used by [1993FEL/RAI]. Therefore to obtain data for the double salts and the anionic thorium fluoride complexes, and to develop a comprehensive model consistent with all of the available information, it was necessary to reinterpret these data, as discussed in detail in Sections VIII.1.2 and VIII.1.3. Based on the thermodynamic data selected/fitted from [1993FEL/RAI] (Tables VIII-8 and VIII-9), comparisons of the observed [1993FEL/RAI] and predicted concentrations are presented in Figures VIII-3 and VIII-4 and in Table A-73 to Table A-76.

Table A-73: Experimental and predicted concentrations for the solubility of ThF_4(cr, hyd) at 25°C in NaF solutions (data from [1993FEL/RAI]) using the thermodynamic model selected in this review (Tables VIII-8 and VIII-9); data plotted in Figure VIII-3b.

Experimental concentrations (m)		Predicted concentrations (m)							
NaF $\times10^3$	Th $_{\text{total}}$ $\times10^7$	Th $_{\text{total}}$ $\times10^7$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^{+}	ThF_4(aq)	ThF_2^{6-}	F^- $\times10^3$
0.1720	9.052	7.235	0	3.187×10^{-12}	2.850×10^{-9}	4.990×10^{-8}	6.707×10^{-7}	8.562×10^{-11}	0.1684
0.1750	9.526	7.226	0	3.035×10^{-12}	2.758×10^{-9}	4.908×10^{-8}	6.707×10^{-7}	8.851×10^{-11}	0.1712
0.4990	6.466	6.892	0	1.437×10^{-13}	3.525×10^{-10}	1.734×10^{-8}	6.707×10^{-7}	7.620×10^{-10}	0.4964
0.4690	6.810	6.902	0	1.726×10^{-13}	3.986×10^{-10}	1.845×10^{-8}	6.707×10^{-7}	6.718×10^{-10}	0.4663
0.9410	5.690	6.829	0	0	1.044×10^{-10}	9.346×10^{-9}	6.707×10^{-7}	2.778×10^{-9}	0.9387
0.9620	5.690	6.829	0	0	9.998×10^{-11}	9.145×10^{-9}	6.707×10^{-7}	2.905×10^{-9}	0.9597
5.000	7.974	7.582	0	0	4.684×10^{-12}	1.902×10^{-9}	6.707×10^{-7}	8.555×10^{-8}	4.997
5.000	8.405	7.581	0	0	4.684×10^{-12}	1.902×10^{-9}	6.707×10^{-7}	8.554×10^{-8}	4.996
10.00	11.21	10.34	0	0	1.376×10^{-12}	1.003×10^{-9}	6.707×10^{-7}	3.627×10^{-7}	9.995
10.00	7.716	10.35	0	0	1.375×10^{-12}	1.003×10^{-9}	6.707×10^{-7}	3.628×10^{-7}	9.996

Table A-74: Experimental and predicted concentrations for the solubility of $ThF_4\cdot NaF\cdot H_2O$(cr) at 25°C in NaF solutions (data from [1993FEL/RAI]) using the thermodynamic model selected in this review (Tables VIII-8 and VIII-9); data plotted in Figure VIII-4a.

Experimental concentrations (m)		Predicted concentration (m)							
NaF$\times10^2$	Th $_{\text{total}}\times10^8$	Th $_{\text{total}}\times10^8$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^{+}	ThF_4(aq)	ThF_2^{6-}	$F^-\times10^2$
5.000	4.052	1.917	0	0	0	3.870×10^{-13}	1.073×10^{-9}	1.810×10^{-8}	5.000
5.000	4.095	1.917	0	0	0	3.870×10^{-13}	1.073×10^{-9}	1.810×10^{-8}	5.000
10.00	1.595	2.370	0	0	0	0	2.988×10^{-10}	2.340×10^{-8}	10.00
10.00	2.931	2.370	0	0	0	0	2.988×10^{-10}	2.340×10^{-8}	10.00
20.00	1.336	3.236	0	0	0	0	8.409×10^{-11}	3.228×10^{-8}	20.00
20.00	2.026	3.236	0	0	0	0	8.409×10^{-11}	3.228×10^{-8}	20.00

Table A-75: Experimental and predicted concentrations for the solubility of ThF_4(cr, hyd) at 25°C in NH_4F solutions (data from [1993FEL/RAI]) using the thermodynamic model selected in this review (Tables VIII-8 and VIII-9); data plotted in Figure VIII-3a.

Experimental concentrations (m)		Predicted concentrations (m)							
$NH_4F\times10^3$	$Th_{total}\times10^7$	$Th_{total}\times10^7$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	ThF_2^{6-}	$F^-\times10^3$
0.100	8.620	5.059	0	1.140×10^{-12}	1.279×10^{-9}	2.814×10^{-8}	4.764×10^{-7}	9.708×10^{-11}	0.2126
0.100	6.770	5.012	0	6.890×10^{-13}	9.125×10^{-10}	2.375×10^{-8}	4.764×10^{-7}	1.370×10^{-10}	0.2523
0.500	2.740	4.885	0	7.773×10^{-14}	2.085×10^{-10}	1.123×10^{-8}	4.764×10^{-7}	6.529×10^{-10}	0.5449
0.500	5.820	4.899	0	1.115×10^{-13}	2.657×10^{-10}	1.269×10^{-8}	4.764×10^{-7}	5.094×10^{-10}	0.4817
1.00	5.260	4.850	0	0	6.739×10^{-11}	6.326×10^{-9}	4.764×10^{-7}	2.179×10^{-9}	0.9859
1.00	3.790	4.849	0	0	6.325×10^{-11}	6.127×10^{-9}	4.764×10^{-7}	2.326×10^{-9}	1.018
5.00	6.640	5.386	0	0	3.326×10^{-12}	1.351×10^{-9}	4.764×10^{-7}	6.080×10^{-8}	4.997
5.00	7.370	5.385	0	0	3.326×10^{-12}	1.351×10^{-9}	4.764×10^{-7}	6.079×10^{-8}	4.997
10.00	8.280	7.349	0	0	9.766×10^{-13}	7.125×10^{-10}	4.764×10^{-7}	2.578×10^{-7}	9.996
10.00	2.970	7.350	0	0	9.762×10^{-13}	7.123×10^{-10}	4.764×10^{-7}	2.579×10^{-7}	9.998

Table A-76: Experimental and predicted concentrations for the solubility of $ThF_4\cdot NH_4F$(cr) at 25°C in NH_4F solutions (data from [1993FEL/RAI]) using the thermodynamic model selected in this review (Tables VIII-8 and VIII-9); data plotted in Figure VIII-4b.

Experimental concentrations (m)		Predicted concentrations (m)							
$NH_4F\times10$	$Th_{total}\times10^7$	$Th_{total}\times10^7$	Th^{4+}	ThF^{3+}	ThF_2^{2+}	ThF_3^+	ThF_4(aq)	ThF_2^{6-}	$F^-\times10$
0.5000	0.4570	0.6007	0	0	0	1.208×10^{-12}	3.355×10^{-9}	5.671×10^{-8}	0.5000
0.5000	0.4400	0.6007	0	0	0	1.208×10^{-12}	3.355×10^{-9}	5.671×10^{-8}	0.5000
1.000	0.2800	0.7412	0	0	0	1.863×10^{-13}	9.301×10^{-10}	7.319×10^{-8}	1.000
1.000	0.3190	0.7412	0	0	0	1.863×10^{-13}	9.301×10^{-10}	7.319×10^{-8}	1.000
2.000	0.3710	1.009	0	0	0	0	2.598×10^{-10}	1.006×10^{-7}	2.000
2.000	0.6640	1.009	0	0	0	0	2.598×10^{-10}	1.006×10^{-7}	2.000
5.000	2.440	1.764	0	0	0	0	4.760×10^{-11}	1.764×10^{-7}	5.000
5.000	2.410	1.764	0	0	0	0	4.760×10^{-11}	1.764×10^{-7}	5.000
10.000	15.60	3.253	0	0	0	0	1.269×10^{-11}	3.253×10^{-7}	10.000
10.000	16.20	3.253	0	0	0	0	1.269×10^{-11}	3.253×10^{-7}	10.000

[1994BAG/FOU]

The solubility of well characterised $Th_3(PO_4)_4$(s) was measured at different concentrations of perchloric acid from 0.01 to 1 M. The temperature was presumably "room-temperature", 20−25°C, but the ionic strength seems to have varied between the different test solutions used. Equilibrium was attained after 8 hours and the solubility remained constant for periods of several weeks. Care was taken to ensure that the solubility was not compromised by the presence of colloids. The authors also checked that the solid phase did not change in contact with the aqueous phase. When analysing the experimental solubility data, Baglan *et al.* [1994BAG/FOU] used auxiliary data for the protonation of phosphate and the hydrolysis of Th(IV) that are in good agreement with those selected in the present review. The authors suggest that the solubility product is $\log_{10} K^{\circ}_{s,0} = -(112 \pm 2.1)$ for the reaction:

$$\mathrm{Th_3(PO_4)_4(s)} \rightleftharpoons 3\mathrm{Th^{4+}} + 4\mathrm{PO_4^{3-}}$$

but the procedure used to obtain the solubility product at zero ionic strength is not clear. The proposed solubility product is much lower than reported in [1956CHU/STE], $\log_{10} K^{\circ}_{s,0} = -(79 \pm 1)$. The total concentration of phosphate is so small both in [1994BAG/FOU] and [1956CHU/STE] that one can neglect the formation of phosphate complexes.

[1994OST/BRU]

Östhols *et al.* [1994OST/BRU] made a systematic solubility study with hydrous thorium oxide in carbonate solution to determine the stoichiometry and equilibrium constants of the thorium complexes with carbonate. The solid phase has been dried at room temperature for one week in a vacuum desiccator and characterised as X-ray amorphous, microcrystalline $\mathrm{ThO_2{\cdot}}x\mathrm{H_2O(s)}$ with a water content of $x = 2.4$. The solubility has been determined in equilibrium with 0, 10 and 100% $\mathrm{CO_2(g)}$ and also in batch experiments where the ratio of carbonate/bicarbonate was varied at constant total concentration of carbonate + bicarbonate ($C_{\mathrm{tot}} = 0.1$ M). All experiments were performed at 25°C and constant ionic strength ($I = 0.5$ M, $\mathrm{NaClO_4}$ medium). The authors have given detailed information about the experimental procedures and primary data. The equilibrium constants used to calculate the concentration of $\mathrm{OH^-}$, $\mathrm{HCO_3^-}$ and $\mathrm{CO_3^{2-}}$ from the measured the $\mathrm{H^+}$ concentration were taken from [1992GRE/FUG]. The ion interaction (SIT) coefficients used for ionic strength corrections are the same as or close to those selected in the present review.

Östhols *et al.* have also reanalysed the experimental data in [1987JOA/BIG2]; they point out that the Th(IV) EDTA complex used to evaluate the equilibrium constant for the formation of $\mathrm{Th(CO_3)_5^{6-}}$ is $\mathrm{Th(EDTA)(OH)^-}$, not Th(EDTA)(aq), but it is not clear from [1994OST/BRU] how they arrived at the recalculated value of $\log_{10} \beta_{105}$; this review has therefore reanalysed the data in [1987JOA/BIG2] as described in the Appendix A entry for that paper.

1. Solubility in carbonate-free solution

From the experimental solubility data in carbonate-free solution at $-\log_{10}[\mathrm{H^+}] = 3.3 - 4.1$, Östhols *et al.* [1994OST/BRU] calculated a solubility constant of $\log_{10} {}^{*}K_{s,0} = (9.37 \pm 0.13)$ in 0.5 M $\mathrm{NaClO_4}$ and $\log_{10} {}^{*}K^{\circ}_{s,0} = (7.3 \pm 0.3)$ at zero ionic strength.

However, the hydrolysis model with the species $Th(OH)^{3+}$, $Th(OH)_3^+$, $Th(OH)_4(aq)$, $Th_2(OH)_2^{2+}$ and $Th_2(OH)_3^{5+}$, and some of the hydrolysis constants taken from [1976BAE/MES], [1991GRE/LAG2] and converted to I = 0.5 M with the SIT, differ considerably from the selections in the present review. Therefore, the solubility constant is re-evaluated using the hydrolysis constants and SIT coefficients selected by this review. The recalculated value, $\log_{10} {}^*K^\circ_{s,0} = (8.0 \pm 0.5)$, is included in the selection of the solubility constant for ThO_2(am, hyd). It is comparable to that derived from a solid phase prepared in the same way by [2002NEC/MUL] and to aged thorium oxyhydroxide precipitates (*cf.* Section VII.4.1.1). Polynuclear hydroxide complexes are minor species in the test solutions of [1994OST/BRU] at $-\log_{10}[H^+] = 3.3-4.1$ (*cf.* Figure VII-14).

2. Solubility under 0.1 and 1.0 bar $CO_2(g)$

The solubility measured by Östhols *et al.* [1994OST/BRU] under $CO_2(g)$ partial pressures of 0.1 bar ($-\log_{10}[H^+] = 4.6-7.4$) and 1.0 bar ($-\log_{10}[H^+] = 4.1-6.3$) has been interpreted by the formation of a single ternary complex, (131) = $Th(OH)_3(CO_3)^-$, according to:

$$ThO_2(\text{am, hyd}) + H^+ + H_2O(l) + CO_3^{2-} \rightleftharpoons Th(OH)_3(CO_3)^- \qquad (A.85)$$

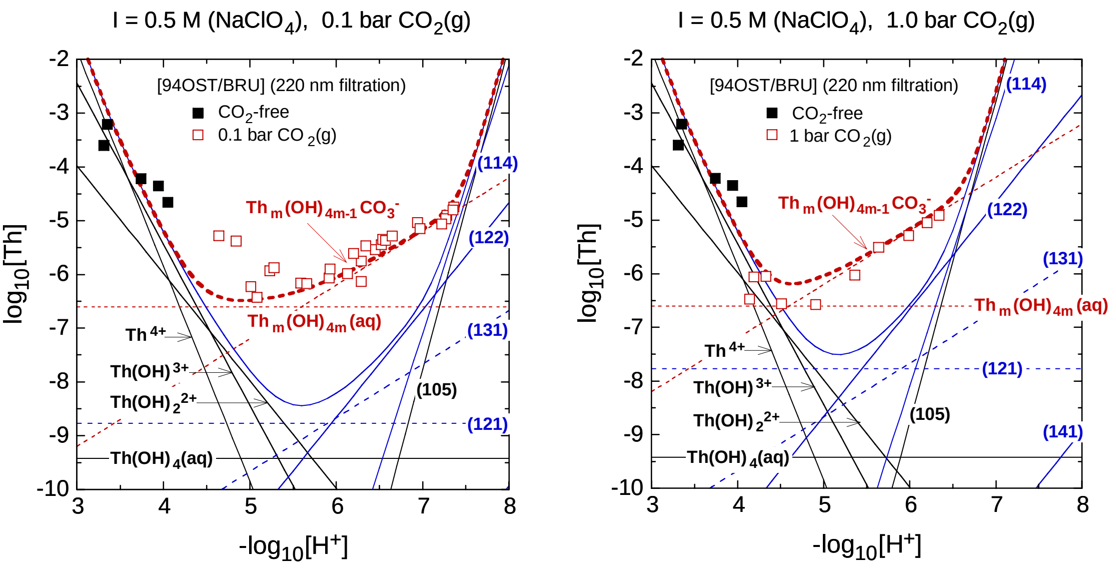
with $\log_{10} {}^*K_{s,(131)}$ (A.85) = (6.1 ± 0.2) at I = 0.5 M, corresponding to $\log_{10} {}^*K^\circ_{s,(131)}$ (A.85) = (6.8 ± 0.3) at zero ionic strength [1994OST/BRU]. Combined with the solubility constant of $\log_{10} {}^*K^\circ_{s,0} = (8.0 \pm 0.5)$ recalculated by this review from the solubility data in carbonate-free solution, this gives a formation constant of $\log_{10} \beta^\circ_{131} = (40.8 \pm 0.3)$ for the reaction:

$$Th^{4+} + 3OH^- + CO_3^{2-} \rightleftharpoons Th(OH)_3(CO_3)^- \qquad (A.86)$$

The data have been reanalysed by Altmaier *et al.* [2005ALT/NEC] who identified that the discrepancies between their study and [1994OST/BRU] were due to the presence of colloidal particles (or possibly large polynuclear ternary complexes) that had passed through the filter used by Östhols *et al.* In agreement with the conclusions in [2005NEC/ALT], this review has not accepted the equilibrium constant for the formation of $Th(OH)_3(CO_3)^-$ proposed by Östhols *et al.*

The thorium concentrations measured in the range pH = 4.6−6.5 after 220 nm filtration are comparable to those measured in [2005ALT/NEC] under the same conditions without removing colloidal or polynuclear species. However, [2005ALT/NEC] measured considerably lower thorium concentrations after 1.2 nm ultrafiltration and ultracentrifugation, indicating that the concentrations in [1994OST/BRU] for the pH region 4.6 to 6.5 do not refer to $Th(OH)_4(aq)$ and $Th(OH)_3(CO_3)^-$ but to colloids or large polymers. Thus the thorium concentrations predicted with the equilibrium constants selected by this review (solid lines in Figure A-35) are lower than the experimental data of [1994OST/BRU].

Figure A-35: Solubility of ThO_2(am, hyd) under 0.1 and 1.0 bar CO_2(g) in 0.5 M $NaClO_4$ [1994OST/BRU]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review and the solubility constant calculated from the data in carbonate-free solutions, $\log_{10} K^{\circ}_{s,0} = -(48.0 \pm 0.5)$. The dotted curves are calculated with the equilibrium constants proposed by Östhols *et al.* for $Th(OH)_4$(aq) and $Th(OH)_3(CO_3)^-$ (designated here as $Th_m(OH)_{4m}$(aq) and $Th_m(OH)_{4m-1}(CO_3)^-$).



As discussed in Section VII.4.1.2, the concentration of $\log_{10}[Th(OH)_4(aq)] = -6.6$ [1994OST/BRU] is typical for the presence of polynuclear or colloidal species $Th_m(OH)_{4m}$(aq) with $m > 10$. In the presence of carbonate we may additionally assume the formation of carbonate-containing polynuclear species such as $Th_m(OH)_{4m-1}(CO_3)^-$. The solubility data may be described with the reactions:

$$Th(OH)_4(s) \rightleftharpoons (1/m)\ Th_m(OH)_{4m}(aq) \qquad (A.87)$$

and

$$Th_m(OH)_{4m}(aq) + CO_3^{2-} \rightleftharpoons Th_m(OH)_{4m-1}(CO_3)^- + OH^- \qquad (A.88)$$

with $\log_{10} K_{s,(4m,m)}$ (A.87) = −6.6 [1994OST/BRU] and $\log_{10} K$ (A.88) = −1.1. However, it should be noted that the "equilibrium constants" for Reactions (A.87) and (A.88) are fitting parameters; no equilibrium constants for polynuclear species such as $Th_m(OH)_{4m}$(aq) and $Th_m(OH)_{4m-1}(CO_3)^-$ have been selected by this review.

3. Solubility in carbonate/bicarbonate buffers at C_{tot} = 0.1 M

The analysis of the experimental data in the carbonate/bicarbonate buffers at C_{tot} = 0.1 M and $-\log_{10}[H^+] = 8.2 - 10.5$ is not affected by the filtration procedure because of the much higher solubility. Based on the knowledge from the previous literature where $\mathrm{Th(CO_3)_5^{6-}}$ has been identified as limiting thorium carbonate complex, Östhols *et al.* interpreted their data with the reaction:

$$\mathrm{ThO_2(am, hyd) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} + 2H_2O(l)} \qquad \text{(A.89)}$$

with

$$\log_{10}[\mathrm{Th(CO_3)_5^{6-}}] - 4\log_{10}[\mathrm{H^+}] = \log_{10}{}^{*}K_{s,(105)} + 5\log_{10}[\mathrm{CO_3^{2-}}] \qquad \text{(A.90)}$$

and obtained $\log_{10}{}^{*}K_{s,(105)}$ (A.89) = (42.12 ± 0.32) at I = 0.5 M, corresponding to $\log_{10}{}^{*}K^{\circ}_{s,(105)}$ (A.89) = (39.64 ± 0.4) [1994OST/BRU] at zero ionic strength and to $\log_{10}\beta^{\circ}_{105}$ = (31.64 ± 0.64), if combined with the solubility constant of $\log_{10}{}^{*}K^{\circ}_{s,0}$ = (8.0 ± 0.5) recalculated by this review from the solubility data in carbonate-free solution.

The slope of 5 in the plot of $\{\log_{10}[\mathrm{Th(CO_3)_5^{6-}}] - 4\log_{10}[\mathrm{H^+}]\}$ *vs.* $\log_{10}[\mathrm{CO_3^{2-}}]$ (Figure A-36-a) is consistent the presence of $\mathrm{Th(CO_3)_5^{6-}}$ as dominant species. On the other hand, [2005ALT/NEC] claimed that $\mathrm{Th(OH)(CO_3)_4^{5-}}$ is the major complex under these conditions. As shown in Figure A-36-b, the corresponding interpretation of the solubility data in [1994OST/BRU]:

$$\mathrm{ThO_2(am, hyd) + 3H^+ + 4CO_3^{2-} \rightleftharpoons Th(OH)(CO_3)_4^{5-} + H_2O(l)} \qquad \text{(A.91)}$$

with

$$\log_{10}[\mathrm{Th(OH)(CO_3)_4^{5-}}] - 3\log_{10}[\mathrm{H^+}] = \log_{10}{}^{*}K_{s,(114)} + 4\log_{10}[\mathrm{CO_3^{2-}}] \qquad \text{(A.92)}$$

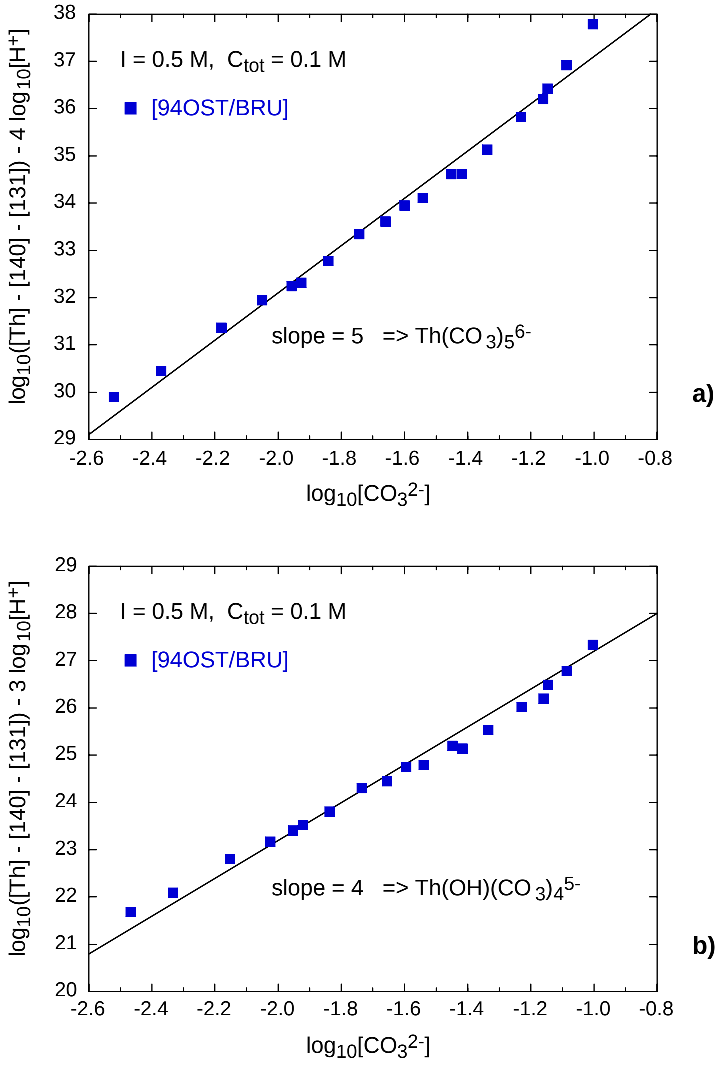
is also consistent with the slope of 4 expected for the plot of $\{\log_{10}[\mathrm{Th(OH)(CO_3)_4^{5-}}] - 3\log_{10}[\mathrm{H^+}]\}$ *vs.* $\log_{10}[\mathrm{CO_3^{2-}}]$.

This data set alone does not allow a final conclusion as to the dominant complex under these conditions. Using the additional information from the solubility of $\mathrm{ThO_2}$(am, hyd) under a wider range of experimental conditions at I = 0.5 M [2005ALT/NEC], from an EXAFS spectrum of a saturated solution under very similar conditions at C_{tot} = 0.1 M and $-\log_{10}[\mathrm{H^+}] = -9.16$ in 0.5 M $\mathrm{NaHCO_3}$-$\mathrm{Na_2CO_3}$-NaCl [2006ALT/NEC] and from further EXAFS studies at higher carbonate and bicarbonate concentrations [1997FEL/RAI], [2006ALT/NEC], the present review has selected $\log_{10}\beta^{\circ}_{105}(\mathrm{Th(CO_3)_5^{6-}}) = (31.0 \pm 0.7)$. This value is somewhat lower than the value of (31.6 ± 0.6) derived above, based on the data interpretation in [1994OST/BRU].

Figure A-36 [1]: Evaluation of the solubility data of [1994OST/BRU] for ThO_2(am, hyd) at I = 0.5 M ($NaHCO_3$-Na_2CO_3-$NaClO_4$) and a total carbonate concentration of C_{tot} = 0.1 M assuming two different dominant reactions:

$$\text{a) } ThO_2(am, hyd) + 4H^+ + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} + 2H_2O(l)$$

$$\text{b) } ThO_2(am, hyd) + 3H^+ + 4CO_3^{2-} \rightleftharpoons Th(OH)(CO_3)_4^{5-} + H_2O(l)$$



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[1] In the plots of Figure A-36 the total thorium concentration in the test solutions is corrected for the contributions from the species $Th(OH)_4(aq)$ and $Th(OH)_3(CO_3)^-$ which are, however, very small compared to those of the dominant complexes $Th(CO_3)_5^{6-}$ or $Th(OH)(CO_3)_4^{5-}$.

[1995JOA/BUR]

In this paper, João *et al.* have reinvestigated the Th(IV)-carbonate system using the same experimental method as in their previous study [1987JOA/BIG2]; in addition they have also investigated the Ce(IV)-carbonate system. The experiments were made at three different ionic strengths, 0.025, 0.050 and 0.70 M; there is no information about the temperature and this review has assumed that the experiments refer to "room temperature", (22 ± 2) °C. In this study the authors have taken the formation of the ternary complex $Th(EDTA)(OH)^-$ into account and have also determined the equilibrium constant, K_{111} for the reaction.

$$Th(EDTA)(aq) + H_2O(l) \rightleftharpoons Th(EDTA)(OH)^- + H^+ \qquad (A.93)$$

The experimental value at ionic strength 0.05, $\log_{10} K_{111} = (7.7 \pm 0.2)$ is in fair agreement with the value reported in [1989SMI/MAR], but the difference between this and the value at ionic strength 0.025, $\log_{10} K_{111} = (9.3 \pm 0.2)$ seems too large for the rather small change in ionic strength. The experimental data refer to a pH slightly below 9, much lower than in [1987JOA/BIG2]. The experimental data are given only in graphs and they are therefore difficult to evaluate. The free carbonate concentration range is very small (between *ca.* 8 and 10 mM), so there could be significant errors in the slope analysis used in [1995JOA/BUR]. The equilibrium constants for the reaction

$$Th^{4+} + 5CO_3^{2-} \rightleftharpoons Th(CO_3)_5^{6-} \qquad (A.94)$$

$\log_{10} \beta_5 = 22.0$, 21.6 and 21.4, at ionic strengths 0.025, 0.050 and 0.70 M, respectively, reported in [1995JOA/BUR] are much smaller than that reported in [1987JOA/BIG2] and also those selected in this review. The reason for this seems to be an error in the equation (10), p. 178 in [1995JOA/BUR], where the equation:

$$\frac{D^C}{D^Y} = \frac{K_{111}^Y[\text{EDTA}][\text{H}_Y^+]^3}{\beta_5^C[\text{CO}_3^{2-}]^5[\text{H}_C^+]^4}$$

was transformed into

$$\frac{D^C}{D^Y} = \frac{K_{111}^Y[\text{EDTA}]}{\beta_5^C[\text{CO}_3^{2-}]^5} \times 10^3(10\text{pH}_C - \text{pH}_Y)\,.$$

This transformation implies the simple mathematical error that

$$[\text{H}_Y^+]^3/[\text{H}_C^+]^4 = 10^4\text{pH}_C - 10^3\text{pH}_Y = 10^3(10\text{pH}_C - \text{pH}_Y)$$

instead of the correct $10^{(4\text{pH}_C)}/10^{(3\text{pH}_Y)} = 10^{(4\text{pH}_C - 3\text{pH}_Y)}$. For this reason the equilibrium constants have not been accepted by this review. It is also notable that the Ce(IV) system is claimed to form the complex $Ce(CO_3)_2(aq)$ in the same concentration range where $Th(CO_3)_5^{6-}$ is assumed to be predominant. Ce(IV) forms much stronger hydroxide complexes than Th(IV) and presumably also stronger carbonate complexes. One can therefore not rule out the formation of ternary Ce(IV)-hydroxide-carbonate complexes.

The following experimental observations indicate that the data might be affected by systematic errors:

- The ionic strength dependence of Reaction (A.94) is very large; the values of $\log_{10} K$ at I = 0.025, 0.050 and 0.70 are: –9.3, –7.7 and –7.0, respectively; this is not what one expects from the SIT model where the ionic strength effect in this case is determined mainly by the Debye-Hückel term.
- The equilibrium constant for the formation of the assumed complex $Th(CO_3)_5^{6-}$ differs considerably from that obtained in the previous study [1987JOA/BIG2] using the same experimental method (after the correction discussed above). The equilibrium constant also differs significantly from the values reported in [1994OST/BRU] and [1997FEL/RAI]. There are large similarities in chemical properties of the different actinide(IV) ions and one therefore expects similar equilibrium constants for the complexes formed. This is not the case for the value reported in [1995JOA/BUR].
- It is very surprising to find that the Ce(IV) carbonate system is so different from Th(IV) system. Ce(IV) is much more strongly hydrolysed and under the conditions of the experiment one would expect the formation of ternary hydroxide-carbonate complexes. The formation of $Ce(CO_3)_2(aq)$ does in the opinion of this review not make chemical sense.
- Using the experimental data in [2005ALT/NEC] and a comparison of with the corresponding U(IV) carbonate system it seems unlikely that the complex $Th(CO_3)_5^{6-}$ is predominant in the range $-2.05 < \log_{10}[CO_3^{2-}] < -0.30$.

For these reasons this review has not accepted the equilibrium constants proposed in [1995JOA/BUR].

[1995OST]

The solubility of microcrystalline ThO_2 was measured in the pH range 5 to 13 in the presence of 0.01 and 0.1 M phosphate and in the range 10.5 to 13 in the absence of phosphate. The ionic medium was 1.00 M $NaClO_4$ and the batch solubility experiments were made at 25°C. The author noted that the solubility in the pH range 5 to 10, $[Th]_{tot} = 10^{-6.4}$ M, was close to that predicted using published hydrolysis constants and solubility products. A small increase in solubility was noticed in the presence of 0.1 M phosphate in the pH range 10.5 to 13. The author has analysed the solid phase after equilibrium in the phosphate test solutions and observed that it contained small amounts of phosphate; however no major transformation to solid thorium phosphate phases had taken place. There is no information on equilibrium constants for phosphate complexes in this study, but the author observes that the phosphate complexes cannot compete with the stronger hydroxide complexes under the experimental conditions used. He also suggests that the influence of phosphate on the solubility of Th(IV) in most natural water systems will not be significant; the present review accepts these conclusions.

[1995RAI/FEL]

Rai *et al*. [1995RAI/FEL] measured the solubility of ThO_2(am, hyd) and UO_2(am, hyd) at room temperature (*ca*. 22°C) in $NaHCO_3$ and Na_2CO_3-NaOH or K_2CO_3-NaOH solutions of various carbonate and hydroxide concentrations.

Thorium test solutions:

a. 0.005 − 1.0 M $NaHCO_3$
b. 0.1 − 2.0 M Na_2CO_3
c. 0.001 − 2.0 M Na_2CO_3 containing 0.1 NaOH
d. 1.0 M Na_2CO_3 containing 0.01 − 0.5 M NaOH

Uranium test solutions:

a. 0.02 − 1.0 M $NaHCO_3$ and 0.1 − 2.0 M Na_2CO_3
b. 0.0003 − 2.0 M Na_2CO_3 containing 0.01 NaOH
c. 0.0003 − 2.0 M Na_2CO_3 containing 0.01 NaOH
d. 2.7 M K_2CO_3 containing 0.01 − 0.1 M NaOH

The results show the expected tendency that the solubility of ThO_2(am, hyd) is considerably greater than that of UO_2(am, hyd) at comparable conditions. This paper does not contain a quantitative interpretation but only reports the following qualitative conclusions: The pentacarbonate complex $\mathrm{An(CO_3)_5^{6-}}$ is expected to be dominant at high carbonate concentrations while the variation of the solubility with the NaOH concentration (at fixed total carbonate concentration) indicates the formation of ternary complexes like $\mathrm{An(OH)_4(CO_3)^{2-}}$ or $\mathrm{An(OH)_3(CO_3)^-}$. Quantitative models for the solubility of Th(IV) and U(IV) in carbonate solution are reported in the later papers [1997FEL/RAI] and [1998RAI/FEL], respectively. The evaluation of the solubility data for ThO_2(am, hyd) is discussed in detail in the Appendix A entry for [1997FEL/RAI].

[1996BEN/BRA]

Synthesis of $Th_4(PO_4)_4P_2O_7$ was achieved only with a controlled thorium to phosphorus ratio of 2/3 in the starting materials. Mixtures of $Th_4P_6O_{23}$ and ThO_2 were observed at thorium to phosphorus ratios of $>2/3$ and of $Th_4P_6O_{23}$ and ThP_2O_7 for ratios of $<2/3$. The compound was characterised by powder and single crystal X-ray diffraction, chemical analyses, and infrared spectroscopy. No thermodynamic data were reported.

[1996BOI/COL]

The exploding wire technique was used to measure some physical properties of Th(cr) and Th(l) up to the vicinity of the thorium boiling point (*ca.* 5000 K). The main details of the paper concern the volume expansion and electrical resistivity, which are reported as a function of enthalpy, since no temperatures were measured. This restricts their usefulness for current purposes, since the enthalpy of thorium is not known above 3400 K. However, the results did show relatively distinct breaks at the α to β and melting transformations, from which the authors deduced transition enthalpies of 3.5 and 13.9 kJ·mol^{-1}, in excellent agreement with existing data.

[1996KON]

The infrared spectrum of $ThF_4(g)$ heated to 1300 to 1370 K was recorded with a resolution of 0.5 cm^{-1} using an optical gas cell with silicon windows. The ν_4 fundamental was found at 116 cm^{-1} in a low intensity band. This is close to the value of 114 cm^{-1} for $UF_4(g)$ found earlier by the same team.

[1996RON/HIE]

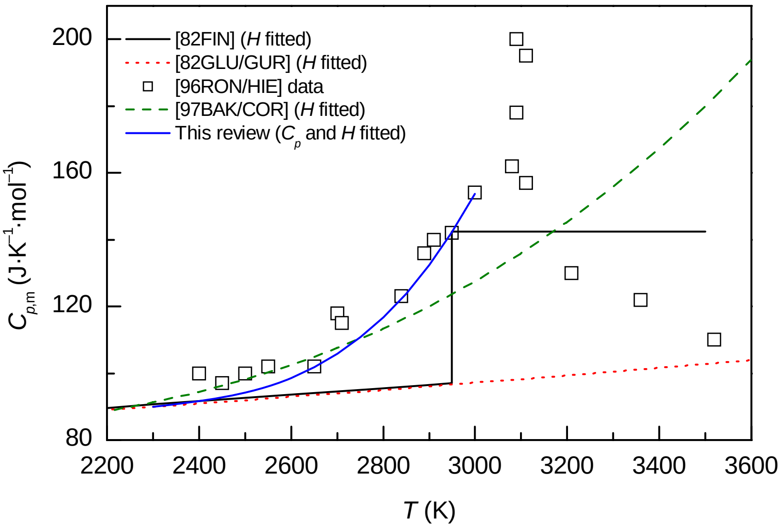
This paper describes a study of some thermophysical properties of $ThO_2(cr)$ at temperatures of 2500 to 4000 K. Small spheres (*ca.* 1 mm diameter) of ThO_2 (99.9% pure) were pulse heated in an autoclave filled with different gases by four symmetrically oriented Nd-YAG laser beams of equal intensity. This heated a shell of the sphere approximately 0.3 mm thickness to temperatures above the melting point and the sample cooling curve was then recorded by a fast multichannel pyrometer. The heat capacity was obtained from the sample cooling rate and any thermodynamic phase transitions occurring were identified from the analysis of the corresponding thermal arrest traces on the cooling curves.

The melting point of essentially stoichiometric thoria was shown to be (3651 ± 17) K, with a pre-melting transition at (3091 ± 6) K. These temperatures are weakly influenced by chemical reduction of the sample. While virtually stoichiometric thoria melts congruently, in the hypostoichiometric oxide the liquidus and solidus temperatures could be clearly observed at O/Th = 1.98.

Ronchi and Hiernaut found that the heat capacity in the region of the pre-melting shows a typical, but broad λ peak, rising from *ca.* 110 $\text{J·K}^{-1}\text{·mol}^{-1}$ at 2400 K to a peak of over 200 $\text{J·K}^{-1}\text{·mol}^{-1}$ at (3090 ± 10) K, falling again to *ca.* 115 $\text{J·K}^{-1}\text{·mol}^{-1}$ at 3450 K as shown in Figure A-37. The data suggest that these features can be described by a defect model, where cooperative effects lead to a critical order-disorder transition in the oxygen sublattice. A similar second-order transition occurs in a number of compounds with the fluorite structure.

However, the noticeable decrease in the heat capacity above 3100 K is not consistent with the more accurate enthalpy data of Fisher *et al.* [1981FIS/FIN] who made measurements up to 3400 K, and derived an essentially linear $C_{p,\mathrm{m}}$ of 142.3 J·K^{-1}·mol^{-1} from 2950 to 3400 K. The reason for this discrepancy is not clear and further work is required to establish which of these interpretations is correct. But for the purposes of this review, data for $C_{p,\mathrm{m}}$(ThO$_2$,cr) is only required up to 3000 K, in order to process the vapour pressure data, and we have restricted our treatment of the high temperature enthalpy and heat capacity data to this temperature, where the inconsistency is acceptable.

Figure A-37: Fit to C_p and $H(T)-H(298.15\text{ K})$ for ThO$_2$(cr) from 2300 to 3000 K – Heat capacity.



For this, we have made a simultaneous fit of the heat capacity and enthalpy data from 2300 to 3000 K for $C_{p,\mathrm{m}}$ and $H(T)-H(298.15\text{ K})$ to a cubic equation (for $C_{p,\mathrm{m}}$), with the constraints that $C_{p,\mathrm{m}}$(2300 K) and $H(2300\text{ K})-H(298.15\text{ K})$ are identical to the values from our selected data below 2300 K (essentially the same as those of [1982GLU/GUR]). The fitting used the 15 $C_{p,\mathrm{m}}$ data points from [1996RON/HIE] and 13 data points for $H(T)-H(298.15\text{ K})$, 5 from [1961HOC/JOH] and 8 from [1981FIS/FIN].

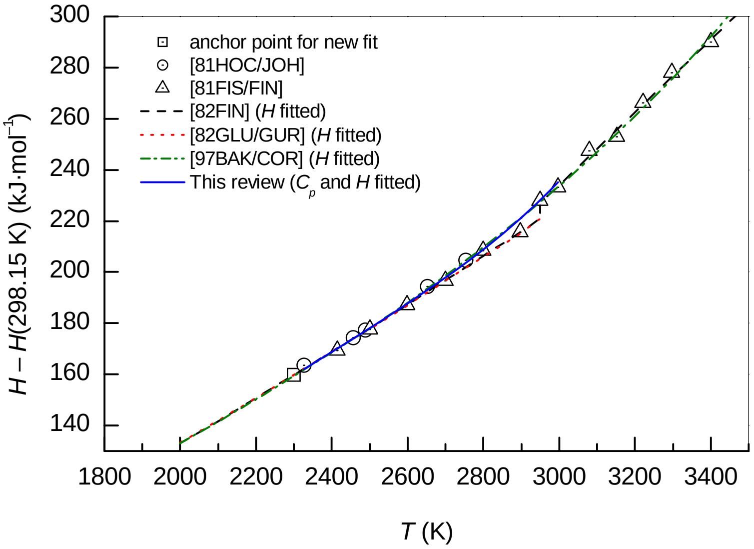
The uncertainty in the measurements of [1981FIS/FIN] is estimated to be at least ±2%, since their calibration differed from a standard sample of NBS molybdenum by 1.5% even at 2500 K, and their errors are likely to increase with temperature. Their reproducibility for duplicate runs was about 0.5%. The uncertainty of the $C_{p,\mathrm{m}}$ measurements by [1996RON/HIE] is much more difficult to estimate, but from their reproducibility (see Figure A-37), we estimate the uncertainty to be at least 6%.

The enthalpy data were therefore given a weighting factor of three in the fitting. The average deviation of the $C_{p,\mathrm{m}}$ data from the fit is +3.6%, with a standard deviation of ±3.9%, while for the enthalpy data, these values are −0.23% and ±0.85%, which reflect satisfactorily the relative accuracies of the two data sets.

The resulting fit to the heat capacity is shown in Figure A-37, together with earlier assessments, which have fitted the enthalpy only. The corresponding enthalpy values are shown in Figure A-38 These two figures include the data up to 3500 K, although no data above 3000 K were used in the fitting for this review.

Ronchi and Hiernaut also report the spectral emissivity of the thoria samples, measured during heating up to 4000 K.

Figure A-38: Fit to C_p and $H(T)-H(298.15\ \mathrm{K})$ for $\mathrm{ThO_2}$(cr) from 2300 to 3000 K – Enthalpy.



[1997FEL/RAI]

This paper (based on experimental data from [1995RAI/FEL]) is discussed together with [1999FEL/RAI].

The solubility data determined by Rai *et al.* [1995RAI/FEL] in 0.01−0.25 M $\mathrm{NaHCO_3}$, in 1.0 M $\mathrm{Na_2CO_3}$ containing 0.01−0.5 M NaOH and in 0.001−2.0 M $\mathrm{Na_2CO_3}$ containing 0.1 NaOH, were used by Felmy *et al.* [1997FEL/RAI] to derive a model for the solubility of $\mathrm{ThO_2}$(am, hyd) in carbonate solution. This model is based on the ion interaction approach of Pitzer [1991PIT] and includes two thorium complexes, the pentacarbonate complex $\mathrm{Th(CO_3)_5^{6-}}$ and the ternary complex $\mathrm{Th(OH)_3(CO_3)^-}$ proposed by

Östhols *et al.* [1994OST/BRU]. The equilibrium constant $\log_{10}{}^{*}K^{\circ}_{s,(131)}$)(A.95) = 6.78 for the reaction:

$$\text{ThO}_2(\text{am, hyd}) + \text{H}^+ + \text{H}_2\text{O(l)} + \text{CO}_3^{2-} \rightleftharpoons \text{Th(OH)}_3(\text{CO}_3)^- \qquad \text{(A.95)}$$

was adopted from [1994OST/BRU]; Pitzer parameters for this complex are not reported. The equilibrium constant $\log_{10}{}^{*}K^{\circ}_{s,(105)}$ (A.96) = 37.6 calculated by [1997FEL/RAI] for the reaction:

$$\text{ThO}_2(\text{am, hyd}) + 4\text{H}^+ + 5\,\text{CO}_3^{2-} \rightleftharpoons \text{Th(CO}_3)_5^{6-} + 2\text{H}_2\text{O(l)} \qquad \text{(A.96)}$$

differs by two $\log_{10}$ units from the value of $\log_{10}{}^{*}K^{\circ}_{s,(105)}$ (A.96) = (39.6 ± 0.4) calculated in [1994OST/BRU] with the SIT approach. The binary Pitzer parameters reported by Felmy *et al.* [1997FEL/RAI] for the pair Na^+- $\text{Th(CO}_3)_5^{6-}$ ($\beta^{(0)} = 1.31$, $\beta^{(1)} = 30$ kg·mol^{-1}) are reasonable for interactions parameters between ions of these charges. These parameters were applicable to model the solubility of ThO_2(am, hyd) in the investigated NaHCO_3 and Na_2CO_3-NaOH solutions [1995RAI/FEL] within an uncertainty range of ± 0.5 $\log_{10}$-units. However, the modelling of the solubility data determined by Östhols *et al.* [1994OST/BRU] at $C_{\text{tot}} = 0.1$ M and $I = 0.5$ M in NaClO_4 media required in addition a mixing parameter with an extremely large value of $\theta(\text{Th(CO}_3)_5^{6-} - \text{ClO}_4^-) = 5.5$ kg·mol^{-1}.

In a later study Felmy *et al.* [1999FEL/RAI] extended their model to alkaline Na_2CO_3-NaCl solutions. The experimental solubility data determined with ThO_2(am, hyd) in 2.33 and 4.67 m NaCl containing 0.1 − 2.3 M Na_2CO_3 and 0.1 M NaOH were fitted with mixing parameters of $\theta(\text{Th(CO}_3)_5^{6-}\text{-Cl}^-) = 1.8$ kg·mol^{-1} and $\psi(\text{Th(CO}_3)_5^{6-}\text{-Cl}^-\text{-Na}^+) = 0.3$ kg^2·mol^{-2}, indicating that the activity coefficients of $\text{Th(CO}_3)_5^{6-}$ in Na_2CO_3-NaCl solutions differ considerably from those in Na_2CO_3-NaClO_4 solutions.

It should be noted that the model of Felmy *et al.* is neither consistent with the complexes and equilibrium constants selected in the present review nor with the speciation calculated with the SIT approach. Therefore the equilibrium constants selected in the present review must not be used in combination with the Pitzer parameters of Felmy *et al.* [1997FEL/RAI], [1999FEL/RAI].

The predictive capability of the equilibrium constants and SIT coefficients selected in the present review for the ternary Th(IV)-hydroxide-carbonate complexes and $\text{Th(CO}_3)_5^{6-}$ is demonstrated in Figure A-39, Figure A-40 and Figure A-41 for the solubility of ThO_2(am, hyd) under the experimental conditions in [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI]. The model calculations are in good agreement with the solubility of ThO_2(am, hyd) at high OH^- and Na_2CO_3 concentrations up to 1.0 M (Figure A-39). At carbonate concentrations above $[\text{CO}_3^{2-}] = 1.0$ M and $I > 3$ mol·kg^{-1} (Figure A-39), in particular in solutions with additions of NaCl (Figure A-40), the predicted thorium concentrations are up to about 1.5 orders of magnitude lower than the experimental values. As shown by the dashed concentration lines for the species (124) in Figure A-39 and Figure A-40, the solubility at high carbonate concentration and ionic strength can be better described by assuming the formation of the additional ternary complex $\mathrm{Th(OH)_2(CO_3)_4^{6-}}$ with $\log_{10}\beta^{\circ}_{124}$ = (34.3 ± 0.6) and $\varepsilon(\mathrm{Th(OH)_2(CO_3)_4^{6-}}, \mathrm{Na^+}) = -(0.3 \pm 0.2)\ \mathrm{kg{\cdot}mol^{-1}}$ as estimated in [2005ALT/NEC]. However, these conditions are beyond the validity range of the SIT model. Moreover, changing $\varepsilon(\mathrm{Th(OH)(CO_3)_4^{5-}}, \mathrm{Na^+})$ or $\varepsilon(\mathrm{Th(CO_3)_5^{6-}}, \mathrm{Na^+})$ within their uncertainty ranges would also yield a better fit. Therefore the complex $\mathrm{Th(OH)_2(CO_3)_4^{6-}}$ is not selected by the present review.

Felmy *et al.* [1997FEL/RAI] also present EXAFS measurements of Th(IV) in carbonate solutions. The sample compositions are given as 1.0 M $\mathrm{Na_2CO_3}$ + 0.1 M NaOH and 1.0, 0.5, 0.25, 0.17 and 0.10 $\mathrm{NaHCO_3}$, with thorium concentrations ranging from 8.6 mM to 0.1 mM. The thorium concentration of 0.02 mM in a 0.07 M $\mathrm{NaHCO_3}$ solution was too low for XAS analysis. The composition of the first sample (designated as Th-15) cannot be correct, because the solubility of $\mathrm{ThO_2}$(am, hyd) is below 10^{-5} M under these conditions (*cf.*, Figure A-39). Moreover, in another EXAFS study of this group [1997HES/FEL], which is the basis for the EXAFS data reported in [1997FEL/RAI], the composition of sample Th-15 is reported to be 2.0 M $\mathrm{Na_2CO_3}$ + 0.1 M NaOH. The EXAFS parameters derived from the $\mathrm{NaHCO_3}$ solutions, in particular the coordination numbers N_O, N_C and N_{Od}, differ somewhat from those reported for the same samples (Th-76, Th-74 and Th-71) in [1997HES/FEL], but this does not affect the general conclusions. In the $\mathrm{Na_2CO_3}$ solution and in 1.0 and 0.5 M $\mathrm{NaHCO_3}$ the complex $\mathrm{Th(CO_3)_5^{6-}}$ is the dominant species (N_O = (10.5 ± 2.7) at $d_{\mathrm{Th-O}}$ = (2.49 ± 0.02) Å, N_C = (4.4 ± 1.4) at $d_{\mathrm{Th-C}}$ = (3.00 ± 0.02) Å, and $N_{\mathrm{O_d}}$ = (5.9 ± 1.8) at $d_{\mathrm{Th-O_d}}$ = (4.23 ± 0.02) Å). In the 0.25 and 0.17 M $\mathrm{NaHCO_3}$ solutions the distances $d_{\mathrm{Th-O}}$ = (2.50 ± 0.02) Å, $d_{\mathrm{Th-C}}$ = (2.98 ± 0.02) Å, $d_{\mathrm{Th-O_d}}$ = (4.22 ± 0.02) Å (O_d represents a distal carbonate oxygen atom), and the coordination number of the first oxygen shell (N_O = (10 ± 1)) remain approximately constant, while the average number of $\mathrm{CO_3^{2-}}$ ligands (N_C and N_{Od}) decreases to values between 5 and 4. This is consistent with the formation of $\mathrm{Th(OH)(CO_3)_4^{5-}}$. In the 0.10 M $\mathrm{NaHCO_3}$ solution $d_{\mathrm{Th-O}}$ decreases to (2.46 ± 0.02) Å, N_O to (8.4 ± 2.4), and the number of $\mathrm{CO_3^{2-}}$ ligands to N_{Od} = (2.2 ± 0.7) [1997FEL/RAI] (or (3.2 ± 1.5) [1997HES/FEL]), indicating the presence of ternary Th(IV)-hydroxide-carbonates complexes with smaller numbers of carbonate ligands, such as $\mathrm{Th(OH)_3(CO_3)^-}$ or $\mathrm{Th(OH)_2(CO_3)_2^{2-}}$, which must noticeably contribute to the speciation. With regard to the large uncertainties of the coordination numbers determined by EXAFS, these results are fairly consistent with the speciation diagram in Figure A-41 that is calculated with the complexes and equilibrium constants selected by this review.

Figure A-39: Solubility of ThO_2(am, hyd) in 1.0 M Na_2CO_3 containing 0.01 − 1.0 M NaOH and in 0.001 − 2.0 M Na_2CO_3 containing 0.1 M NaOH: Experimental data from [1995RAI/FEL], [1997FEL/RAI], [2005ALT/NEC] and calculations based on the equilibrium constants, SIT coefficients and $\log_{10} K^{o}_{s,0}$ (aged ThO_2(am, hyd)) = − 47.5 selected in the present review, taking into account the variation of the solution composition and ionic strength.

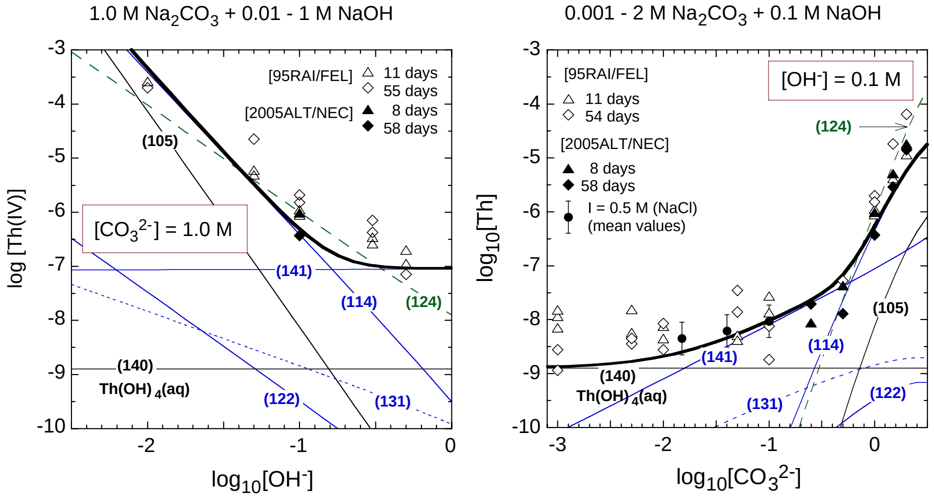


Figure A-40: Solubility of ThO_2(am, hyd) in 2.33 and 4.67 m NaCl containing 0.1 – 2.3 M Na_2CO_3 and 0.1 M NaOH [1999FEL/RAI]. The calculations are based on the equilibrium constants, SIT coefficients and $\log_{10} K^{o}_{s,0}$ (aged ThO_2(am, hyd)) = – 47.5 selected in the present review, taking into account the variation of the solution composition and ionic strength.

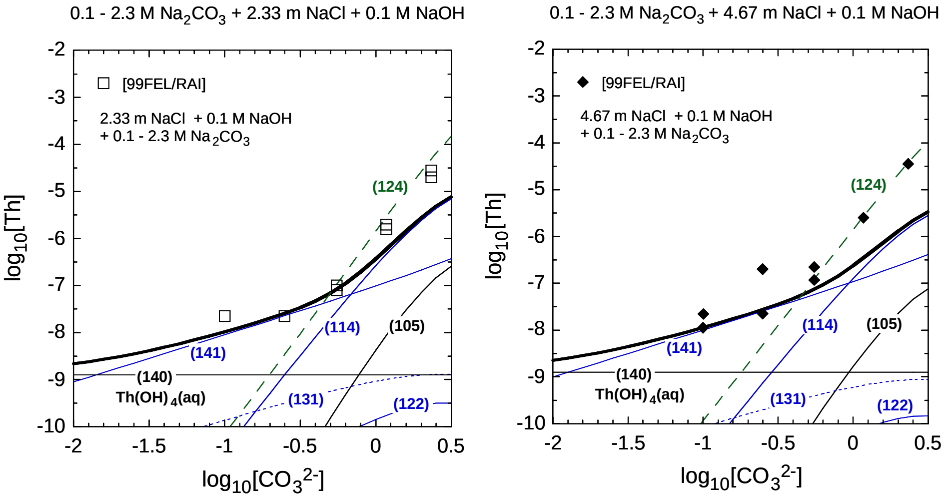
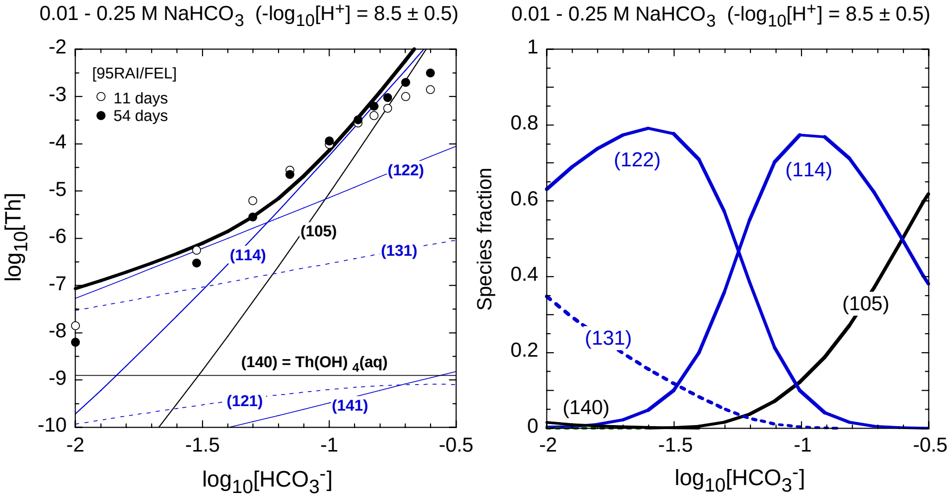


Figure A-41: Solubility of ThO_2(am, hyd) and speciation in 0.01 − 0.25 M $NaHCO_3$ [1995RAI/FEL], [1997FEL/RAI]. The calculations are based on the equilibrium constants, SIT coefficients and $\log_{10} K^{o}_{s,0}$ (aged ThO_2(am, hyd)) = − 47.5 selected in the present review, taking into account the variation of the solution composition and ionic strength.



[1997HES/FEL]

In this conference proceedings paper Hess *et al.* [1997HES/FEL] present an EXAFS study of Th(IV) solutions in sodium carbonate and bicarbonate solutions. In three samples, with the solution compositions given as 2 M Na_2CO_3 containing 0.1, 0.5 and 1.0 M NaOH and 1.0 mM Th, the pentacarbonate complex $Th(CO_3)_5^{6-}$ has been identified from the coordination numbers of the first and distal oxygen shells: $N_O = (10 \pm 1)$ ($d_{Th–O}$ = (2.49 ± 0.02) Å, $d_{Th–C}$ = (2.99 ± 0.02) Å) and $N_{Od} = 5$($d_{Th–Od}$ = (4.26 ± 0.02) Å). The fitted number of second shell carbon atoms appears to be too small (N_C = 3.1 − 3.4 at a distance of $d_{Th–C}$ = (3.00 ± 0.02) Å). However, the reported sample compositions cannot be correct, because in these highly alkaline solutions the solubility of ThO_2(am, hyd) is below 10^{-5} M (*cf.* Figure 4 in [1995RAI/FEL] and Figure 1 in [1997FEL/RAI]), much too low for EXAFS analysis.

In the 0.25 and 0.1 M $NaHCO_3$ solutions (pH 9.3 − 9.4) containing 7 mM and 0.1 mM Th, respectively, the distance $d_{Th–O}$ and N_O are approximately the same, but the number of CO_3^{2-} ligands decreases to about (3 ± 1) and the authors postulate the formation of a ternary complex $ThO_{2-x}(CO_3)_3(OH)_x^{(6-x)-}$. However the coordination numbers have large uncertainties and a clear-cut identification of the ternary complexes is not possible.

[1997HOV]

As noted in Appendix A of [2003GUI/FAN], this is an important study as it is a precise determination of the partial molar heat capacity and volume of a M^{4+} ion. By selecting Th(IV) the author has been able to minimise the experimental difficulties due to hydrolysis. The procedure, the data (10 to 55°C) and the data treatment are detailed in the paper. The consistency of the results for the system $Th(ClO_4)_4$ + $HClO_4$ has been tested using Young's rule and the Pitzer ion-interaction model with concordant result over the entire concentration range 1.0 to 2.9 m investigated. Hovey reports $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}, 298.15\ \mathrm{K}) = -(224 \pm 5)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

In his calculations, the author uses a fit of the existing literature data for the partial molar quantities of $HClO_4$. These calculations are compatible with a value of $C^{\circ}_{p,\mathrm{m}}(\mathrm{ClO}_4^-) = -(25.45 \pm 0.60)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

The author has also reviewed the previous attempts by [1976MOR/MCC] and [1975APE/SAH] to estimate the partial molar heat capacity of Th^{4+} and finds that the results deviate strongly from his own experimental data. The data of Morss and MacCue [1976MOR/MCC] based on integral enthalpies of dilution of $Th(NO_3)_4{\cdot}5H_2O(cr)$ in 0.01 M $HClO_4$ at 15, 25 and 35°C, recalculated using a new value of the partial molar heat capacity of NO_3^-, $C^{\circ}_{p,\mathrm{m}} = -72\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ [1988HOV/HEP], gives $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}, 298.15\ \mathrm{K}) = -(60 \pm 11)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, close to the value selected by [1992GRE/FUG] for U^{4+}, $[C^{\circ}_{p,\mathrm{m}}]^{473\mathrm{K}}_{298\mathrm{K}}(\mathrm{U}^{4+}) = -(48 \pm 15)\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. The data of Apelbat and Sahar [1975APE/SAH] at 30°C based on measurement of bulk heat capacity of $Th(NO_3)_4$ solutions, given as a linear function of $m^{1/2}$ for the range 0 to 2.9 m, lead to $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+}, 303.15\ \mathrm{K}) = 111\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, as calculated by Hovey using $C^{\circ}_{p,\mathrm{m}}(\mathrm{NO}_3^-) = -63.7\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ from [1989HOV/HEP]. Hovey plausibly argues that the discrepancy is not surprising, given the fact that specific molalities and heat capacities are not reported and also the improbability of a simple linear equation being able to represent heat capacities over such a wide range of temperature. Hovey [1997HOV] gives additional important data on the variations of $C^{\circ}_{p,\mathrm{m}}(\mathrm{Th}^{4+})$ with the temperature and on the structure of the Th^{4+} aqueous ion.

The experimental conditions chosen by Hovey, which lead to little hydrolysis and no complexation, are preferable to those of [1976MOR/MCC].

A related paper, [1986HOV/TRE] refers to $C^{\circ}_{p,\mathrm{m}}(\mathrm{Al}^{3+})$, where $C^{\circ}_{p,\mathrm{m}}(\mathrm{Al}^{3+})$ was found to be $-119\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, while the Criss-Cobble equation, [1964CRI/COB2] leads to $16\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$.

It seems that the Criss-Cobble equation for heat capacity from entropy breaks down for highly charged ions. As Hovey noticed, the correspondence between the result of Morss and McCue for Th^{4+} and the Criss-Cobble prediction for U^{4+} could be fortuitous.

[1997KLA/SCH]

These authors claimed the first experimental evidence for the formation of the Th^{3+} ion in aqueous solution, as a result of the reduction of Th^{4+} by hydrazoic acid. The solution was prepared by mixing 7.38 mmol of $ThCl_4$ in 10 mL water with 15mL of a 2.0 M HN_3 solution under nitrogen. An amber solution was obtained immediately and gaseous evolution was observed.

The process was ascribed to the reaction

$$Th^{4+} + HN_3(aq) \rightarrow Th^{3+} + 1.5N_2(g) + H^+ \qquad (A.97)$$

based on a value of −3.54 V for the potential corresponding to the reaction

$$1.5N_2(g) + H^+ + e^- \rightarrow HN_3(aq) \qquad (A.98)$$

at pH 3.5 and 298.15 K (calculated from the data in [1982WAG/EVA]) and on an estimated value [1986BRA/LAG] of −3.0 V for the Th^{4+}/Th^{3+} standard potential.

However, the experimental observations indicate a rapid reaction and this is contrary to what one would expect for the redox reaction (A.98) that involves $N_2(g)$. The $N_2(g)/HN_3(aq)$ couple is strongly irreversible, as indicated by the stability of HN_3 in dilute aqueous solution, hence the proposed reduction of Th^{4+} would not be thermodynamically controlled as suggested in [1997KLA/SCH].

The Th^{3+} solution was reported to be stable for more than one hour; after that time, slow oxidation by water was reported, with the formation of a white gel-like precipitate assumed to be "thorium oxide hydroxide".

The absorption spectrum (UV-visible, 180−1300 nm) of the solution was characterised by a broad band below 650 nm with a maximum at 460 nm, followed at lower wavelengths by a very intense band with maxima at *ca.* 332 (shoulder), 190, and 185 nm. These features were assigned to $f \rightarrow d$ and metal → ligand allowed transitions. The ESR spectrum of a frozen solution showed a very broad signal with a main g value of 2.19 that the authors indicated to be similar to other f^1 systems.

The conclusions of [1997KLA/SCH] regarding the formation of the Th^{3+} in their experiments were seriously questioned by Ionova *et al.* [1998ION/MAD] (see Appendix A).

[1997RAI/FEL]

This paper is discussed together with [1991FEL/RAI].

[1997SOU/KUS]

Souter *et al.* [1997SOU/KUS] have identified the four gaseous thorium hydride species ThH_n (n = 1 to 4) by examining the IR spectra of the products condensed from the reaction of laser-ablated thorium with $H_2(g)$ in solid argon matrices. In some experiments, a discharge was passed through the Ar-$H_2(g)$ mixture, using a low-power microwave source, to provide a source of H atoms. After deposition, the samples were annealed at 20 − 40 K. Isotopic substitution with deuterium confirmed the spectral assignments. Estimates of the vibration frequencies by DFT calculations, including quasi-relativistic effects, gave good theoretical support for the assignments and provided additional data on the structures of the hydride molecules.

The resultant structures and vibration frequencies assigned are summarised in Table A-77.

It will be seen from Table A-77, that [1997SOU/KUS] unfortunately only give the calculated vibration frequencies for the IR active modes, so no complete calculation of the thermodynamic properties of the higher hydrides is possible.

Table A-77: Properties of gaseous thorium hydride molecules.

Species	Symmetry and multiplicity of ground state	*r*(Th–H) (Å)	H–Th angle °	Vibration frequencies (cm^{-1})	
				Experimental	DFT calculation
ThH(g)	C∞, doublet	1.985	180	1485.2	1496
ThH_2(g)	C_{2v}, triplet	2.040	114	$\upsilon_1 = 1480.1$	$\upsilon_1 = 1454$
				$\upsilon_3 = 1455.6$	$\upsilon_3 = 1399$
ThH_3(g)	C_{3v}, doublet	2.047	114	$\upsilon_1 = 1435$	$\upsilon_1 = 1475$
					$\upsilon_3 = 1409$
ThH_4(g)	$T_{d,}$, singlet	2.058	109.5	$\upsilon_1 = 1444$	$\upsilon_1 = 1504$
					$\upsilon_3 = 1413$

[1997STE/FEL]

This is one of a series of documents from Felmy and co-workers that use of Gibbs energy minimisation approach combined with nonlinear parameter optimisation to analyse a variety of experimental data to simultaneously solve chemical equilibria involving large number of components and associated species. This particular publication describes a model that allows parameter evaluation for both Pitzer and ESP[1] electrolyte models. A reader interested in these codes should also see [1989FEL/RAI] and [1995FEL]. The fitting code (NONLINT), described in these publications, was upgraded by Felmy[2], to include the capability for simultaneously evaluating SIT parameters and fitting chemical potentials of different chemical species from a variety of experimental data. This modified code is referred to as the “NONLINT-SIT code”. The types of data that can be evaluated using the “NONLINT-SIT code” include: solvent extraction, solubility, ion-exchange, potentiometric, and solid solution.

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[1] Environmental Simulation Program

[2] A. R. Felmy, personal communication, Pacific Northwest National Laboratory, September 2004

[1998BRA/DAC]

The paper presents several different methods of preparing $Th_4(PO_4)_4P_2O_7$, but no thermodynamic data are reported.

[1998ION/MAD]

This paper is a well-documented criticism of the claim of [1997KLA/SCH] (see Appendix A) of the first observation of a Th^{3+} ion in aqueous solution from the reaction

$$Th^{4+} + HN_3(aq) \rightarrow Th^{3+} + 1.5N_2(g) + H^+ \qquad (A.99)$$

in a slightly acidic solution (pH ≈ 3.5).

The authors questioned the value of E^{o} (Th^{4+}/Th^{3+}), −3.0 V, chosen by [1997KLA/SCH] from the estimation of [1986BRA/LAG] based on an ionic model which took account the stabilisation of *d* electrons by crystal field effects. A re-evaluation of the crystal field stabilisation effects by [1998ION/MAD] led these authors to propose −3.82 V and −3.35 V as limiting values for this potential, consistent with the earlier estimate −3.7 V by [1973NUG/BAY].

Moreover, [1998ION/MAD] recommended the value of −2.80 V for the standard potential of the reaction

$$1.5N_2(g) + H^+ + e^- \rightarrow HN_3(aq) \qquad (A.100)$$

as listed by Jones [1973JON], instead of that of −3.54 V used by [1997KLA/SCH].

With the potential values adopted by [1998ION/MAD], the reduction of Th^{4+} by hydrazoic acid according to Reaction (A.99) would not be thermodynamically feasible. Moreover, as noted in the Appendix A review of [1997KLA/SCH], the redox couple $N_2(g)/HN_3(aq)$ is highly irreversible and dilute aqueous HN_3 is therefore unlikely to act as a fast reducing agent.

The attribution to Th^{3+} species ($f \rightarrow d$ and Th → ligand allowed transitions) of the features in the absorption spectra observed by [1997KLA/SCH] was also criticised by [1998ION/MAD], who showed that these features could be equally well be assigned to a $N_3^- \rightarrow Th^{4+}$ transition and to the $Cl^- \rightarrow Th^{4+}$ charge transfer.

As far as the ESR spectrum reported by [1997KLA/SCH], [1998ION/MAD] suggested that a sensible discussion was not possible without the measurement of the concentration of spins.

[1998KON/HIL]

An analysis of vapour pressure measurements of a number of actinide tetrahalides is used to infer their molecular structure. The results offer no evidence for deviations from tetrahedral symmetry.

For this analysis a set of consistent spectroscopic data and molecular constants for these species is presented based on recent results of IR spectroscopic measurements for $UCl_4(g)$, $UF_4(g)$ and $ThF_4(g)$. For the thorium tetrahalides, these estimates of molecular parameters have been somewhat overtaken by theoretical calculations using density functional theory. These confirm the tetrahedral structure of the species, and on the whole, the current review has preferred these calculated values to the correlative estimates presented in this paper.

[1998WIE/HEL]

Wierczinski *et al.* [1998WIE/HEL] carried out solubility and sorption experiments at 22°C and 55°C in alkaline cement pore waters of pH 13.22 and 12.45 ($I \approx 0.01$ M). The solubility experiments were performed with microcrystalline ThO_2(am, hyd) prepared and dried as described by [1994OST/BRU]. Thorium concentrations were analysed by ICP-MS and pH was measured with a glass electrode calibrated against pH 10 buffer and 0.1 M NaOH, but the phase separation which may be connected with sorption effects is not reported. During short term experiments (5 hours to 5 days) the authors measured thorium concentrations in the range of 4×10^{-9} to 5×10^{-7} M, while those measured after 11−25 days were in the range of 10^{-10} to 10^{-9} M. The mean values of $\log_{10}[\text{Th}]$ calculated from the data given in Table 5 of [1998WIE/HEL] are $-(9.6 \pm 0.4)$ at 22°C and $-(10.0 \pm 0.1)$ at 55°C. These concentrations are comparable with those measured by Jernström *et al.* [2002JER/VUO] ($\log_{10}[\text{Th}] = -(9.5 \pm 1.2)$ at pH 7−13 and 22°C) with a ThO_2(am, hyd) solid prepared in the same way.

[1999BHA/MIS]

The authors measured the equilibrium constant of the reaction:

$$BaThO_3(cr) + H_2O(g) \rightleftharpoons ThO_2(cr) + Ba(OH)_2(g) \qquad (A.101)$$

from 1548 to 1683 K by the transpiration method. The $BaThO_3$ solid was prepared by heating the nitrates of barium and thorium with citric acid, which acts as an ignition agent. X-ray diffraction showed only the presence of a cubic (actually pseudo-cubic) phase with $a = 4.499$ Å; no other analysis is given. There was no measurable mass loss when the material was heated *in vacuo* to 1750 K, but there was a measurable loss when heated in $H_2O(g)$. The mass loss at 1643 K as a function of the partial pressure of water was closely proportional to p_{H_2O}, indicating the reaction was that given by the above equation. X-ray diffraction on partially evaporated samples showed them to be a mixture of $BaThO_3(cr)$ and $ThO_2(cr)$ as anticipated. The calculated equilibrium constants from 15 experimental points are well represented by the equation $\ln K = -20306/T + 5.37$. Thus the Gibbs energy of the above reaction is $\Delta_r G_m$ ((A.101), T) = 168834 − 44.648 T (J·mol^{-1}). However, the Gibbs energy of formation of $Ba(OH)_2(g)$ is rather uncertain –Gurvich *et al.* [1994GUR/VEY] report derived enthalpies of formation which vary by more than 60 kJ·mol^{-1}, finally associating an uncertainty of ±20 kJ·mol^{-1} with their selected value. However, Ali (Basu) *et al.* [2001ALI/MIS2] have recently measured the pressures of $Ba(OH)_2(g)$ in the reaction $BaO(cr) + H_2O(g) \rightleftharpoons Ba(OH)_2(g)$ from 1346 to 1451 K in exactly the same apparatus as that used by [1999BHA/MIS], to give for:

$$BaO(cr) + H_2O(g) \rightleftharpoons Ba(OH)_2(g) \tag{A.102}$$

$$[\Delta_r G_m]_{1346K}^{1451K}\ ((A.102), T) = 139620 - 41.074\ T\ (J{\cdot}mol^{-1})$$

By using these data, we can derive the Gibbs energy of the formation reaction of $BaThO_3(cr)$ from the component oxides directly, eliminating some of the possible experimental errors as well as uncertainties in the thermal function of $Ba(OH)_2(g)$. Thus we find:

$$BaO(cr) + ThO_2(cr) \rightarrow BaThO_3(cr) \tag{A.103}$$

$$[\Delta_r G_m]_{1548K}^{1683K}\ ((A.103), T) = -29214 + 3.574\ T\ (J{\cdot}mol^{-1})$$

Although the authors suggest an uncertainty of only $\pm 3.6\ kJ{\cdot}mol^{-1}$ for these values, we recall the large scatter in the data for $\Delta_f H_m^o$ ($Ba(OH)_2$, g, 298.15 K) and prefer to increase the uncertainty quite substantially to $\pm$ 20 $kJ{\cdot}mol^{-1}$.

These data for $\Delta_r G_m$ (A.103) are compared with those obtained by Knudsen effusion measurements of the pressure of BaO(g) from the decomposition of $BaThO_3(cr)$ by [1999MIS/ALI] in Section XII.1.1.2.

[1999FEL/RAI]

This paper of Felmy and Rai presents an overview on the application of Pitzer's ion interaction equations for modelling the aqueous thermodynamics of actinides. The section on the modelling of thorium in carbonate solution is discussed together with [1997FEL/RAI] in the Appendix A entry for that paper. The Pitzer parameters for the Th^{4+} ion and Th(IV) sulphate and fluoride complexes are discussed in the corresponding main text sections and in the Appendix A entries for [1991FEL/RAI], [1992FEL/RAI] and [1993FEL/RAI].

[1999FOU/LAG]

Fourest *et al.* have prepared and carefully characterised the solid $Th_4(PO_4)_4{\cdot}P_2O_7(s)$ and subsequently measured its solubility in the pH range 0 to 10.5; the temperature was 25°C and the ionic medium 0.1 M $NaClO_4$. The authors have used different analytical methods to determine the solubility and the stoichiometry of the solid phases, all of which are described in detail. The experimental solubility curve, Figure 3 in [1999FOU/LAG], has been divided in three linear sections: at pH < 1.5 the slope of $\log_{10} [Th]_{tot}$ *vs.* pH is -1.10, between $1.5 < pH < 5$, the slope is -0.6 and above pH 5 the slope is zero. The division of the solubility curve seems arbitrary to this review, and the solubility might well be a continuous function of pH. To complicate matters the authors note that $Th_4(PO_4)_4{\cdot}P_2O_7(s)$ is not formed from the over-saturation side and accordingly the system is not in true equilibrium; the diphosphate ion is also not a stable species and will transform to monophosphate species with a rate that depends on pH and temperature. The authors have used experimental data obtained after an equilibration time of one day and assumed that they can be used to describe an "apparent" equilibrium. The authors have considered the possibility of phase transformation of $Th_4(PO_4)_4{\cdot}P_2O_7(s)$ to form $Th(HPO_4)_2(s)$ and $Th(OH)_4(s)$. It is difficult to judge from the information presented if this has taken place, or not (there does not seem to be an analysis of the solid phases at different pH). The present review is not convinced by the analysis made by Fourest *et al.* but a phase transformation seems possible.

[1999KUS/AND]

The paper deals mainly with the vibrational frequencies of NMO molecules which are formed when laser-ablated Zr, Hf, and Th atoms react with NO. However, additional frequencies at 735.0 and 787.3 cm^{-1} for the experiments involving ^{16}O species and Th were attributed to ThO_2 molecules. These values are essentially the same as those observed by Gabelnick *et al.* [1974GAB/REE].

[1999MIS/ALI]

The authors measured the decomposition pressure of $BaThO_3(cr)$ according to the reaction:

$$BaThO_3(cr) \rightleftharpoons ThO_2(cr) + BaO(g) \tag{A.104}$$

from 1770 to 2136 K by weight-loss Knudsen effusion from tungsten cells. The $BaThO_3$ solid was prepared by heating the nitrates of barium and thorium with citric acid, which acts as an ignition agent. The purity, stated to be >99.9% was checked by unspecified chemical analyses and X-ray diffraction. Moisture was removed from the sample before use by heating to 1673 K in flowing argon. X-ray diffraction on partially evaporated samples showed them to be a mixture of $BaThO_3(cr)$ and $ThO_2(cr)$ as anticipated. The thermodynamic data for the Ba−O system indicate that there are negligible amounts of species other than BaO(g) in the vapour under the experimental conditions. The calculated decomposition pressures from 31 experimental points are well represented by the equation $\log_{10} p_{BaO}/\text{bar} = -21943/T + 6.705$. The Gibbs energy of the above reaction is thus $\Delta_r G_m$ ((A.104), T) = 420104 − 128.376 T ($J{\cdot}mol^{-1}$). The Gibbs energy of the reaction $BaO(cr) \rightleftharpoons BaO(g)$ over the experimental temperature range is given by 398684 – 131.434 T ($J{\cdot}mol^{-1}$), where the data are taken from the recent assessment by [1994GUR/VEY]. Their values for BaO(cr) at 298.15 K differ very slightly from those in Table IV-1), but these differences would be reflected in the data for BaO(g) also. The Gibbs energy of the formation reaction of $BaThO_3(cr)$ from the component oxides is thus:

$$[\Delta_r G_m]_{1770\text{K}}^{2136\text{K}} \text{((A.104), } T) = -21420 - 3.058\,T\ (J{\cdot}mol^{-1})$$

The small value of the entropy change of this all-solid reaction gives confidence in the experimental results.

[1999MOL/DEN]

The structure of M^{4+} and MF^{3+}, where M = U and Th were determined using L_{III} edge EXAFS in test solutions of 1.5 M $HClO_4$, where the total concentration of Th(IV) was 0.03 and 0.05 M. A standard analysis of the scattering data indicated (10.8 ± 0.5) water molecules in the first coordination sphere of both M^{4+} ions and a Th−O distance of (2.45 ± 0.01) Å. The authors suggest that the most likely coordination number is (10 ± 1) for both ions and this review accepts this estimate as it is in good agreement with previous large angle X-ray scattering data [1968JOH2] and theoretical data [2001YAN/TSU], [2002YAN/TSU]. In the fluoride test solutions the EXAFS data gave Th−F and Th−O distances of (2.14 ± 0.01) Å and (2.48 ± 0.01) Å, respectively; the first sphere coordination number is still (10 ± 1). There are indications of an asymmetric distribution of the Th−O distances as expected for both tricapped trigonal bipyramid and square antiprism geometries.

[2000ALI/MIS]

The authors measured the decomposition pressure of $Cs_2ThO_3(cr)$ according to the reaction:

$$Cs_2ThO_3(cr) \rightleftharpoons ThO_2(cr) + Cs_2O(g) \qquad (A.105)$$

from 1100 to 1254 K by weight-loss Knudsen effusion. The Cs_2ThO_3 solid was prepared by heating caesium iodide and hydrated thorium nitrate with citric acid, which acts as an ignition agent. The purity was checked by unspecified chemical analyses and X-ray diffraction; TGA and DSC were also used. The total carbon content was 0.08 wt%. Moisture was removed from the sample before use by heating to 1250 K in the Knudsen cell. X-ray diffraction on partially evaporated samples showed them to be a mixture of $Cs_2ThO_3(cr)$ and $ThO_2(cr)$ as anticipated, (but no details are given). The thermodynamic data for the Cs-O system indicate that there are quite negligible amounts of species other than $Cs_2O(g)$ in the vapour under the experimental conditions. The initial rate of effusion of Cs-bearing species was high, but fell rapidly and remained constant after a few minutes. This behaviour was attributed to the formation of CsOH(g) from the residual water vapour in the system. The subsequent contribution of CsOH(g) to the pressure was estimated to be less than 1%. The calculated decomposition pressures from ten experimental points are well represented by the equation $\log_{10} p_{Cs_2O}/\text{bar} = -13942/T + 6.939$. The Gibbs energy of the above reaction is thus $\Delta_r G_m$ (A.105) = 266916 − 132.842 T ($J\cdot mol^{-1}$). The Gibbs energy of the reaction $Cs_2O(l) \rightleftharpoons Cs_2O(g)$ over the experimental temperature range is given by 152692 − 107.587 T ($J\cdot mol^{-1}$); where the data are taken from the equilibrium constant given in [1982GLU/GUR], adjusted to 1 bar standard state. The Gibbs energy of the formation reaction of $Cs_2ThO_3(cr)$ from the component oxides is thus:

$$Cs_2O(l) + ThO_2(cr) \rightarrow Cs_2ThO_3(cr) \qquad (A.106)$$

$$[\Delta_r G_m]_{1100\text{K}}^{1254\text{K}}((A.106), T) = -114224 + 25.254\,T\,(J\cdot mol^{-1})$$

Since the entropy of fusion of Cs_2O is 26.042 $J \cdot mol^{-1} \cdot K^{-1}$, the entropy change for the metastable reaction involving $Cs_2O(cr)$ would be close to zero, which gives confidence in the experimental results. Combination of the values in the above equation with the values for $\Delta_f G^\circ_m$ (Cs_2O, l) [1982GLU/GUR] and $\Delta_f G^\circ_m$ (ThO_2, l) (this review) gives finally:

$$[\Delta_f G_m]^{1254\text{K}}_{1100\text{K}} (Cs_2ThO_3, \text{cr}, T) = -\ 1780323 + 441.26\ T\ (J \cdot mol^{-1})$$

where the standard state for Cs is Cs(g) in this temperature range. The uncertainty in these values is estimated to be at least 20 $kJ \cdot mol^{-1}$, mainly from the uncertainty in $\Delta_f H^\circ_m$ (Cs_2O, g, 298.15 K) which is given as 15 $kJ \cdot mol^{-1}$ by [1982GLU/GUR].

Since there are no other thermodynamic data for $Cs_2ThO_3(cr)$, no further processing of these results is possible, and no values are selected for the review.

[2000BUN/KNO]

This paper is discussed with [2003NEC/ALT].

[2000EKB/ALB]

This is a study of the hydrolysis of Th^{4+} that includes potentiometric titration data and liquid-liquid extraction data of the type previously described in [1992ENG/ALB]. In the latter case the extractant, acetylacetonate, forms both binary complexes ThL_n^{4-n}, and presumably ternary complexes $ThL_n(OH)_m^{4-n-m}$ in the aqueous phase; the possible formation of ternary thorium-acetylacetonate-hydroxide complexes was not considered in [2000EKB/ALB]. The potentiometric experiments have been made at three different temperatures, 15.0, 25.0 and 35.0°C in a 1 M $NaClO_4$ ionic medium; the liquid-liquid extraction experiments have been performed at 25°C. The potentiometric data have been collected using standard methods, with $[Th]_{tot}$ varying between 10^{-5} and 10^{-4} M in the pH range $3.23 - 4.47$. The measured pH values have been converted to $-\log_{10} [H^+]$. The authors have used very small concentrations of total thorium and under these conditions the experiments are strongly dependent on the presence of protolytic impurities in the ionic medium, the presence of 10 ppm Fe or Al will result in a concentrations of about 0.02 mM in 1 M $NaClO_4$; impurity levels of this magnitude are common in commercial sodium perchlorate. The Sillén group therefore developed special techniques to prepare $NaClO_4$. The primary experimental data are given in the paper and they have been analysed using the MINIQUAD least-squares program with simultaneous minimisation of $[H_{tot,calc} - H_{tot,exp}]^2$ and $[Th_{tot,calc} - Th_{tot,exp}]^2$; the standard deviation of the fit is given in Table II of [2000EKB/ALB] but is not defined, nor is there a comparison between experimental and calculated values of H_{tot} and Th_{tot} that would allow identification of systematic errors. The equilibrium constants and the estimated uncertainty deduced from potentiometry are given in Table A-78; the uncertainties in the $\log_{10} {}^*\beta_{n,m}$ values are seriously underestimated and should be increased by at least a factor five as judged by this review.

The enthalpy and entropy of reaction have been estimated from $\log_{10}{}^{*}\beta_{n,m}$ at 15, 25 and 35°C assuming $\Delta_{\mathrm{r}}C_{p,\mathrm{m}} = 0$; the uncertainties in these values are also underestimated in the opinion of this review.

Table A-78: Potentiometric equilibrium constants $\log_{10}{}^{*}\beta_{n,m}(\mathrm{Th}_m(\mathrm{OH})_n^{4m-n})$, for thorium hydroxide complexes in 1 M $NaClO_4$.

t (°C)	Total concentrations of Th (mM)	Species (n,m)	$\log_{10}{}^{*}\beta_{n,m}$ (± 1σ)	$\Delta_{\mathrm{r}}H_{\mathrm{m}}$ (kJ·mol^{-1})	$\Delta_{\mathrm{r}}S_{\mathrm{m}}$ (J·K^{-1}·mol^{-1})
15	0.0096 – 0.104	(1,1)	– 3.34 ± 0.05		
		(2,1)	– 8.78 ± 0.02		
		(8,4)	– 20.55 ± 0.01		
		(15,6)	– 41.44 ± 0.03		
25	0.0093 – 0.0989	(1,1)	– 3.35 ± 0.06	38 ± 6	60 ± 20
		(2,1)	– 8.55 ± 0.02	36 ± 1	– 44 ± 4
		(8,4)	– 19.18 ± 0.01	191 ± 3	280 ± 10
		(15,6)	– 39.01 ± 0.04	410 ± 60	600 ± 200
25	0.0116 – 0.123	(2,1)	– 8.54 ± 0.02		
		(8,4)	– 18.95 ± 0.01		
		(15,6)	– 40.07 ± 0.04		
35	0.0104 – 0.103	(1,1)	– 3.19 ± 0.07		
		(2,1)	– 8.36 ± 0.04		
		(8,4)	– 17.86 ± 0.01		
		(15,6)	– 36.58 ± 0.04		

In order to determine a precise value of the first mononuclear hydrolysis constant, additional potentiometric measurements were performed at each temperature in the pH range 1.8 − 3.1. Besides a minor contribution from $\mathrm{Th}_4(\mathrm{OH})_8^{8+}$, the mononuclear complex ThOH^{3+} was the only hydroxide complex observed in this pH range. The following equilibrium constants were calculated:

$$\log_{10}{}^{*}\beta_{1,1}\,(1.0\ \mathrm{M\ NaClO_4,}\ 15°\mathrm{C}) = -(3.6 \pm 0.1),$$
$$\log_{10}{}^{*}\beta_{1,1}\,(1.0\ \mathrm{M\ NaClO_4}\ 25°\mathrm{C}) = -(3.3 \pm 0.1),$$
$$\log_{10}{}^{*}\beta_{1,1}\,(1.0\ \mathrm{M\ NaClO_4}\ 35°\mathrm{C}) = -(3.2 \pm 0.1).$$

The liquid-liquid extraction study has been made at $[\mathrm{Th}]_{\mathrm{tot}}$ below 10^{-5} M, typically at 10^{-7} M; under these conditions the formation of polynuclear complexes and colloids should be minimised. The experimental data have been evaluated in the same way as in [1992ENG/ALB] – that is, the formation of ternary complexes has not been considered. The method requires a simultaneous determination of the equilibrium constants for the binary Th(IV)-OH– and Th(IV)-acetylacetonate systems as indicated in Eqs. (1) and (2) of [2000EKB/ALB]. The authors do not report the total concentration of HL (acetylacetone) used and only some of the experimental $\log_{10}D$ – $\log_{10}[\mathrm{H}^+]$ data are given in Table AII of [2000EKB/ALB]). The equilibrium constants for the acetylacetonate complexes differ significantly from those in [1992ENG/ALB] and the reported uncertainty is much smaller. This may not be the result of improved experimental technique, but the use of a smaller range of total concentrations of acetylacetone (but there is no information on this in the paper). The authors have divided the analysis of the extraction data into two parts, where data below pH 8.3 are assumed to be dominated by the formation of acetylacetonato complexes; these data were used to determine the equilibrium constants for ThL_n^{4-n}. The data at higher pH were then used to determine the equilibrium constants for $\mathrm{Th(OH)}_3^+$ and $\mathrm{Th(OH)_4}$. This review has objections to this procedure; ternary complexes have not been taken into account and the authors have not considered the possibility of formation of ThL_5^- that also will result in a decrease of $\log_{10}D$. The following speciation diagram (Figure A-42) illustrates these points. The assumption that binary hydroxide complexes are negligible is only justified at $-\log_{10}[\mathrm{H}^+] < 6$ (varies with the total concentration of acetylacetone). The equilibrium constants for the formation of $\mathrm{Th(OH)}_3^+$ and $\mathrm{Th(OH)_4(aq)}$ suggested are $\log_{10}{}^*\beta(\mathrm{Th(OH)}_3^+) = -(14.9 \pm 2.8)$ and $\log_{10}{}^*\beta\,(\mathrm{Th(OH)_4},\ \mathrm{aq}) = -(22.0 \pm 0.4)$. The equilibrium constants have been determined also at 15 and 35°C.

Figure A-42 illustrates the effect of assuming that, in addition to the complexes ThL_n^{4-n} (with $\log_{10}\beta_{1,n,0}$ = 9.0, 16.7, 22.8 and 27.4 for n = 1 − 4 and 25°C [2000EKB/ALB]), the negatively charged complexes ThL_5^- (with $\log_{10}\beta_{1,5,0} = 27.4$) and $\mathrm{ThL_4(OH)^-}$ (with $\log_{10}{}^*\beta_{1,4,1} = 16.0$) are formed. These estimated equilibrium constants correspond to the sums of $\log_{10}\beta_{1,4,0}$ and the following stepwise constants for the reactions:

$$\mathrm{ThL_4} + \mathrm{L}^- \rightleftharpoons \mathrm{ThL}_5^- \qquad \log_{10}K = 0.6$$

$$\mathrm{ThL_4} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{ThL_4(OH)^-} + \mathrm{H}^+ \qquad \log_{10}{}^*K = -11.4.$$

It is obvious that these constants have a noticeable effect on the distribution curve at high pH and accordingly on the model used in [2000EKB/ALB].

The overall results proposed by Ekberg *et al.* [2000EKB/ALB] in Table V of their paper, combining both potentiometric and solvent extraction data, are summarised in Table A-79. The equilibrium constant for $\mathrm{Th_4(OH)}_8^{8+}$ at 25°C is in good agreement with the value calculated from potentiometric data of [1954HIE], [1954KRA/HOL], [1965BAE/MEY] in 1.0 M $\mathrm{NaClO_4}$ at 25°C. The equilibrium constant proposed for $\mathrm{Th_6(OH)}_{15}^{9+}$ at 25°C differs considerably and is about 2 $\log_{10}$-units lower. The enthalpies and entropies of reaction differ significantly from those reported in [1965BAE/MEY].

The equilibrium constants for the mononuclear hydroxide complexes, including the values for $\mathrm{Th(OH)}_3^+$ and $\mathrm{Th(OH)_4(aq)}$ which are exclusively derived from the solvent extraction study, were found to be consistent with solubility data for $\mathrm{ThO_2}$(am, hyd) [2001NEC/KIM], [2002NEC/MUL]. However, the stoichiometry of the complexes and their equilibrium constants are based on the assumption that the species ThL_5^- and $\text{ThL}_4(\text{OH})^-$ are not formed in significant amounts and this has not been verified.

Figure A-42: Speciation diagram for the Th(IV) acetylacetonate system at 25°C, based on the equilibrium constants for ThL_n^{4-n} (n = 1−4) from [2000EKB/ALB] and the values estimated by this review for ThL_5^- and $\text{ThL}_4(\text{OH})^-$. The total concentration of L is constant at 0.05 M and that of Th at 10^{-7} M. Note that the binary hydroxide complexes have not been included in this diagram. They start to influence the species distribution around pH 6.

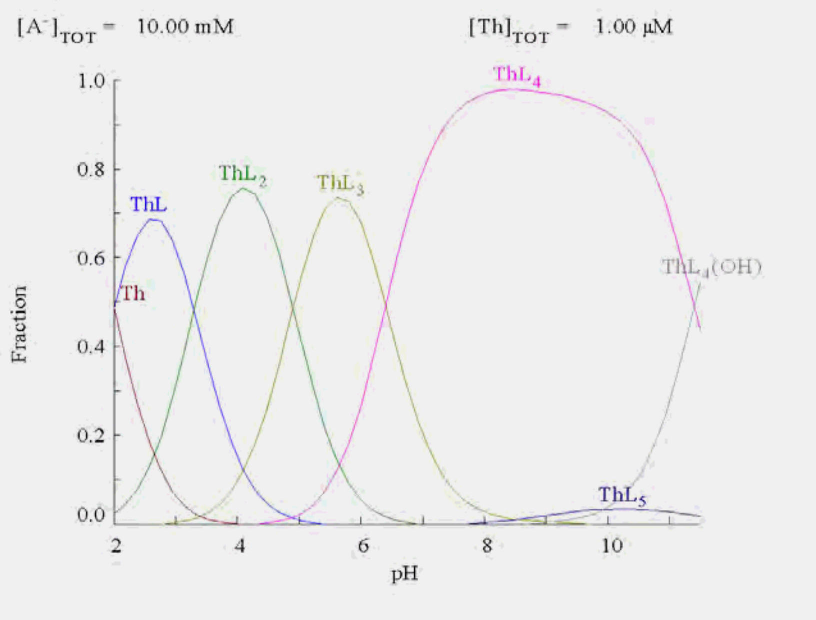


Table A-79: Equilibrium constants, enthalpies and entropies of reaction proposed in [2000EKB/ALB] for the formation of Th(IV) hydroxide complexes in 1.0 M NaClO_4.

Complex	$-\log_{10}{}^*\beta_{n,m}$			Δ_rH_m	Δ_rS_m
	15°C	25°C	35°C	(kJ·mol^{-1})	(J·K^{-1}·mol^{-1})
ThOH^{3+}	3.6 ± 0.1	3.3 ± 0.1	3.2 ± 0.1	38 ± 6	60 ± 20
Th(OH)_2^{2+}	8.8 ± 0.1	8.6 ± 0.1	8.4 ± 0.1	36 ± 1	– 44 ± 4
Th(OH)_3^+	14.9 ± 2.8	14.2 [a]	12.7 ± 3.5	190 ± 40	300 ± 100
$\text{Th(OH)}_4\text{(aq)}$	22.0 ± 0.4	19.4 ± 0.5	17.8 ± 0.4	360 ± 40	800 ± 100
$\text{Th}_4\text{(OH)}_8^{8+}$	20.2 ± 0.3	19.1 ± 0.1	18.0 ± 0.1	191 ± 3	280 ± 10
$\text{Th}_6\text{(OH)}_{15}^{9+}$	41.4 ± 0.2	39.5 ± 0.2	36.6 ± 0.2	410 ± 60	600 ± 200

a: Estimated from other data for mononuclear hydroxide complexes at 25°C and the values for Th(OH)_3^+ at 15°C and 35°C.

[2000FAR/GRE]

This study describes the rate and mechanism of water exchange between $\mathrm{U(H_2O)_{10}^{4+}}$, $\mathrm{UF(H_2O)_9^{3+}}$, $\mathrm{Th(H_2O)_{10}^{4+}}$ and the solvent water as studied by ^{17}O NMR. The rate of exchange is significantly larger for $\mathrm{Th^{4+}}$, $k_{ex} > 5 \times 10^7\ \mathrm{s^{-1}}$ than for the $\mathrm{U^{4+}}$, $k_{ex} = 5.4 \times 10^6\ \mathrm{s^{-1}}$. The mechanism for the exchange depends on the coordination number; for $\mathrm{Th(H_2O)_9^{4+}}$ the theoretical data in [2002YAN/TSU] indicate that a dissociative mechanism can be excluded as the energy of the dissociative intermediate is much higher in energy than that for the associative intermediate. On the other hand if $\mathrm{Th^{4+}}$ is ten-coordinated, $\mathrm{Th(H_2O)_{10}^{4+}}$, the reaction mechanism is most probably dissociative.

[2000FOU/VIN]

Fourest *et al.* [2000FOU/VIN] performed leaching experiments at 25°C and 90°C with $\mathrm{ThO_2(cr)}$ powder in pure water and four synthetic granite waters ($I = 0.01 - 0.3$ M) at pH 6.6 − 9.2 and carbonate/bicarbonate concentrations corresponding to carbon dioxide partial pressures of $p_{\mathrm{CO_2}} = 10^{-6}$ bar for solutions 1 (final pH = 8.0, 25°C) and 3 (pH = 9.2, 90°C) and 10^{-3} bar for solutions 2 (pH = 6.6, 25°C) and 4 (pH = 7.1, 90°C). The crystalline thorium dioxide was prepared from oxalate calcined up to 1600°C. After 31 days, the thorium concentrations in the batch samples were measured by ICP-MS analysis after centrifugation at 3500 rpm and subsequent ultracentrifugation at 50000 rpm. An effect of carbonate was not observed, which is consistent with the data on Th(IV) carbonate complexes reported by [1994OST/BRU], [1997FEL/RAI] and [2005ALT/NEC].

The mean values of $\log_{10}[\mathrm{Th}]$ calculated from the data given in Table 4 of [2000FOU/VIN] are $-(10.3 \pm 0.7)$ at 25°C and $-(8.3 \pm 0.4)$ at 90°C. These values are orders of magnitude higher than expected from $\Delta_f G_m^\circ$ ($\mathrm{ThO_2}$, cr, 298.15 K) = $-(1169.0 \pm 3.5)\ \mathrm{kJ \cdot mol^{-1}}$, corresponding to $\log_{10} {}^*K_{s,0}^\circ$ ($\mathrm{ThO_2}$, cr, 298.15 K) = (1.77 ± 1.11), and $\log_{10} {}^*\beta_{4,1}^\circ = -(17.4 \pm 0.7)$ selected by this review. These values yield an equilibrium constant of $\log_{10} K_{s,4}^\circ$ ($\mathrm{ThO_2}$, cr) = $-(15.6 \pm 1.3)$ for the reaction:

$$\mathrm{ThO_2(cr) + 2H_2O(l) \rightleftharpoons Th(OH)_4(aq)}.$$

The thorium concentrations determined by Fourest *et al.* [2000FOU/VIN] with crystalline thorium dioxide are close to experimental $\log_{10} K_{s,4}$ values for amorphous hydroxides or hydrous oxides $\mathrm{ThO_2(am, hyd)}$.

[2000GAG/SKY]

Six different DFT functionals have been used to predict the structure and molecular properties of the four thorium tetrahalides gaseous molecules, giving reasonably consistent values. All the gaseous species are predicted to have tetrahedral symmetry. The calculated interatomic distances agree in general with the experimental electron diffraction results to within 0.05 Å. For the harmonic vibration frequencies, agreement with the four known values (ν_3 and ν_4 for $\mathrm{ThF_4}$ and ν_3 for $\mathrm{ThCl_4}$ and $\mathrm{ThBr_4}$) is within 15% for all the models. The authors suggest that for thermodynamic calculations, the vibration frequencies from the B3LYP functional should be preferred to empirical estimates.

[2000RAI/MOO]

The solubility of the following thorium oxide phases was studied in 0.1 M NaCl as a function of time and pH (activity scale) at two different temperatures, (23 ± 2) and (90 ± 2)°C: a) an amorphous ThO_2(am, hyd) precipitate purified by washing with water, b) crystalline ThO_2(cr) prepared by heating thorium oxalate at 750°C, and c) a microcrystalline phase obtained by thermal transformation of the amorphous phase at 90°C, designated as ThO_2(am→cr). Preparation and characterisation of the solid phases as well as the experimental procedures for measuring the solubility are described in detail, as are the details about the calculations.

The solubility of amorphous ThO_2(am, hyd) was determined from undersaturation at 23°C and pH 4 − 5 after equilibration of the suspensions for 5 − 22 days. Analogous experiments were performed with crystalline ThO_2(cr) in the pH range 1.3 to 3.5 at 23°C (equilibration times: 11 − 794 days) and 90°C (equilibration time: 12 days). At 23°C the solubility of the amorphous phase was greater than 10^{-2} M at pH < 4 while that of the crystalline phase decreased to values below 10^{-9} at pH > 3. The solubility data determined with ThO_2(cr) at 23°C in the pH range 1.3 to 2.0, where hydrolysis is negligible, decreased approximately with the slope of − 4 as expected for $\log_{10} [Th^{4+}]$ *vs*. pH. However, the authors were not sure whether equilibrium was reached and considered the measured thorium concentrations as lower limit for the solubility of ThO_2(cr) at 23°C. The thorium concentrations measured at pH 2.0 − 3.5 after equilibration at 23°C for more than two years were unexpectedly high and independent of pH, indicating that they were not equilibrium values. They decreased to the expected values after storing the samples for two weeks at 90°C and readjusting them for 1 day at 23°C. This observation was ascribed to the crystallinisation of small amorphous fractions of the bulk solid.

A similar observation, the thermal transformation of the initially amorphous ThO_2(am, hyd) precipitate into a microcrystalline solid phase, was made at 90°C and pH 1.5 − 3.0. The equilibrium between this ThO_2(am→cr) phase and Th^{4+} was reached from the direction of oversaturation. The solubility data measured with this ThO_2(am→cr) phase after 52 − 76 days at 90°C show the expected dependence on pH, however, but at a solubility about 2.2 $\log_{10}$-units higher level than the value determined with ThO_2(cr) from undersaturation.

Rai *et al.* have used the Pitzer model to interpret the solubility data and calculate the solubility products for the different thorium oxide phases: $\log_{10} K^{\circ}_{s,0}$ = – (44.9 ± 0.5) for ThO_2(am) at 23°C, ≥ – 56.9 for ThO_2(cr) at 23°C, –(51.4 ± 0.2) for ThO_2(cr) at 90°C, and –(49.2 ± 0.2) for ThO_2(am→cr) at 90°C. The corresponding interaction parameters are taken from an earlier study [1997RAI/FEL]. However, as shown in Figure VI-5, Section VI.3.2, the activity coefficient calculated with these interaction coefficients for Th^{4+} in 0.1 M NaCl differs by about two orders of magnitude from $\gamma_{Th^{4+}}$ calculated with the SIT and $\varepsilon(Th^{4+},Cl^-)$ = (0.25 ± 0.03) $kg\cdot mol^{-1}$. In addition, Rai *et al.* have not taken hydrolysis into account when evaluating the solubility products. Only part of the experimental solubility data have been obtained in a pH range where hydrolysis can be neglected. Therefore this review has used the SIT and the selected data for Th(IV) hydroxide complexes to recalculate the solubility constants from the experimental data in [2000RAI/MOO].

The re-evaluation of the solubility data for fresh ThO_2(am, hyd) at 23°C is shown in Figure A-43. Using the hydrolysis constants and SIT coefficients selected in the present review, the tetranuclear complex $Th_4(OH)_{12}^{4+}$ is found to be the predominant species in saturated solutions at pH 4−5 in 0.1 M NaCl and the solubility constant at zero ionic strength is calculated to be $\log_{10}{}^*K^{\circ}_{s,0} = (9.8 \pm 0.3)$, $\log_{10} K^{\circ}_{s,0} = -(46.2 \pm 0.3)$. This value is about 0.5−1.5 $\log_{10}$-units higher than the values derived from similar solubility studies in earlier papers of this group [1987RYA/RAI], [1991FEL/RAI], [1997RAI/FEL].

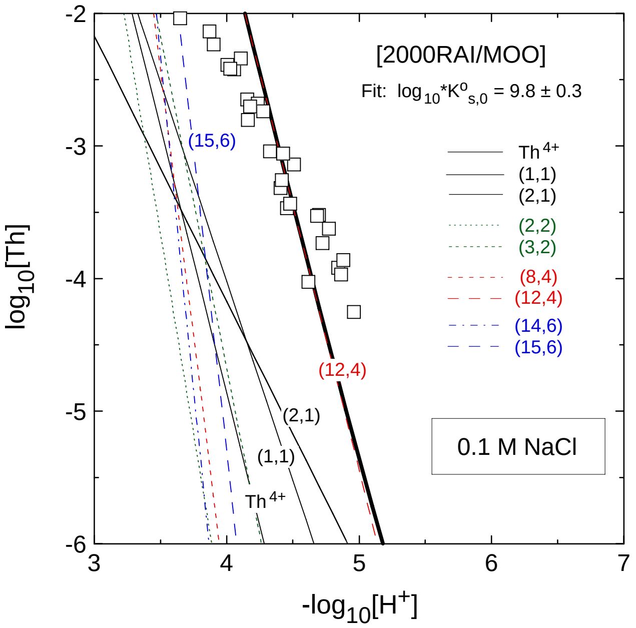
The solubility studies with ThO_2(cr) are performed at low pH where hydrolysis is negligible. As proposed by [2000RAI/MOO] the solubility constant $\log_{10}{}^*K_{s,0}$ (0.1 M NaCl, 23°C) ≥ 2.3, derived from data in the pH range 1.3 to 2.0, is considered as a lower limit. Extrapolation to $I = 0$ with the SIT and $\varepsilon(Th^{4+}, Cl^-)$ = (0.25 ± 0.03) $kg\cdot mol^{-1}$ selected by this review gives $\log_{10}{}^*K^{\circ}_{s,0} \geq 1.0$ ($\log_{10} K^{\circ}_{s,0} \geq -55.0$) at 23°C.

The solubility constants $\log_{10}{}^*K_{s,0}$ (0.1 M NaCl, 90°C) for ThO_2(cr) and ThO_2(am→cr) are calculated from the experimental values of $\log_{10}[Th^{4+}]$ and pH (activity scale) in the range 1.3 to 2.5 according to:

$$\log_{10}{}^*K_{s,0} = \log_{10}[Th^{4+}] + 4\,(pH + \log_{10}\gamma_{H^+}) \qquad (A.107)$$

with $\log_{10}\gamma_{H^+} = -0.12$ at 90°C. Ionic strength corrections are made with the SIT (*cf.* [1997GRE/PLY2] and [2003GUI/FAN]) using the Debye-Hückel constants *A* and *B* listed in Appendix B of [2003GUI/FAN]. The temperature derivative of the activity of water, $L_1 = -RT^2(\partial \ln a_w/\partial T) = 0.00\ kJ\cdot mol^{-1}$ for 0.1 M NaCl, and $\varepsilon_L(H^+,Cl^-) = (\partial(\varepsilon(H^+, Cl^-))/\partial T) = -(1.0 \pm 0.1)\cdot 10^{-3}\ kg\cdot mol^{-1}\cdot K^{-1}$ [1997GRE/PLY2] have no significant effect at I = 0.1 M (HCl-NaCl). The unknown value of $\varepsilon_L(Th^{4+},Cl^-)$ is set equal to zero assuming an uncertainty of $\pm 5\cdot 10^{-3}\ kg\cdot mol^{-1}\cdot K^{-1}$. The following solubility constants, with the uncertainty given as 2σ, are obtained at 90°C: $\log_{10}{}^*K_{s,0}$ (0.1 M NaCl) = (1.3 ± 0.4) and $\log_{10}{}^*K^{\circ}_{s,0} = -(0.2 \pm 0.4)$ for ThO_2(cr), $\log_{10}{}^*K_{s,0}$ (0.1 M NaCl) = (3.5 ± 0.4) and $\log_{10}{}^*K^{\circ}_{s,0} = (2.0 \pm 0.4)$ for ThO_2(am→cr).

Figure A-43: Solubility data for ThO_2(am, hyd) at 23°C in 0.1 M NaCl [2000RAI/MOO]: Recalculation of the solubility constant and aqueous speciation using the hydrolysis constants and SIT coefficients selected in the present review.



The solubility constants derived at 23 and 90°C for the different thorium oxides are summarised in Table A-80, together with the values calculated for ThO_2(cr) from thermochemical data and the corresponding solubility constants calculated by Rai *et al*. [2000RAI/MOO]. The solubility constants calculated by this review from the undersaturation solubility experiments with crystalline ThO_2(cr), $\log_{10} K^{\circ}_{s,0} \geq -55.0$ at 23°C and $\log_{10} K^{\circ}_{s,0} = -(49.9 \pm 0.4)$ at 90°C are consistent with the thermochemical values of $\log_{10} K^{\circ}_{s,0} = -(54.2 \pm 1.1)$ at 25°C and $-(51.6 \pm 1.2)$ at 90°C. The solubility constant calculated for the ThO_2(am→cr) phase from solubility data determined at 90°C from oversaturation, after transformation of initially amorphous precipitate into a microcrystalline solid, is 2.2 $\log_{10}$-units higher than the value for crystalline ThO_2(cr) at this temperature. This difference can be attributed to the effect of particle size. The reported X-ray diffraction pattern clearly shows that the crystallite size in the ThO_2(am→cr) phase is much smaller than in the crystalline ThO_2(cr). From the line broadening one can estimate crystallite sizes of $d = (4 \pm 1)$ nm for ThO_2(am→cr) and $d = (17.5 \pm 1.0)$ nm for the crystalline ThO_2(cr) prepared at 750°C. Applying the equation of Schindler (*cf.* Section VII.4.3) to the solubility constant of ThO_2(cr) at 90°C, the variation with particle size d is given by:

$$\log_{10} K^{\circ}_{s,0}\ (\text{ThO}_2, \text{particle size } d) = -\,(51.6 \pm 1.2) + 21.6\,/\,d(\text{nm}) \qquad (\text{A.108})$$

Table A-80: Solubility constants $\log_{10} K^{\circ}_{s,0}$ calculated by [2000RAI/MOO] and this review from solubility data for ThO_2(am, hyd), microcrystalline ThO_2(am→cr) and ThO_2(cr) at 23 and 90°C in 0.1 M HCl-NaCl and from thermochemical data for anhydrous ThO_2(cr).

Solid	t (°C)	Method	$\log_{10} K^{\circ}_{s,0}$	$\log_{10} K^{\circ}_{s,0}$ [a]	$\log_{10} {}^{*}K^{\circ}_{s,0}$
			[2000RAI/MOO]	This review (SIT)	
ThO_2(am)	23	sol, undersat.	– (44.9 ± 0.5)	– (46.2 ± 0.3)	(9.8 ± 0.3)
ThO_2(cr)	23	sol, undersat.	≥ –56.9	≥ –55.0	≥ 1.0
ThO_2(cr)	90	sol, undersat.	– (51.4 ± 0.2)	– (49.9 ± 0.4)	– (0.2 ± 0.4)
ThO_2(am→cr)	90	sol, oversat.	– (49.2 ± 0.2)	– (47.7 ± 0.4)	(2.0 ± 0.4)
ThO_2(cr)	25	calculated	– 54.2 [c]	– (54.2 ± 1.1)	(1.8 ± 1.1) [b]
	90	calculated	(– 50.8 / – 51.6) [c]	– (51.6 ± 1.2)	– (1.9 ± 1.1) [b]

a: Calculated from $\log_{10} {}^{*}K^{\circ}_{s,0}$ with $\text{p}K^{\circ}_{\text{w}}$ = 14.00 at 25°C and 12.42 at 90°C.

b: Calculated from standard state thermodynamic data for Th(cr), ThO_2(cr) and Th^{4+} selected in the present review. The value at 90°C is calculated according to Eq. (X.19) in [1997ALL/BAN] (Chapter X, p. 434), with a constant value of $\Delta_{\text{r}} C^{\circ}_{p,\text{m}} = -\,(135 \pm 15)\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

c: The thermochemical values calculated by Rai *et al.* [2000RAI/MOO] are based on slightly different thermodynamic data (CODATA, [1976FUG/OET], [1982WAG/EVA]).

Taking into account this dependence on particle size (or better: crystallite size) we calculate a solubility product of $\log_{10} K^{\circ}_{s,0}$ (ThO_2(am→cr), 363 K) = −(46.2 ± 1.9) for the microcrystalline ThO_2(am→cr) phase with d = (4 ± 1) nm and $\log_{10} K^{\circ}_{s,0}$ (ThO_2, cr, 363 K) = −(50.4 ± 1.2) for d = (17.5 ± 1) nm. Both calculated values are, within the uncertainties, consistent with the solubility products derived from the experimental data ($\log_{10} K^{\circ}_{s,0}$ = −(47.7 ± 0.4) and −(49.9 ± 0.4), respectively). However, because of the large uncertainties and because of the fact that the crystallite size estimated above and the particle size in Eq. (A.108) are not identical quantities, these calculations must be considered as semi-quantitative approximations.

[2000THO/DAC]

Normalised leaching rate of thorium phosphate-diphosphate ($Th_4(PO_4)_4P_2O_7$) as a function of temperature, hydrogen ion, and phosphate concentrations are reported. No raw data are available. The leach data are presented in graphical form for the most part as $\text{g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ and it is reported that $Th_4(PO_4)_4P_2O_7$ is not the equilibrium phase and that the leach rates are governed by thorium phosphate-hydrogen phosphate ($Th_2(PO_4)_2HPO_4\cdot H_2O$). Equilibrium thermodynamic values are not reported, and no experimental data are available to calculate either the solubility products of any of the solids used in the study or the phosphate complexes of thorium.

[2000WAN/GUO]

Using a direct synthesis calorimeter operating at (1473 ± 2) K, these authors determined the enthalpies of formation of $ThAl_2$(cr), $ThSi_2$(cr), $ThGe_2$(cr) and Th_5Sn_3(cr).

The instrument used was a single-unit differential microcalorimeter described in detail in an earlier publication [1989KLE/TOP]. The calibration of the calorimeter was achieved by dropping high purity copper wires from room temperature (298.15 K) into the calorimeter at its working temperature and using literature value for the enthalpy of copper [1973HUL/DES]. Results were reproducible within 1%. All experiments were conducted in an atmosphere of argon from which traces of oxygen and nitrogen had been eliminated by passing it over a titanium sponge at 1173 K. The actual calorimetric syntheses were carried out in boron nitride crucibles. For each run, both the unreacted mixture and the actual final product were dropped from 298.15 K to the reacting temperature and the enthalpies measured; the difference between these values therefore gives the enthalpy of formation at 298.15 K.

Samples for calorimetry were prepared by mixing the two component powders, accurately weighed according to the appropriate stoichiometry, and pressing the mixture into 4 mm diameter pellets. The purity of the commercial materials used was given as 99.5% for Si and Al, 99.8% for Th, 99.995 for Ge and 99.999% for Sn, without further details. The authors mention precautions in handling the easily oxidised thorium metal powder. X-ray diffraction measurement suggested that the thorium samples might contain up to 3.5% ThO_2. However, this value could be considered as an upper limit representing the outer layers of the thorium powder (100 mesh size), given the low penetration of the X-rays into the thorium metal. X-ray examination of the samples after calorimetric reaction showed, for all compounds for which an enthalpy of formation was reported, the absence of unreacted materials. About 5% of ThO_2 were detected in all compounds. In the case of $ThAl_2$, minor amounts of $ThAl_3$ were detected. For $ThSi_2$, three weak unknown peaks were detected. For Th_5Sn_3, minor quantities of Th_5Sn_4 were identified. In the absence of standard X-ray diffraction patterns for the Th-Sn alloys in the ASTM powder diffraction file, the authors resorted to a commercial software program to obtain ideal diffraction patterns for the various compounds in the Th-Sn system. In the case of $ThGe_2$, no extraneous lines could be identified, although the authors report that their compound did not match the standard X-ray diffraction pattern for this compound, or for any other Th-Ge compound.

The calorimetric results are the average of four to six individual measurements and the overall uncertainties on the results are reported as the combined standard deviation taking in account the uncertainties of the calibration runs and are given as:

$$\Delta_f H_m^\circ(\mathrm{ThAl_2, cr, 298.15\ K}) = -(140.4 \pm 6.3)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{ThSi_2, cr, 298.15\ K}) = -(166.8 \pm 6.0)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m^\circ(\mathrm{ThGe_2, cr, 298.15\ K}) = -(216.6 \pm 4.2)\ \mathrm{kJ\cdot mol^{-1}}$$

$$\Delta_f H_m^\circ(\text{Th}_5\text{Sn}_3, \text{cr}, 298.15\text{ K}) = -(510.4 \pm 16.0)\text{ kJ·mol}^{-1}.$$

The authors discuss their results in the light of values predicted by semi-empirical models for intermetallic compounds and with earlier experimental literature results for the enthalpy of formation of these and related compounds.

[2001ALI/MIS]

The authors measured the pressure of Sr(g) obtained by heating $SrThO_3$(cr) in a tungsten cell from 1677 to 2419 K by mass loss Knudsen effusion. X-ray examination of the residue after partial decomposition showed that the condensed phases were different in different temperature ranges. As well as $SrThO_3$(cr), W(cr) and ThO_2(cr), Sr_2WO_5(cr) was present from 1677 to 2047 K, but $SrWO_4$(cr) was found in experiments from 2138 to 2419 K. Since $SrWO_4$ would be molten at these higher temperatures, Energy Dispersive X-ray analysis was carried out to determine whether there was any solubility of thorium species in this melt. Less than 10% ThO_2 was detected, but the authors were not clear whether this was due to dissolution of *e.g.* $SrThO_3$ or from interference from neighbouring ThO_2 particles. Thus $SrWO_4$(l) was treated as a pure phase in the subsequent analysis, as was ThO_2(cr), although the solubility of SrO in ThO_2 (cr) at 2273 K is reported to be as high as 13 mol%. The uncertainty resulting from these assumptions was estimated by the authors to be 2.6 kJ·mol^{-1}. The authors discuss and dismiss the possible loss of oxygen to form phases containing lower-valent tungsten, such as $SrWO_3$(cr).

The relevant reactions were thus assumed to be:

$$5\text{SrThO}_3(\text{cr}) + \text{W(cr)} \rightleftharpoons \text{Sr}_2\text{WO}_5(\text{cr}) + 5\text{ThO}_2(\text{cr}) + 3\text{Sr(g)} \qquad 1677 \text{ to } 2047\text{ K} \quad (\text{A.109})$$

and

$$4\text{SrThO}_3(\text{cr}) + \text{W(cr)} \rightleftharpoons \text{SrWO}_4(\text{l}) + 4\text{ThO}_2(\text{cr}) + 3\text{Sr(g)} \qquad 2138 \text{ to } 2419\text{ K} \quad (\text{A.110})$$

Measurements were also made below 1670 K, but the establishment of the equilibrium (probably with Sr_3WO_6(cr)) was too slow for the results to be reliable. The $SrThO_3$ solid was prepared by "sol-gel combustion" as described by [2000PUR/TYA]. This involves heating the nitrates of strontium and thorium with citric acid, which acts as an ignition agent. X-ray diffraction showed the presence of a monoclinic cell with parameters in good accord with other determinations [2000PUR/TYA], [1947NAR]. The calculated decomposition pressures for Reactions (A.109) and (A.110) are well represented by the equations $\log_{10} p_{Sr}/\text{bar} = -19291/T + 5.280$ and $\log_{10} p_{Sr}/\text{bar} = -21719/T + 6.166$. The Gibbs energy of the above reactions are thus

$$\Delta_r G_m((\text{A.109}), T) = 1107989 - 303.240\,T \quad (\text{J·mol}^{-1})$$

and

$$\Delta_r G_m((\text{A.110}), T) = 1247401 - 354.041\,T \quad (\text{J·mol}^{-1}).$$

The Gibbs energy of the reaction $\text{Sr(g)} + 0.5\text{O}_2(\text{g}) \rightleftharpoons \text{SrO(cr)}$ over the experimental temperature range is given by $-726189 + 185.253\,T$ (J·mol^{-1}), where the data are taken from the recent assessment by [1994GUR/VEY], adjusted slightly to accord with Table IV-1. The only experimental data for the Gibbs energies of formation of $SrWO_4$(cr) and Sr_2WO_5(cr) are those for the reactions:

$$\mathrm{SrO(cr) + W(cr) + 1.5O_2(g) \rightleftharpoons SrWO_4(cr)}, \quad \Delta_r G_m = -1031495 + 234.443\,T\ (\mathrm{J \cdot mol^{-1}})$$

and

$$\mathrm{2SrO(cr) + W(cr) + 1.5\,O_2(g) \rightleftharpoons Sr_2WO_5(cr)}, \quad \Delta_r G_m = -1090350 + 246.019\,T\ (\mathrm{J \cdot mol^{-1}})$$

given by Levitskii and Skolis [1974LEV/SKO] for temperatures from 1100 to 1500 K, based on emf measurements. These have been assumed to apply at the appreciably higher temperatures of the current experiments. For Reaction (A.110), we also require the Gibbs energy of fusion of $SrWO_4$, which is not known. The authors used an estimated enthalpy of fusion of 30 $\mathrm{kJ \cdot mol^{-1}}$, which we have accepted together with the melting point of 1808 K, giving $\Delta_{fus} G_m$ ($SrWO_4$) = 30000 − 16.593 T ($\mathrm{J \cdot mol^{-1}}$). Manipulation of the appropriate equations gives for the Gibbs energy of the formation reaction of $SrThO_3$(cr) from the component oxides:

$$\mathrm{SrO(cr) + ThO_2(cr) \rightarrow SrThO_3(cr)} \qquad \text{(A.111)}$$

$[\Delta_r G_m]_{1670\mathrm{K}}^{2040\mathrm{K}}$ ((A.111), T) = − 3955 − 1.300 T ($\mathrm{J \cdot mol^{-1}}$) from Reaction (A.109), and

$[\Delta_r G_m]_{2135\mathrm{K}}^{2420\mathrm{K}}$ ((A.111), T) = − 17583 + 4.033 T ($\mathrm{J \cdot mol^{-1}}$) from Reaction (A.110)

Considering the extrapolations involved, and the uncertain activities for Reaction (A.110), it is not surprising the enthalpy and entropy values differ, but in fact the Gibbs energy of the formation reaction from the oxides at the intermediate temperature 2100 K, − (6.7 ± 4.0) and −(9.1 ± 10.0) $\mathrm{kJ \cdot mol^{-1}}$ agree remarkably well. The uncertainties are those estimated by the authors.

This is a lower stability than $BaThO_3$(cr) but is appreciably more negative than the trends in the actinide(IV) mixed oxides would suggest. Indeed [1993FUG/HAI], estimated $\Delta_r H_m^\circ$ ((A.111), 298.15 K) to be +(20.0 ± 8.5) $\mathrm{kJ \cdot mol^{-1}}$, and Smith and Welch [1960SMI/WEL] were unable to prepare $SrThO_3$ by heating a mixture of ThO_2(cr) and $SrCO_3$(cr) in air at 1273 to 1923 K and suggested that the XRD pattern attributed to $SrThO_3$(cr) by [1947NAR] fitted better to the two components SrO(cr) and ThO_2(cr). Similarly, Smith and Welch indicated that the diffraction pattern given by [1947NAR] for his reported $CaThO_3$(cr) agrees well with that for a mixture of ThO_2 and hydrated lime. Keller [1976KEL] has also thrown doubt on some of the results of [1947NAR].

Although the sol-gel technique provides intermediate products of much smaller particle size, and thus more readily reactive, we also note that no detailed analyses to confirm the positive identification of the final product as $SrThO_3$(cr) were made by either [2000PUR/TYA] or [2001ALI/MIS]. We also note the equation given by the authors for $\Delta_r G_m$ (A.111) from Reaction (A.109), based on different auxiliary data, $\Delta_r G_m$ ((A.111), T) = − 4900 + 3.0 T ($\mathrm{J \cdot mol^{-1}}$) would actually make $SrThO_3$(cr), metastable with respect to the component oxides in the temperature range of their experiments.

The data from Reaction (A.109) are the less uncertain; these correspond to the Gibbs energy of formation from the elements: $[\Delta_f G_m]_{1670\text{K}}^{2040\text{K}}$ ($SrThO_3$, cr, T) = − 194680 + 36.23 T, where the standard state for strontium in this temperature range is Sr(g). However, owing to the uncertainties in the assessment noted above and in the identification of $SrThO_3$(cr), these data are given for information only.

[2001BEE/DYK]

Ultraviolet photoelectron spectra of UBr_4 and $ThBr_4$ were recorded in the gas phase and interpreted using relativistic density functional calculations. Supporting matrix isolation infrared experiments were also carried out under very similar vaporisation conditions to those used in the photoelectron spectroscopy experiments to check the composition of the vapour beams used. In these experiments, the T_2 stretching modes of $ThBr_4$ and UBr_4 have been measured to be (230 ± 2) and (239 ± 2) cm^{-1}, respectively. Both the photoelectron and infrared matrix isolation spectra are consistent with an effective tetrahedral geometry for UBr_4(g) and $ThBr_4$(g).

[2001BRA/DAC]

This review paper deals with the syntheses of uranium and thorium phosphates and discusses at length the syntheses of $Th_4(PO_4)_4P_2O_7$ for storing radioactive wastes. No thermodynamic data are reported.

[2001BRA/DAC2]

The authors report the syntheses of $Th_2(PO_4)_2HPO_4 \cdot H_2O$ and $Th(OH)PO_4$ from aqueous solutions under hydrothermal conditions at temperatures around 150°C. A combination of techniques (SEM, XRD, IR, electron probe microanalyses, DTA and TGA) are used. It is indicated that the dissolution reactions of $Th_4(PO_4)_4P_2O_7$ in water results in the formation of $Th_2(PO_4)_2HPO_4 \cdot H_2O$. No original thermodynamic data were obtained in this study.

[2001HUB/BAR]

Hubert *et al.* [2001HUB/BAR] performed leaching experiments with crystalline ThO_2(cr) in 0.1 M $HClO_4$-$NaClO_4$ at room temperature (assumed to be 20−25°C). Aqueous thorium concentrations were determined by ICP-MS after phase separation by ultracentrifugation The solids used were prepared from different precursors (hydroxide, nitrate and oxalate) and calcined at different temperatures (600, 900, 1300 and 1600°C). This resulted in different properties (specific surface area, surface state, size of aggregates) that govern the dissolution kinetics. As previously reported by Greiling and Lieser [1984GRE/LIE], who studied the dissolution kinetics of ThO_2(cr) in 7.5 M HNO_3, using solids prepared by calcination of hydroxide and oxalate precipitates at 450 to 1400°C, increasing calcination temperature and the use of thorium oxalate as a precursor leads to lower specific surface area and lower dissolution rates in acidic solution. For the solids studied by [2001HUB/BAR] at pH 1 to 3, equilibrium was not reached after 123 days.

Contrary to the data at low pH, the Th concentrations measured at pH 5.3 − 7.2 after only 10 days are already orders of magnitude higher than $\log_{10}[\text{Th}] = \log_{10} K^{\circ}_{s,4}(\text{ThO}_2, \text{cr}) = -(15.6 \pm 1.3)$ as calculated for the reaction:

$$\text{ThO}_2(\text{cr}) + 2\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Th(OH)}_4(\text{aq})$$

using $\Delta_f G^{\circ}_m(\text{ThO}_2, \text{cr}, 298.15\ \text{K}) = -(1169.0 \pm 3.5)\ \text{kJ·mol}^{-1}$ ($\log_{10}{}^{*}K^{\circ}_{s,0}(\text{ThO}_2, \text{cr}, 298.15\ \text{K}) = (1.77 \pm 1.11)$) and $\log_{10}{}^{*}\beta^{\circ}_{4,1} = -(17.4 \pm 0.7)$ selected by this review. The mean values of $\log_{10}[\text{Th}]$ extracted from Figure 4 of [2001HUB/BAR] for ThO_2(cr) prepared from hydroxide ($-(10.3 \pm 0.2)$), nitrate ($-(9.6 \pm 0.4)$) and oxalate ($-(10.6 \pm 0.6)$) at 900 and 1600°C are close to experimental $\log_{10} K_{s,4}$ values for amorphous hydroxides or hydrous oxides ThO_2(am, hyd).

[2001MOU/AME]

This is an interesting article describing the use of electrospray-ionisation mass spectrometry for the identification of hydroxide complexes of Th(IV). The method involves injection of 1 mM Th(IV) solutions in 1, 0.1, 0.01 and 0.001 M HClO_4 through an electro-spray nozzle into the high-vacuum system of a mass spectrometer where a rapid evaporation takes place and the ions formed are analysed in a quadrupole mass spectrometer. The authors briefly describe the methodology and discuss various factors that might affect the interpretation of the resulting mass spectra. The ions formed have a charge of + 1 and their stoichiometry can be identified by their mass and their relative amounts by the intensity of the peaks in the mass spectra. The authors demonstrate that the mass distribution varies with the speciation in the injected solution, indicating that the method might be useful as a speciation probe and even to obtain equilibrium information. From the mass spectra they find that the following stoichiometry for the major peaks:

- At pH = 0: $\text{Th(ClO}_4)_3(\text{H}_2\text{O})_3^+$, indicating a coordination number of 9 for Th^{4+}, assuming bidentate coordination of perchlorate.
- At pH = 2: $\text{Th(ClO}_4)_3(\text{H}_2\text{O})_3^+$; $\text{Th(OH)(ClO}_4)_2(\text{H}_2\text{O})_2^+$ and $\text{Th(OH)(ClO}_4)_2(\text{H}_2\text{O})_3^+$; the latter indicating coordination numbers of seven and eight.
- At pH = 3: $\text{Th(OH)}_2(\text{ClO}_4)(\text{H}_2\text{O})^+$; $\text{Th(OH)}_2(\text{ClO}_4)(\text{H}_2\text{O})_2^+$, with coordination numbers of five and six.

It is interesting to note that the species at pH = 0 and 2 seem to have coordination numbers that are consistent with those found in solution and the solid state. There is also a quantitative estimate of the relative amounts of different species that was used to estimate equilibrium constants for the formation of $\mathrm{Th(OH)^{3+}}$, $\mathrm{Th(OH)_2^{2+}}$ and $\mathrm{Th(OH)_3^{+}}$. These values are $\log_{10}{}^{*}\beta^{\circ}_{n,1}(\mathrm{Th(OH)}_n^{4-n}) = -(2.0 \pm 0.2)$, $-(4.5 \pm 0.5)$ and $-(7.5 \pm 1.0)$ for n = 1, 2 and 3, respectively. These values, in particular $\log_{10}{}^{*}\beta^{\circ}_{2,1}$ and $\log_{10}{}^{*}\beta^{\circ}_{3,1}$, differ appreciably from those determined by other methods, which is not surprising. At the present stage this method does not seem to provide quantitative equilibrium information, but it seems to have the potential for identification of possible hydrolytic species.

[2001NEC/KIM]

The authors review the solubility and hydrolysis of tetravalent actinides using experimental data and semi-empirical estimates among the series of tetravalent actinides Th(IV), U(IV), Np(IV) and Pu(IV). They present a set of selected equilibrium constants that are based preferentially on experimental data using trace concentration of the actinides. The rationale for this is based on experience of studies of colloid formation using laser-induced breakdown detection [1999KNO/NEC], [2000BUN/KNO], [2001NEC/KIM2], [2002NEC/MUL].

The authors also use semi-empirical methods to estimate the equilibrium constants for mononuclear An(IV) hydroxide complexes. Two methods are suggested: Model A assumes a linear correlation between the formation constants $\log_{10}\beta^{\circ}_{n,1}(\mathrm{ML}_n)$ and the ion potential $Z/d_{\mathrm{An–OH}}$, while Model B is based on an electrostatic approach described in detail in [2000NEC/KIM]. The model assumes a relationship between the consecutive equilibrium constants of the form:

$$\log_{10}\beta^{\circ}_{n,1} = n\log_{10}\beta^{\circ}_{1,1} - {}^{\mathrm{rep}}E_{\mathrm{L}}/\mathrm{R}T\ln 10$$

where

$${}^{rep}E_L = N_A\, e^2\,(1/2)\sum_L \frac{z_L z_{L'}}{d_{L-L'}\varepsilon_{L-L'}}$$

N_A is Avogadro's number, e the electron charge, Z_L and $Z_{L'}$ the charges of ligands L and L', $d_{L-L'}$ the distance between the centres of the two ligands calculated from the distance between M and L and the geometry of the complex (octahedral, tetrahedral *etc.*), $\varepsilon_{L-L'}$ is a factor describing the electrostatic shielding between the ligands L and L' that is determined by fitting a "virial" equation. The present review does not select equilibrium constants based on correlations of this type, but [2001NEC/KIM] provides an important discussion of the chemistry of tetravalent actinides (*cf.* [2003GUI/FAN]).

The authors note that potentiometric studies performed with Th(IV) by different authors are interpreted by different sets of species and ascribe this to colloid formation. The present review does not share this opinion, precise potentiometric data, $\bar{n}_{\mathrm{OH}}$ ($\log_{10}[\mathrm{H^+}]$), agree very well with each other if obtained by specialists, provided the same ionic medium is used, *cf.* [1964HIE/SIL] and [1965BAE/MEY]. Neck and Kim [2001NEC/KIM] select hydrolysis constants and ion interaction (SIT) coefficients for the Th(IV) hydroxide complexes $\mathrm{Th_2(OH)_2^{6+}}$, $\mathrm{Th_4(OH)_8^{8+}}$, $\mathrm{Th_4(OH)_{12}^{4+}}$, and $\mathrm{Th_6(OH)_{15}^{9+}}$ from the potentiometric titration studies of Baes *et al.* [1965BAE/MEY], [1976BAE/MES], Brown *et al.* [1983BRO/ELL], Grenthe and Lagerman [1991GRE/LAG2], and Ekberg *et al.* [2000EKB/ALB]. The equilibrium constants for the mononuclear species $\mathrm{Th(OH)_3^+}$, $\mathrm{Th(OH)_2^{2+}}$ and $\mathrm{Th(OH)^{3+}}$ are taken from the potentiometric and solvent extraction studies of [1983BRO/ELL], [1984NAK/ZIM], [2000EKB/ALB] and the semi-empirical estimates discussed above. The SIT coefficients for the mononuclear species were estimated according to charge type analogies and systematics in the actinide series. The equilibrium constant for $\mathrm{Th(OH)_4(aq)}$ is derived from the pH-independent solubility of Th(IV) hydrous oxide at pH to 14 [1987RYA/RAI], [1989MOO], [1991FEL/RAI]: $\log_{10} K^{\circ}_{s,4} = -(8.5 \pm 0.6)$.

Using these hydrolysis constants and ion interaction coefficients listed in Table A-81, Neck and Kim re-evaluated the solubility data reported by [1964NAB/KUD], [1987RYA/RAI], [1989MOO], [1991FEL/RAI] at 17 to 25°C and calculated a mean value of $\log_{10} K^{\circ}_{s,0}$ ($\mathrm{Th(OH)_4}$, am) = $-(47.0 \pm 0.8)$ ($\log_{10} {}^{*}K^{\circ}_{s,0}$ ($\mathrm{Th(OH)_4}$, am) = (9.0 ± 0.8)). The solubility constant for $\mathrm{ThO_2(cr)}$, $\log_{10} K^{\circ}_{s,0}$ ($\mathrm{ThO_2}$, cr, 298.15 K) = $-(54.2 \pm 1.3)$ is adopted from Rai *et al.* [1987RAI/SWA] and based on thermochemical data which are only slightly different from those selected in the present review.

An important observation discussed in [2001NEC/KIM] is that experimental solubility data in neutral and alkaline solutions are approximately the same for amorphous hydroxides $\mathrm{An(OH)_4}$(am, hyd) or hydrous oxides $\mathrm{AnO_2}$(am, hyd) and crystalline oxides $\mathrm{AnO_2}$(cr), although their solubility constants differ by 6−7 orders of magnitude. Solubility data determined with $\mathrm{AnO_2}$(cr) at pH > 5 do not reflect an equilibrium with the bulk solid but with amorphous fractions or an amorphous surface layer.

Table A-81: Hydrolysis constants $\log_{10} {}^{*}\beta^{\circ}_{n,m}$ at zero ionic strength and ion interaction (SIT) coefficients ε_{ij} (kg·mol^{-1}) selected in [2001NEC/KIM]. (In this paper the equilibrium constants $\log_{10} \beta^{\circ}_{n,m}$ have been reported for the reactions $m\mathrm{Th^{4+}} + n\mathrm{OH^-} \rightleftharpoons \mathrm{Th}_m\mathrm{(OH)}_n^{4m-n}$).

$\mathrm{Th}_m\mathrm{(OH)}_n^{4m-n}$	$\log_{10} {}^{*}\beta^{\circ}_{n,m}$	$\varepsilon(\mathrm{Th}_m\mathrm{(OH)}_n^{4m-n}, \mathrm{ClO_4^-})$	$\varepsilon(\mathrm{Th}_m\mathrm{(OH)}_n^{4m-n}, \mathrm{Cl^-})$
$\mathrm{Th^{4+}}$	–	0.67 ± 0.1	0.25 ± 0.03 [b]
$\mathrm{Th(OH)^{3+}}$	– 2.2 ± 0.2	0.45 ± 0.1	0.2 ± 0.1 [c]
$\mathrm{Th(OH)_2^{2+}}$	– 6.0 ± 0.6	0.3 ± 0.1	0.1 ± 0.1 [c]
$\mathrm{Th(OH)_3^{+}}$	– 11.0 ± 1	0.15 ± 0.1	0.05 ± 0.1 [c]
$\mathrm{Th(OH)_4(aq)}$	– 17.5 ± 1	0	0
$\mathrm{Th_2(OH)_2^{6+}}$	– 5.7	1.3	
$\mathrm{Th_4(OH)_8^{8+}}$	–20.4	1.7	
$\mathrm{Th_4(OH)_{12}^{4+}}$	– 26.7	0.4	
$\mathrm{Th_6(OH)_{15}^{9+}}$	– 34.0	5.6 ± 1.9	

[2001THO/DAC]

The authors have studied the rate of dissolution of solid solutions of U(IV) and Th(IV) phosphate phases. The paper contains information on the proposed dissolution mechanism and also extensive information on phase characterisation. Of particular interest is the solid $Th_2(PO_4)_2(HPO_4)\cdot H_2O$; this pure phase and the solid solutions were characterised using XRD, IR, UV-visible spectrophotometry, electron probe microanalysis, SEM and TEM. There is no thermodynamic information on the pure $Th_2(PO_4)_2(HPO_4)\cdot H_2O$ phase except for a value of its solubility product at zero ionic strength, $\log_{10} K^{\circ}_{s,0} = -(66.6 \pm 1.2)$ for which a reference is given to a forthcoming publication; as this is not available to the present review this solubility product is not accepted.

[2001VEN/NAG]

The authors measured the heat capacity of $BaThO_3$(cr) from *ca.* 320 to 820 K by DSC. The $BaThO_3$ solid was prepared by combustion synthesis from the nitrates of barium and thorium using citric acid as an ignition agent, initially by heating to 573 K, then to 1173 K to remove residual carbon and hydrogen, with final homogenisation at 1673 K for 60 hours. The product was described as single-phase $BaThO_3$(cr), as characterised by X-ray diffraction. Absolute values of the heat capacity were obtained by using sapphire as a standard. The heat capacity of ThO_2(cr) was also measured as a check; the values obtained were in good agreement with the assessment by [1997BAK/COR], and thus with the selected values. The results of 26 measurements were fitted to the expression:

$$[C_{p,\mathrm{m}}]^{820\mathrm{K}}_{320\mathrm{K}}(\mathrm{BaThO_3, cr}, T) = 137.9046 + 5.272\times10^{-2}\,T - 2.432487\times10^{6}\,T^{-2}\quad \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

However, this corresponds to a large $\Delta_f C_{p,\mathrm{m}}$ of the formation reaction from the solid oxides in the range of temperature measurement; the calculated values for this $\Delta_f C_{p,\mathrm{m}}$ are 20.0 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at 320 K and 50.9 $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$ at 820 K; even larger values would be obtained by extrapolation of the equation to higher temperatures. These large values must throw doubt on the validity of the results and these data are mentioned for information only.

[2001YAN/TSU]

This paper of Yang *et al.* is discussed together with [2002YAN/TSU].

Both these papers describe the use of quantum chemical and molecular dynamics simulations to study the structure of the first and second coordination spheres of Th(IV) and to determine the residence time of water in the second coordination sphere. In the second paper the authors discuss the entry of chloride into the second coordination sphere at different concentrations of chloride. The starting point in these studies is the determination of the geometry and relative energy of different hydration isomers of Th(IV) using *ab initio* quantum mechanics. When the ratio $(H_2O)/(Th^{4+})$ is nine, the most stable structure, $[Th(H_2O)_9^{4+}]$ has a C_{4v} geometry (a capped square antiprism), followed by $[\mathrm{Th(H_2O)_9^{4+}}]$ with a D_{2d} geometry (a bicapped trigonal prism) 17 kJ·mol^{-1} higher in energy. The least stable isomer $[\mathrm{Th(H_2O)_8^{4+}}]$,(H$_2$O) has a C_{2v} geometry and an energy that is 52 kJ·mol^{-1} above the C_{4v} isomer; this isomer is eight-coordinated with one water in the second coordination sphere. The most stable structure when the ratio (H$_2$O)/(Th^{4+}) is ten, is $[\mathrm{Th(H_2O)_9^{4+}}]$,(H$_2$O) with C_{4v} geometry (a capped square anti-prism), followed by $[\mathrm{Th(H_2O)_{10}^{4+}}]$ only 3 kJ·mol^{-1} higher in energy; the latter has D_{4d} geometry. The other isomers are significantly higher in energy. The structure and dynamics of the second (and third) coordination spheres are studied using molecular dynamics (the AMBER code) with the hydrated ion concept, assuming the $[\mathrm{Th(H_2O)_9^{4+}}]$ geometry and describing the interaction potential between this unit and surrounding solvent molecules using empirical potentials (one Coulomb and one Lennard-Jones part). The calculated Th^{4+}–OH$_2$ distance is in good agreement with experimental data [1991JOH/MAG], [1999MOL/DEN] where the concentration used in [1991JOH/MAG] is closer to the conditions used in the simulations. The second coordination sphere contains 18.9 water molecules with a residence time of 423 picoseconds; the number of second sphere water molecules is in good agreement with that in [1991JOH/MAG]. By increasing the number of chloride ions in the simulations the authors investigated the conditions under which water in the second coordination sphere can be replaced by chloride. At room temperature chloride enters the second coordination sphere only when the chloride concentration is around 2.6 m. In this simulation it was assumed that chloride did not enter the first coordination sphere, an assumption supported by the experimental results of Johansson *et al*. [1991JOH/MAG], who found that chloride entered the first coordination sphere only at very high concentrations, 7.4 M. Entry of chloride in the second coordination sphere also resulted in a shortening of the residence time of water. The most important conclusion of these two studies is that they establish the coordination number and coordination geometry of the Th(IV) aquo ion to be $[\mathrm{Th(H_2O)_9^{4+}}]$ or $[\mathrm{Th(H_2O)_{10}^{4+}}]$ with a coordination geometry based on a capped square antiprism. It is also of interest to note that if the coordination geometry is $[\mathrm{Th(H_2O)_9^{4+}}]$ the exchange of water between the first and second coordination sphere is most likely associative; the energy difference between the ground state and the associative intermediate is 3 kJ·mol^{-1} and that between the ground state and the dissociative intermediate 52 kJ·mol^{-1}. If the coordination in the ground state is $[\mathrm{Th(H_2O)_{10}^{4+}}]$, the water exchange is dissociative as suggested by Farkas *et al*. [2000FAR/GRE].

The second sphere residence times in $(\mathrm{Th(H_2O)_9^{4+}})$ and $(\mathrm{Th(H_2O)_{10}^{4+}})$ are very different, 398 ps *vs.* 1500 ps; if the residence time could be determined experimentally this would offer a possibility to determine the coordination number. On the other hand equilibrium between isomers with two different coordination numbers is also possible.

[2002ABD]

The study describes the solubility of monazite in aqueous solutions of ammonium carbonate/bicarbonate at different pressure and temperature. The recovery of Th(IV) in the leach process is surprisingly high, ranging from 18.7% at 70°C to 99.8% at 150 to 175°C. These observations confirm the formation of strong carbonate complexes. However, there are no quantitative thermodynamic data in this communication.

[2002BRA/DAC]

The authors report the syntheses of several different thorium phosphate solids ($ThFPO_4 \cdot H_2O$, $Th_2(PO_4)_2SO_4 \cdot 2H_2O$, $Th_4(PO_4)_4SiO_4$, $CsTh_2(PO_4)_3$, $BaTh(PO_4)_2$) from aqueous solutions under hydrothermal conditions. The chemical composition of the solids was established by electron probe microanalysis and/or particle induced X-ray emission. The X-ray diffraction patterns and/or infrared spectra were given. No thermodynamic data are reported.

[2002DAC/CHA]

This work is part of a broad effort to evaluate the potential of phosphate matrices for radioactive waste storage. It concerns the synthetic methods for preparing $Th_4(PO_4)_4P_2O_7$, thorium phosphate diphosphate (TPD) and the study of its physical, thermal, and thermomechanical properties and chemical durability during leaching tests. Only the determination of the specific heat of the compound between room temperature and 1073 K is of relevance to this review. These measurements were made in an argon atmosphere on powdered samples in an alumina holder using a Setaram Differential Scanning Calorimeter (model 111), with calibration against sapphire provided by NIST as a reference material. Data were taken between 293 and 1073 K, with steps of 20 K and an acquisition time of 600 s. The heating rate between two steps was 5 $K \cdot min^{-1}$. Individual experimental values were given only on a C_p *vs.* T graph. The equation for the fit to the specific heat in the text seems to be in error, and we have refitted the original values of the specific heat, kindly provided by the authors,

$$C_p = 0.46262 + 6.94205 \times 10^{-5}\, T - 1.2367 \times 10^{-10}\, T^2 - 9402.0\, T^{-2}\ \mathrm{J \cdot K^{-1} \cdot g^{-1}}$$

which for a molecular weight of 1505.981 corresponds to the molar heat capacity equation:

$$[C_{p,\mathrm{m}}]_{298.15\mathrm{K}}^{1073\mathrm{K}} = 696.70 + 0.10455\, T - 1.8625 \times 10^{-7}\, T^2 - 1.4159 \times 10^{7}\, T^{-2}\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

[2002FAN/NEC]

The authors discuss systematic trends and specific phenomena on the solubility of hydroxides and oxides of tri-, tetra-, penta- and hexavalent actinides. The reported solubility constants of amorphous ThO_2(am, hyd), microcrystalline and crystalline ThO_2(cr), the conclusions on the solubility controlling solid phase and the solubility increasing effect of eigencolloids are taken from [2001NEC/KIM], [2002NEC/MUL], [2003NEC/ALT]. Experimental solubility constants of Th(IV) oxides/hydroxides of different crystallinity are illustrated as a function of particle size in comparison with calculations based on Schindler's equation [1967SCH].

Experimental data are discussed in the Appendix A reviews of [2001NEC/KIM], [2002NEC/MUL], [2003NEC/ALT].

[2002JER/VUO]

In this report the solubility of thorium was investigated in 0.1 M NaCl solution and in saline and fresh anoxic synthetic reference groundwater (I = 0.5 and 0.002 M, respectively, major electrolyte: NaCl) containing 10^{-6} to 10^{-5} M total carbonate. Different sets of solubility experiments in the pH range of 6 to 13 were performed at 20.5 − 23°C from oversaturation and, with $ThO_2{\cdot}xH_2O(s)$ prepared and dried as described by Östhols *et al.* [1994OST/BRU], from undersaturation. The solid phases were studied by X-ray diffraction, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The XRD patterns showed slight indications of microcrystalline fractions. The low carbonate concentrations of $10^{-5}-10^{-6}$ M have no effect on the solubility and aqueous thorium speciation, but IR spectrometry gave an indication that carbonate might be sorbed onto the solid phase.

The samples were kept in an inert gas glove box and equilibrated for 10 to 200 days. The thorium concentration was determined by ICP-MS after phase separation by centrifugation or 450 nm pre-filtration and subsequent 50000 MWCO (Molecular Weight Cut-Off) ultrafiltration and pH was measured with a combination electrode calibrated against commercial pH buffers. Nearly all the 42 solubility data in the different solutions and at different pH values were in the range $10^{-10}-10^{-8}$ M. There is no significant effect of pH and equilibration time.

If the mean value of the measurements in [2002JER/VUO], $\log_{10}[\mathrm{Th}] = -(9.5 \pm 1.2)$ (2σ), is ascribed to the reaction $ThO_2(am, hyd) + 2H_2O \rightleftharpoons Th(OH)_4(aq)$ and combined with the solubility constant of a ThO_2(am, hyd) solid prepared and pretreated the same way ($\log_{10} {}^*K^{\circ}_{s,0} = (8.2 \pm 0.6)$, calculated by this review from the solubility data of [1994OST/BRU] and [2002NEC/MUL] at pH 3.2 − 4.5), we obtain the hydrolysis constant of $\log_{10} {}^*\beta^{\circ}_{4,1}$ ($Th(OH)_4$, aq) = −(17.7 ± 1.3). This value agrees with the $\log_{10} {}^*\beta^{\circ}_{4,1}$ values calculated by this review from solubility studies of other authors (−(17.6 ± 0.6) [1987RYA/RAI], −(17.6 ± 0.4) [1989MOO], −(17.2 ± 1.2) [1991FEL/RAI], −(16.9 ± 1.0) [2002NEC/MUL], [2004ALT/NEC]).

[2002JOS/SIV]

Partial pressures of different species present in the vapour phase over ThO_2, UO_2, UC, were studied at very high temperature (> 3000 K), by transient heating of the sample with a 532 nm laser pulse of *ca.* 8 ns duration with time-resolved mass-spectrometric detection. The surface temperature was varied by changing the laser incident power on the sample. For ThO_2, the authors give partial pressures of Th(g), ThO(g), ThO_2(g) and O(g) at 5146 and 6253 K. Since in this type of experiment, it is difficult to establish reliably the relevant temperatures, these data have not been used in the analysis. Nevertheless, the extrapolation of these data down to the melting point of ThO_2 (3650 K), gives a value in good agreement with the selected data, extrapolated upwards.

This study gives the first information on the vaporisation of thoria at very high temperatures.

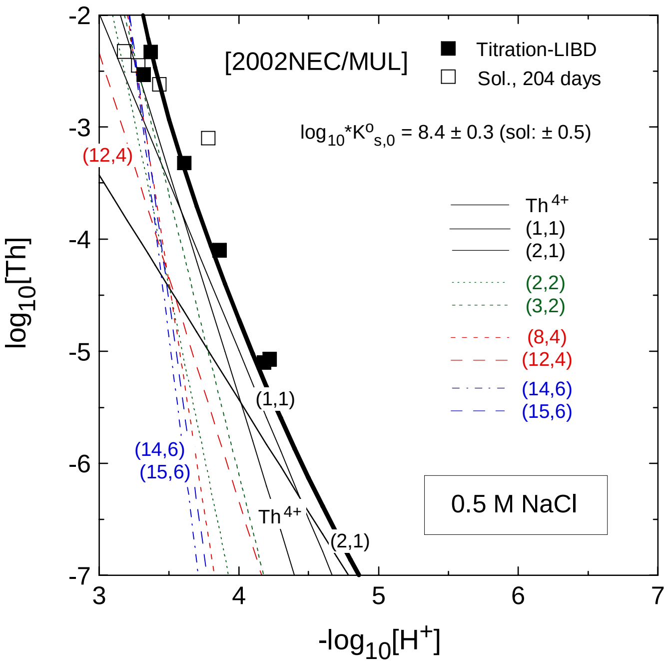
[2002NEC/MUL]

Neck *et al.* [2002NEC/MUL] studied the solubility of amorphous Th(IV) hydrous oxide at pH 3.0 − 13.5 in 0.5 M NaCl and 25°C. The authors performed solubility measurements with $ThO_2{\cdot}xH_2O(am)$ from undersaturation (equilibration times: 5 − 211 days) and used laser-induced breakdown detection (LIBD) to detect the initial formation of thorium hydroxide colloids during the coulometric titration of $10^{-2} - 10^{-5}$ M thorium solutions in the $-\log_{10}[H^+]$ range 2.7 − 4.5. The temperature and ionic medium were the same as in [2000BUN/KNO]. The experimental solubility product given by the authors, $\log_{10} K_{s,0} = -(44.48 \pm 0.24)$ and $\log_{10} K^{\circ}_{s,0} = -(47.8 \pm 0.3)$, is much larger than that obtained for ThO_2 colloids in acid solution ($-(52.8 \pm 0.3)$) [2000BUN/KNO], and corresponds to the solubility products obtained for amorphous thorium hydroxide phases. There are other important observations in this study: colloids that were formed in the coulometric experiment as a result of local excess of hydroxide redissolved if outside the stability region for colloid formation; similar observations have been made in previous potentiometric titrations.

When evaluating the solubility product in the investigated $-\log_{10}[H^+]$ region it is necessary to take the formation of hydroxide complexes into account. The authors have used the hydrolysis constants and SIT coefficients selected in the literature review of [2001NEC/KIM] (*cf.* Table A-81). As seen in Figure 4 of [2002NEC/MUL], the complex $Th(OH)^{3+}$ is predominant in the test solutions and the selected hydrolysis constants, in particular the value of $\log_{10} {}^{*}\beta^{\circ}_{1,1} = -2.2$ (which is higher than $\log_{10} {}^{*}\beta^{\circ}_{1,1} = -2.5$ selected in the present review) affects the calculation of $\log_{10} K^{\circ}_{s,0}$. Calculating the aqueous speciation with the hydrolysis constants and SIT coefficients selected in the present review, the solubility constant of $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.3)$ is obtained from the titration-LIBD data. The same value, but with an increased uncertainty ($\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$), is obtained from the solubility data determined at $pH_c = 3 - 4$ with an X-ray amorphous $ThO_2{\cdot}xH_2O$ ($x \approx 2.4$) dried for one week in a vacuum desiccator. This value is in agreement with $\log_{10} K^{\circ}_{s,0} = -(48.0 \pm 0.5)$ calculated by this review from solubility data of [1994OST/BRU] with a solid phase $ThO_2{\cdot}xH_2O$ ($x \approx 2.5$) prepared and dried with the same procedures, but considerably lower than the mean value of $\log_{10} K^{\circ}_{s,0} = -(46.7 \pm 0.9)$ selected in the present review for fresh amorphous precipitates not dried but only washed with water.

The solubility data measured at pH < 3 were not used for the evaluation of $\log_{10} K^{\circ}_{s,0}$, because they obviously refer to a more crystalline solid consisting of larger particles (*cf.* discussion in Section VII.4.3). The mean value of the thorium concentrations at pH > 10 (given with a 2σ uncertainty interval), $\log_{10}[Th] = -(8.2 \pm 0.9)$, is consistent with the value of $\log_{10}[\text{Th(OH)}_4\text{(aq)}] = -(8.5 \pm 0.6)$ selected in [2001NEC/KIM] from literature data. However, due to possible problems arising from incomplete removal of colloids by centrifugation, Neck *et al.* [2002NEC/MUL] assumed that the concentration of mononuclear $\text{Th(OH)}_4\text{(aq)}$ is more likely represented by the lower values at $\log_{10}[\text{Th}] \approx -9$.

Figure A-44: Solubility data for ThO_2(am, hyd) in 0.5 M NaCl [2002NEC/MUL]. Recalculation of the solubility constant and aqueous speciation using hydrolysis constants and SIT coefficients selected in the present review



In a separate section the authors describe EXAFS measurements in hydrolysed Th(IV) solutions and on the amorphous solid phase. Details of these measurements were published in [2002ROT/DEN]. The EXAFS data of the Th^{4+} ion in 1.5 M HClO_4 are taken from a previous study [1999MOL/DEN]. The authors indicate that their observations support the selected speciation scheme. Their arguments can be questioned, since their solution B1 ($[\text{Th}] = 5.0 \times 10^{-3}$ M, $-\log_{10}[\text{H}^+] = 3.02$) contains 59% Th^{4+} and 31% Th(OH)^{3+}, but the speciation is strongly dependent on the selected hydrolysis constants. By using the values selected in this review the fraction of Th(OH)^{3+} is lower and that of $\text{Th}_2\text{(OH)}_2^{6+}$ is higher. It is well known that bond distances of OH^- and F^- to metal ions are very similar in the solid state. One would therefore expect the Th–OH^- distance to be close to that of Th–F^-, equal to 2.20 Å; if the test solution contained 31% of $Th(OH)^{3+}$ one should be able to detect this distance, as in [1999MOL/DEN]. The EXAFS spectra of samples B2, C2 and particularly sample C1 (at H^+ and Th concentrations exceeding the solubility limit, but in the stability range of colloids) are significantly different from that of Th^{4+} and sample B1. The presence of large amounts of polynuclear Th(IV) species or colloids with highly asymmetric Th–O coordination is indicated by a broad asymmetric Th–O FT peak, similar to that for the EXAFS spectrum of the amorphous oxyhydroxide solid $ThO_n(OH)_{4-2n}\cdot xH_2O$(am).

[2002PER/RIG]

The authors report the solubility of $ThO_2\cdot xH_2O$(am) in 1) 0.1 M $NaClO_4$ as a function of pH, 2) 0.001, 0.01, 0.08, and 0.14 M Na_2SiO_3 solutions at 25°C and at selected pH values ranging from 4 to 12, and 3) 0.08 and 0.14 M Na_2SiO_3 solutions at 90°C and at a few selected pH values ranging between 4 and 12. They report that their measured solubilities of $ThO_2\cdot xH_2O$(am) in the absence of silica are similar to those previously reported in the literature, although their limiting solubilities ($10^{-10.4}$) at pH values >6 are lower than previously reported. They state that the observed aqueous thorium concentrations, ranging between 10^{-5} and 10^{-7} M at pH $6-12$ in the presence of silica, result from the formation of a thorium hydroxo-silicate compound.

No thermodynamic data are reported in this paper. No characterisation data, other than bulk analysis, are available for the so-called thorium hydroxo-silicate compound. Based on data reported in [2005MAZ/USH] and [2005RAI/YUI], no thorium silicate-based solids are expected to be precipitated, at least not at high pH values. At the high concentrations of silica ($>>$0.01 M) used in these experiments, it is expected that SiO_2(am) will precipitate in the entire range of pH values investigated in this study. Therefore the solid observed in their study may be just a mixture of $ThO_2\cdot xH_2O$(am) and SiO_2(am) rather than a single solid phase as they propose. The Na_2SiO_3 reagent generally has significant carbonate impurities. The authors do not state whether they checked their solution for carbonate. The level of carbonate impurities generally present in Na_2SiO_3 is expected to affect significantly the thorium concentrations, especially in the relatively concentrated Na_2SiO_3 solutions and in the pH region around 8 and 9. Carbonate impurities are not expected to have an impact at higher pH values (*e.g.* 11 and 12). Therefore, there are large uncertainties in the reported data, especially for pH values below about 9 and in relatively concentrated silicate solutions (≥ 0.08 M) due to possible complexation of Th with carbonate. There is a large scatter in the thorium concentrations as a function of pH and at 0.08 and 0.14 M Na_2SiO_3 concentrations, the only data where the suspensions were filtered through low MW membrane filters, which is not conducive to any meaningful reinterpretation of this data. However, a general significant increase in thorium concentrations at high pH values (around 11 and 12) might indicate the possible existence of thorium complexes with polynuclear silica species.

[2002ROB/DAC]

The authors have studied the dissolution of thorium phosphate diphosphate (TPD) with and without trivalent actinides; they also studied a solid solution of Th(IV)/Pu(IV) phosphate diphosphate. The experiments consist of leaching studies where the rate of dissolution has been measured as a function of pH. This study does not provide any information on the solubility product of TPD. There is information on estimated equilibrium constants for $MPO_4(s)$ phases, where M = Am, Cm, Ce and Pr. These are secondary phases formed in the leach system.

[2002TOR/FAR]

The complexation of Th(IV) and various Ln(III) by glycolic acid ($HO\text{-}CH_2\text{-}COO^-$) has been investigated in 3.0 M $NaClO_4$ by potentiometry, ^{13}C-NMR spectroscopy and EXAFS. Glycolate may be bonded in two ways: either through the carboxyl group or by formation of a chelate. The formation of mononuclear complexes $Th(HO\text{-}CH_2\text{-}COO^-)_n$; $n = 1 - 4$, were identified in the $-\log_{10}[H^+]$ range 2.5 − 4.5 and the equilibrium constants of these complexes were determined using least squares refinement. The multinuclear complexes $Th_2(OH)_2(HO\text{-}CH_2\text{-}COO^-)_n$ were also established from potentiometric results and ^{13}C-NMR spectra.

The chelate-bonded complexes, $M_4(O\text{-}CH_2\text{-}COO^-)_n(OH\text{-}CH_2\text{-}COO^-)_{8-n}$; $n = 6$, 8 for Th(IV) and 6 − 8 for Ln(III), were identified in the higher $-\log_{10}[H^+]$ range. The structural model of these tetranuclear complexes having a tetranuclear core $M_4(O\text{-}CH_2\text{-}COO^-)_4$ with the triple-bridging was proposed from the information from ^{13}C-NMR spectroscopy and EXAFS. The EXAFS data give a Th–Th distance of 3.97 Å, with oxygen in the deprotonated OH-group as the bridging atom. The distance is close to that found in the polynuclear hydroxide system [1968JOH2]. The equilibrium constants proposed in this study refer to complexes with organic ligands and are therefore not included among the selected constants. However, the study demonstrates the role that ternary hydroxide complexes may play.

[2002YAN/TSU]

This paper of Yang *et al.* is discussed together with [2001YAN/TSU] from the same group of authors using quantum mechanical and molecular dynamical simulations to study the hydration sphere of Th^{4+}.

[2003AGA/PRA]

Enthalpy increments of $ThO_2(cr)$ were measured using a high temperature Calvet drop calorimeter from 376 to 940 K (20 measurements). The $ThO_2(cr)$, prepared by the oxalate route, contained less than 1000 ppm impurity, presumably including the 500 ppm MgO deliberately added as a sintering aid.

The results were fitted to an equation which leads to the heat capacity expression:

$$[C_{p,\mathrm{m}}]^{940\mathrm{K}}_{376\mathrm{K}}\,(\mathrm{ThO_2,cr},\,T) = 71.6726 + 8.2532\times10^{-3}\,T + 1.116094\times10^{6}\,T^{-2}\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$$

These data are very similar to the many other consistent measurements of the enthalpy increments of ThO_2(cr).

Similar measurements were made on four ThO_2-rich $Th_xU_{1-x}O_2$ compositions.

[2003BIT/MUL]

Bitea *et al.* [2003BIT/MUL] discuss the stability of thorium colloids generated by coulometric titration of 10^{-5} to 10^{-2} M thorium solutions at pH 3 − 5 in 0.5 M NaCl. Using laser-induced breakdown detection (LIBD) and ultrafiltration the colloids formed above the solubility limit of Th(IV) hydroxide were found to be stable within the time period of investigation (up to more than 400 days). Dilution of colloid containing test solutions at constant pH leads to the degradation of colloids into soluble ionic species, whereas dilution with neutral 0.5 M NaCl results in increased over-saturation and colloid formation, as recognised by a pH shift to lower values. This observation was ascribed to the simplified reaction:

$$\mathrm{Th(OH)}_n^{4-n} + (4-n)\,\mathrm{H_2O(l)} \rightleftharpoons \text{"Th(OH)}_4\text{(coll)"} + (4-n)\,\mathrm{H^+} \qquad (\mathrm{A.112})$$

Finally pH, ionic thorium species and colloids were found to approach a steady state which is comparable to the solid-liquid equilibrium of amorphous Th(IV) hydroxide determined in [2002NEC/MUL] with the coulometric titration-LIBD method.

[2003HEL/NAV]

The enthalpies of formation of three brannerite compositions, namely, $CeTi_2O_6$(cr), $U_{0.97}Ti_{2.03}O_6$(cr), and $ThTi_2O_6$(cr), have been measured by high temperature drop calorimetry at 976 K, using a solvent with the composition $3Na_2O\cdot4MoO_3$. The interest in these compounds is related to the potential of titanate-based ceramics for the immobilisation of actinides. The calorimetric procedure is described and the calorimeter is calibrated using the heat content of α-Al_2O_3. Drop solution enthalpic effects were measured by dropping pellets (about 5 mg) of the powdered samples from room temperature (presumably 25°C) into the solvent at the calorimeter temperature. Solution enthalpies were measured after equilibration of sample pellets above the solvent at the calorimeter temperature. In this way, the heat content increments could be taken in account.

The brannerite samples were prepared by sintering ball-mixed stoichiometric amounts of the oxides, namely, for the thorium compound, ThO_2(cr) and TiO_2(anatase) in air at 1773 K for more than 100 hours. X-ray powder diffraction of the compounds showed that they are monoclinic, belonging to space group *C*2/*m*. The lattice parameters reported for the thorium compound $ThTi_2O_8$ were a = (9.8046 ± 0.0008) Å, b = (3.8187 ± 0.0003) Å, c = (7.0229 ± 0.0005) Å, and β = (118.852 ± 0.005)°, giving, as expected, a slightly larger cell volume than that obtained for the corresponding uranium compound. Quantitative analysis by the Rietveld method indicated a sample composition of (0.991 ± 0.003) weight fraction $ThTi_2O_6$ and (0.009 ± 0.001) weight fraction

ThO_2 These results were confirmed by back-scattered electron images which gave 0.9902 weight fraction $ThTi_2O_6$ and 0.0098 weight fraction ThO_2. Electron microprobe analysis with wavelength dispersion spectroscopy indicated that the thorium and titanium contents were, within the uncertainties, equal to stoichiometric values. After correction for the small thorium dioxide impurity, a value of (19.4 ± 1.6) $kJ\cdot mol^{-1}$ was reported for Reaction (A.113) corresponding to the enthalpy of the formation reaction of thorium brannerite from the binary oxides,

$$ThO_2(cr, 298.15\ K) + 2TiO_2(rutile, 298.15\ K) \rightarrow ThTi_2O_6(cr, 298.15\ K) \qquad (A.113)$$

This result indicates that Th-brannerite is entropy-stabilised and may be stable at high temperature only.

Taking this value, with slightly increased uncertainty limits, namely, (19.4 ± 2.0) $kJ\cdot mol^{-1}$ and making use of the values selected in this review for $\Delta_f H^\circ_m$ (ThO_2, cr, 298.15 K) = – (1226.4 ± 3.5) $kJ\cdot mol^{-1}$ and (TiO_2, rutile, 298.15 K) = – (944.0 ± 0.8) $kJ\cdot mol^{-1}$ yields the value:

$$\Delta_f H^\circ_m (ThTi_2O_6, cr, 298.15\ K) = -(3095.0 \pm 4.3)\ kJ\cdot mol^{-1}$$

which is the selected value.

The authors report also values of (29.6 ± 3.6) $kJ\cdot mol^{-1}$ and – (7.7 ± 2.8) $kJ\cdot mol^{-1}$, respectively, for the enthalpies of the formation reaction of $CeTi_2O_6$(cr) and $U_{0.97}Ti_{2.03}O_6$(cr) from the binary oxides.

Thus the results indicate that both the thorium and the cerium titanates are entropy stabilised compounds and are probably stable at high temperature only, while uranium titanate is presumably stable at ambient conditions.

[2003NEC/ALT]

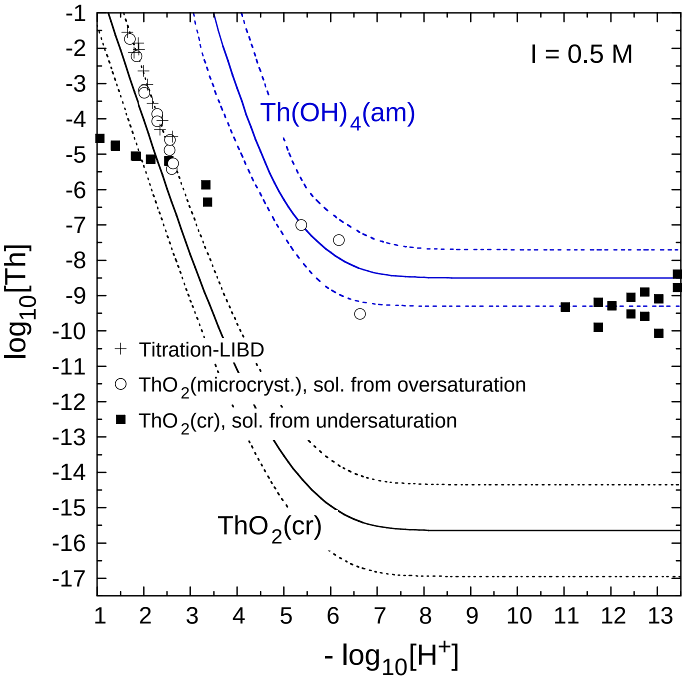
This review concerns the two related papers by [2000BUN/KNO] and [2003NEC/ALT] on the formation of colloids in the precipitation of microcrystalline ThO_2(s, hyd). In the first study, Bundschuh *et al.* [2000BUN/KNO] have used coulometric titration in combination with the LIBD (Laser Induced Breakdown Detection) method to detect the onset of colloid formation and also to estimate the number of particles formed and their average size. The data have been obtained at 25°C in 0.50 M NaCl, where the colloid formation has been measured as a function of $-\log_{10}[H^+]$ at total thorium concentrations varying between 9×10^{-5} and 2.9×10^{-2} M. The $-\log_{10}[H^+]$ range varied between 1.6 and 2.6. It turns out that ThO_2 colloids are formed at low pH, well before precipitation can be observed experimentally. The detection of the point where colloids are formed also indicates the point where equilibrium between solid and solution is attained. The calculated solubility product, $\log_{10} K_{s,0} = -(49.54 \pm 0.23)$ at the 2σ-level, was recalculated to zero ionic strength using the SIT: $\log_{10} K^\circ_{s,0} = -(52.8 \pm 0.3)$. This value refers to a colloidal hydrous oxide with a particle size in the range of 16 to 23 nm [2000BUN/KNO].

The same titration-LIBD method and equipment is used in a second study of this group [2003NEC/ALT] to confirm the reproducibility of these results by three additional titration experiments at thorium concentrations of 7.6×10^{-3}, 5.0×10^{-5} and 3.2×10^{-5} M. The mean value of the solubility product calculated from the data determined in both studies is found to be $\log_{10} K_{s,0} = -(49.6 \pm 0.5)$ (2σ) in 0.5 M NaCl and $\log_{10} K^{\circ}_{s,0} = -(52.9 \pm 0.5)$ at zero ionic strength. In addition, the formation of visible precipitates was observed after storing the colloidal ThO_2 suspensions produced in the titration-LIBD experiments of [2000BUN/KNO] and [2003NEC/ALT]. The microcrystalline nature of these ThO_2(cr, hyd) precipitates obtained at pH 1.5 − 2.5 was confirmed by EXAFS and XRD analyses. The H^+ and Th concentrations were measured 19 − 160 days after precipitation; they decrease with a slope of − 4 in a logarithmic solubility plot, indicating that these solubility data determined from the direction of oversaturation actually refer to the equilibrium between microcrystalline ThO_2(cr, hyd) and Th^{4+}. The corresponding solubility product of $\log_{10} K_{s,0} = -(49.9 \pm 0.4)$ in 0.5 M NaCl and $\log_{10} K^{\circ}_{s,0} = -(53.2 \pm 0.4)$ (uncertainties given as 2σ) is somewhat lower than the value obtained by the titration-LIBD method. Using the equations of Schindler [1967SCH], the solubility product for a crystalline phase with large particle size is estimated to be 1.0 to 1.4 logarithmic units lower. Accordingly, the experimental solubility constants of $\log_{10} K^{\circ}_{s,0}$ (particle size d = 16 − 23 nm) = − 52.8 to − 53.2 are in reasonable agreement with the value calculated from thermochemical data for crystalline ThO_2(cr), $\log_{10} K^{\circ}_{s,0} = -(54.2 \pm 1.3)$.

The findings of [2000BUN/KNO], [2003NEC/ALT] are important for solubility measurements because colloids result in a measured solubility that is too large, if the colloidal fraction cannot be removed prior to the thorium analysis (this is usually done using filtration or ultracentrifugation). However, the conclusion of [2000BUN/KNO] who assumed that the much higher solubility data reported in the literature for amorphous Th(IV) hydroxide or hydrous oxide must be affected by inclusion of colloids, is not correct. It is certainly possible to prepare colloid-free thorium solutions at higher pH and thorium concentrations as observed in a later study of these authors [2002NEC/MUL]. The observed formation of microcrystalline ThO_2 colloids at pH < 2.5 has no implications for the analysis of potentiometric data at pH > 2.5.

The second study [2003NEC/ALT] also includes a solubility study with commercially obtained anhydrous ThO_2(cr). The study was performed from undersaturation in 0.1 and 0.5 M HCl-NaCl solutions and in 0.5 M NaOH-NaCl solutions ($-\log_{10}[H^+]$ = 11.0 − 13.5). However, as in an analogous study of [2001HUB/BAR], the thorium concentrations measured in acidic solutions after 79 − 318 days were not equilibrium values. The values of $\log_{10}[Th]$ in the range of $-\log_{10}[H^+]$ = 1.0 − 2.5 show only a slight pH-dependence, whereas equilibrium values of $\log_{10}[Th^{4+}]$ are expected to decrease with a slope of − 4. The thorium concentration at pH 1 is several orders of magnitude lower than the calculated equilibrium value (*cf.* Figure A-45).

Figure A-45: Experimental data determined in [2000BUN/KNO], [2003NEC/ALT] for ThO_2 colloids using the titration-LIBD method. The solubility from oversaturation after precipitation of microcrystalline ThO_2(cr, hyd) and from undersaturation with crystalline ThO_2(cr) are compared to the solubility curves calculated for ThO_2(cr) and $Th(OH)_4$(am) (from [2003NEC/ALT]).



The thorium concentrations measured in [2003NEC/ALT] with crystalline ThO_2(cr) after 71 and 122 days in the alkaline range are orders of magnitude higher than the value of $\log_{10}[Th(OH)_4(aq)] = -(15.6 \pm 1.3)$ expected for the reaction:

$$ThO_2(cr) + 2H_2O(l) \rightleftharpoons Th(OH)_4(aq) \qquad (A.114)$$

from the solubility constant $\log_{10} {}^*K^{\circ}_{s,0}$ (ThO_2, cr, 298.15 K) = (1.8 ± 1.1) and $\log_{10} {}^*\beta^{\circ}_{4,1} = -(17.4 \pm 0.7)$ selected by this review. The mean value, $\log_{10}[Th] = -(9.3 \pm 0.8)$ (given with an uncertainty of $\pm 2\sigma$), is close to the solubility of $Th(OH)_4$(am) (*cf.* Figure A-45). Similar values for crystalline ThO_2(cr) in neutral and alkaline solution were reported in [1989MOO], [1998WIE/HEL] [2000FOU/VIN] [2001HUB/BAR]. These experimental findings may be caused by small amounts of amorphous fractions of the otherwise crystalline solid. Neck *et al.* [2001NEC/KIM], [2002FAN/NEC], [2003NEC/ALT] assumed that the slow dissolution of ThO_2(cr) followed by the very fast hydrolysis reactions of the Th^{4+} ions might result in an irreversible dissolution reaction. They suggest that the back-reaction, *i.e.*, the sorption or precipitation of monomeric or polynuclear hydroxide complexes $\mathrm{Th}_m(\mathrm{OH})_n^{4m-n}$ on the surface of crystalline ThO_2(cr), would lead to an amorphous, solubility controlling surface layer of "$Th(OH)_4$(am)".

[2003OKA/MOC]

This is a theoretical study using *ab initio* quantum mechanics in combination with a polarisable continuum model (PCM) for the solvent. The theoretical approach is satisfactory both for the determination of structures and energetic in the ground and transition states; the latter refer to the transfer of a proton from water coordinated in the first, to water in the second coordination sphere. The reactions studied are:

$$\mathrm{Th(H_2O)}_N^{4+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Th(OH)(H_2O)}_{N-1}^{3+} + \mathrm{H_3O^+}$$

$$\mathrm{Th(OH)(H_2O)}_{N-1}^{3+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Th(OH)_2(H_2O)}_{N-2}^{2+} + \mathrm{H_3O^+}$$

$$\mathrm{Th(OH)_2(H_2O)}_{N-2}^{2+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Th(OH)_3(H_2O)}_{N-3}^{+} + \mathrm{H_3O^+}$$

where $N = 1 - 4$ for the first reaction and $N = 4$ for the second and third reaction. As the coordination number of Th^{4+} is $9 - 11$ according to the previous theoretical [2001YAN/TSU], [2002YAN/TSU] and experimental studies [1968JOH2], [1999MOL/DEN], it is clear that the chemical model is not appropriate to describe experimental data. The authors are aware of this and note that they were not able to study the transition state of systems with larger coordination numbers; this review suggests that it should be feasible to study the thermodynamics of the reactions. In view of shortcomings of the chemical model the calculated reaction energies are not in good agreement with experimental data.

[2003SAW/SHA]

The hydrolytic behaviour of thorium(IV) and dioxo-uranium(VI) was studied using potentiometric determinations of the hydrogen ion concentration at 25°C in 1.0 M $NaClO_4$; only the thorium data will be discussed here. Seven different titrations with total concentrations of thorium(IV), $[\mathrm{Th}]_{\mathrm{tot}}$ = 0.045, 0.214, 1.05, 1.07, 1.09, 1.14, and 1.09 mM were made; in one of them a small amount of fluoride, about 1% of $[\mathrm{Th}]_{\mathrm{tot}}$ was added. The pH range studied in the different titrations varied but the overall variation was from 1.5 to 5.1. The titrations were made by adding successive amounts of a NaOH solution to test solutions with the initial concentrations given above. Hence the total concentration varied throughout the titration. The authors report pH values but they determined the E° value of the glass electrode using the Gran method. The methodology was tested by determination of the dissociation constant of acetic acid and $\mathrm{p}K_{\mathrm{w}}$ of water. Titration with NaOH is not the best experimental approach due to the risk of local precipitation when the titrant is added; it is then important to ensure that equilibrium has been attained and it seems to this review that a longer equilibration time than one minute, used in most titrations, is necessary. The authors also note that a titration where the equilibration time was 10 minutes had to be rejected because these data could not be refined using their least-squares approach. This suggests that equilibrium might not have been attained after one minute. The experimental data were refined using HYPERQUAD where the program fitted each experimental titration curve by a certain chemical model, in this case the equilibrium constants for two complexes $\mathrm{Th(OH)^{3+}}$ and $\mathrm{Th(OH)_3^+}$. The average values are $\log_{10} {}^*\beta_{1,1} = -(3.51 \pm 0.03)$ and $\log_{10} {}^*\beta_{3,1} = -(10.75 \pm 0.14)$. From a scrutiny of Figure 6 in [2003SAW/SHA] it is obvious that this model does not fit the experimental titration curve very well; unfortunately the authors have not stated to which experiment this curve belongs. At first sight, the fit seems good because of the large scale used, but closer scrutiny reveals noticeable and systematic discrepancies, in particular at low pH.

There is strong evidence from other investigations discussed in the present review that polynuclear thorium complexes are formed in the $[\mathrm{Th}]_{\mathrm{tot}}$-pH range investigated, complexes that have not been found by Sawant *et al.* This review considers this as an indication of unidentified errors in [2003SAW/SHA] and does therefore not accept the equilibrium constants proposed.

The authors have also made titrations where a small amount of fluoride was added to the test solutions; the rationale for this is not clear and the suggestion that fluoride addition should result in the prevention of colloid formation is not quantified.

[2003TOR/GRE]

The complex formation in the binary Th(IV)-5-sulphosalicylate ($\mathrm{SSA^{3-}}$) system and in the corresponding ternary fluoride system was investigated using potentiometry and proton and fluorine NMR spectroscopy. The equilibrium constants for the reactions

$$p\,\mathrm{Th^{4+}} + r\,\mathrm{SSA^{3-}} \rightleftharpoons \mathrm{Th}_p\mathrm{H}_{-q}(\mathrm{SSA})_r^{4p-q-3r} + q\,\mathrm{H^+}$$

were determined at 25°C in an ionic medium with constant concentration of $\mathrm{Na^+}$ equal to 1.00 M. Three mononuclear complexes $\mathrm{Th(HSSA)^{2+}}$, $\mathrm{Th(SSA)^{+}}$ and $\mathrm{Th(SSA)_2^{2-}}$, were identified in the $-\log_{10}[\mathrm{H^+}]$ range 1.7−3.5. The NMR data indicate that the SSA ligand in $\mathrm{Th(HSSA)^{2+}}$ is only coordinated *via* the carboxylate group, *i.e.* the aromatic OH-group is not deprotonated. In the other two complexes the OH-group is deprotonated, resulting in the formation of very stable chelate complexes. Two additional fluoride ions can coordinate to $\mathrm{Th(SSA)^{+}}$ and $\mathrm{Th(SSA)_2^{2-}}$, even at low total concentrations of fluoride. At $-\log_{10}[\mathrm{H^+}] > 3.5$ bi- and tetranuclear complexes, $\mathrm{Th_2(OH)_2(SSA)_4^{6-}}$ and $\mathrm{Th_4(OH)_4(SSA)_{10}^{18-}}$, were identified by using a combination of potentiometry and NMR data. The binuclear complex can bind three additional fluoride ions, indicating nine-fold coordination around the Th, where the thorium ions are linked with a double hydroxide bridge. The complex $\mathrm{Th_4(OH)_4(SSA)_{10}^{18-}}$ cannot bind additional fluoride ions, indicating that Th is eight coordinated. From the stoichiometry of the complex and the NMR data the authors conclude that the complex contains a cubane-like "$\mathrm{Th_4(OH)_4}$" core, similar to the ones suggested in binary hydroxide systems [1969BAC/BRO].

A comparison of the data presented in [2002TOR/FAR] and [2003TOR/GRE] shows that much stronger complexes are formed with organic ligands containing aromatic OH-groups (like 5-sulphosalicylate) than those containing aliphatic ones (like glycolate). This observation is important when modelling the complex formation between actinides and humic and fulvic acids.

Toraishi and Grenthe [2003TOR/GRE] provide information that the formation of polynuclear Th(IV) complexes is not restricted to the binary Th(IV)-hydroxide system. They also show that fluoride binds strongly to Th(IV) even in the presence of other ligands. These are chemical aspects that need to be considered when modelling the speciation of Th(IV) in aquatic systems. As the present review does not include organic ligands the equilibrium constants determined in [2003TOR/GRE] are not listed.

[2003YAN/TSU]

This paper is discussed together with [2003TSU/YAN].

Both these studies discuss the structure and coordination number of the Th(IV) aquo ion, $\mathrm{Th(OH_2)}_n^{4+}$ by the use of quantum chemical methods, where the solvent has been described by using a continuum model. In this, the solvent is described as a conductor-like polarisable continuum with the same dielectric constant as water. Standard quantum chemical methods have been used with the core electrons replaced by effective relativistic core-potentials. The structure and relative energy of aquo ions with different coordination number and coordination geometry have been compared. Calculated $\mathrm{Th^{4+}}$-$\mathrm{OH_2}$ bond distances are in fair agreement with experimental data. The calculations indicate that the $\mathrm{Th^{4+}}$ aquo ion has the stoichiometry $\mathrm{Th(OH_2)}_9^{4+}$ with D_{3h} symmetry as judged by a comparison of the relative energy of $[\mathrm{Th(OH_2)}_9^{4+}]$ and $[\mathrm{Th(OH_2)}_8^{4+}],(\mathrm{H_2O})$, where the latter complex with one water in the second coordination sphere has the higher electronic energy. A similar comparison between $[\mathrm{Th(OH_2)}_{10}^{4+}]$ and $[\mathrm{Th(OH_2)}_9^{4+}],(\mathrm{H_2O})$ shows that the first complex is marginally more stable, by *ca.* 1 $\mathrm{kJ{\cdot}mol^{-1}}$, far less than the uncertainty in this type of calculations. A comparison between $[\mathrm{Th(OH_2)}_9^{4+}],(\mathrm{H_2O})_3$ and $[\mathrm{Th(OH_2)}_{10}^{4+}],(\mathrm{H_2O})_2$ shows that the latter is less stable by 7 $\mathrm{kJ{\cdot}mol^{-1}}$. Comparisons of the relative energy of the different complexes should be made by using the difference in Gibbs energy, rather than the electronic energy. However, this is often not possible because of the high computational cost for the estimate of vibration energy levels required for the molecular partition functions. The energy difference between eight- and nine-coordinated aquo-ions is sufficiently large to conclude that the nine-coordinated species is the more stable one. The difference between nine and ten-coordination is so small that it is difficult to decide on their relative stability, the two species might even be in equilibrium in solution as found among the trivalent lanthanide aquo-ions. In the second study, [2003YAN/TSU], there is also a discussion of the mechanism for the exchange of water between the first and second coordination spheres of Th(IV). The authors have also discussed the structure and rate of water exchange in $[\mathrm{Th(OH)(OH_2)_8}]^{3+}$. Both studies provide information on the chemical properties of the Th(IV) aquo ion but no thermodynamic data. These studies contain essentially the same information as in [2001YAN/TSU] and [2002YAN/TSU].

[2004ALT/NEC]

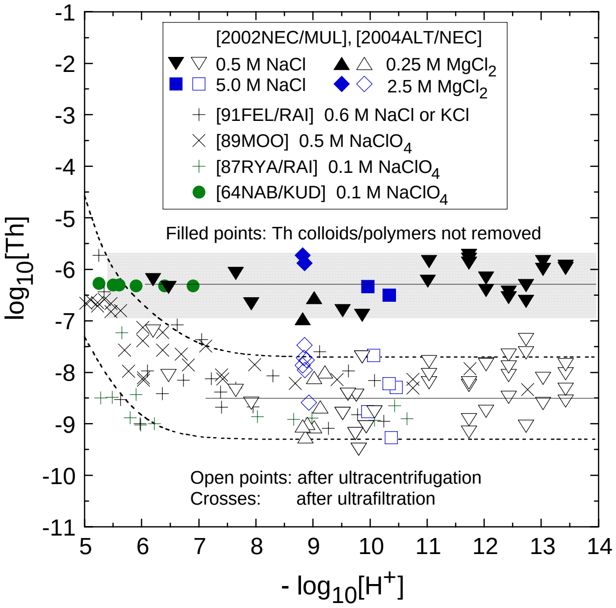
Altmaier *et al.* [2004ALT/NEC] describe the solubility of crystalline ThO_2(cr) and amorphous Th(IV) oxyhydroxide and the colloid formation (determined from the Th concentration in the supernatant and after ultracentrifugation) in concentrated NaCl and $MgCl_2$ solutions (brines) at (22 ± 2)°C. These solutions are models for the brines present in rock salt formations. The solubility increasing effect of long-time stable Th(IV) colloids previously studied in 0.5 M NaCl solutions [2002NEC/MUL] is observed also in 5 M NaCl, 0.25 M $MgCl_2$ and 2.5 M $MgCl_2$. The ionic strength has no influence on the stability of these colloids. The solubility increasing effect of Th(IV) eigencolloids is fairly large at $pH > 7$ and corresponds to a total concentration of $[Th]_{tot} \approx [Th]_{coll} = 10^{-6.3 \pm 0.5}$ M, which was ascribed to the equilibrium reaction:

$$Th(OH)_4(am) \rightleftharpoons Th(OH)_4(coll) = 1/m\ Th_m(OH)_{4m}(aq) \qquad (A.115)$$

In 4.5 M $MgCl_2$ solutions saturated with $Mg_2(OH)_3Cl(s)$, magnesium oxychloride colloids are formed that sorb Th(IV) species strongly, resulting in an increase of the total thorium concentration to 10^{-5} M. These findings are discussed with regard to geochemical modelling of colloidal Th(IV) and Pu(IV) concentrations.

The total thorium concentrations observed in both over- and undersaturation experiments with amorphous Th(IV) precipitates were analysed by ultracentrifugation which showed that the removal of Th(IV) eigencolloids requires a large centrifugal force of about 1.5×10^5 g (rotation velocities of 50000 rpm). Increasing the rotation velocity to about 5×10^5 g (90000 rpm) did not lead to a further decrease of the thorium concentration, indicating that the thorium remaining dissolved is present as small aqueous species. As shown in Figure A-46, the thorium concentration measured by Nabivanets and Kudritskaya [1964NAB/KUD] at pH 6 − 7 after centrifugation at 10000 rpm, $\log_{10}[Th] = -6.3$ is equal to that determined by [2002NEC/MUL], [2004ALT/NEC] in the supernatant solutions without removing polymeric or colloidal species. The centrifugal force used by [1964NAB/KUD] is not sufficient to remove small Th(IV) polymers or colloids. This reproducible Th concentration is two orders of magnitude higher than those determined at pH 6 to 14 after ultrafiltration (pore size 1.3 − 2 nm) [1987RYA/RAI], [1989MOO], [1991FEL/RAI] or ultracentrifugation at 5×10^5 g [2002NEC/MUL], [2004ALT/NEC] and obviously not caused by $Th(OH)_4(aq)$ but by polymeric species $Th_m(OH)_{4m}(aq)$ in the range 1.5 − 2 nm.

Figure A-46: The pH-independent thorium concentrations determined in neutral to alkaline solutions at 17 to 25°C. Filled points (hatched area): Thorium colloids/polymers not removed [2002NEC/MUL], [2004ALT/NEC], [1964NAB/KUD]. Open points: Data measured after ultracentrifugation for one hour at at 5×10^5 g [2002NEC/MUL], [2004ALT/NEC]. Crosses: Data measured after ultrafiltration (pore size 1.3 – 2 nm) [1987RYA/RAI], [1989MOO], [1991FEL/RAI].



[2004BEN/BOU]

This study has been made using potentiometry, the measurement of pH at 25°C, in a 0.1 M NaClO$_4$ ionic medium; the pH range 3.82 – 9.73 was investigated. The test solution had a total thorium concentration of 0.10 mM and it was titrated with 0.1 M or 1.0 M NaOH. It is obvious that no reliable data can be obtained under these conditions, *i.e.*, at Th concentrations up to 4 orders of magnitude above the solubility of ThO$_2$(am, hyd). Nevertheless, the authors have used their experimental data in a least-squares program that suggested that the following species are formed: $\mathrm{Th(OH)_2^{2+}}$, $\mathrm{Th(OH)_3^{+}}$, Th(OH)$_4$(aq) and $\mathrm{Th_2(OH)_7^{+}}$ with the equilibrium constants, $\log_{10} {}^*\beta_{2,1}(\mathrm{Th(OH)_2^{2+}}) = -(8.36 \pm 0.11)$, $\log_{10} {}^*\beta_{3,1}(\mathrm{Th(OH)_3^{+}}) = -(11.63 \pm 0.09)$, $\log_{10} {}^*\beta_{4,1}$ (Th(OH)$_4$, aq) = $-(18.24 \pm 0.13)$ and $\log_{10} {}^*\beta_{7,2}(\mathrm{Th_2(OH)_7^{+}}) = -(24.32 \pm 0.08)$. The authors do not report any test of alternative chemical models and there is no comparison between experimental and calculated titration curve.

The literature survey provided is very incomplete and most of the important previous studies are not mentioned, including the monograph of Baes and Mesmer [1976BAE/MES]. The introduction of the paper gives strong evidence that the authors are not familiar with solution and coordination chemistry. The data given in [2004BEN/BOU] are not useful.

[2004HEI/HUB]

Heisbourg *et al.* [2004HEI/HUB] prepared mixed Th(IV)-U(IV) oxides, $Th_{1-x}U_xO_2$(cr) with $x = 0.24$, 0.37, 0.53, 0.67, and 0.81, and investigated their dissolution behaviour under oxidising conditions at room temperature in 0.1 M HNO_3-KNO_3 ($-\log_{10}[H^+] = 1$, 2, 3, and 4) and in 1 and 5 M HNO_3. The results were presumably obtained at 20 − 25ºC. The solids were investigated by XRD, particle induced X-ray emission analysis (PIXE) and electron probe micro analysis (EPMA). X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) were used to determine the oxidation state of uranium. The dissolution behaviour was studied up to 800 days and the aqueous thorium and uranium concentrations were determined by ICP-MS after phase separation by centrifugation at 13000 rpm.

The dissolution rates observed for low and high fractions of thorium are discussed in comparison with those of pure ThO_2(cr) and UO_2(cr) and a possible mechanism is proposed including dissolution kinetics and kinetics of uranium oxidation. The authors observed enrichment of thorium in the mixed oxides and assumed that a protective surface layer of hydrated thorium oxide is formed as secondary phase. Heisbourg *et al.* [2004HEI/HUB] used the steady state thorium concentrations in 0.1 M HNO_3-KNO_3 reached after 100 days to calculate the solubility products of the ThO_2(s) secondary phase. The $\log_{10} K^{\circ}_{s,0}$ values extrapolated to $I = 0$ (Table A-82) are in the range of experimental values for crystalline or microcrystalline thorium dioxide: $\log_{10} K^{\circ}_{s,0} \geq -55.0$ [2000RAI/MOO] and $\log_{10} K^{\circ}_{s,0} = -(53.2 \pm 0.4)$ [2003NEC/ALT] (extrapolated to $I = 0$ with the SIT). However, the calculated $\log_{10} K^{\circ}_{s,0}$ values in Table A-82 evidently increase with pH, and the values calculated from the data in 0.1 M HNO_3 are even lower than $\log_{10} K^{\circ}_{s,0}$ (ThO_2, cr) = $-(54.2 \pm 1.1)$ calculated from thermochemical data selected in the present review. This indicates either a certain stabilisation of thorium oxide in the solid solutions $Th_{1-x}U_xO_2$(cr) or, similarly as in the dissolution studies with ThO_2(cr) [2001HUB/BAR], that the thorium concentrations do not represent equilibrium values.

Table A-82: Solubility products $\log_{10} K^{\circ}_{s,0}$ (ThO_2 secondary phase) calculated in [2004HEI/HUB] from the dissolution experiments with $Th_{1-x}U_xO_2$(cr) at I = 0.1 M ($HNO_3 - KNO_3$).

	$-\log_{10}[H^+] = 1$	$-\log_{10}[H^+] = 2$	$-\log_{10}[H^+] = 3$	$-\log_{10}[H^+] = 4$
$Th_{0.76}U_{0.24}O_2$(cr)				$-(51.2 \pm 0.2)$
$Th_{0.33}U_{0.67}O_2$(cr)	$-(56.3 \pm 0.2)$	$-(53.3 \pm 0.2)$	$-(51.4 \pm 0.2)$	
$Th_{0.19}U_{0.81}O_2$(cr)	$-(56.2 \pm 0.2)$	$-(53.3 \pm 0.2)$	$-(51.9 \pm 0.2)$	

[2004KON]

The heat capacity data of the actinide(IV) oxides, fluorides and chlorides have been analysed, and the data expressed as the sum of three contributions: from the lattice vibrations, from *f*-electron excitation and from a residual term, probably arising from the interaction of *d*-electrons. It is demonstrated that the latter contribution becomes zero around $T = 500$ to 600 K. A similar approach is given for the entropies, from which the standard entropies of a number of An(IV) compounds have been estimated.

These estimates have been used in selecting the data at 298.15 K for β-$ThCl_4$. Unfortunately, this paper does not include estimates for the bromide and iodide, but such values are included in the later overview by Konings *et al.* [2006KON/MOR], and these have been selected by this review.

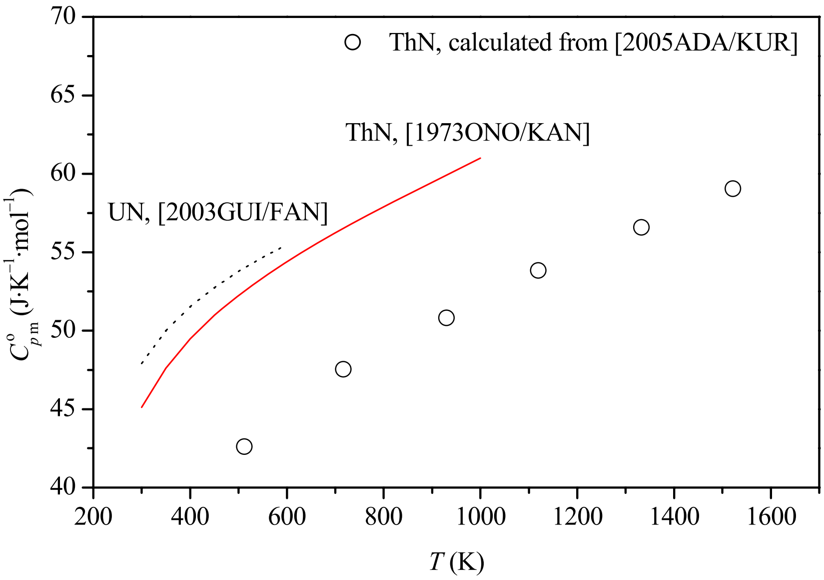
[2005ADA/KUR]

A molecular dynamics calculation was performed for thorium mononitride ThN(cr) in the temperature range from 300 to 2800 K to evaluate the thermophysical properties, *viz*. the lattice parameter, linear thermal expansion coefficient, compressibility, heat capacity ($C^{\circ}_{\mathrm{v,m}}$), and thermal conductivity. A Morse-type function added to the Busing-Ida type potential was employed as the potential function for interatomic interactions. The interatomic potential parameters were semi-empirically determined by fitting to the experimental variation of the lattice parameter with temperature.

For the heat capacity, only the lattice vibration and dilatational contributions could be evaluated from the molecular dynamics calculations. An electronic contribution of $C_{\mathrm{el}}(T) = 3.12 \times 10^{-3}\,T$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$) was added, based on the very low temperature results of de Novion and Costa [1970NOV/COS].

Figure A-47 shows a comparison of the authors' calculated values (presented only graphically in the paper) with the experimental values for $C^{\circ}_{p,\mathrm{m}}$ (ThN,cr) by [1973ONO/KAN], and also the assessed values for UN(cr) from [2003GUI/FAN]. It seems that the authors' predicted values of the total heat capacity are too low by *ca*. 10 $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, perhaps due to an underestimation of the electronic contribution.

Figure A-47: Heat capacity of ThN(cr).



[2005ALT/NEC]

This is a careful experimental study of the solubility of ThO_2(am, hyd) and the complex formation in the ternary Th(IV)-hydroxide-carbonate system and an equally careful analysis and discussion of some previous publications, [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], and [1999FEL/RAI]. Altmaier *et al.* [2005ALT/NEC] have performed solubility studies with a $ThO_2{\cdot}xH_2O$(am) phase described in [2002NEC/MUL], very similar to that used by [1994OST/BRU], at 22°C and constant ionic strength of $I = 0.5$ M (NaCl media) under CO_2(g) partial pressures of 0.1 and 1.0 bar and in carbonate/bicarbonate buffers, partly with additions of NaOH. A few additional solubility measurements at high pH and carbonate concentrations are consistent with the results reported by Rai *et al.* [1995RAI/FEL]. The experimental procedures are described in detail. The equilibrium constants used to calculate the concentration of OH^-, HCO_3^- and CO_3^{2-} from the measured H^+ concentration were taken from the NEA-TDB review [2003GUI/FAN] and the unknown ion interaction coefficients $\varepsilon(Na^+, Th(OH)_y(CO_3)_z^{4-y-2z})$ were estimated (from known values for actinide complexes of analogous charge and similar size) to be: 0.1, 0.05, 0, −0.05, − 0.1, −0.15. − 0.2, −0.25 and −0.3 kg·mol^{-1} for Th(IV) complexes of charge +2, +1, 0, −1, −2, −3, −4, −5 and −6, respectively (estimated uncertainty: ±0.2 kg·mol^{-1}).

The conclusions drawn in [2005ALT/NEC] are accepted by this review, based on the arguments in Section XI.1.3.2. The choice of equilibrium constants is justified due to the close agreement between the experimental solubility data and the solubilities calculated using the selected speciation model, *cf.* Figures XI.2 – XI.4. Additional comparison between experimental data and model calculations are given in Figure A-48 to Figure A-51. The equilibrium constants reported in [2005ALT/NEC] and those selected in the present value are listed in Table A-83.

Figure A-48 to Figure A-50 show the comparison between model calculations and experimental data from Altmaier *et al.* [2005ALT/NEC] under various conditions at $I = 0.5$ M, under $CO_2(g)$ ($p_{CO_2} = 0.1$ and 1.0 bar, $-\log_{10}[H^+] = 4.4 - 7.6$) and in carbonate/bicarbonate buffers ($C_{tot} = 0.10$, 0.04 and 0.015 M, $-\log_{10}[H^+] = 8.7 - 13.0$) and from [2006ALT/NEC] at $I = 0.1 - 4.0$ M and $C_{tot} = 0.02$ M and 0.10 M). Figure A-49 includes further comparable experimental data from [1994OST/BRU] and [1995RAI/FEL]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review, including the pentacarbonate complex $Th(CO_3)_5^{6-}$ which is not included in the speciation model of Altmaier *et al.*

Figure A-48 to Figure A-51 also show the contributions of the various complexes to the measured solubility. It is obvious that the relative contributions of the various complexes vary strongly with the experimental conditions. The species $Th(OH)(CO_3)_4^{5-}$ (114), $Th(OH)_2(CO_3)_2^{2-}$ (122) and $Th(OH)_4(CO_3)^{2-}$ (141) contribute significantly to the measured solubility in most of the experiments; these equilibrium constants are therefore accepted by this review. The contributions of the species $Th(OH)_2(CO_3)(aq)$ (121) and $Th(OH)_3(CO_3)^-$ (131) are limited to only a few experimental conditions where they amount to less than 50% of the total thorium concentrations; these equilibrium constants are therefore not selected but only recommended as guidance. The upper limits given in Table A-83 for numerous other complexes should not be used even in scoping calculations. These species give no contributions to the thorium concentrations in [1994OST/BRU], [1995RAI/FEL], [1997FEL/RAI], [1999FEL/RAI], [2005ALT/NEC] and [2006ALT/NEC]. If these species exist under other conditions (not covered in these studies), their equilibrium constants could be orders of magnitude lower than the reported upper limits. The stoichiometry and structure of the complexes formed in the ternary Th(IV)-OH^--CO_3^{2-} system are still not completely known. However the set of equilibrium constants proposed by [2005ALT/NEC] is in the judgment of this review the best available.

Table A-83: Equilibrium constants $\log_{10} K_{s,1yz}$ and $\log_{10} \beta_{1yz}$ and upper limits calculated in [2005ALT/NEC] for the formation of (1*yz*) complexes $\mathrm{Th(OH)}_y(\mathrm{CO}_3)_z^{4-y-2z}$ at $I = 0.5$ M and $I = 0$ (25°C). The equilibrium constants (uncertainties $\pm 2\sigma$) refer to:

$$\mathrm{Th(OH)_4(am)} + z\,\mathrm{CO}_3^{2-} \rightleftharpoons \mathrm{Th(OH)}_y(\mathrm{CO}_3)_z^{4-y-2z} + (4-y)\,\mathrm{OH}^- \qquad \log_{10} K_{s,1yz}$$

$$\mathrm{Th}^{4+} + y\,\mathrm{OH}^- + z\,\mathrm{CO}_3^{2-} \rightleftharpoons \mathrm{Th(OH)}_y(\mathrm{CO}_3)_z^{4-y-2z} \qquad \log_{10} \beta_{1yz}$$

Complex	$\log_{10} K_{s,1yz}$	$\log_{10} K^{o}_{s,1yz}$ ($I = 0.5$ M)	$\log_{10} \beta^{o}_{1yz}$	$\log_{10} \beta^{o}_{1yz}$ This review
Hydroxide complexes				
(110)			11.8 ± 0.2 [a]	11.5 ± 0.5
(120)			21.4 ± 0.2 [a]	21.8 ± 0.5
(130)			30.6 ± 1.0 [a]	
(140)			39.0 ± 0.5 [a]	38.6 ± 0.7
Carbonate complexes				
(101)	< -35.3	< -35.8	< 12.0 [b]	
(102)	< -27.7	< -26.8	< 21.0 [b]	
(103)	< -21.5	< -20.6	< 27.2 [b]	
(104)	< -17.1	< -17.6	< 30.2 [b]	
(105)	< -13.2	< -16.6	< 31.2 [b]	31.0 ± 0.7
(111)	< -26.3	< -26.2	< 21.6 [b]	
(112)	< -19.2	< -18.4	< 29.4 [b]	
(113)	< -14.1	< -14.0	< 33.8 [b]	
(114)	-10.0 ± 0.1	-12.0 ± 0.2	35.8 ± 0.3 [b]	35.6 ± 0.5
(121)	-17.5 ± 0.2	-17.1 ± 0.3	30.7 ± 0.4 [b]	30.5 ± 0.6
(122)	-11.2 ± 0.1	-10.8 ± 0.2	37.0 ± 0.4 [b]	36.8 ± 0.5
(123)	< -8.9	< -9.9	< 37.9 [b]	
(124)	< -7.8	< -11.6	< 36.2 [b]	
		≤ -13.3 [c]	≤ 34.5 [b]	
(131)	-9.7 ± 0.5	-9.3 ± 0.5	38.5 ± 0.6 [b]	38.3 ± 0.7
(132)	< -7.7	< -8.0	< 39.8 [b]	
		< -8.4 [c]	< 39.4 [b]	

(Continued on next page)

Table A-83: (continued)

Complex	$\log_{10} K_{s,1yz}$	$\log_{10} K^{\circ}_{s,1yz}$ (I = 0.5 M)	$\log_{10} \beta^{\circ}_{1yz}$	$\log_{10} \beta^{\circ}_{1yz}$ This review
Ternary hydroxide carbonate complexes				
(133)	< -6.8	< -9.2	< 38.6 [b]	
		< -10.9 [c]	< 36.9 [b]	
(141)	-7.2 ± 0.3	-7.2 ± 0.3	40.6 ± 0.5 [b]	40.4 ± 0.6
(142)	< -6.0	< -7.4	< 40.4 [b]	
		< -9.1 [c]	< 38.7 [b]	

a: Hydrolysis constants from [2000EKB/ALB], [2001NEC/KIM], [2002NEC/MUL].

b: The formation constants und upper limits given in [2005ALT/NEC] for $\log_{10} \beta^{\circ}_{1yz}$ are related to the solubility constant $\log_{10} K^{\circ}_{s,0} = -(47.8 \pm 0.3)$ that is based on hydrolysis constants which differ from those selected by this review. For reasons of consistency, the solubility constant is recalculated with the hydrolysis constants and SIT coefficients selected in the present review: $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$. This recalculated value is used to calculate the selected formation constants $\log_{10} \beta^{\circ}_{1yz}$ from the $\log_{10} K^{\circ}_{s,1yz}$ values in [2005ALT/NEC].

c: Calculated from solubility data in Na_2CO_3-NaOH solutions at [CO_3^{2-}] = 1 M.

Figure A-48: Solubility of ThO_2(am, hyd) under 0.1 bar CO_2(g) in 0.5 M NaCl [2005ALT/NEC]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review and $\log_{10} K^{\circ}_{s,0} = -(47.6 \pm 0.5)$ recalculated in the present review from the authors' solubility data in carbonate-free solution.

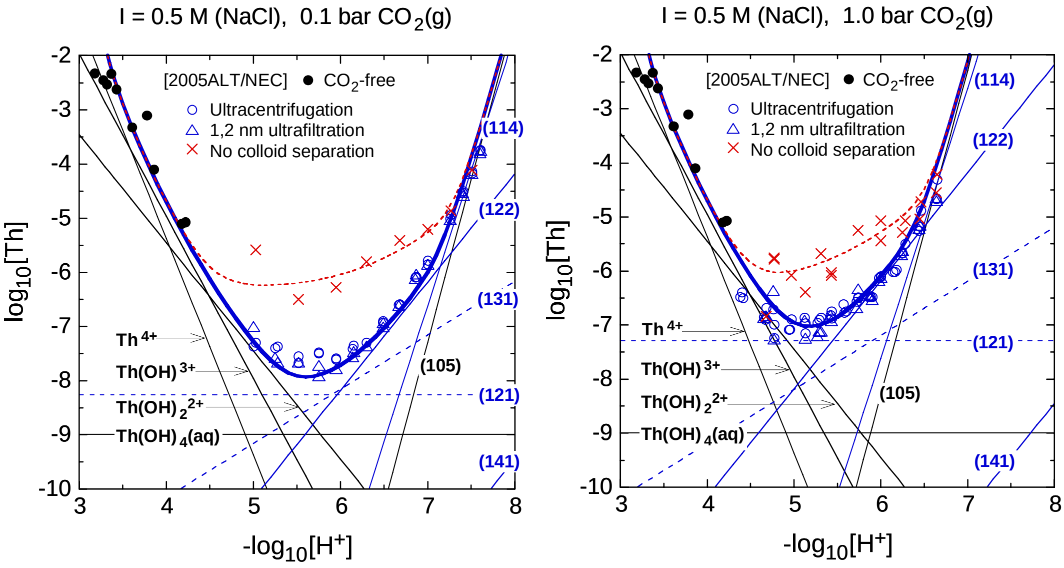


Figure A-49: Solubility of ThO_2(am, hyd) at *I* = 0.5 M ($NaHCO_3$-Na_2CO_3-NaOH-NaCl) and a total carbonate concentration of C_{tot} = 0.1, 0.04 and 0.015 M [2005ALT/NEC]. The corresponding data of [1994OST/BRU] at C_{tot} = 0.1 and *I* = 0.5 M ($NaClO_4$ media) and those determined in C_{tot} = 0.1 M ($NaHCO_3$-Na_2CO_3) without additional background electrolyte [1995RAI/FEL], [2005ALT/NEC] are shown for comparison.

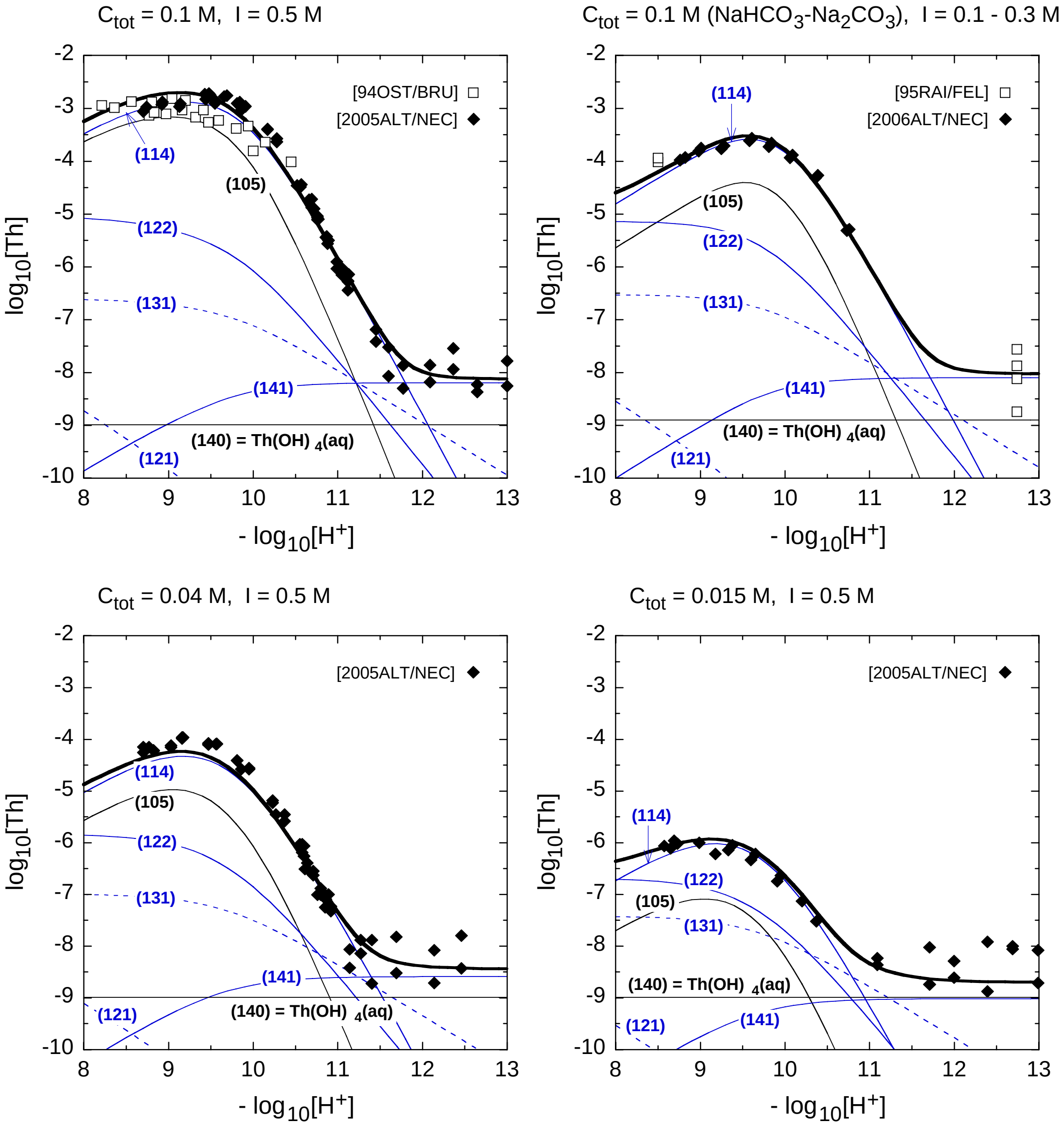


Figure A-50: Solubility of ThO_2(am, hyd) at a total carbonate concentration of C_{tot} = 0.02 M and constant ionic strengths of I = 0.1, 0.5, 2.0 and 4.0 M ($NaHCO_3$-Na_2CO_3-NaCl) [2006ALT/NEC]. The calculations are based on the equilibrium constants, SIT coefficients and $\log_{10} K^{\circ}_{s,0}$ (aged ThO_2(am, hyd)) = – 47.5 selected in the present review.

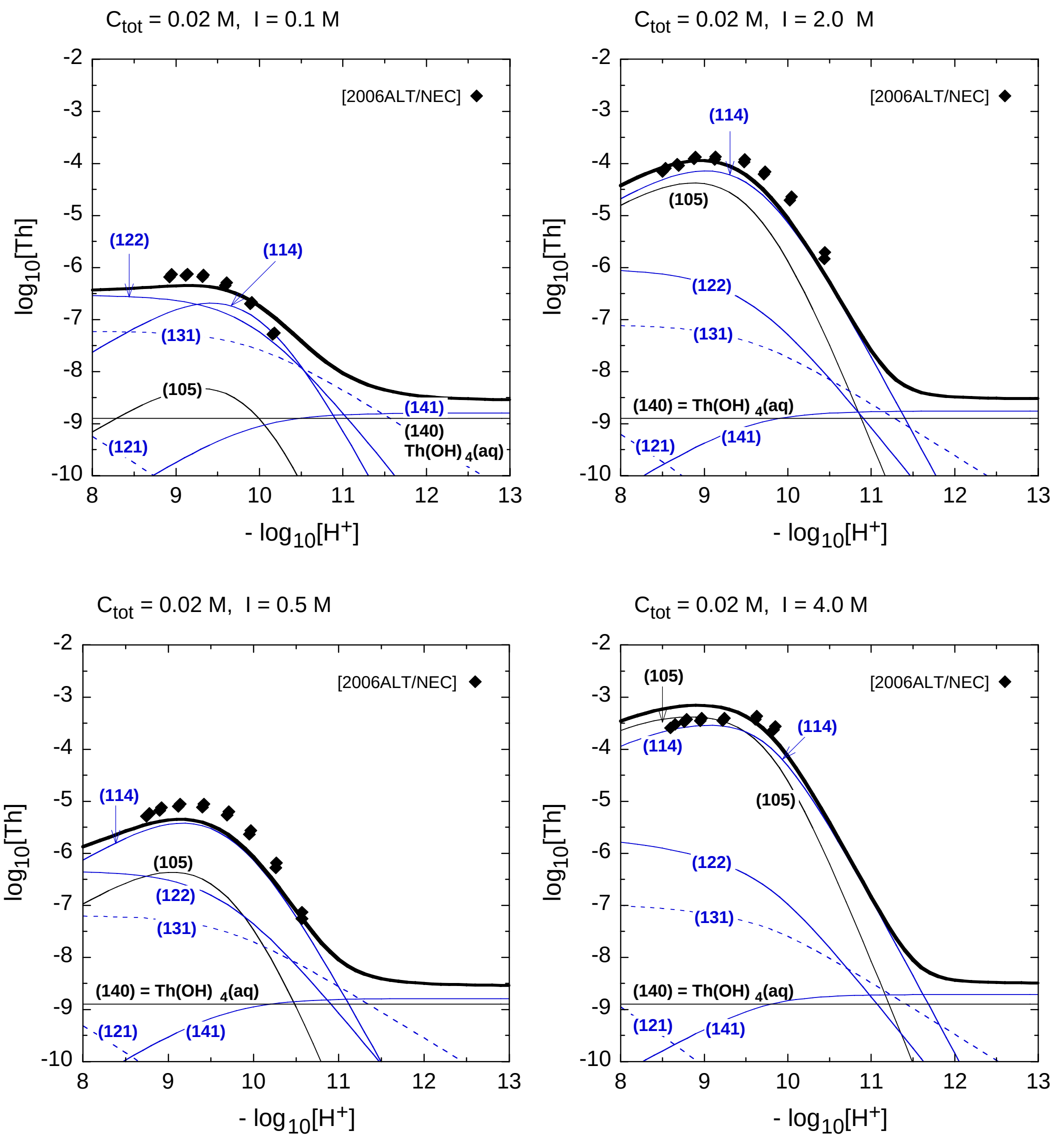
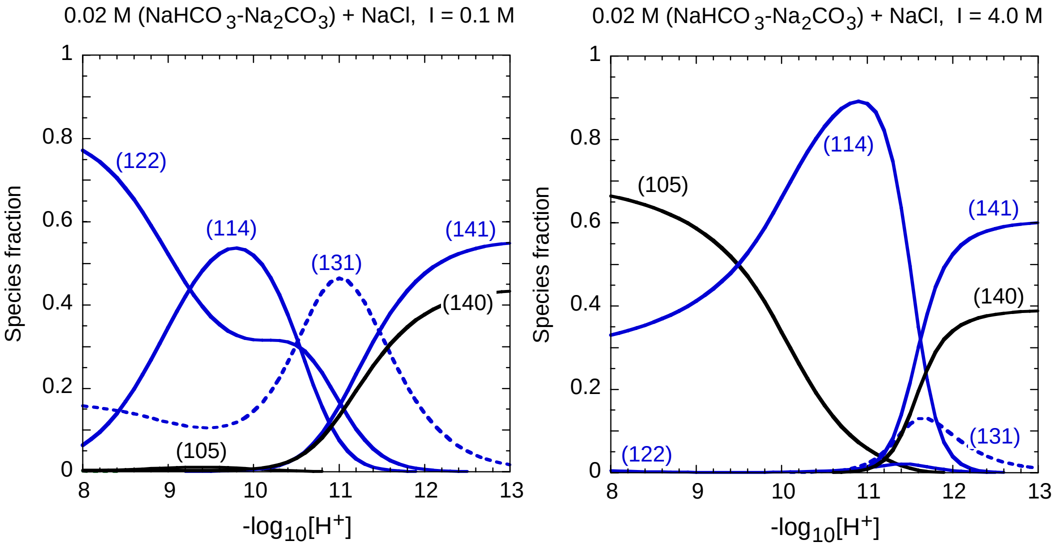


Figure A-50 shows the strong effect of ionic strength on the solubility. At constant carbonate and H^+ concentration of C_{tot} = 0.02 M and $-\log_{10}[H^+]$ = 9.5, the solubility $\log_{10}$[Th] increases from −6.2 to −3.4 when ionic strength is increased from I = 0.1 to 4.0 M. This effect is well predicted. It is due to the dramatic effect of ionic strength on the species distribution as illustrated in Figure A-51: Higher ionic strength favours the formation of the higher charged complexes $Th(CO_3)_5^{6-}$ and $Th(OH)(CO_3)_4^{5-}$ compared to $Th(OH)_2(CO_3)_2^{2-}$.

Figure A-51: Speciation at a total carbonate concentration of C_{tot} = 0.02 M and constant ionic strengths of I = 0.1 and 4.0 M ($NaHCO_3$-Na_2CO_3-NaCl) [2006ALT/NEC]. The calculations are based on the equilibrium constants and SIT coefficients selected in the present review and refer to solutions saturated with ThO_2(am, hyd).



[2005DAS/SIN]

The authors measured the pressure of CO_2(g) in the reaction Rb_2ThO_3(cr) according to the reaction:

$$ThO_2(cr) + Rb_2CO_3(cr) \rightleftharpoons Rb_2ThO_3(cr) + CO_2(g) \qquad (A.116)$$

The three solid phase compounds were mixed, pelleted, dried and heated in an alumina boat in a quartz tube attached to an all-metal vacuum system and the resultant CO_2(g) pressures measured manometrically at ten temperatures between 952 and 1098 K. Equilibration times were 200−400 h and attainment of equilibrium was checked by removal of some CO_2(g) and allowing the equilibrium to be attained again.

The Rb_2ThO_3 solid was prepared by heating rubidium nitrate and hydrated thorium nitrate with citric acid, which acts as an ignition agent, as described by [2000PUR/TYA] for $SrThO_3$(cr) and $BaThO_3$(cr). The X-ray diffraction pattern of the product were said to agree closely with those for the (hexagonal) cell reported by [1970HOP/SEE], but no details are given. The diffraction patterns of the mixture after equilibration showed no additional peaks from the initial mixture.

The calculated decomposition pressures from ten experimental points are well represented by the equation $\log_{10} p_{CO_2}/\text{bar} = -13031/T + 8.915$. The Gibbs energy of the above reaction is thus $\Delta_r G_m$ ((A.116), T) = 249476 − 170.680 T ($J{\cdot}mol^{-1}$). The Gibbs energy of the reaction $Rb_2O(l) + CO_2(g) \rightleftharpoons Rb_2CO_3(cr)$ over the experimental temperature range is given by −413796 + 173.100 T ($J{\cdot}mol^{-1}$), where the data are taken from [1982GLU/GUR], adjusted to 1 bar standard state. The Gibbs energy of the formation reaction of Rb_2ThO_3(cr) from the component oxides is thus:

$$Rb_2O(l) + ThO_2(cr) \rightarrow Rb_2ThO_3(cr) \qquad (A.117)$$

$$[\Delta_r G_m]_{952K}^{1058K}\ ((A.117), T) = -164320 + 2.420\,T\ \ (J{\cdot}mol^{-1})$$

Since the enthalpy of fusion of Rb_2O at 778 K is 20.0 $kJ{\cdot}mol^{-1}$, [1982GLU/GUR], the Gibbs energy change for the metastable reaction involving Rb_2O(cr) would be approximately −144320 − 23.287 T ($J{\cdot}mol^{-1}$) with an appreciable entropy change. Combination of the values for Reaction (A.117) with the values for $\Delta_f G^\circ_m$ (Rb_2O, l) from [1982GLU/GUR] and $\Delta_f G^\circ_m$ (ThO_2, cr) (this review) gives finally for the Gibbs energy of the formation reactions:

$$2Rb(l) + Th(cr) + 1.5O_2(g) \rightarrow Rb_2ThO_3(cr) \qquad (A.118)$$

$$[\Delta_r G_m]_{952K}^{1058K}\ ((A.118), T) = -1688657 + 276.470\,T\ (J{\cdot}mol^{-1})$$

and

$$2Rb(g) + Th(cr) + 1.5O_2(g) \rightarrow Rb_2ThO_3(cr) \qquad (A.119)$$

$$[\Delta_r G_m]_{952K}^{1058K}\ ((A.119), T) = -1831523 + 424.248\,T\ (J{\cdot}mol^{-1})$$

Both these equations are given since the pressure of Rb(g) over Rb(l) reaches 1 bar at *ca*. 967 K. The uncertainty in these values is estimated to be at least 11 $kJ{\cdot}mol^{-1}$, mainly from the uncertainty in $\Delta_f H^\circ_m$ (Rb_2O, cr, 298.15 K) which is given as 8 $kJ{\cdot}mol^{-1}$ by [1982GLU/GUR]. These expressions correspond to a very negative value for the Gibbs energy of formation of Rb_2ThO_3, in comparison with the results reported in Section XII.1.2.2 for Cs_2ThO_3.

Since there are no other thermodynamic data for Rb_2ThO_3(cr), no further processing of these results is possible, and no values are selected for the review.

[2005HEN/TUT]

The study of the U(IV)-chloride system is relevant for the discussion of chloride complexes also for other tetravalent actinides, *viz.* Th^{4+}. The study describes the use of EXAFS methods to determine the composition and bond distances in the first coordination sphere of uranium. The complexes studied are weak and the authors have used factor analysis to separate the spectra for the two species present in the EXAFS test solutions. The number of coordinated water and chloride ligands was determined from these spectra. The authors report two alternative interpretations of their EXAFS results:

$[Cl^-]$ (M)	Number of H_2O ligands		Number of Cl^- ligands	
	Model 1	Model 2	Model 1	Model 2
3.0	8.5	8.5	0.3	0.3
6.0	7.6	6.7	0.8	1.4
9.0	6.1	5.2	2.1	2.7

The experimental U^{4+}–Cl^- distance indicates very clearly that chloride complexes are formed. The number of coordinated chloride ligands can be used to estimate the equilibrium constant; however, the coordination number is uncertain with an error of at least 20%. Using the data in 3 M chloride solution (HCl + LiCl), this review obtains:

$$K = \frac{0.3}{0.7 \times 3.0}\ \mathrm{M}^{-1} = 0.14\ \mathrm{M}^{-1}$$

This value is of the same order of magnitude as those obtained using equilibrium analytical methods. The conclusion of this review is that Hennig *et al.* have clearly demonstrated that U(IV) forms inner-sphere chloride complexes; this provides very strong indications that chloride complexes are formed also by Th^{4+}.

[2005MAZ/USH]

The standard enthalpies of formation of the two forms of $ThSiO_4$, thorite (tetragonal) and huttonite (monoclinic), and, independently, the enthalpy of transition between these two polymorphs, were obtained from high temperature calorimetry. Results were reported as averages of several experiments.

Crystals of the compounds were grown by the thermal gradient flux technique, using $Li_2O{\cdot}2WO_3$ as solvent, at 1473 K for thorite and at 1673 K for huttonite. For these syntheses SiO_2 (α-quartz) with a reported purity greater than 99.9% and ThO_2(cr) with a reported purity greater than 99.99% (on the basis of the thorium content), thoroughly dried before use, were employed.

To obtain samples for analysis and calorimetry, crystals were ground (in an alumina mortar), washed with ethanol and dried at 1273 K. X-ray data showed that the tetragonal thorite samples were single phase, with lattice parameters a = (7.129 ± 0.001) Å and c = (6.319 ± 0.001) Å. As grown, huttonite crystals contained 8%

thorite, which could be entirely eliminated by a thermal treatment at 1773 K. The reported parameters of the pure monoclinic phase were: a = (6.774 ± 0.002) Å, b = (6.962 ± 0.002) Å, c = (6.495 ± 0.003) Å, β = (105.0 ± 0.1)°. For both species, reported lattice parameters were close to the literature values. Microprobe analyses indicated that the compounds were nearly stoichiometric, namely $Th_{1.005(3)}Si_{0.994(3)}O_4$ for thorite, and $Th_{1.011(5)}$ $Si_{0.989(2)}O_4$, for huttonite.

Using commercial equipment, samples of both thorite and huttonite were heated from 298.15 K to (1774 ± 1) K. This temperature was chosen so that the conversion of thorite to huttonite was complete during the calorimetric run. In these experiments, the samples were of the same volume as that of the 5 mg α-alumina pellets used for the calibration of the equipment, and the completeness of the conversion of thorite to huttonite was checked by XRD.

The difference between the measured enthalpy contents gave the enthalpy of the transition of thorite to huttonite, with the assumption that the heat contents of the two isomorphs are the same. The experimental data (Table 2 of [2005MAZ/USH]) give a value of $\Delta_{trs}H_m$ ((A.120), 298.15 K) = (7.2 ± 7.4) kJ·mol^{-1} for the reaction:

$$ThSiO_4\ (\text{thorite}) \rightarrow ThSiO_4\ (\text{huttonite}) \qquad (A.120)$$

although the authors report a value of (7.4 ± 7.5) kJ·mol^{-1} in their text.

For the determination of the enthalpies of formation of the two polymorphs, a custom-built Tian-Calvet calorimeter was used, operating at 1080 K. The solvent, contained in a platinum crucible, was $2PbO{\cdot}B_2O_3$. This instrument was calibrated using the heat content of platinum between 298 and 1080 K. Attempts to measure solution enthalpies after equilibration of sample pellets above the solvent at the calorimeter temperature had to be abandoned as the melt vapours reacted with the samples. The reported results thus arise from experiments in which samples at room temperature (presumably 298.15 K) were dropped into the solvent at the calorimeter temperature.

For the reaction:

$$ThO_2(\text{cr}, 298.15\ \text{K}) + SiO_2(\alpha, 298.15\ \text{K}) \rightarrow ThSiO_4\ (\text{thorite or huttonite}, 298.15\ \text{K}) \qquad (A.121)$$

values of $\Delta_r H^\circ_m$ ((A.121), 298.15 K) = (19.6 ± 2.0) kJ·mol^{-1} for thorite and (26.3 ± 3.0) kJ·mol^{-1} for huttonite were obtained. This gives, for the transition, $\Delta_{trs}H^\circ_m$ ((A.120), 298.15 K) = (6.7 ± 3.6) kJ·mol^{-1}, a value in agreement with that obtained from the heat content measurements, but more precise and involving fewer assumptions.

According to these results, both compounds are metastable towards quartz and thorium dioxide under standard conditions. Use of the values selected in this review for $\Delta_f H^\circ_m$ (ThO_2, cr, 298.15 K) = −(1226.4 ± 3.5) kJ·mol^{-1} and $\Delta_f H^\circ_m$ (SiO_2, α, 298.15 K) = −(910.7 ± 1.0) kJ·mol^{-1} yields the values:

$$\Delta_f H^\circ_m\ (ThSiO_4,\ \text{thorite},\ 298.15\ \text{K}) = -(2117.5 \pm 4.2)\ \text{kJ·mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{ThSiO}_4, \text{huttonite}, 298.15\ \text{K}) = -(2110.8 \pm 4.7)\ \text{kJ}\cdot\text{mol}^{-1}$$

The authors also discuss the relationship between the standard enthalpies of the formation reactions of the various zircon-type orthosilicates $MSiO_4$ from the binary oxides and the ionic radii of the tetravalent M cations.

[2005RAI/YUI]

The paper discusses the solubility of Th-doped borosilicate glass containing 48.6% SiO_2 and 0.99% Th in a wide range of solutions with pH values from 0.5 to 12 and carbonate and bicarbonate concentrations up to 6.2 m and 1.0 m respectively. Equilibration times varied up to 93 days. The solubility was also approached from the over-saturation direction by spiking Th-doped glass suspensions with soluble thorium and following the changes in thorium concentrations with time. Membrane filters (0.0018 µm pore size) were used to separate solutions from suspensions in order to determine aqueous concentrations. A combination of X-ray diffraction and X-ray absorption spectroscopy (XAS) was used to characterise the solids and aqueous solutions. X-ray diffraction analyses did not detect any crystalline thorium solids indicating that the solids must be amorphous. No thermodynamic data are presented in the paper. Observed aqueous concentrations, a gradual decrease in aqueous thorium concentrations from the over-saturation direction, and XAS data strongly suggest that thorium in the solid and the aqueous phases around pH 1, is associated with silica. The data also indicate that thorium hydrous oxide is the possible solubility-controlling phase in the highly alkaline region.

[2006ALT/NEC]

In this study Altmaier *et al.* [2006ALT/NEC] extended their solubility measurements with $ThO_2\cdot xH_2O(am)$ in carbonate/bicarbonate buffers at $I = 0.5$ M [2005ALT/NEC] to a wider range of ionic strength, $I = 0.1, 0.5, 2.0$ and 4.0 M ($NaHCO_3$-Na_2CO_3-NaCl) and $I = 0.1-0.3$ M (0.1 M $NaHCO_3$-Na_2CO_3 without additional background electrolyte). The authors derived an interaction coefficient of $\varepsilon(\text{Na}^+, \text{Th(OH)(CO}_3)_4^{5-}) = -(0.22 \pm 0.13)\ \text{kg}\cdot\text{mol}^{-1}$ for the dominant (114) complex from their experimental data at $I = 0.1-4.0$ M ($\log_{10} K^\circ_{s,114} = -(11.9 \pm 0.2)$, $\Delta\varepsilon = (0.22 \pm 0.05)\ \text{kg}\cdot\text{mol}^{-1}$). This experimental SIT coefficient, close to the estimated value of $\varepsilon(\text{Na}^+, \text{Th(OH)(CO}_3)_4^{5-}) = -0.25\ \text{kg}\cdot\text{mol}^{-1}$ used in [2005ALT/NEC], is selected in the present review. The close agreement between the experimental solubility data of [2006ALT/NEC] and the solubility calculated with the equilibrium constants and SIT coefficients selected in this review (including the pentacarbonate complex $\text{Th(CO}_3)_5^{6-}$ not taken into account by Altmaier *et al.*) are shown in the Appendix A entry for [2005ALT/NEC].

In addition, [2006ALT/NEC] contains a brief section on EXAFS measurements. The spectrum of a thorium solution in 1.0 M Na_2CO_3 / 0.1 M $NaHCO_3$ is consistent with those measured in [1997FEL/RAI] for thorium solutions at high carbonate or bicarbonate concentrations. The different EXAFS spectrum of a saturated solution taken from the solubility study at $I = 0.5$ M ($NaHCO_3$-Na_2CO_3-NaCl), $C_{tot} = 0.1$ M, and

$-\log_{10}[H^+] = 9.16$ shows that the pentacarbonate complex is not the dominant species in this sample which is consistent with the interpretation of the solubility data.

[2006NEC/ALT]

In this study ion interaction (SIT) coefficients for the Th^{4+} ion and trace activity coefficients in $NaClO_4$, $NaNO_3$ and NaCl solution were determined by solvent extraction with tri-*n*-butyl phosphate (TBP) at 22°C. The liquid-liquid phase equilibria between dilute to concentrated $NaClO_4$, $NaNO_3$ and NaCl solutions containing 0.01 – 0.02 M H^+ and $(1 - 8) \times 10^{-3}$ M Th^{4+} and organic phases consisting of 10 – 50 vol.% TBP in *n*-dodecane are given by:

$$Th^{4+}(aq) + 4\ X^-(aq) + n\ TBP(org) \rightleftharpoons ThX_4(TPB)_n(org) \tag{A.122}$$

with $X^- = ClO_4^-$, NO_3^- and Cl^-. The thorium concentrations in the aqueous and organic phases were measured by ICP-MS. The organic phases were pre-equilibrated with corresponding aqueous HX-NaX solutions. To ensure that co-extraction of acids and sodium salts does not affect the free TBP concentration in the organic phase, the concentrations of HX and NaX in the organic phases were measured as well. Except of the experiments at higher perchlorate concentrations, which were not included in the data evaluation, this effect was found to be negligible. The conditional equilibrium constants $'K$ for a given aqueous ionic medium

$$'K = K\,[TBP(org)]^n = \frac{[ThX_4(TPB)_n(org)]}{[Th^{4+}]\,[X^-]^4} \tag{A.123}$$

were extrapolated to zero ionic strength by linear SIT regression:

$$\log_{10}{'K} + 20D = \log_{10}{'K^\circ} + \varepsilon(Th^{4+}, X^-)\,m_{X^-} + 4\,\varepsilon(Na^+, X^-)\,m_{Na^+} \tag{A.124}$$

The experimental data in 0.05 – 1.5 m $NaClO_4$ and in 0.05 – 3 m $NaNO_3$ yielded:

$$\varepsilon(Th^{4+}, NO_3^-) + 4\,\varepsilon(Na^+, NO_3^-) = (0.15 \pm 0.02)\ kg\cdot mol^{-1}$$

$$\varepsilon(Th^{4+}, ClO_4^-) + 4\,\varepsilon(Na^+, ClO_4^-) = (0.74 \pm 0.04)\ kg\cdot mol^{-1}$$

and, with $\varepsilon(Na^+, NO_3^-) = -(0.04 \pm 0.03)\ kg\cdot mol^{-1}$ and $\varepsilon(Na^+, ClO_4^-) = (0.01 \pm 0.01)\ kg\cdot mol^{-1}$, the following interaction coefficients for the Th^{4+} ion:

$$\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)\ kg\cdot mol^{-1}$$

$$\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.06)\ kg\cdot mol^{-1}.$$

The interaction coefficient with perchlorate is in excellent agreement with $\varepsilon(Th^{4+}, ClO_4^-) = (0.70 \pm 0.10)\ kg\cdot mol^{-1}$ estimated from the correlation between $\varepsilon(An^{4+}, ClO_4^-)$ and the ionic radii of the An^{4+} ions (*cf.* Section VI-3). The interaction coefficient $\varepsilon(Th^{4+}, NO_3^-) = (0.31 \pm 0.12)\ kg\cdot mol^{-1}$ [2006NEC/ALT] differs considerably from $\varepsilon(Th^{4+}, NO_3^-) = (0.11 \pm 0.02)\ kg\cdot mol^{-1}$ [1980CIA] adopted in the previous

NEA-TDB reviews. As the value of $\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = (0.31 \pm 0.12)$ kg·mol^{-1} follows the linear correlation between known values of $\varepsilon(\mathrm{M}^{Z+}, \mathrm{NO}_3^-)$ and $\varepsilon(\mathrm{M}^{Z+}, \mathrm{ClO}_4^-)$, it is considered to be more reliable than the value of $\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = (0.11 \pm 0.02)$ kg·mol^{-1} which strongly deviates from this correlation (*cf.* Section VI-3).

For aqueous phases containing NaCl, the distribution coefficients D_{Th} at m_{NaCl} < 3 mol·kg^{-1} were too low to evaluate SIT coefficients in NaCl solution by linear regression, but the data determined by [2006NEC/ALT] in 2.5 − 5.0 m NaCl were found to be compatible with the SIT coefficients selected in the NEA-TDB reviews, $\varepsilon(\mathrm{Th}^{4+},\mathrm{Cl}^-) + 4\,\varepsilon(\mathrm{Na}^+,\mathrm{Cl}^-) = (0.37 \pm 0.04)$ kg·mol^{-1}.

The method used in [2006NEC/ALT] was also tested for the extraction of $\mathrm{HClO_4}$ and $\mathrm{HNO_3}$ from aqueous $\mathrm{NaClO_4}$ and $\mathrm{NaNO_3}$ solutions and U(VI) in dilute to concentrated $\mathrm{NaClO_4}$, $\mathrm{NaNO_3}$ and chloride solutions (NaCl, $\mathrm{MgCl_2}$, $\mathrm{CaCl_2}$). The variation of the distribution coefficients was in excellent agreement with calculations based on SIT coefficients from the NEA-TDB reviews: $\varepsilon(\mathrm{H}^+,\mathrm{ClO}_4^-) = (0.14 \pm 0.02)$ kg·mol^{-1}, $\varepsilon(\mathrm{H}^+, \mathrm{NO}_3^-) = (0.07 \pm 0.01)$ kg·mol^{-1}, $\varepsilon(\mathrm{UO}_2^{2+}, \mathrm{ClO}_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}, $\varepsilon(\mathrm{UO}_2^{2+}, \mathrm{NO}_3^-) = (0.24 \pm 0.03)$ kg·mol^{-1}, and $\varepsilon(\mathrm{UO}_2^{2+}, \mathrm{Cl}^-) = (0.21 \pm 0.02)$ kg·mol^{-1} [1992GRE/FUG], [2003GUI/FAN].

It is to be noted that the ion interaction coefficients for Th^{4+} and UO_2^{2+} discussed above refer to a strict ion interaction approach which does not account for the formation of chloride and nitrate complexes. This review has re-evaluated the Th(IV) extraction data from aqueous nitrate phases using also the complexation model. Figure A-52 shows that the experimental data of [2006NEC/ALT] in 0.05 − 3 M $\mathrm{NaNO_3}$ + 0.02 M $\mathrm{HNO_3}$ can be described equally well with both approaches.

Using the complexation model (Figure A-52-b), the interaction coefficient of Th^{4+} in nitrate solution is set equal to the interaction coefficient in non-complexing perchlorate solution:

$$\varepsilon(\mathrm{Th}^{4+}, \mathrm{NO}_3^-) = \varepsilon(\mathrm{Th}^{4+}, \mathrm{ClO}_4^-) = (0.70 \pm 0.10)\ \mathrm{kg \cdot mol^{-1}}$$

and the interaction of Th^{4+} with nitrate is ascribed to the reactions:

$$\mathrm{Th}^{4+} + n\,\mathrm{NO}_3^- \rightleftharpoons \mathrm{Th(NO_3)}_n^{4-n} \qquad \text{(A.125)}$$

with $\Delta\varepsilon_{n=1} = -(0.21 \pm 0.05)$ kg·mol^{-1} and $\Delta\varepsilon_{n=2} = -(0.41 \pm 0.13)$ kg·mol^{-1} in $\mathrm{HNO_3}$ media and $\Delta\varepsilon_{n=1} = -(0.10 \pm 0.10)$ kg·mol^{-1} and $\Delta\varepsilon_{n=2} = -(0.19 \pm 0.16)$ kg·mol^{-1} in $\mathrm{NaNO_3}$ media adopted from the analogous reactions of U(IV) [1992GRE/FUG]. Up to nitrate concentrations of 1.0 M, the distribution coefficients D_{Th} are well described with the equilibrium constant $\log_{10} \beta_1^{\circ}$ ((A.125), $n = 1$) $= (1.5 \pm 0.2)$ (dotted line in Figure A-52-b). The fit including experimental data at higher nitrate concentrations (dashed line in Figure A-52-b) gives also the formation constants of the complexes $\mathrm{Th(NO_3)}_2^{2+}$ and $\mathrm{Th(NO_3)}_3^{+}$:

$\log_{10} \beta_1^{\circ}$ (A.125) = (1.3 ± 0.2),

$\log_{10} \beta_2^{\circ}$ (A.125) = (2.3 ± 0.4), and

$\log_{10} \beta_3^{\circ}$ (A.125) = (3.0 ± 0.5).

An estimate of $\varepsilon(\mathrm{Th(NO_3)_3^+}, \mathrm{NO_3^-}) = \varepsilon(\mathrm{Th(NO_3)_3^+}, \mathrm{ClO_4^-})$ = (0.25 ± 0.15) kg·mol^{-1}, *i.e.*, $\Delta\varepsilon_{n=3}$ = −(0.33 ± 0.20) kg·mol^{-1} in NaNO$_3$ solution, is used for ionic strength corrections of the third complex which becomes significant at $[\mathrm{NO_3^-}] > 2$ M. The equilibrium constants for the first and second complex are close to the values selected in the NEA-TDB review of uranium for the analogous U(IV) nitrate complexes which have been studied by different authors and different experimental methods at widely varying ionic strength ($\log_{10} \beta_1^{\circ}(\mathrm{U(NO_3)^{3+}})$ = (1.47 ± 0.13), $\log_{10} \beta_2^{\circ}(\mathrm{U(NO_3)_2^{2+}})$ = (2.30 ± 0.35) [1992GRE/FUG]).

A considerably different value of $\log_{10} \beta_1^{\circ}(\mathrm{Th(NO_3)^{3+}})$ = 2.0 was obtained from the TTA extraction study of [1950DAY/STO] who calculated β_1 = 4.73 M^{-1} from the variation of the distribution coefficient in 0.5 M HClO$_4$-HNO$_3$. The alternative evaluation of their experimental data with the ion interaction approach yields a strongly negative value of $\varepsilon(\mathrm{Th^{4+}}, \mathrm{NO_3^-})$ = −0.61 kg·mol^{-1}(*cf.* Appendix review of [1950DAY/STO]). Figure A-53 shows that both the calculations with the data obtained from the study of [1950DAY/STO], either using $\varepsilon(\mathrm{Th^{4+}}, \mathrm{NO_3^-})$ = −0.61 kg·mol^{-1} (ion interaction model) or using $\log_{10} \beta_2^{\circ}$ = 2.0 and $\Delta\varepsilon_{n=1}$ = − (0.21 ± 0.05) kg·mol^{-1} [1992GRE/FUG] (nitrate complexation model) significantly overpredict the effect of nitrate interaction or complexation on the distribution coefficients determined by [2006NEC/ALT] for aqueous phase containing 0.05 – 3 M NaNO$_3$ + 0.02 M HNO$_3$. In particular the negative value of $\varepsilon(\mathrm{Th^{4+}}, \mathrm{NO_3^-})$ = − 0.61 kg·mol^{-1} is extremely inappropriate to model the results at nitrate concentrations above 0.5 M.

Figure A-52: Distribution coefficients of Th(IV) in the TBP extraction study of [2006NEC/ALT] (aqueous phase: 0.05 − 3 M $NaNO_3$ + 0.02 M HNO_3; organic phase: TBP/*n*-dodecane). Experimental data and recalculation a) with the ion interaction model, b) with the nitrate complexation model. (All calculations are performed on the molal scale and back-transformed to the molar scale for direct comparison with the experimental data.)

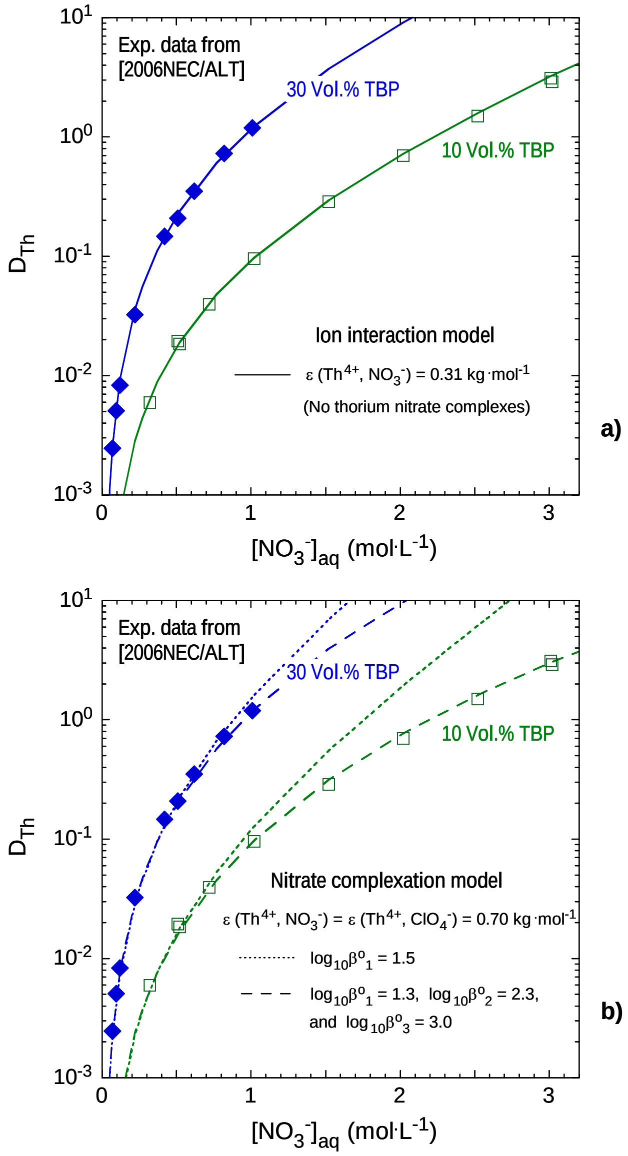
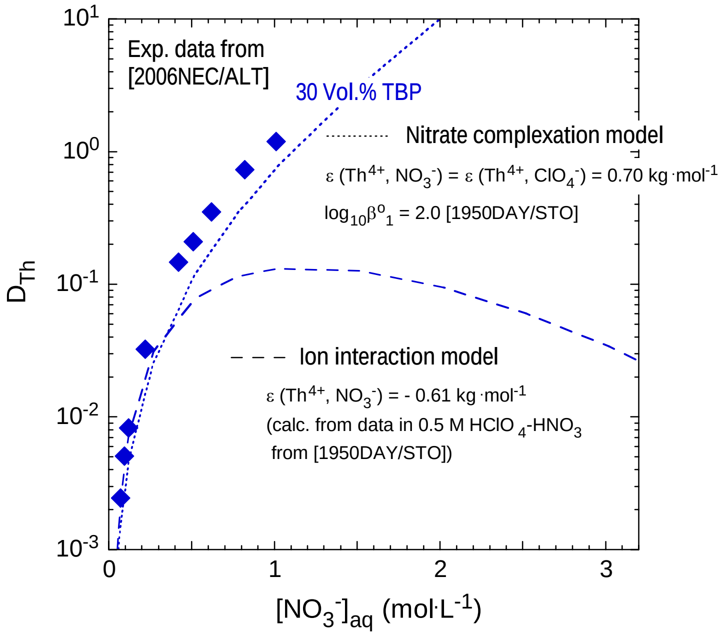


Figure A-53: Comparison of experimental distribution coefficients of Th(IV) in the TBP extraction study of [2006NEC/ALT] (aqueous phase: 0.05 – 3 M $NaNO_3$ + 0.02 M HNO_3; organic phase: TBP/*n*-dodecane) and calculations with the data obtained from the TTA extraction study of [1950DAY/STO], either $\varepsilon(Th^{4+}, NO_3^-) = -0.61$ (ion interaction model) or $\log_{10}\beta_1^\circ = 2.0$ (nitrate complexation model).



[2007BRE/ALT]

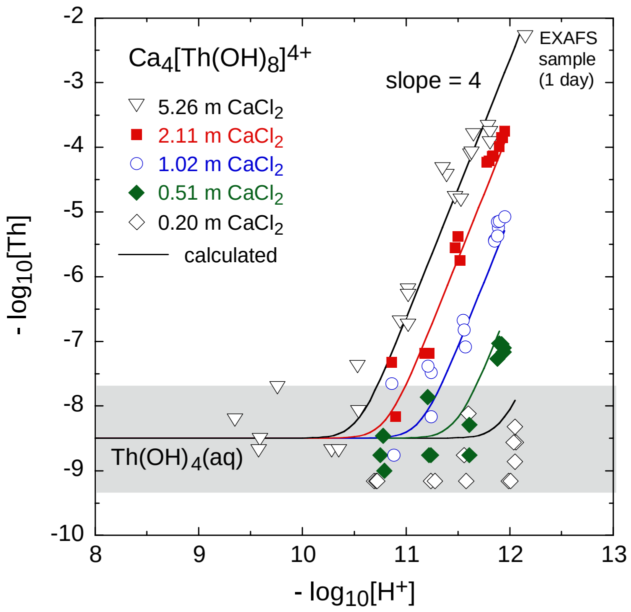
Brendebach *et al.* [2007BRE/ALT] report unexpectedly high solubilities of Zr(IV) and Th(IV) hydrous oxides in alkaline $CaCl_2$ solutions kept under an argon atmosphere at (22 ± 2)°C (for Zr(IV) at $-\log_{10}[H^+]$ = 10 to 12 in 0.2, 0.5 and 2.0 M $CaCl_2$ and for Th(IV) at $-\log_{10}[H^+]$ = 11 to 12 in 0.5 to 4.5 M $CaCl_2$). The dominant aqueous species are identified as ternary Ca-M(IV)-OH complexes, $Ca_3[Zr(OH)_6]^{4+}$ and $Ca_4[Th(OH)_8]^{4+}$, respectively. The EXAFS spectra of four Zr(IV) solutions and a 4.3×10^{-3} M Th(IV) solution at $-\log_{10}[H^+]$ = 12.2 in 4.5 M $CaCl_2$ (the latter is oversaturated with regard to the solubility of calcium hydroxychlorides at this pH) show two coordination shells. The numbers of oxygen atoms in the first coordination sphere detected by EXAFS, N_O = (6.6 ± 1.2) for Zr and N_O = (8.6 ± 1.2) for Th, are consistent with 6 and 8 OH^- ligands as derived from the respective slopes of 2 and 4 in the solubility curves of $\log_{10}[M]_{tot}$ versus $-\log_{10}[H^+]$. The EXAFS spectra also show a second co-ordination shell of Ca^{2+} ions, with N_{Ca} = 3 (2.7 ± 0.6) at a distance of $R_{Zr\text{-}Ca}$ = (3.38 ± 0.02) Å for the zirconium complex and N_{Ca} = 4 (3.8 ± 0.5) at a distance of $R_{Th\text{-}Ca}$ = (3.98 ± 0.02) Å for the thorium complex. The presence of dominating amounts of polynuclear hydrolysis species and the formation of complexes with chloride ligands can be excluded. The ternary $Ca_3[Zr(OH)_6]^{4+}$ and $Ca_4[Th(OH)_8]^{4+}$ complexes, where the central $[Zr(OH)_6^{2-}]$ and $[Th(OH)_8^{4-}]$ complexes are stabilised by associated Ca^{2+} ions, probably have distorted rutile- and fluorite-type structures with the Ca^{2+} ions bound to coordination polyhedra edges.

The authors have used the SIT to describe the measured solubilities. The thorium data (Figure A-54) are well described with an equilibrium constant of $\log_{10} K^{o}_{s,(4,1,8)} = (1.8 \pm 0.5)$ for the reaction

$$Th(OH)_4(am) + 4Ca^{2+} + 4OH^- \rightleftharpoons Ca_4[Th(OH)_8]^{4+}$$

and $\varepsilon(Ca_4[Th(OH)_8]^{4+}, Cl^-) = -(0.01 \pm 0.10)$ kg·mol^{-1}. However, the ion interaction coefficient depends strongly on the data in 4.5 M $CaCl_2$, *i.e.* at $I_m = 15.8$ mol·kg^{-1} which is far above the validity range of the SIT. The data reported in [2007BRE/ALT] may be used as guidance in estimating the solubility of thorium in salt solutions containing cementitious waste forms.

Figure A-54: Experimental solubility data reported in [2007BRE/ALT] for Th(IV) hydrous oxide in 0.2 to 4.5 M $CaCl_2$ solutions (after equilibration times of 14 to 198 days, except of the EXAFS sample which was measured after only one day); the calculated curves are based on the proposed SIT model parameters.



[2007HEN/SCH]

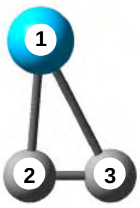
Hennig *et al.* have investigated test solutions of 0.05 M Th(IV) at pH close to 1 and with total concentrations of sulphate in the range $0.90 \le [\mathrm{SO}_4^{2-}] + [\mathrm{HSO}_4^{-}] \le 2.0$ M, using EXAFS methodology to obtain information on the stoichiometry, geometry and mode of coordination in the Th(IV) sulphato complexes formed under these experimental conditions; only the EXAFS results of Th(IV) sulphato complexes will be discussed.

There are two S–Th distances at 3.81 and 3.14 Å, respectively, consistent with a complex that contains both unidentate and bidentate sulphate coordination. The numbers of unidentate Th–S distances reported in the two test solutions are 3.7 and 3.8, respectively; the numbers of bidentate Th–S distances in the same solutions are 0.9 and 1.6, respectively. These numbers indicate the presence of complexes with the stoichiometry $\mathrm{Th(SO_4\text{-}uni)_4(SO_4\text{-}bi)(OH_2)}_x$ and $\mathrm{Th(SO_4\text{-}uni)_4(SO_4\text{-}bi)_2(OH_2)}_y$. The number of coordinated oxygen atoms is close to 9, indicating that there are some coordinated water ligands present in the sulphato complexes. However, the uncertainty in the number of Th–S and Th–O distances is fairly large (± 15%), making a more quantitative estimate of the constitution of the complexes difficult. It is of interest to note that the proposed mode of sulphate coordination is similar to that found in the structure of $\mathrm{Cs_2[Th(SO_4)_3]\cdot(H_2O)_3}$, *cf.* Figure IX-1) where there are three bidentate and two unidentate sulphato ligands and two water coordinated to Th. The composition of the test solutions and the measured pH in the test solutions are consistent with the formation of strong sulphato complexes, but it is not possible to use these data to estimate equilibrium constants.

[2008KOV/KON]

The geometry and vibrations of the $\mathrm{ThC_2}$ and $\mathrm{ThC_4}$ gaseous molecules have been derived from quantum chemical calculations, using second-order perturbation theory. The results indicate an asymmetric essentially L-shaped structure for $\mathrm{ThC_2(g)}$ and a symmetric planar fan-type structure (with C_{2v} symmetry) for $\mathrm{ThC_4(g)}$.

The details of the structures are given in Table A-84, where the numbering of the carbon atoms is as follows in the schematic models:



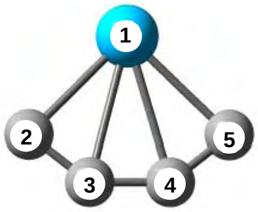


Table A-84: Molecular parameters of ThC_2(g) and ThC_4(g).

Parameter	ThC_2(g)	ThC_4(g)
	Symmetry C_s	Symmetry C_{2v}
r (Th-C2) (Å)	2.155	2.365
r (Th-C3) (Å)	2.473	2.532
Angle Th-C2-C3	88.1°	82.1°
Angle C2-Th-C3	31.3°	30.2°
Angle C2-Th-C5		91.6°
Angle C3-Th-C4		31.2°
Harmonic vibration frequencies (degeneracies) (cm^{-1})	632(1) 210(1) 1649(1)	1818(1) 1706(1) 1054(1) 642(1) 475(1) 393(1) 372(1) 499(1) 280(1)

[1995ROS/BAL] and [1996ROS/BAL] have found from similar *ab initio* calculations that YC_2(g) and LaC_2(g) have symmetrical C_{2v} fan-shaped structures. Kovács and Konings indicate that for ThC_2(g), this structure is stable, but lies *ca.* 7.7 $kJ \cdot mol^{-1}$ (644 cm^{-1}) above the asymmetric configuration described above.

The effective charge on the thorium atom is found to be 1.66 for ThC_2(g) and 1.60 for ThC_4(g). For this reason, [2008KOV/KON] used the electronic levels of ThO(g), where the thorium atom is divalent, in calculating the thermal functions of the carbide molecules, and we have followed the same procedure, as discussed in sections XI.1.2.1 and XI.1.2.2. However, as noted there, the calculated entropies of the reactions Th(g) + nC(cr) $\rightleftharpoons$ ThC_n(g), $n = 2, 4$ are noticeably different (by *ca.* 30 and −17 $J \cdot K^{-1} \cdot mol^{-1}$ respectively) from those derived from the vaporisation experiments of [1964JAC/BAR] and [1974KOH/STE].

Appendix B

Ionic strength corrections[1]

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 $m_{\text{B}} = m^{\text{o}} = 1\ \text{mol}\cdot\text{kg}^{-1}$, and in which the activity coefficient γ_{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 theory.
- 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

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[1] 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.

introducing ion pairing between the medium ions and the species involved in the equilibrium reactions. Earlier, this approach has been used extensively in 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 Data Base review is a medium-dependent expression for the activity coefficients, which is the specific ion interaction theory 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 M, *cf.* Figure B-1, while in other cases, notably for cations of high charge ($\geq +4$ and ≤ -4), the lowest available ionic strength is often 0.2 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 units 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 theory are described below.

- **Assumption 1:** The activity coefficient γ_j of an ion j of charge z_j in the solution of ionic strength I_m may be described by Eq. (B.1):

$$\log_{10}\gamma_j = -z_j^2 D + \sum_k \varepsilon(j,k,I_m)\, m_k \qquad \text{(B.1)}$$

D is the Debye-Hückel term:

$$D = \frac{A\sqrt{I_m}}{1 + B a_j \sqrt{I_m}} \qquad \text{(B.2)}$$

where I_m is the molal ionic strength:

$$I_m = \frac{1}{2}\sum_i m_i\, z_i^2$$

A and B are constants which are temperature and pressure dependent, and a_j is an ion size parameter ("distance of closest approach") for the hydrated ion j. The Debye-Hückel limiting slope, A, has a value of $(0.509 \pm 0.001)\ \text{kg}^{\frac{1}{2}}\cdot\text{mol}^{-\frac{1}{2}}$ at 25°C and 1 bar, (*cf.* Section B.1.2). The term Ba_j in the denominator of the Debye-Hückel term has been assigned a value of $Ba_j = 1.5\ \text{kg}^{\frac{1}{2}}\cdot\text{mol}^{-\frac{1}{2}}$ at 25°C and 1 bar, as proposed by Scatchard [1976SCA] and accepted by Ciavatta [1980CIA]. This value has been found to minimise, for several species, the ionic strength dependence of $\varepsilon(j,k,I_m)$ between I_m = 0.5 m and I_m = 3.5 m. It should be mentioned that some authors have proposed different values for Ba_j ranging from Ba_j = 1.0 [1935GUG] to Ba_j = 1.6 [1962VAS]. However, the parameter Ba_j is empirical and as such is correlated to the value of $\varepsilon(j,k,I_m)$. Hence, this variety of values for Ba_j does not represent an uncertainty range, but rather indicates that several different sets of Ba_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 25°C listed in Table B-4, Table B-5, Table B-6 and Table B-7 have thus to be used with $Ba_j = 1.5\ \text{kg}^{\frac{1}{2}}\cdot\text{mol}^{-\frac{1}{2}}$.

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 ε, 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.

Eq. (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 ± 0.03 $\text{kg}\cdot\text{mol}^{-1}$ or greater, Ciavatta [1980CIA] proposed the use of Equation (B.3)

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m \tag{B.3}$$

However, even if the value of ε calculated in this way describes the variation with ionic strength slightly better than a constant value, this equation has no theoretical basis; ε_2 is a fitting parameter and the term $\varepsilon_2 \log_{10} I_\text{m}$ goes to minus infinity at the limiting value $I_\text{m} = 0$. This expression for the concentration dependence of ε should be avoided, even though the term $\varepsilon\cdot m = (\varepsilon_1 + \varepsilon_2\log_{10}I_\text{m})\cdot m$ (in the calculation of activity coefficients) is zero at $I_\text{m} = 0$. 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. This conclusion was reached at a time when the present review, wherein we have used the two-epsilon model for a few systems, was nearly complete. However, it is expected that the one- and two-epsilon models will provide similar calculated results for the $\log_{10} K^\circ$. To confirm this, we remodelled a few important cases (solubility of solids containing $Th(SO_4)_2$) as a function of Li_2SO_4 or Na_2SO_4 concentrations (*cf.* Section IX.1.3.3) using a one-epsilon model. Our results show, as expected, that the calculated values of $\log_{10} K^\circ$ using the one- and two-epsilon models differ insignificantly (identical in the Li system and less than 0.028 $\log_{10}$ units for the Na system, far less than the overall uncertainty in the $\log_{10} K^\circ$). As the two-epsilon model has been used in the current and previous volumes, the relevant parameters have been retained 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 theory. The use of the theory 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 theory is illustrated below for a general case of a complex formation reaction. Charges on all species except the hydrogen ions are omitted for brevity.

$$m\,\mathrm{M} + q\,\mathrm{L} + n\,\mathrm{H_2O(l)} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n + n\,\mathrm{H}^+$$

The formation constant of $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$, ${}^*\beta_{q,n,m}$, 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, ${}^*\beta^{\mathrm{o}}_{q,n,m}$ by Eq.(B.4).

$$\begin{aligned}\log_{10}{}^*\beta_{q,n,m} = \log_{10}{}^*\beta^{\mathrm{o}}_{q,n,m} + m\log_{10}\gamma_{\mathrm{M}} + q\log_{10}\gamma_{\mathrm{L}} + n\log_{10}a_{\mathrm{H_2O}} \\ -\log_{10}\gamma_{q,n,m} - n\log_{10}\gamma_{\mathrm{H^+}}\end{aligned} \tag{B.4}$$

The subscript (q,n,m) denotes the complex ion, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$. If the concentrations of N and X are much greater than the concentrations of M, L, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$ 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, γ_{M}, Eq. (B.5) is obtained at 25°C and 1 bar.

$$\log_{10}\gamma_{\mathrm{M}} = \frac{-z^2_{\mathrm{M}}\,0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} + \varepsilon(\mathrm{M,X},I_m)m_{\mathrm{X}} \tag{B.5}$$

Under these conditions, $I_m \approx m_{\mathrm{X}} = m_{\mathrm{N}}$ Substituting the $\log_{10}\gamma_j$ values in Eq. (B.4) with the corresponding forms of Eq. (B.5) and rearranging leads to:

$$\log_{10}{}^*\beta_{q,n,m} - \Delta z^2 D - n\log_{10}a_{\mathrm{H_2O}} = \log_{10}{}^*\beta^{\mathrm{o}}_{q,n,m} - \Delta\varepsilon\, I_m \tag{B.6}$$

where, at 25°C and 1 bar:

$$\Delta z^2 = (m\,z_{\mathrm{M}} - q\,z_{\mathrm{L}} - n)^2 + n - mz^2_{\mathrm{M}} - q\,z^2_{\mathrm{L}} \tag{B.7}$$

$$D = \frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \tag{B.8}$$

$$\Delta\varepsilon = \varepsilon(q,n,m,\mathrm{N\ or\ X}) + n\,\varepsilon(\mathrm{H,\,X}) - q\,\varepsilon(\mathrm{N,\,L}) - m\,\varepsilon(\mathrm{M,\,X}) \tag{B.9}$$

Here $(m z_M - q z_L - n)$, z_M and z_L are the charges of the complex, $M_mL_q(OH)_n$, the metal ion M and the ligand L, respectively.

Equilibria involving $H_2O(l)$ as a reactant or product require a correction for the activity of water, a_{H_2O}. The activity of water in an electrolyte mixture can be calculated as:

$$\log_{10} a_{H_2O} = \frac{-\phi_m \sum_k m_k}{\ln(10) \cdot 55.508} \tag{B.10}$$

where ϕ_m is the osmotic coefficient of the mixture, 55.508 (mol·kg^{-1}) is the molality of pure water, 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 $I_m \approx m_{NX}$, Eq. (B.10) becomes:

$$\log_{10} a_{H_2O} = \frac{-2\, m_{NX}\, \phi_m}{\ln(10) \times 55.508} \tag{B.11}$$

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, $N_{\nu_+}X_{\nu_-}$, 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]).

$$\begin{aligned} 1-\phi_m = {} & \frac{A\ln(10)|z_+z_-|}{I_m(Ba_j)^3}\left[1+Ba_j\sqrt{I_m}-2\ln(1+Ba_j\sqrt{I_m})-\frac{1}{1+Ba_j\sqrt{I_m}}\right] \\ & -\ln(10)\ \varepsilon(\mathrm{N,X})\, m_{NX}\left(\frac{\nu_+\nu_-}{\nu_+ + \nu_-}\right) \end{aligned} \tag{B.12}$$

where ν_+ and ν_- are the number of cations and anions in the salt formula $(\nu_+z_+ = \nu_-z_-)$ and in this case:

$$I_m = \frac{1}{2}|z_+z_-|\, m_{NX}(\nu_+ + \nu_-)$$

Table B-1: Water activities a_{H_2O} for the most common ionic media at various concentrations applying Pitzer’s ion interaction approach 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.

Water activities a_{H_2O} at 298.15 K								
c (M)	$HClO_4$	$NaClO_4$	$LiClO_4$	NH_4ClO_4	$Ba(ClO_4)_2$	HCl	NaCl	LiCl
0.10	0.9966	0.9966	0.9966	0.9967	0.9953	0.9966	0.9966	0.9966
0.25	0.9914	0.9917	0.9912	0.9920	0.9879	0.9914	0.9917	0.9915
0.50	0.9821	0.9833	0.9817	0.9844	0.9740	0.9823	0.9833	0.9826
0.75	0.9720	0.9747	0.9713	0.9769	0.9576	0.9726	0.9748	0.9731
1.00	0.9609	0.9660	0.9602	0.9694	0.9387	0.9620	0.9661	0.9631
1.50	0.9357	0.9476	0.9341	0.9542	0.8929	0.9386	0.9479	0.9412
2.00	0.9056	0.9279	0.9037		*0.8383*	0.9115	0.9284	0.9167
3.00	0.8285	0.8840	0.8280		*0.7226*	0.8459	0.8850	0.8589
4.00	0.7260	0.8331	*0.7309*			0.7643	0.8352	0.7991
5.00	*0.5982*	*0.7744*				0.6677	0.7782	0.7079
6.00	*0.4513*	*0.7075*				*0.5592*		*0.6169*
c (M)	KCl	NH_4Cl	$MgCl_2$	$CaCl_2$	NaBr	HNO_3	$NaNO_3$	$LiNO_3$
0.10	0.9966	0.9966	0.9953	0.9954	0.9966	0.9966	0.9967	0.9966
0.25	0.9918	0.9918	0.9880	0.9882	0.9916	0.9915	0.9919	0.9915
0.50	0.9836	0.9836	0.9744	0.9753	0.9830	0.9827	0.9841	0.9827
0.75	0.9754	0.9753	0.9585	0.9605	0.9742	0.9736	0.9764	0.9733
1.00	0.9671	0.9669	0.9399	0.9436	0.9650	0.9641	0.9688	0.9635
1.50	0.9500	0.9494	0.8939	0.9024	0.9455	0.9439	0.9536	0.9422
2.00	0.9320	0.9311	0.8358	0.8507	0.9241	0.9221	0.9385	0.9188
3.00	0.8933	0.8918	0.6866	0.7168	0.8753	0.8737	0.9079	0.8657
4.00	0.8503	0.8491	0.5083	0.5511	*0.8174*	0.8196	0.8766	0.8052
5.00		*0.8037*		*0.3738*	*0.7499*	0.7612	0.8446	0.7390
6.00					*0.6728*	*0.7006*	*0.8120*	*0.6696*

(Continued on next page)

Table B-1: (continued)

c (M)	NH_4NO_3	Na_2SO_4	$(NH_4)_2SO_4$	Na_2CO_3	K_2CO_3	NaSCN
0.10	0.9967	0.9957	0.9958	0.9956	0.9955	0.9966
0.25	0.9920	0.9900	0.9902	0.9896	0.9892	0.9915
0.50	0.9843	0.9813	0.9814	0.9805	0.9789	0.9828
0.75	0.9768	0.9732	0.9728	0.9720	0.9683	0.9736
1.00	0.9694	0.9653	0.9640	0.9637	0.9570	0.9641
1.50	0.9548	0.9491	0.9455	0.9467	0.9316	0.9438
2.00	0.9403		0.9247	0.9283	0.9014	0.9215
3.00	0.9115		0.8735		0.8235	0.8708
4.00	0.8829		0.8050		0.7195	*0.8115*
5.00	*0.8545*				*0.5887*	*0.7436*
6.00	*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_{H_2O} 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 $H_2O(l)$ 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 NaCl as the dominant electrolyte.

In more complex solutions of high ionic strengths with more than one electrolyte at significant concentrations, *e.g.*, (Na^+, Mg^{2+}, Ca^{2+}) (Cl^-, 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, $H^+ + e^- \rightleftharpoons \frac{1}{2}H_2(g)$, is necessary (*cf.* Example B.3).

B.1.2 Ionic strength corrections at temperatures other than 298.15 K

Values of the Debye-Hückel parameters *A* and *B* in Eqs. (B.2) and (B.12) are listed in Table B-2 for a few 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 may be calculated from the static dielectric constant and the density of water as a function of temperature and pressure, and are also found for example in Refs. [1974HEL/KIR], [1979BRA/PIT], [1981HEL/KIR], [1984ANA/ATK], [1990ARC/WAN].

The term, Ba_j, in the denominator of the Debye-Hückel term, *D*, *cf.* Eq. (B.2), has been assigned in this review a value of 1.5 $\text{kg}^{½}\cdot\text{mol}^{-½}$ at 25°C and 1 bar, *cf.* Section B.1.1 At temperatures and pressures other than the reference and standard state, the following possibilities exist:

- The value of Ba_j is calculated at each temperature assuming that ion sizes are independent of temperature and using the values of *B* listed in Table B-2.
- The value Ba_j is kept constant at 1.5 $\text{kg}^{½}\cdot\text{mol}^{-½}$. Due the variation of *B* with temperature, *cf.* Table B-2, this implies a temperature dependence for ion size parameters. Assuming for the ion size is in reality constant, then it is seen that this simplification introduces an error in *D*, which increases with temperature and ionic strength (this error is less than ± 0.01 at $t \leq 100$°C and $I < 6$ m, and less than ± 0.006 at $t \leq 50$°C and $I \leq 4$ m).
- The value of Ba_j is calculated at each temperature assuming a given temperature variation for a_j and using the values of *B* listed in Table B-2. For example, in the aqueous ionic model of Helgeson and co-workers ([1988TAN/HEL], [1988SHO/HEL], [1989SHO/HEL], [1989SHO/HEL2]) ionic sizes follow the relation: $a_j(T) = a_j(298.15\text{ K, 1 bar}) + |z_j|\,g(T,p)$ [1990OEL/HEL], where $g(T, p)$ is a temperature and pressure function which is tabulated in [1988TAN/HEL], [1992SHO/OEL], and is approximately zero at temperatures below 175°C.

The values of $\varepsilon(j,k,I_m)$, obtained with the methods described in Section B.1.3 at temperatures other than 25°C, will depend on the value adopted for Ba_j. 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°C) the choice $Ba_j = 1.5\ \text{kg}^{½}\cdot\text{mol}^{-½}$ is the simplest one 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 ≤ 0.005 $\text{kg}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ for temperatures below 200°C. Therefore, if values of $\varepsilon(j,k,I_m)$ obtained at 25°C are used in the temperature range 0 to 50°C to perform ionic strength corrections, the error in $\log_{10}\gamma_j / I_m$ will be ≤ 0.13. It is clear that in order to reduce the uncertainties in solubility calculations at $t \neq 25$°C, studies on the variation of $\varepsilon(j,k,I_m)$ values with temperature should be undertaken.

Table B-2: Debye-Hückel constants 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 ± 0.001 at 25°C, and ± 0.006 at 300°C, while for the B parameter the estimated uncertainty ranges from ± 0.0003 at 25°C to ± 0.001 at 300°C.

t(°C)	p(bar)	A ($\mathrm{kg^{1/2}\cdot mol^{-1/2}}$)	$B \times 10^{-10}$ ($\mathrm{kg^{1/2}\cdot mol^{-1/2}\cdot m^{-1}}$)
0	1.00	0.491	0.3246
5	1.00	0.494	0.3254
10	1.00	0.498	0.3261
15	1.00	0.501	0.3268
20	1.00	0.505	0.3277
25	1.00	0.509	0.3284
30	1.00	0.513	0.3292
35	1.00	0.518	0.3300
40	1.00	0.525	0.3312
50	1.00	0.534	0.3326
75	1.00	0.564	0.3371
100	1.013	0.600	0.3422
125	2.32	0.642	0.3476
150	4.76	0.690	0.3533
175	8.92	0.746	0.3593
200	15.5	0.810	0.365
250	29.7	0.980	0.379
300	85.8	1.252	0.396

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 $\varepsilon(\mathrm{H^+},\mathrm{Cl^-})$ can be obtained from published values of $\gamma_{\pm,\,\mathrm{HCl}}$ *versus* m_{HCl} :

$$\begin{aligned}
2\log_{10}\gamma_{\pm,\,\mathrm{HCl}} &= \log_{10}\gamma_{\mathrm{H^+}} + \log_{10}\gamma_{\mathrm{Cl^-}} \\
&= -D + \varepsilon(\mathrm{H^+},\mathrm{Cl^-})\,m_{\mathrm{Cl^-}} \;-D \;+\; \varepsilon(\mathrm{Cl^-},\mathrm{H^+})\,m_{\mathrm{H^+}} \\
\log_{10}\gamma_{\pm,\,\mathrm{HCl}} &= -D + \varepsilon(\mathrm{H^+},\mathrm{Cl^-})\,m_{\mathrm{HCl}}
\end{aligned}$$

By plotting $(\log_{10} \gamma_{\pm,\mathrm{HCl}} + D)$ *versus* m_{HCl} a straight line with the slope $\varepsilon(\mathrm{H}^+, \mathrm{Cl}^-)$ 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:

$$\mathrm{UO_2^{2+}} + \mathrm{Cl^-} \rightleftharpoons \mathrm{UO_2Cl^+} \qquad \text{(B.13)}$$

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) [(a)]	$\log_{10} \beta_{1,m}$ [(b)]	$\log_{10} \beta_{1,m} + 4D$
0.10	– 0.17 ± 0.10	– 0.174	0.264 ± 0.100
0.20	– 0.25 ± 0.10	– 0.254	0.292 ± 0.100
0.26	– 0.35 ± 0.04	– 0.357	0.230 ± 0.040
0.31	– 0.39 ± 0.04	– 0.397	0.220 ± 0.040
0.41	– 0.41 ± 0.04	– 0.420	0.246 ± 0.040
0.51	– 0.32 ± 0.10	– 0.331	0.371 ± 0.100
0.57	– 0.42 ± 0.04	– 0.432	0.288 ± 0.040
0.67	– 0.34 ± 0.04	– 0.354	0.395 ± 0.040
0.89	– 0.42 ± 0.04	– 0.438	0.357 ± 0.040
1.05	– 0.31 ± 0.10	– 0.331	0.491 ± 0.100
1.05	– 0.277 ± 0.260	– 0.298	0.525 ± 0.260
1.61	– 0.24 ± 0.10	– 0.272	0.618 ± 0.100
2.21	– 0.15 ± 0.10	– 0.193	0.744 ± 0.100
2.21	– 0.12 ± 0.10	– 0.163	0.774 ± 0.100
2.82	– 0.06 ± 0.10	– 0.112	0.860 ± 0.100
3.50	0.04 ± 0.10	– 0.027	0.974 ± 0.100

(a) Equilibrium constants for Reaction (B.13) in aqueous $\mathrm{NaClO_4}$ 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, corrected from molarity to molality units as described in Section II.2

The following formula is deduced from Eq. (B.6) for the extrapolation to $I = 0$:

$$\log_{10} \beta_1 + 4D = \log_{10} \beta_1^{\circ} - \Delta\varepsilon I_m \qquad \text{(B.14)}$$

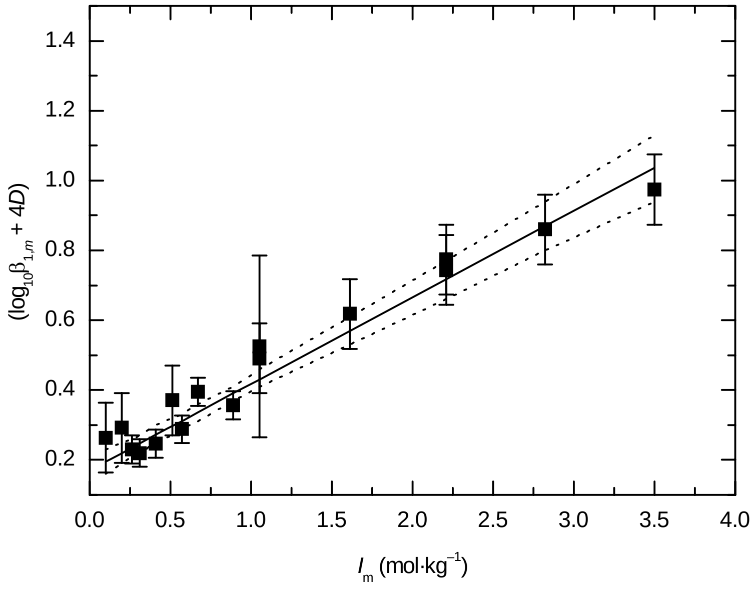
The linear regression is done as described in Appendix C. The following results are obtained:

$$\log_{10} \beta_1^{\circ} = (0.170 \pm 0.021)$$

$$\Delta\varepsilon(\text{B.13}) = -\,(0.248 \pm 0.022)\ \text{kg}\cdot\text{mol}^{-1}.$$

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 $I = 4$ m.



Example B.3:

When using the specific ion interaction theory, the relationship between the redox potential of the couple, $\mathrm{PuO_2^{2+}/Pu^{4+}}$, in a 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:

$$\mathrm{Pt} \left| \mathrm{H_2(g, r)} \right| \mathrm{H^+(r)} \left\| \mathrm{PuO_2^{2+}, Pu^{4+}, H^+, H_2O(l)} \right| \mathrm{Pt}$$

is:

$$\mathrm{PuO_2^{2+} + H_2(g, r) + 4H^+ - 2H^+(r) \rightleftharpoons Pu^{4+} + 2H_2O(l)} \qquad \text{(B.15)}$$

where "r" is used to indicate that $H_2(g)$ and H^+ are at the chemical conditions in the reference electrode compartment, *i.e.*, standard conditions when the reference electrode is the SHE. However, activities of H^+, $H_2O(l)$ and the ratio of activity of $\mathrm{PuO_2^{2+}}$ to $\mathrm{Pu^{4+}}$ depend on the conditions of the experimental measurements (*i.e.*, non-standard conditions, usually high ionic strength to improve the accuracy of the measurement).

For Reaction (B.15):

$$\log_{10} K^{\circ} = \log_{10}\left(\frac{a_{\mathrm{Pu^{4+}}} \cdot a^2_{\mathrm{H_2O}} \cdot a_{\mathrm{H^+(r)}}}{a_{\mathrm{PuO_2^{2+}}} \cdot a^4_{\mathrm{H^+}} \cdot f_{\mathrm{H_2(r)}}}\right).$$

Since by definition of the SHE, $f_{\mathrm{H_2(r)}} = 1$ and $\gamma_{\mathrm{H^+(r)}} = 1$,

$$\log_{10} K^{\circ} = \log_{10} K + \log_{10}\gamma_{\mathrm{Pu^{4+}}} - \log_{10}\gamma_{\mathrm{PuO_2^{2+}}} - 4\log_{10}\gamma_{\mathrm{H^+}} + 2\log_{10} a_{\mathrm{H_2O}},$$

and

$$\log_{10}\gamma_{\mathrm{Pu^{4+}}} = -16D + \varepsilon(\mathrm{Pu^{4+}, ClO_4^-})\ m_{\mathrm{ClO_4^-}}$$

$$\log_{10}\gamma_{\mathrm{PuO_2^{2+}}} = -4D + \varepsilon(\mathrm{PuO_2^{2+}, ClO_4^-})\ m_{\mathrm{ClO_4^-}}$$

$$\log_{10}\gamma_{\mathrm{H^+}} = -D + \varepsilon(\mathrm{H^+, ClO_4^-})\ m_{\mathrm{ClO_4^-}}$$

Hence,

$$\begin{aligned}\log_{10} K^{\circ} = \log_{10} K - 8D + (\varepsilon(\mathrm{Pu^{4+}, ClO_4^-}) - \varepsilon(\mathrm{PuO_2^{2+}, ClO_4^-}) \\ - 4\varepsilon(\mathrm{H^+, ClO_4^-}))\, m_{\mathrm{ClO_4^-}} + 2\log_{10} a_{\mathrm{H_2O}}\end{aligned} \qquad \text{(B.16)}$$

The relationship between the equilibrium constant and the redox potential is:

$$\ln K = \frac{nF}{\mathrm{R}T} E^{\circ\prime} \qquad \text{(B.17)}$$

$$\ln K^{\circ} = \frac{nF}{\mathrm{R}T} E^{\circ}. \qquad \text{(B.18)}$$

$E^{\circ\prime}$ is the redox potential in a medium of ionic strength I, E° 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):

$$E^{o'} - (8D - 2\log_{10} a_{H_2O})\left(\frac{RT\ln(10)}{nF}\right) = E^{o} - \Delta\varepsilon\; m_{ClO_4^-}\left(\frac{RT\ln(10)}{nF}\right) \tag{B.19}$$

For $n = 2$ in the present example and $T = 298.15$ K, Eq.(B.19) becomes:

$$E^{o'}[\mathrm{mV}] - 236.6\ D + 59.16\log_{10} a_{H_2O} = E^{o}[\mathrm{mV}] - 29.58\,\Delta\varepsilon\ m_{ClO_4^-}$$

where

$$\Delta\varepsilon = \varepsilon(\mathrm{Pu}^{4+},\ \mathrm{ClO}_4^-)\ - \varepsilon(\mathrm{PuO}_2^{2+},\ \mathrm{ClO}_4^-)\ - 4\,\varepsilon(\mathrm{H}^+,\ \mathrm{ClO}_4^-)\,.$$

The value of a_{H_2O} can be taken from experimental data or calculated from equations (B.11) and (B.12).

In general, formal potentials are reported with reference to the standard hydrogen electrode, *cf.* Section II.1.6.5, as exemplified in Tables V.2 and V.3 of the uranium NEA review [1992GRE/FUG]. In that case, the H^+ appearing in the reduction reaction is already at standard conditions. For example, experimental data are available on the formal potentials for reactions:

$$\mathrm{PuO}_2^{2+} +\ 4\mathrm{H}^+ + 2\,\mathrm{e}^- \ \rightleftharpoons\ \mathrm{Pu}^{4+} +\ 2\,\mathrm{H_2O(l)} \tag{B.20}$$

and

$$\mathrm{PuO}_2^{2+} +\ \mathrm{e}^- \ \rightleftharpoons\ \mathrm{PuO}_2^{+}\,. \tag{B.21}$$

While Reaction (B.20) corresponds to (B.15), Reaction (B.21) is equivalent to:

$$\mathrm{PuO}_2^{2+} +\ \frac{1}{2}\mathrm{H_2(g)} \ \rightleftharpoons\ \mathrm{PuO}_2^{+} +\ \mathrm{H}^+ \tag{B.22}$$

where the designator "(r)" has been omitted, since in these equations only the H^+ in the reference compartment is relevant.

The cations in Reaction (B.15) represent aqueous species in the ionic media used during the experiments. In Reaction (B.22) H^+ represents the cation in the standard hydrogen electrode, and therefore it is already in standard conditions, and its activity coefficient must not be included in any extrapolation to $I = 0$ of experimental values for Reaction (B.21). Reactions (B.21) and (B.22) are equivalent, as are Reactions (B.15) and (B.20), as can be seen if any of these equations are combined with Reaction (II.27). Hence Eq. (B.19) can be obtained more simply by using Eq. (II.34) for Reaction (B.20).

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 ε, 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 theory described. Table B-4 contains cation interaction coefficients with Cl^-, ClO_4^- and NO_3^-, Table B-5 anion interaction coefficients with Li^+, Na^+ (or NH_4^+) and 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.3. 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 $\varepsilon(j,k)$ (kg·mol^{-1}) for cations j with k = Cl$^-$, ClO_4^- and NO_3^-. 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 $\varepsilon(M^{n+}, Cl^-)$ and $\varepsilon(M^{n+}, NO_3^-)$ reported by Ciavatta [1980CIA] were evaluated without taking chloride and nitrate complexation into account, as discussed in Section B.2.

j	k	$\varepsilon(j,\kappa)$	Comments
H^+	Cl^-	0.12 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.14 ± 0.02	
	NO_3^-	0.07 ± 0.01	
NH_4^+	Cl^-	-0.01 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	$-0.08 \pm 0.04^\dagger$	
	NO_3^-	$-0.06 \pm 0.03^\dagger$	
H_2gly^+	Cl^-	-0.06 ± 0.02	Reported by Ciavatta [1988CIA].
	ClO_4^-	—	
	NO_3^-	—	
H_5edta^+	Cl^-	-0.23 ± 0.15	See Section VIII.3.7 of [2005HUM/AND].
	ClO_4^-	-0.23 ± 0.15	
	NO_3^-	-0.23 ± 0.15	
Tl^+	Cl^-	—	
	ClO_4^-	$-0.21 \pm 0.06^\dagger$	
	NO_3^-	—	
$ZnHCO_3^+$	Cl^-	0.2	Taken from Ferri *et al.* [1985FER/GRE].
	ClO_4^-	—	
	NO_3^-	—	
$CdCl^+$	Cl^-	—	
	ClO_4^-	0.25 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
CdI^+	Cl^-	—	
	ClO_4^-	0.27 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$CdSCN^+$	Cl^-	—	
	ClO_4^-	0.31 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
$HgCl^+$	Cl^-	—	
	ClO_4^-	0.19 ± 0.02	Reported by Ciavatta [1988CIA].
	NO_3^-	—	
Cu^+	Cl^-	—	
	ClO_4^-	0.11 ± 0.01	Reported by Ciavatta [1980CIA].
	NO_3^-	—	
Ag^+	Cl^-	—	
	ClO_4^-	0.00 ± 0.01	Reported by Ciavatta [1980CIA].
	NO_3^-	– 0.12 ± 0.05†	
$NiOH^+$	Cl^-	– 0.01 ± 0.07	Evaluated in [2005GAM/BUG] (Section V.3.1.1) for the reaction $Ni^{2+} + H_2O \rightleftharpoons NiOH^+ + H^+$ from $\Delta\varepsilon$ in chloride media / perchlorate media.
	ClO_4^-	0.14 ± 0.07	
	NO_3^-	—	
NiF^+	Cl^-	—	
	ClO_4^-	0.34 ± 0.08	Derived from $\Delta\varepsilon = \varepsilon(NiF^+,ClO_4^-) - \varepsilon(Ni^{2+},ClO_4^-) - \varepsilon(Na^+,F^-) = -(0.049$ ((0.060) $kg{\cdot}mol^{-1}$ (see Section V.4.2.3 of [2005GAM/BUG]).
	NO_3^-	—	
$NiCl^+$	Cl^-	—	
	ClO_4^-	0.47 ± 0.06	See details in Section V.4.2.4 of [2005GAM/BUG].
	NO_3^-	—	
$NiNO_3^+$	Cl^-	—	
	ClO_4^-	0.44 ± 0.14	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.
	NO_3^-	—	
$Ni(H_2cit)^+$	Cl^-	—	
	ClO_4^-	0.12 ± 0.5	See Section VII.7 in [2005HUM/AND].
	NO_3^-	—	
$NiBr^+$	Cl^-	—	
	ClO_4^-	0.59 ± 0.10	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.
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$NiHS^+$	Cl^-	—	
	ClO_4^-	-0.85 ± 0.39	See details in [2005GAM/BUG], Section V.5.1.1.2.
	NO_3^-	—	
$NiSCN^+$	Cl^-	—	
	ClO_4^-	0.31 ± 0.04	Derived from $\Delta\varepsilon = \varepsilon(NiSCN^-, Na^+) - \varepsilon(SCN^-, Na^+) - \varepsilon(Ni^{2+}, ClO_4^-) = -(0.109 \pm 0.025)\ kg{\cdot}mol^{-1}$ (see [2005GAM/BUG], Section V.7.1.3.1).
	NO_3^-	—	
YCO_3^+	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	
$Am(OH)_2^+$	Cl^-	-0.27 ± 0.20	Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from Δε (in NaCl solution) for the reactions $An^{3+} + nH_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + n\,H^+$.
	ClO_4^-	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
AmF_2^+	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmSO_4^+$	Cl^-	—	
	ClO_4^-	0.22 ± 0.08	Evaluated in [1995SIL/BID].
	NO_3^-	—	
$AmCO_3^+$	Cl^-	0.01 ± 0.05	Evaluated in [2003GUI/FAN] (Section 12.6.1.1.1) from Δε (in NaCl solution) for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-n)}$ (based on $\varepsilon(Am^{3+}, Cl^-) = (0.23 \pm 0.02)\ kg{\cdot}mol^{-1}$ and $\varepsilon(Na^+, CO_3^{2-}) = -(0.08 \pm 0.03)\ kg{\cdot}mol^{-1}$.
	ClO_4^-	0.17 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$Am(ox)^+$	Cl^-	—	
	ClO_4^-	0.08 ± 0.10	See Section VI.13 of [2005HUM/AND].
	NO_3^-	—	

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Table B-4: (continued)

j	*k*	$\varepsilon(j,\kappa)$	Comments
PuO_2^+	Cl^-	—	
	ClO_4^-	0.24 ± 0.05	Derived from $\Delta\varepsilon = \varepsilon(PuO_2^{2+},ClO_4^-) - \varepsilon(PuO_2^+,ClO_4^-) = (0.22 \pm 0.03)$ kg·mol^{-1} [1995CAP/VIT]. In [1992GRE/FUG], $\varepsilon(PuO_2^+,ClO_4^-) = (0.17 \pm 0.05)$ kg·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_3^-	—	
PuO_2F^+	Cl^-	—	
	ClO_4^-	0.29 ± 0.11	Estimated in [2001LEM/FUG] by analogy with Δε of the corresponding Np(IV) reaction.
	NO_3^-	—	
PuO_2Cl^+	Cl^-	—	
	ClO_4^-	0.50 ± 0.09	From Δε evaluated by Giffaut [1994GIF].
	NO_3^-	—	
NpO_2^+	Cl^-	0.09 ± 0.05	See Section 12.1 of [2001LEM/FUG].
	ClO_4^-	0.25 ± 0.05	Derived from $\Delta\varepsilon = \varepsilon(NpO_2^{2+},ClO_4^-) - \varepsilon(NpO_2^+,ClO_4^-) = (0.21 \pm 0.03)$ kg·mol^{-1} [1987RIG/VIT], [1989RIG/ROB] and [1990RIG].
	NO_3^-	—	
NpO_2OH^+	Cl^-	—	
	ClO_4^-	− 0.06 ± 0.40	Estimated in [2001LEM/FUG].
	NO_3^-	—	
$(NpO_2)_3(OH)_5^+$	Cl^-	—	
	ClO_4^-	0.45 ± 0.20	See Section 8.1.2 of [2001LEM/FUG].
	NO_3^-	—	
NpO_2F^+	Cl^-	—	
	ClO_4^-	0.29 ± 0.12	Estimated in [2001LEM/FUG] by analogy with Δε of the corresponding U(IV) reaction.
	NO_3^-	—	
NpO_2Cl^+	Cl^-	—	
	ClO_4^-	0.50 ± 0.14	Estimated in [2001LEM/FUG] by analogy with Δε of the corresponding Pu(VI) reaction.
	NO_3^-	—	
$NpO_2IO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(NpO_2IO_3^+,ClO_4^-) \approx \varepsilon(UO_2IO_3^+,ClO_4^-)$.
	NO_3^-	—	

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Table B-4: (continued)

j	*k*	$\varepsilon(j,\kappa)$	Comments
$Np(SCN)_3^+$	Cl^-	—	
	ClO_4^-	0.17 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(Np(SCN)_3^+, ClO_4^-) \approx \varepsilon(AmF_2^+, ClO_4^-)$.
	NO_3^-	—	
UO_2^+	Cl^-	—	
	ClO_4^-	0.26 ± 0.03	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, ClO_4^-) = (0.46 \pm 0.03)$ kg·mol^{-1}.
	NO_3^-	—	
UO_2OH^+	Cl^-	—	
	ClO_4^-	-0.06 ± 0.40	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ kg·mol^{-1}, where X = Cl^-, ClO_4^- and NO_3^-.
	NO_3^-	0.51 ± 1.4	
$(UO_2)_3(OH)_5^+$	Cl^-	0.81 ± 0.17	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ kg·mol^{-1}, where X = Cl^-, ClO_4^- and NO_3^-.
	ClO_4^-	0.45 ± 0.15	
	NO_3^-	0.41 ± 0.22	
UF_3^+	Cl^-	0.1 ± 0.1	Estimated in [1992GRE/FUG].
	ClO_4^-	0.1 ± 0.1	
	NO_3^-	—	
UO_2F^+	Cl^-	0.04 ± 0.07	Taken from Riglet *et al.* [1989RIG/ROB], where the following assumptions were made: $\varepsilon(Np^{3+}, ClO_4^-) \approx \varepsilon(Pu^{3+}, ClO_4^-) =$ 0.49 kg·mol^{-1} as for other (M^{3+}, ClO_4^-) interactions, and $\varepsilon(NpO_2^{2+}, ClO_4^-) \approx \varepsilon(PuO_2^{2+}, ClO_4^-) \approx \varepsilon(UO_2^{2+}, ClO_4^-) = 0.46$ kg·mol^{-1}.
	ClO_4^-	0.28 ± 0.04	See Section 9.4.2.2.1 of [2003GUI/FAN].
	NO_3^-	—	
UO_2Cl^+	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+}, X) = (0.46 \pm 0.03)$ kg·mol^{-1}, where X = Cl^-, ClO_4^- and NO_3^-.
	NO_3^-	—	
$UO_2ClO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
UO_2Br^+	Cl^-	—	
	ClO_4^-	0.24 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2BrO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$UO_2IO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2N_3^+$	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$UO_2NO_3^+$	Cl^-	—	
	ClO_4^-	0.33 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
UO_2SCN^+	Cl^-	—	
	ClO_4^-	0.22 ± 0.04	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$Th(OH)_3^+$	Cl^-	0.06 ± 0.05	See Table VII-16 in Section VII.3.6.1 of this review.
	ClO_4^-	0.15 ± 0.10	
	NO_3^-	0.05 ± 0.15	
ThF_3^+	Cl^-	—	
	ClO_4^-	0.1 ± 0.1	See Table VIII-8 in Section VIII.1.2.1 of this review.
	NO_3^-	0.0 ± 0.2	
$Th(NO_3)_3^+$	Cl^-	—	
	ClO_4^-	0.25 ± 0.15	Evaluated in Section X.1.3.3 of this review, using $\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)$ kg·mol^{-1} where X = ClO_4^- and NO_3^-.
	NO_3^-	0.25 ± 0.15	
H_6edta^{2+}	Cl^-	-0.20 ± 0.16	Evaluated in [2005HUM/AND] (Section VIII.3.7).
	ClO_4^-	-0.20 ± 0.16	
	NO_3^-	-0.20 ± 0.16	
Pb^{2+}	Cl^-	—	
	ClO_4^-	0.15 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.20 \pm 0.12^{\dagger}$	
$AlOH^{2+}$	Cl^-	0.09	Taken from Hedlund [1988HED].
	ClO_4^-	0.31	
	NO_3^-	—	
$Al_2CO_3(OH)_2^{2+}$	Cl^-	0.26	Taken from Hedlund [1988HED].
	ClO_4^-	—	
	NO_3^-	—	
Zn^{2+}	Cl^-	—	
	ClO_4^-	0.33 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.16 ± 0.02	

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Table B-4: (continued)

j	*k*	$\varepsilon(j,k)$	Comments
$ZnCO_3^{2+}$	Cl^-	0.35 ± 0.05	Taken from Ferri *et al.* [1985FER/GRE].
	ClO_4^-	—	
	NO_3^-	—	
Cd^{2+}	Cl^-	—	
	ClO_4^-	—	
	NO_3^-	0.09 ± 0.02	Reported by Ciavatta [1980CIA].
Hg^{2+}	Cl^-	—	
	ClO_4^-	0.34 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.1 \pm 0.1^{\dagger}$	
Hg_2^{2+}	Cl^-	—	
	ClO_4^-	0.09 ± 0.02	Reported by Ciavatta [1980CIA].
	NO_3^-	$-0.2 \pm 0.1^{\dagger}$	
Cu^{2+}	Cl^-	0.08 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.32 ± 0.02	
	NO_3^-	0.11 ± 0.01	
Ni^{2+}	Cl^-	0.17 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.370 ± 0.032	Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $Ni(ClO_4)_2$ solution ([2005GAM/BUG], Section V.4.3).
	NO_3^-	0.182 ± 0.010	Derived from the ionic strength dependence of the osmotic and mean activity coefficient of $Ni(NO_3)_2$ solution ([2005GAM/BUG], Section V.6.1.2.1).
Co^{2+}	Cl^-	0.16 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.34 ± 0.03	
	NO_3^-	0.14 ± 0.01	
$FeOH^{2+}$	Cl^-	—	
	ClO_4^-	0.38	Taken from Spahiu [1983SPA].
	NO_3^-	—	
$FeSCN^{2+}$	Cl^-	—	
	ClO_4^-	0.45	Taken from Spahiu [1983SPA].
	NO_3^-	—	
Mn^{2+}	Cl^-	0.13 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	—	
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$YHCO_3^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	
$AmOH^{2+}$	Cl^-	-0.04 ± 0.07	Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from $\Delta\varepsilon$ (in NaCl solution) for the reactions $An^{3+} + n\,H_2O(l) \rightleftharpoons An(OH)_n^{(3-n)} + n\,H^+$.
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
AmF^{2+}	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmCl^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
AmN_3^{2+}	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmNO_2^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmNO_3^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmH_2PO_4^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
$AmSCN^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [1995SIL/BID].
	NO_3^-	—	
PuO_2^{2+}	Cl^-	—	
	ClO_4^-	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_3^-	—	

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Table B-4: (continued)

j	*k*	$\varepsilon(j,\kappa)$	Comments
PuF_2^{2+}	Cl^-		
	ClO_4^-	0.36 ± 0.17	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	
$PuCl^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.16	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Am(III) reaction.
	NO_3^-	—	
PuI^{2+}	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(PuI^{2+},ClO_4^-) \approx \varepsilon(AmSCN^{2+},ClO_4^-)$ and $\varepsilon(I^-,NH_4^+) \approx \varepsilon(SCN^-,Na^+)$.
	NO_3^-	—	
$PuSCN^{2+}$	Cl^-	—	
	ClO_4^-	0.39 ± 0.04	Estimated in [2001LEM/FUG] by assuming $\varepsilon(PuSCN^{2+},ClO_4^-) \approx \varepsilon(AmSCN^{2+},ClO_4^-)$.
	NO_3^-	—	
NpO_2^{2+}	Cl^-	—	
	ClO_4^-	0.46 ± 0.05	By analogy with $\varepsilon(UO_2^{2+},ClO_4^-)$ as derived from isopiestic measurements noted in [1992GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
$(NpO_2)_2(OH)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.57 ± 0.10	See Section 8.1.2 in [2001LEM/FUG].
	NO_3^-	—	
NpF_2^{2+}	Cl^-	—	
	ClO_4^-	0.38 ± 0.17	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	
$NpSO_4^{2+}$	Cl^-	—	
	ClO_4^-	0.48 ± 0.11	Estimated on Section 10.1.2.1 of [2001LEM/FUG].
	NO_3^-	—	
$Np(SCN)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.38 ± 0.20	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
UO_2^{2+}	Cl^-	0.21 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.46 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.24 ± 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 *et al*. used $\varepsilon(UO_2^{2+},X) = (0.46 \pm 0.03)$ kg·mol^{-1}, for X = Cl^-, ClO_4^- and NO_3^-.
$(UO_2)_2(OH)_2^{2+}$	Cl^-	0.69 ± 0.07	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+},X) = (0.46 \pm 0.03)$ kg·mol^{-1}, where X = Cl^-, ClO_4^- and NO_3^-.
	ClO_4^-	0.57 ± 0.07	
	NO_3^-	0.49 ± 0.09	
$(UO_2)_3(OH)_4^{2+}$	Cl^-	0.50 ± 0.18	Evaluated in [1992GRE/FUG], using $\varepsilon(UO_2^{2+},X) = (0.46 \pm 0.03)$ kg·mol^{-1}, where X = Cl^-, ClO_4^- and NO_3^-.
	ClO_4^-	0.89 ± 0.23	
	NO_3^-	0.72 ± 1.0	
UF_2^{2+}	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	Estimated in [1992GRE/FUG].
	NO_3^-	—	
USO_4^{2+}	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	Estimated in [1992GRE/FUG].
	NO_3^-	—	
$U(NO_3)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.49 ± 0.14	Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+},X) =$ (0.76 ± 0.06) kg·mol^{-1}.
	NO_3^-	—	
$Th(OH)_2^{2+}$	Cl^-	0.13 ± 0.05	Calculated in Section VII.3.6.1 of this review.
	ClO_4^-	0.33 ± 0.10	
	NO_3^-	0.10 ± 0.15	
ThF_2^{2+}	Cl^-	—	
	ClO_4^-	0.3 ± 0.1	See Table VIII-8 in Section VIII.1.2.1 of this review.
	NO_3^-	0.15 ± 0.20	
$ThSO_4^{2+}$	Cl^-	0.14 ± 0.15	See Section IX.1.3.2 of this review.
	ClO_4^-	0.3 ± 0.1	
	NO_3^-	—	
$Th(N_3)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.40 ± 0.15	Estimated in Section X.1.2 of this review.
	NO_3^-	—	

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Table B-4: (continued)

j	*k*	$\varepsilon(j,\kappa)$	Comments
$Th(NO_3)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.43 ± 0.18	Estimated in Section X.1.3.3 of this review, using $\varepsilon(Th^{4+}, X) = (0.70 \pm 0.10)\ kg{\cdot}mol^{-1}$ for X = ClO_4^- and NO_3^-.
	NO_3^-	0.43 ± 0.18	
$Th(H_2PO_4)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.4 ± 0.1	Estimated in Section X.2.3.2 of this review.
	NO_3^-	—	
$Th(SCN)_2^{2+}$	Cl^-	—	
	ClO_4^-	0.38 ± 0.20	See Section XI.1.3.6.1 of this review.
	NO_3^-	—	
Mg^{2+}	Cl^-	0.19 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.33 ± 0.03	
	NO_3^-	0.17 ± 0.01	
Ca^{2+}	Cl^-	0.14 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.27 ± 0.03	
	NO_3^-	0.02 ± 0.01	
Ba^{2+}	Cl^-	0.07 ± 0.01	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.15 ± 0.02	
	NO_3^-	-0.28 ± 0.03	
Al^{3+}	Cl^-	0.33 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	—	
	NO_3^-	—	
Ni_2OH^{3+}	Cl^-	—	
	ClO_4^-	0.59 ± 0.15	By assuming $\varepsilon(Ni_2OH^{3+}, ClO_4^-) \approx \varepsilon(Be_2OH^{3+}, ClO_4^-)$, see Section V.3.1.1 in [2005GAM/BUG].
	NO_3^-	—	
Fe^{3+}	Cl^-	—	
	ClO_4^-	0.56 ± 0.03	Reported by Ciavatta [1980CIA].
	NO_3^-	0.42 ± 0.08	
Cr^{3+}	Cl^-	0.30 ± 0.03	Reported by Ciavatta [1980CIA].
	ClO_4^-	—	
	NO_3^-	0.27 ± 0.02	Reported by Ciavatta [1980CIA].
La^{3+}	Cl^-	0.22 ± 0.02	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.47 ± 0.03	
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$La^{3+} \rightarrow Lu^{3+}$	Cl^-	—	
	ClO_4^-	0.47 → 0.52	Taken from Spahiu [1983SPA].
	NO_3^-	—	
Am^{3+}	Cl^-	0.23 ± 0.02	The $\varepsilon(An^{3+},Cl^-)$ for An = Am and Cm is assumed to equal to $\varepsilon(Nd^{3+},Cl^-)$ which is calculated from trace activity coefficients of Nd^{3+} ion in 0–4 m NaCl. These trace activity coefficients are based on the ion interaction Pitzer parameters evaluated in [1997KON/FAN] from osmotic coefficients in aqueous $NdCl_3$ – NaCl and $NdCl_3$ – $CaCl_2$.
	ClO_4^-	0.49 ± 0.03	Estimated in [1995SIL/BID].
	NO_3^-	—	
Pu^{3+}	Cl^-	—	
	ClO_4^-	0.49 ± 0.05	Estimated by analogy with $\varepsilon(Ho^{3+},ClO_4^-)$ [1983SPA] as in [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
$PuOH^{3+}$	Cl^-	—	
	ClO_4^-	0.50 ± 0.05	Estimated in [2001LEM/FUG].
	NO_3^-	—	
PuF^{3+}	Cl^-	—	
	ClO_4^-	0.56 ± 0.11	Estimated in [2001LEM/FUG].
	NO_3^-	—	
$PuCl^{3+}$	Cl^-	—	
	ClO_4^-	0.85 ± 0.09	Derived from the $\Delta\varepsilon$ evaluated in [2001LEM/FUG].
	NO_3^-	—	
$PuBr^{3+}$	Cl^-	—	
	ClO_4^-	0.58 ± 0.16	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction, and by assuming $\varepsilon(Br^-,H^+) \approx \varepsilon(Br^-,Na^+)$.
	NO_3^-	—	
Np^{3+}	Cl^-	—	
	ClO_4^-	0.49 ± 0.05	Estimated by analogy with $\varepsilon(Ho^{3+},ClO_4^-)$ [1983SPA] as in previous books in this series [1992GRE/FUG], [1995SIL/BID]. The uncertainty is increased because the value is estimated by analogy.
	NO_3^-	—	
$NpOH^{3+}$	Cl^-	—	
	ClO_4^-	0.50 ± 0.05	Estimated in [2001LEM/FUG].
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
NpF^{3+}	Cl^-	—	
	ClO_4^-	0.58 ± 0.07	Evaluated in [2001LEM/FUG].
	NO_3^-	—	
$NpCl^{3+}$	Cl^-	—	
	ClO_4^-	0.81 ± 0.09	Derived from the $\Delta\varepsilon$ selected in [2001LEM/FUG].
	NO_3^-	—	
NpI^{3+}	Cl^-	—	
	ClO_4^-	0.77 ± 0.26	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) chloride reaction, and by assuming $\varepsilon(I^-, H^+) \approx \varepsilon(I^-, Na^+)$.
	NO_3^-	—	
$NpSCN^{3+}$	Cl^-	0.76 ± 0.12	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.
	ClO_4^-	—	
	NO_3^-	—	
U^{3+}	Cl^-	—	
	ClO_4^-	0.49 ± 0.05	Evaluated in [2001LEM/FUG] by analogy with $\varepsilon(Am^{3+}, ClO_4^-)$.
	NO_3^-	—	
UOH^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Evaluated in [1992GRE/FUG].
	NO_3^-	—	
UF^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Estimated in [1992GRE/FUG].
	NO_3^-	—	
UCl^{3+}	Cl^-	—	
	ClO_4^-	0.50 ± 0.10	Estimated in [2001LEM/FUG] by analogy with $\Delta\varepsilon$ of the corresponding Pu(VI) reaction and using $\varepsilon(U^{4+}, X) = (0.76 \pm 0.06)$ $kg\cdot mol^{-1}$ for $X = Cl^-$ and ClO_4^-.
	NO_3^-	—	
UBr^{3+}	Cl^-	—	
	ClO_4^-	0.52 ± 0.10	Estimated in [1992GRE/FUG] using $\varepsilon(U^{4+}, X) = (0.76 \pm 0.06)$ $kg\cdot mol^{-1}$, for $X = Br^-$ and ClO_4^-.
	NO_3^-	—	
UI^{3+}	Cl^-	—	
	ClO_4^-	0.55 ± 0.10	Estimated in [1992GRE/FUG] using $\varepsilon(U^{4+}, X) = (0.76 \pm 0.06)$ $kg\cdot mol^{-1}$, for $X = I^-$ and ClO_4^-.
	NO_3^-	—	
	NO_3^-	0.56 ± 0.14	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
UNO_3^{3+}	Cl^-	—	
	ClO_4^-	0.62 ± 0.08	Evaluated in [1992GRE/FUG] using $\varepsilon(U^{4+},X) = (0.76 \pm 0.06)$ kg·mol^{-1} for X = NO_3^- and ClO_4^-.
	NO_3^-	—	
$Th(OH)^{3+}$	Cl^-	0.19 ± 0.05	See Table VII-18 in Section VII.3.6.1 of this review.
	ClO_4^-	0.48 ± 0.08	
	NO_3^-	0.20 ± 0.15	
ThF^{3+}	Cl^-	—	
	ClO_4^-	0.48 ± 0.08	Estimated in Section VIII.1.2.1 of this review (Table VIII-8).
	NO_3^-	0.25 ± 0.20	
$ThCl^{3+}$	Cl^-	0.62 ± 0.11	Calculated in Section VIII.2.2.1.2 of this review using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = Cl^- and ClO_4^-
	ClO_4^-	0.62 ± 0.11	
	NO_3^-	—	
$ThClO_3^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.11	Calculated in Section VIII.2.2.2 of this review using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = ClO_3^- and ClO_4^-
	NO_3^-	—	
$ThBr^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.11	Calculated in Section VIII.3.2.1 of this review using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = Br^- and ClO_4^-
	NO_3^-	—	
$ThBrO_3^{3+}$	Cl^-	—	
	ClO_4^-	0.62 ± 0.08	Calculated in Section VIII.3.2.2 of this review using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = BrO_3^- and ClO_4^-
	NO_3^-	—	
ThN_3^{3+}	Cl^-	—	
	ClO_4^-	0.55 ± 0.15	See Section X.1.2 of this review.
	NO_3^-	—	
$Th(NO_3)^{3+}$	Cl^-	—	
	ClO_4^-	0.56 ± 0.14	Calculated in Section X.1.3.3 of this review using $\varepsilon(Th^{4+},X) = (0.70 \pm 0.10)$ kg·mol^{-1}, for X = ClO_4^- and NO_3^-.
	NO_3^-	0.56 ± 0.14	
$Th(H_2PO_4)^{3+}$	Cl^-	—	
	ClO_4^-	0.5 ± 0.1	Estimated in Section X.2.3.2 of this review.
	NO_3^-	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$\mathrm{Th(H_2PO_4)(H_3PO_4)^{3+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.5 ± 0.1	Estimated in Section X.2.3.2 of this review.
	$\mathrm{NO_3^-}$	—	
$\mathrm{Th(SCN)^{3+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.50 ± 0.10	See Section XI.1.3.6.1 of this review.
	$\mathrm{NO_3^-}$	—	
$\mathrm{Be_2OH^{3+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.50 ± 0.05	Taken from [1986BRU], where the following assumptions were made: $\varepsilon(\mathrm{Be^{2+}},\mathrm{ClO_4^-})$ = 0.30 kg·mol^{-1} as for other $\varepsilon(\mathrm{M^{2+}},\mathrm{ClO_4^-})$; $\varepsilon(\mathrm{Be^{2+}},\mathrm{Cl^-})$ = 0.17 kg·mol^{-1} as for other $\varepsilon(\mathrm{M^{2+}},\mathrm{Cl^-})$ and $\varepsilon(\mathrm{Be^{2+}},\mathrm{NO_3^-})$ = 0.17 kg·mol^{-1} as for other $\varepsilon(\mathrm{M^{2+}},\mathrm{NO_3^-})$.
	$\mathrm{NO_3^-}$	—	
$\mathrm{Be_3(OH)_3^{3+}}$	$\mathrm{Cl^-}$	0.30 ± 0.05	Taken from [1986BRU], where the following assumptions were made: $\varepsilon(\mathrm{Be^{2+}},\mathrm{ClO_4^-})$ = 0.30 kg·mol^{-1} as for other $\varepsilon(\mathrm{M^{2+}},\mathrm{ClO_4^-})$; $\varepsilon(\mathrm{Be^{2+}},\mathrm{Cl^-})$ = 0.17 kg·mol^{-1} as for other $\varepsilon(\mathrm{M^{2+}},\mathrm{Cl^-})$ and $\varepsilon(\mathrm{Be^{2+}},\mathrm{NO_3^-})$ = 0.17 kg·mol^{-1} as for other $\varepsilon(\mathrm{M^{2+}},\mathrm{NO_3^-})$.
	$\mathrm{ClO_4^-}$	0.51 ± 0.05	Evaluated in [1992GRE/FUG] using $\varepsilon(\mathrm{U^{4+}},\mathrm{X})$ = (0.76 ± 0.06) kg·mol^{-1}.
	$\mathrm{NO_3^-}$	0.29 ± 0.05	Taken from [1986BRU], where the following assumptions were made: $\varepsilon(\mathrm{Be^{2+}},\mathrm{ClO_4^-})$ = 0.30 kg·mol^{-1} as for other $\varepsilon(\mathrm{M^{2+}},\mathrm{ClO_4^-})$; $\varepsilon(\mathrm{Be^{2+}},\mathrm{Cl^-})$ = 0.17 kg·mol^{-1} as for other $\varepsilon(\mathrm{M^{2+}},\mathrm{Cl^-})$ and $\varepsilon(\mathrm{Be^{2+}},\mathrm{NO_3^-})$ = 0.17 kg·mol^{-1} as for other $\varepsilon(\mathrm{M^{2+}},\mathrm{NO_3^-})$
$\mathrm{Al_3HCO_3(OH)_4^{4+}}$	$\mathrm{Cl^-}$	0.41	Taken from Hedlund [1988HED].
	$\mathrm{ClO_4^-}$	—	
	$\mathrm{NO_3^-}$	—	
$\mathrm{Ni_4(OH)_4^{4+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	1.08 ± 0.08	Derived from $\Delta\varepsilon = 4\varepsilon(\mathrm{H^+},\mathrm{ClO_4^-}) - \varepsilon(\mathrm{Ni_4OH_4^{4+}},\mathrm{ClO_4^-}) - 4\varepsilon(\mathrm{Ni^{2+}},\mathrm{ClO_4^-})$ = (0.16 ± 0.05) kg·mol^{-1} (see [2005GAM/BUG], Section V.3.1.1.1).
	$\mathrm{NO_3^-}$	—	
$\mathrm{Fe_2(OH)_2^{4+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.82	Taken from Spahiu [1983SPA].
	$\mathrm{NO_3^-}$	—	

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$Y_2\,CO_3^{4+}$	Cl^-	—	
	ClO_4^-	0.80 ± 0.04	Taken from Spahiu [1983SPA].
	NO_3^-	—	
Pu^{4+}	Cl^-	0.37 ± 0.05	Calculated in Section VI.3.1 of this review.
	ClO_4^-	0.82 ± 0.07	Derived from $\Delta\varepsilon = \varepsilon(Pu^{4+},ClO_4^-) - \varepsilon(Pu^{3+},ClO_4^-) =$ (0.33 ± 0.035) kg·mol^{-1} [1995CAP/VIT]. Uncertainty estimated in [2001LEM/FUG]. In the [1992GRE/FUG], $\varepsilon(Pu^{3+},ClO_4^-) =$ (1.03 ± 0.05) kg·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.
	NO_3^-	—	
Np^{4+}	Cl^-	—	
	ClO_4^-	0.84 ± 0.06	Derived from $\Delta\varepsilon = \varepsilon(Np^{4+},ClO_4^-) - \varepsilon(Np^{3+},ClO_4^-) =$ (0.35 ± 0.03) kg·mol^{-1} [1989ROB], [1989RIG/ROB], [1990RIG].
	NO_3^-	—	
U^{4+}	Cl^-	—	
	ClO_4^-	0.76 ± 0.06	Estimated in [1992GRE/FUG]. Using the measured value of $\Delta\varepsilon = \varepsilon(U^{4+},ClO_4^-) - \varepsilon(U^{3+},ClO_4^-) =$ (0.35 ± 0.06) kg·mol^{-1} p.89 [1990RIG], where the uncertainty is recalculated in [2001LEM/FUG] from the data given in this thesis, and $\varepsilon(U^{3+},ClO_4^-)$ = (0.49 ± 0.05) kg·mol^{-1}, a value for $\varepsilon(U^{4+},ClO_4^-)$ can be calculated in the same way as is done for $\varepsilon(Np^{4+},ClO_4^-)$ and $\varepsilon(Pu^{4+},ClO_4^-)$. This value, $\varepsilon(U^{4+},ClO_4^-) =$ (0.84 ± 0.06) kg·mol^{-1} is consistent with that tabulated $\varepsilon(U^{4+},ClO_4^-) =$ (0.76 ± 0.06) kg·mol^{-1}, since the uncertainties overlap. The authors of [2001LEM/FUG] do not believe that a change in the previously selected value for $\varepsilon(U^{4+},ClO_4^-)$ is justified at present.
	NO_3^-	—	
Th^{4+}	Cl^-	0.25 ± 0.03	Reported by Ciavatta [1980CIA].
	ClO_4^-	0.70 ± 0.10	Evaluated in Section VI.3.1 of this review.
	NO_3^-	0.31 ± 0.12	Evaluated in Section VI.3.1 of this review.

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Table B-4: (continued)

j	k	$\varepsilon(j,\kappa)$	Comments
$\mathrm{Th_4(OH)_{12}^{4+}}$	$\mathrm{Cl^-}$	0.25 ± 0.20	See Section VII.3.4.1.3 of this review.
	$\mathrm{ClO_4^-}$	0.56 ± 0.42	
	$\mathrm{NO_3^-}$	0.42 ± 0.50	
$\mathrm{Th(H_3PO_4)^{4+}}$	$\mathrm{Cl^-}$	—	
	$\mathrm{ClO_4^-}$	0.7 ± 0.1	Estimated in Section X.2.3.2 of this review.
	$\mathrm{NO_3^-}$	—	
$\mathrm{Al_3(OH)_4^{5+}}$	$\mathrm{Cl^-}$	0.66	Taken from Hedlund [1988HED]
	$\mathrm{ClO_4^-}$	1.30	Taken from Hedlund [1988HED]
	$\mathrm{NO_3^-}$	—	
$\mathrm{Th_2(OH)_3^{5+}}$	$\mathrm{Cl^-}$	0.29 ± 0.09	Calculated in Section VII.3.4.1.1 of this review.
	$\mathrm{ClO_4^-}$	0.91 ± 0.21	
	$\mathrm{NO_3^-}$	0.69 ± 0.25	
$\mathrm{Th_2(OH)_2^{6+}}$	$\mathrm{Cl^-}$	0.40 ± 0.16	Evaluated in Section VII.3.4.1.1 of this review.
	$\mathrm{ClO_4^-}$	1.22 ± 0.24	
	$\mathrm{NO_3^-}$	0.69 ± 0.26	
$\mathrm{Th_4(OH)_8^{8+}}$	$\mathrm{Cl^-}$	0.70 ± 0.20	Evaluated in Section VII.3.4.1.3 of this review.
	$\mathrm{ClO_4^-}$	1.69 ± 0.42	
	$\mathrm{NO_3^-}$	1.59 ± 0.51	
$\mathrm{Th_6(OH)_{15}^{9+}}$	$\mathrm{Cl^-}$	0.72 ± 0.30	See details in Section VII.3.4.1.4 of this review.
	$\mathrm{ClO_4^-}$	1.85 ± 0.74	
	$\mathrm{NO_3^-}$	2.20 ± 0.77	
$\mathrm{Th_6(OH)_{14}^{10+}}$	$\mathrm{Cl^-}$	0.83 ± 0.30	Estimated in Section VII.3.4.1.4 of this review.
	$\mathrm{ClO_4^-}$	2.2 ± 0.3	
	$\mathrm{NO_3^-}$	2.9 ± 0.5	

Table B-5: Ion interaction coefficients, ε(*j*,*k*) (kg·mol^{-1}), for anions *j* with *k* = Li$^+$, Na$^+$ and 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*	ε(*j*,*k*)	Comments
OH$^-$	Li$^+$	− 0.02 ± 0.03†	
	Na$^+$	0.04 ± 0.01	Reported by Ciavatta [1980CIA].
	K$^+$	0.09 ± 0.01	
F$^-$	Li$^+$	—	
	Na$^+$	0.02 ± 0.02	Evaluated in [1992GRE/FUG].
	K$^+$	0.03 ± 0.02	[1988CIA]
HF$_2^-$	Li$^+$	—	
	Na$^+$	− 0.11 ± 0.06	Evaluated in [1992GRE/FUG].
	K$^+$	—	
Cl$^-$	Li$^+$	0.10 ± 0.01	Reported by Ciavatta [1980CIA].
	Na$^+$	0.03 ± 0.01	
	K$^+$	0.00 ± 0.01	
ClO$_3^-$	Li$^+$	—	
	Na$^+$	− 0.01 ± 0.02	Reported by Ciavatta [1980CIA].
	K$^+$	—	
ClO$_4^-$	Li$^+$	0.15 ± 0.01	Reported by Ciavatta [1980CIA].
	Na$^+$	0.01 ± 0.01	
	K$^+$	—	
Br$^-$	Li$^+$	0.13 ± 0.02	Reported by Ciavatta [1980CIA].
	Na$^+$	0.05 ± 0.01	
	K$^+$	0.01 ± 0.02	
BrO$_3^-$	Li$^+$	—	
	Na$^+$	− 0.06 ± 0.02	Reported by Ciavatta [1980CIA].
	K$^+$	—	
I$^-$	Li$^+$	0.16 ± 0.01	Reported by Ciavatta [1980CIA].
	Na$^+$	0.08 ± 0.02	
	K$^+$	0.02 ± 0.01	
IO$_3^-$	Li$^+$	—	
	Na$^+$	− 0.06 ± 0.02	Estimated in [1992GRE/FUG].
	K$^+$	—	
HSO$_4^-$	Li$^+$	—	
	Na$^+$	− 0.01 ± 0.02	Reported by Ciavatta [1980CIA].
	K$^+$	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
N_3^-	Li^+	—	
	Na^+	0.015 ± 0.020	See Section X.1.2 of this review.
	K^+	—	
NO_2^-	Li^+	0.06 ± 0.04†	
	Na^+	0.00 ± 0.02	Reported by Ciavatta [1980CIA].
	K^+	−0.04 ± 0.02	Reported by Ciavatta [1988CIA].
NO_3^-	Li^+	0.08 ± 0.01	Reported by Ciavatta [1980CIA].
	Na^+	− 0.04 ± 0.03†	
	K^+	− 0.11 ± 0.04†	
$H_2PO_4^-$	Li^+	—	
	Na^+	−0.08 ± 0.04†	
	K^+	−0.14 ± 0.04†	
HCO_3^-	Li^+	—	
	Na^+	0.00 ± 0.02	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	−0.06 ± 0.05	Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL].
Hox^-	Li^+	−0.28 ± 0.09	Evaluated in Section VI.3.5 of [2005HUM/AND].
	Na^+	−0.07 ± 0.01	
	K^+	−0.01 ± 0.08	
H_2cit^-	Li^+	−0.11 ± 0.03	Evaluated in Section VII.3.6 of [2005HUM/AND].
	Na^+	−0.05 ± 0.01	
	K^+	−0.04 ± 0.01	
CN^-	Li^+	—	
	Na^+	0.07 ± 0.03	As reported in [1992BAN/BLI].
	K^+	—	
SCN^-	Li^+	—	
	Na^+	0.05 ± 0.01	Reported by Ciavatta [1980CIA].
	K^+	−0.01 ± 0.01	
$HCOO^-$	Li^+	—	
	Na^+	0.03 ± 0.01	Reported by Ciavatta [1980CIA].
	K^+	—	
CH_3COO^-	Li^+	0.05 ± 0.01	Reported by Ciavatta [1980CIA].
	Na^+	0.08 ± 0.01	
	K^+	0.09 ± 0.01	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
H_3edta^-	Li^+	—	
	Na^+	-0.33 ± 0.14	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	K^+	-0.14 ± 0.17	
$SiO(OH)_3^-$	Li^+	—	
	Na^+	-0.08 ± 0.03	Evaluated in [1992GRE/FUG].
	K^+	—	
$Si_2O_2(OH)_5^-$	Li^+	—	
	Na^+	-0.08 ± 0.04	Estimated in [1992GRE/FUG].
	K^+	—	
$B(OH)_4^-$	Li^+	—	
	Na^+	-0.07 ± 0.05†	
	K^+	—	
$Ni(SCN)_3^-$	Li^+	—	
	Na^+	0.66 ± 0.13	Evaluated in [2005GAM/BUG] (see Section V.7.1.3.1).
	K^+	—	
$Ni(cit)^-$	Li^+	—	
	Na^+	0.22 ± 0.5	Evaluated in Section VII.7 of [2005HUM/AND].
	K^+	—	
$Am(SO_4)_2^-$	Li^+	—	
	Na^+	-0.05 ± 0.05	Estimated in [1995SIL/BID].
	K^+	—	
$Am(CO_3)_2^-$	Li^+	—	
	Na^+	-0.14 ± 0.06	Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\varepsilon_n$ in NaCl solution for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-n)}$ based on $\varepsilon(Am^{3+},Cl^-)$ = $(0.23 \pm 0.02)\ kg\cdot mol^{-1}$ and $\varepsilon(Na^+,CO_3^{2-})$ = – $(0.08 \pm 0.03)\ kg\cdot mol^{-1}$.
	K^+	—	
$Am(ox)_2^-$	Li^+	—	
	Na^+	-0.21 ± 0.08	Evaluated in Section VI.13 of [2005HUM/AND].
	K^+	—	
$Am(edta)^-$	Li^+		
	Na^+	0.01 ± 0.16	Evaluated in Section VIII.13.2.1 of [2005HUM/AND].
	K^+	0.01 ± 0.16	Estimated in [2005HUM/AND] Section VIII.13.2.1 by assuming $\varepsilon(Am(edta)^-, K^+) \approx \varepsilon(Am(edta)^-, Na^+)$.

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$PuO_2CO_3^-$	Li^+	—	
	Na^+	-0.18 ± 0.18	Estimated in [2001LEM/FUG] by analogy with $\varepsilon(NpO_2CO_3^-, Na^+)$.
	K^+	—	
$Pu(edta)^-$	Li^+	—	
	Na^+	—	
	K^+	0.01 ± 0.16	Estimated in [2005HUM/AND], Section VIII.12.2.1 by assuming $\varepsilon(Pu(edta)^-, K^+) \approx \varepsilon(Am(edta)^-, Na^+)$.
$NpO_2(OH)_2^-$	Li^+	—	
	Na^+	-0.01 ± 0.07	Estimated in [2001LEM/FUG] (Section 8.1.3).
	K^+	—	
$NpO_2CO_3^-$	Li^+	—	
	Na^+	-0.18 ± 0.15	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	K^+	—	
$NpO_2(ox)^-$	Li^+	—	
	Na^+	-0.4 ± 0.1	Evaluated in Section VI.11.2.3 of [2005HUM/AND].
	K^+	—	
$NpO_2(H_2edta)^-$	Li^+	—	
	Na^+	-0.18 ± 0.16	Evaluated in Section VIII.11.2.3 of [2005HUM/AND].
	K^+	—	
$(NpO_2)_2CO_3(OH)_3^-$	Li^+	—	
	Na^+	0.00 ± 0.05	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	—	
$UO_2(OH)_3^-$	Li^+	—	
	Na^+	-0.09 ± 0.05	Estimated in [1992GRE/FUG].
	K^+	—	
$UO_2F_3^-$	Li^+	—	
	Na^+	-0.14 ± 0.05	Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1.
	K^+	—	
$UO_2(N_3)_3^-$	Li^+	—	
	Na^+	0.0 ± 0.1	Estimated in [1992GRE/FUG].
	K^+	—	
$(UO_2)_2CO_3(OH)_3^-$	Li^+	—	
	Na^+	0.00 ± 0.05	Estimated in [1992GRE/FUG].
	K^+	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
UO_2cit^-	Li^+	—	
	Na^+	-0.11 ± 0.09	Evaluated in [2005HUM/AND].
	K^+	—	
$Th(OH)_3(CO_3)^-$	Li^+	—	
	Na^+	-0.05 ± 0.20	See Section XI.1.3.2 of this review.
	K^+	—	
$Mg(cit)^-$	Li^+	—	
	Na^+	0.03 ± 0.03	Evaluated in [2005HUM/AND].
	K^+	—	
$UO_2(Hedta)^-$	Li^+	—	
	Na^+	-0.18 ± 0.16	Evaluated in Section VIII.10.2.4 of [2005HUM/AND].
	K^+	—	
$Mg(Hedta)^-$	Li^+	—	
	Na^+	0.11 ± 0.20	Estimated in Section VIII.5.1 of [2005HUM/AND]
	K^+	—	
SO_3^{2-}	Li^+	—	
	Na^+	-0.08 ± 0.05†	
	K^+	—	
SO_4^{2-}	Li^+	-0.03 ± 0.04†	
	Na^+	-0.12 ± 0.06†	
	K^+	-0.06 ± 0.02	Reported by Ciavatta [1988CIA].
$S_2O_3^{2-}$	Li^+	—	
	Na^+	-0.08 ± 0.05†	
	K^+	—	
HPO_4^{2-}	Li^+	—	
	Na^+	-0.15 ± 0.06†	
	K^+	-0.10 ± 0.06†	
CO_3^{2-}	Li^+	—	
	Na^+	-0.08 ± 0.03	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	0.02 ± 0.01	Reported by Ciavatta [1980CIA].
ox^{2-}	Li^+	-0.51 ± 0.09	Evaluated in Section VI.3.5 of [2005HUM/AND].
	Na^+	-0.08 ± 0.01	
	K^+	0.07 ± 0.08	
$Hcit^{2-}$	Li^+	-0.17 ± 0.04	Evaluated in Section VII.3.6 of [2005HUM/AND].
	Na^+	-0.04 ± 0.02	
	K^+	-0.01 ± 0.02	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
H_2edta^{2-}	Li^+		
	Na^+	-0.37 ± 0.14	Evaluated in Section VII.3.7 of [2005HUM/AND].
	K^+	-0.17 ± 0.18	
$SiO_2(OH)_2^{2-}$	Li^+	—	
	Na^+	-0.10 ± 0.07	Evaluated in [1992GRE/FUG].
	K^+	—	
$Si_2O_3(OH)_4^{2-}$	Li^+	—	
	Na^+	-0.15 ± 0.06	Estimated in [1992GRE/FUG].
	K^+	—	
$Ni(ox)_2^{2-}$	Li^+	—	
	Na^+	-0.26 ± 0.03	Evaluated in Section VI.7.2 of [2005HUM/AND].
	K^+	—	
$Ni(CN)_4^{2-}$	Li^+	—	
	Na^+	0.185 ± 0.081	Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1).
	K^+	—	
CrO_4^{2-}	Li^+	—	
	Na^+	-0.06 ± 0.04†	
	K^+	-0.08 ± 0.04†	
$NpO_2(HPO_4)_2^{2-}$	Li^+	—	
	Na^+	-0.1 ± 0.1	Estimated in [2001LEM/FUG].
	K^+	—	
$NpO_2(CO_3)_2^{2-}$	Li^+	—	
	Na^+	-0.02 ± 0.14	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	—	
NpO_2cit^{2-}	Li^+	—	
	Na^+	-0.06 ± 0.03	Evaluated in Section VII.11 of [2005HUM/AND].
	K^+	—	
$NpO_2(Hedta)^{2-}$	Li^+	—	
	Na^+	0.07 ± 0.16	Estimated in Section VIII.11.2.3 of [2005HUM/AND].
	K^+	—	
$UO_2F_4^{2-}$	Li^+	—	
	Na^+	-0.30 ± 0.06	Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1.
	K^+	—	
$UO_2(SO_4)_2^{2-}$	Li^+	—	
	Na^+	-0.12 ± 0.06	Estimated in [1992GRE/FUG].
	K^+	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$UO_2(N_3)_4^{2-}$	Li^+	—	
	Na^+	−0.1 ± 0.1	Estimated in [1992GRE/FUG].
	K^+	—	
$UO_2(ox)_2^{2-}$	Li^+	—	
	Na^+	−0.18 ± 0.07	Estimated in Section VI.1.2.4.1 of [2005HUM/AND].
	K^+	—	
UO_2edta^{2-}	Li^+	—	
	Na^+	−0.22 ± 0.18	Estimated in Section VIII.10.2.4 of [2005HUM/AND].
	K^+	—	
$UO_2(CO_3)_2^{2-}$	Li^+	—	
	Na^+	−0.02 ± 0.09	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$(UO_2)_2(OH)_2(SO_4)_2^{2-}$	Li^+	—	
	Na^+	−0.14 ± 0.22	Evaluated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	
ThF_6^{2-}	Li^+	—	
	Na^+	−0.30 ± 0.06	See Table VIII-8 in Section VIII.1.2.1 of this review.
	K^+	—	
$Th(SO_4)_3^{2-}$	Li^+	−0.068 ± 0.003	In combination with ε_2 = (0.093 ± 0.007).
	Na^+	−0.091 ± 0.038	See Section IX.1.3.2 of this review.
	K^+	−0.091 ± 0.038	
$Th(OH)_2(CO_3)_2^{2-}$	Li^+	—	
	Na^+	− 0.1 ± 0.2	See Section XI.1.3.2 of this review.
	K^+	—	
$Th(OH)_4(CO_3)^{2-}$	Li^+	—	
	Na^+	− 0.1 ± 0.2	See Section XI.1.3.2 of this review.
	K^+	—	
$Mg(ox)_2^{2-}$	Li^+	—	
	Na^+	−0.15 ± 0.03	Estimated in Section VI.5.1 of [2005HUM/AND].
	K^+	−0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.1 by assuming $\varepsilon(\mathrm{Mg(ox)_2^{2-}}, \mathrm{K^+}) \approx \varepsilon(\mathrm{Mg(ox)_2^{2-}}, \mathrm{Na^+})$.
$Mg(edta)^{2-}$	Li^+	—	
	Na^+	−0.01 ± 0.15	Evaluated in Section VIII.5.2 of [2005HUM/AND].
	K^+	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$Ca(ox)_2^{2-}$	Li^+	—	
	Na^+	−0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(Ca(ox)_2^{2-}, Na^+) \approx \varepsilon(Mg(ox)_2^{2-}, Na^+)$.
	K^+	−0.15 ± 0.10	Estimated in [2005HUM/AND], Section VI.5.2 by assuming $\varepsilon(Ca(ox)_2^{2-}, K^+) \approx \varepsilon(Mg(ox)_2^{2-}, Na^+)$.
cit^{3-}	Li^+	−0.44 ± 0.15†	
	Na^+	−0.076 ± 0.030†	
	K^+	0.02 ± 0.02	Evaluated in Section VI.3.6 of [2005HUM/AND].
$Hedta^{3-}$	Li^+	—	
	Na^+	−0.10 ± 0.14	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	K^+	0.31 ± 0.18	
PO_4^{3-}	Li^+	—	
	Na^+	−0.25 ± 0.03†	
	K^+	−0.09 ± 0.02	Reported by Ciavatta [1980CIA].
$Si_3O_6(OH)_3^{3-}$	Li^+	—	
	Na^+	−0.25 ± 0.03	Estimated in [1992GRE/FUG].
	K^+	—	
$Si_3O_5(OH)_5^{3-}$	Li^+	—	
	Na^+	−0.25 ± 0.03	Estimated in [1992GRE/FUG].
	K^+	—	
$Si_4O_7(OH)_5^{3-}$	Li^+	—	
	Na^+	−0.25 ± 0.03	Estimated in [1992GRE/FUG].
	K^+	—	
$Ni(CN)_5^{3-}$	Li^+		
	Na^+	0.25 ± 0.14	Evaluated in [2005GAM/BUG] (see Section V.7.1.2.1.1).
	K^+	—	
$Am(CO_3)_3^{3-}$	Li^+	—	
	Na^+	−0.23 ± 0.07	Evaluated Section 12.6.1.1.1 [2003GUI/FAN], from $\Delta\varepsilon_n$ in NaCl solution for the reactions $An^{3+} + n\,CO_3^{2-} \rightleftharpoons An(CO_3)_n^{(3-n)}$ based on $\varepsilon(Am^{3+}, Cl^-)$ = (0.23 ± 0.02) kg·mol^{-1} and $\varepsilon(Na^+, CO_3^{2-})$ = − (0.08 ± 0.03) kg·mol^{-1}.
	K^+	—	
$Am(ox)_3^{3-}$	Li^+	—	
	Na^+	−0.23 ± 0.10	Estimated in [2005HUM/AND], Section VI.13.2.1 by assuming $\varepsilon(Am(ox)_3^{3-}, Na^+) \approx \varepsilon(Am(CO_3)_3^{3-}, Na^+)$.
	K^+	—	

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Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$\mathrm{Np(CO_3)_3^{3-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	—	
	$\mathrm{K^+}$	-0.15 ± 0.07	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.5).
$\mathrm{NpO_2(CO_3)_2^{3-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.33 ± 0.17	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	$\mathrm{K^+}$	—	
$\mathrm{NpO_2(ox)_2^{3-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.3 ± 0.2	Evaluated in Section VI.11.2.3 of [2005HUM/AND].
	$\mathrm{K^+}$	—	
$\mathrm{NpO_2edta^{3-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	0.20 ± 0.16	Estimated in Section VIII.11.2.3 of [2005HUM/AND].
	$\mathrm{K^+}$	—	
$\mathrm{edta^{4-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	0.32 ± 0.14	Evaluated in Section VIII.3.7 of [2005HUM/AND].
	$\mathrm{K^+}$	1.07 ± 0.19	
$\mathrm{P_2O_7^{4-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.26 ± 0.05	Reported by Ciavatta [1988CIA].
	$\mathrm{K^+}$	-0.15 ± 0.05	Reported by Ciavatta [1988CIA].
$\mathrm{Fe(CN)_6^{4-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	—	
	$\mathrm{K^+}$	-0.17 ± 0.03	
$\mathrm{NpO_2(CO_3)_3^{4-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.40 ± 0.19	Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
	$\mathrm{K^+}$	-0.62 ± 0.42	$\varepsilon(\mathrm{NpO_2(CO_3)_3^{4-}}, \mathrm{NH_4^+}) = -(0.78 \pm 0.25)\ \mathrm{kg \cdot mol^{-1}}$ is calculated in [2001LEM/FUG] (Section 12.1.2.2.1).
$\mathrm{NpO_2(CO_3)_2OH^{4-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.40 ± 0.19	Estimated in [2001LEM/FUG] by analogy with $\mathrm{NpO_2(CO_3)_3^{4-}}$.
	$\mathrm{K^+}$	—	
$\mathrm{U(CO_3)_4^{4-}}$	$\mathrm{Li^+}$	—	
	$\mathrm{Na^+}$	-0.09 ± 0.10	These values differ from those estimated in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for $\mathrm{CO_3^{2-}}$ and $\mathrm{HCO_3^-}$ are based on [1980CIA].
	$\mathrm{K^+}$	—	

(Continued on next page)

Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$UO_2(CO_3)_3^{4-}$	Li^+	—	
	Na^+	-0.01 ± 0.11	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$UO_2(ox)_3^{4-}$	Li^+	—	
	Na^+	-0.01 ± 0.11	Estimated in [2005HUM/AND], Section VI.10.2.4.1 by assuming $\varepsilon(UO_2(ox)_3^{4-}, Na^+) \approx \varepsilon(UO_2(CO_3)_3^{4-}, Na^+)$.
	K^+	—	
$(UO_2)_3(OH)_4(SO_4)_3^{4-}$	Li^+	—	
	Na^+	0.6 ± 0.6	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	
$NpO_2(CO_3)_3^{5-}$	Li^+	—	
	Na^+	-0.53 ± 0.19	Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
	K^+	-0.22 ± 0.03	Evaluated in [2003GUI/FAN] (discussion of [1998ALM/NOV] in Appendix A) from Δε for the reactions $KNpO_2CO_3(s) + 2CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + K^+$ (in K_2CO_3–KCl solution) and $K_3NpO_2(CO_3)_2(s) + CO_3^{2-} \rightleftharpoons NpO_2(CO_3)_3^{5-} + 3K^+$ (in K_2CO_3 solution) (based on $\varepsilon(K^+, CO_3^{2-}) = (0.02 \pm 0.01)$ kg·mol^{-1}).
$UO_2(CO_3)_3^{5-}$	Li^+	—	
	Na^+	-0.62 ± 0.15	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$Th(OH)(CO_3)_4^{5-}$	Li^+	—	
	Na^+	-0.22 ± 0.13	Evaluated in Section XI.1.3.2.1 of this review.
	K^+	—	
$Np(CO_3)_5^{6-}$	Li^+	—	
	Na^+	—	
	K^+	-0.73 ± 0.68	Calculated in [2001LEM/FUG] (Section 12.1.2.1.4).
$(NpO_2)_3(CO_3)_6^{6-}$	Li^+	—	
	Na^+	-0.46 ± 0.73	Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
	K^+	—	

(Continued on next page)

Table B-5: (continued)

j	*k*	ε(*j*,*k*)	Comments
$U(CO_3)_5^{6-}$	Li^+	—	
	Na^+	-0.30 ± 0.15	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	-0.70 ± 0.31	Calculated in [2001LEM/FUG] from Pitzer coefficients [1998RAI/FEL].
$(UO_2)_3(CO_3)_6^{6-}$	Li^+		
	Na^+	0.37 ± 0.11	These values differ from those reported in [1992GRE/FUG]. See the discussion in [1995GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [1980CIA].
	K^+	—	
$(UO_2)_2NpO_2(CO_3)_6^{6-}$	Li^+	—	
	Na^+	0.09 ± 0.71	Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.2.1).
	K^+	—	
$(UO_2)_5(OH)_8(SO_4)_4^{6-}$	Li^+	—	
	Na^+	1.10 ± 0.5	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	
$Th(CO_3)_5^{6-}$	Li^+	—	
	Na^+	-0.30 ± 0.15	Estimated in Section XI.1.3.2.1 of this review.
	K^+	—	
$(UO_2)_4(OH)_7(SO_4)_4^{7-}$	Li^+	—	
	Na^+	2.80 ± 0.7	Estimated in Section 9.5.1.1.2 of [2003GUI/FAN].
	K^+	—	

Table B-6: Ion interaction coefficients, $\varepsilon_1(j,k)$ and $\varepsilon_2(j,k)$, both in (kg·mol^{-1}), for cations j with k = Cl^-, ClO_4^- and NO_3^- (first part), and for anions j with k = Li^+, Na^+ and K^+ (second part), according to the relationship $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10}I_m$. The data are taken from Ciavatta [1980CIA], [1988CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level.

j $k \rightarrow$	Cl^-		ClO_4^-		NO_3^-	
↓	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
NH_4^+			−0.088±0.002	0.095±0.012	−0.075±0.001	0.057±0.004
Tl^+			−0.18±0.02	0.09±0.02		
Ag^+					−0.1432±0.0002	0.0971±0.0009
Pb^{2+}					−0.329±0.007	0.288±0.018
Hg^{2+}					−0.145±0.001	0.194±0.002
Hg_2^{2+}					−0.2300±0.0004	0.194±0.002
j $k \rightarrow$	Li^+		Na^+		K^+	
↓	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
OH^-	−0.039±0.002	0.072±0.006				
NO_2^-	0.02±0.01	0.11±0.01				
NO_3^-			−0.049±0.001	0.044±0.002	−0.131±0.002	0.082±0.006
$H_2PO_4^-$			−0.109±0.001	0.095±0.003	−0.1473±0.0008	0.121±0.004
$B(OH)_4^-$			−0.092±0.002	0.103±0.005		
SO_3^{2-}			−0.125±0.008	0.106±0.009		
SO_4^{2-}	−0.068±0.003	0.093±0.007	−0.184±0.002	0.139±0.006		
$S_2O_3^{2-}$			−0.125±0.008	0.106±0.009		
HPO_4^{2-}			−0.19±0.01	0.11±0.03	−0.152±0.007	0.123±0.016
CrO_4^{2-}			−0.090±0.005	0.07±0.01	−0.123±0.003	0.106±0.007
cit^{3-}	−0.55±0.11 [a]	0.3±0.2[a]	−0.15±0.03[a]	0.13±0.03[a]		
PO_4^{3-}			−0.29±0.02	0.10±0.01		

(a): See Section VII.3.6 of [2005HUM/AND].

Table B-7: SIT interaction coefficients ε(*j*,*k*) (kg·mol^{-1}) for neutral species, *j*, with *k*, electroneutral combination of ions.

j *k* → ↓	$Na^+ + ClO_4^-$	$Na^+ + Cl^-$	$K^+ + NO_3^-$
$H_2ox(aq)$	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]
$H_3cit(aq)$	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]	0.00 ± 0.01 [b]
$H_4edta(aq)$	– 0.29 ± 0.14	– 0.29 ± 0.14	– 0.29 ± 0.14
Ni(ox)(aq)	– 0.07 ± 0.03	– 0.07 ± 0.03	
Ni(Hcit)(aq)	– 0.07 ± 0.05		
$Ni(SCN)_2(aq)$	0.38 ± 0.06[a]		
Am(cit)(aq)		0.00 ± 0.05	
Np(edta)(aq)	– 0.19 ± 0.19[g]		
$UO_2ox(aq)$	– 0.05 ± 0.06	– 0.05 ± 0.06	
Uedta(aq)	– 0.19 ± 0.19		
Mg(ox)(aq)		0.00 ± 0.03	0.0 ± 0.1[c]
Mg(Hcit)(aq)	0.02 ± 0.05	0.02 ± 0.05	
Ca(ox)(aq)	0.0 ± 0.1[d]	0.0 ± 0.1[e]	0.0 ± 0.1[f]

(a): See Section V.7.1.3.1 in [2005GAM/BUG].

(b): Basic assumption of this review, see Sections VI.3.5 and VII.3.6 for discussions.

(c): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming ε(Mg(ox)(aq), KNO_3) ≈ ε(Mg(ox)(aq), NaCl).

(d): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming ε(Ca(ox)(aq), $NaClO_4$) ≈ ε(Mg(ox)(aq), NaCl).

(e): Estimated in Section VI.5.1 of [2005HUM/AND] by assuming ε(Ca(ox)(aq), NaCl) ≈ ε(Mg(ox)(aq), NaCl).

(f): Estimated in Section VI.5.2 of [2005HUM/AND] by assuming ε(Ca(ox)(aq), KNO_3) ≈ ε(Mg(ox)(aq), NaCl).

(g): Estimated in Section VIII.11.2.2 of [2005HUM/AND] by assuming ε(Np(edta)(aq), $NaClO_4$) ≈ ε(Uedta(aq), $NaClO_4$).

Appendix C

Assigned uncertainties[1]

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, $r = 1, 2,\ldots, n$, assuming that we know the functional relationship:

$$y = f(k_1, k_2, \ldots k_r \ldots k_n; a_1, a_2, \ldots.) \qquad \text{(C.1)}$$

where a_1, a_2 , *etc.* are quantities that can be varied but whose values (a_{1i}; a_{2i}; *etc.*) are assumed to be known accurately in each experiment from the data sets (y_i, a_{1i}, a_{2i},…), $i = 1, 2, \ldots N$. 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:

$$U = \sum_i w_i \left[y_i - f(k_1 \ldots k_n;\ a_{1i},\ a_{2i} \ldots)\right]^2 \qquad \text{(C.2)}$$

where w_i is the weight of each experimental measurement y_i.

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[1] 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:

$$\frac{\partial U}{\partial k_r} = 0,\ r = 1,.....n \qquad \text{(C.3)}$$

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 $w_i(y_i,\ a_{1i},\ a_{2i},....)$ 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 type 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} … 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 $-\log_{10}[\mathrm{H}^+]$ 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 point with the same estimated uncertainty, σ, 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 Data Base (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, $\bar{X}$:

$$s_X = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(X_i - \bar{X})^2} \qquad \text{(C.4)}$$

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 $\bar{X}$ ± 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, σ. 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, σ, can be calculated with Eq. (C.5), assuming that the systematic errors are independent.

$$\sigma_X = \sqrt{s_X^2 + \sum_j (s_j^2)} \qquad \text{(C.5)}$$

The estimation of the systematic errors s_j (which, of course, have to relate to $\overline{X}$ and be expressed in the same units) can only be made by a person who is familiar with the experimental method. The uncertainty, σ, 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 B.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 σ 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, σ_i, that also includes all systematic errors and represents the 95% confidence level, as described in Section C.3. The weighted mean $\overline{X}$ and its uncertainty, $\sigma_{\overline{X}}$, are then calculated according to Eqs. (C.6) and (C.7).

$$\overline{X} \equiv \frac{\sum_{i=1}^{N}\left(\frac{X_i}{\sigma_i^2}\right)}{\sum_{i=1}^{N}\left(\frac{1}{\sigma_i^2}\right)} \qquad \text{(C.6)}$$

$$\sigma_{\overline{X}} = \sqrt{\frac{1}{\sum_{i=1}^{N}\left(\frac{1}{\sigma_i^2}\right)}} \qquad \text{(C.7)}$$

Eqs. (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 $\sigma_{\overline{X}}$ is directly dependent on the absolute magnitude of the σ_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 σ_i values already represent the 95% confidence level. The selected uncertainty, $\sigma_{\overline{X}}$, 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).

$$\bar{X} = \frac{1}{N}\sum_{i=1}^{N} X_i \tag{C.8}$$

$$\sigma_{\bar{X}} = \frac{\sigma}{\sqrt{N}} \tag{C.9}$$

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 B.3.

i	X_i	σ_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 σ_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, σ_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 σ_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 σ_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 ± 0.21) and of those in Group B, X_B (i = 2, 3) = (26.06 ± 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 B.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 $\sigma_{\overline{X}}$ 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 $\overline{X}$ = (25.5 ± 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 $\overline{X}$ = (25.45 ± 1.05), which is rounded according to the rules in Section B.6.3 to $\overline{X}$ = (25.4 ± 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, $\sigma_{\overline{X}}$, assigned to the selected mean, $\overline{X}$, has to cover the range of expectation of both source data, X_1, X_2, as shown in Eq.(C.10),

$$\sigma_{\overline{X}} = \left| X_i - \overline{X} \right| + \sigma_{\max} \tag{C.10}$$

where i =1, 2, and $\sigma_{\max}$ is the larger of the two uncertainties σ_i, see Example C.1.ii and Example C.2.

Example C.2:

The following credible source data are given:

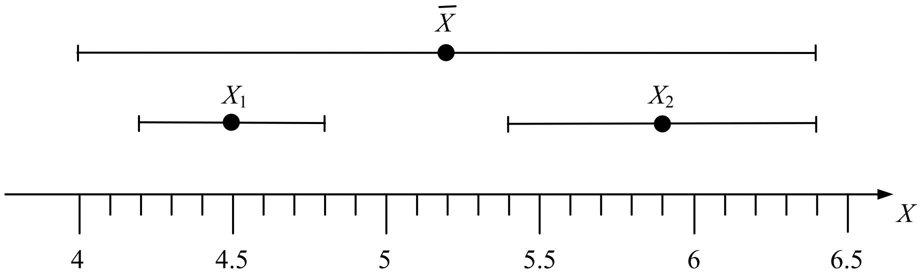
X_1 = (4.5 ± 0.3)

X_2 = (5.9 ± 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	σ_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 B.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 $I = 0$, $\overline{X}^{\mathrm{o}}$, and $\Delta\varepsilon$. The first step is the conversion of the ionic strength from the frequently used molar (mol·dm^{-3}, M) to the molal (mol·kg^{-1}, *m*) scale, as described in Section II.2. The second step is the assignment of an uncertainty, σ_i, to each data point X_i at the molality, $m_{k,i}$, according to the rules described in Section B.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 $\overline{X}^{\mathrm{o}}$ and the slope $-\Delta\varepsilon$:

$$\overline{X}^{\mathrm{o}} = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2}\right) \tag{C.11}$$

$$-\Delta\varepsilon = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2}\right) \tag{C.12}$$

$$\sigma_{\overline{X}^{\mathrm{o}}} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}} \tag{C.13}$$

$$\sigma_{\Delta\varepsilon} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}} \tag{C.14}$$

where

$$\Delta = \sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2} - \left(\sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\right)^2 . \tag{C.15}$$

In this way, the uncertainties, σ_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, $\sigma_{\bar{X}^o}$ and $\sigma_{\Delta\varepsilon}$, in Eqs. (C.13) and (C.14). If the σ_i represents the 95% confidence level, $\sigma_{\bar{X}^o}$ 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, σ_i.

Example C.4:

Ten independent determinations of the equilibrium constant, $\log_{10}{}^*\beta$, for the reaction:

$$UO_2^{2+} + HF(aq) \rightleftharpoons UO_2F^+ + H^+ \tag{C.16}$$

are available in $HClO_4$/$NaClO_4$ media at different ionic strengths. Uncertainties that represent the 95% confidence level have been assigned by the reviewer. A weighted linear regression, ($\log_{10}{}^*\beta$ + 2*D*) *vs.* m_k, according to the formula, $\log_{10}{}^*\beta$ (C.16) + 2*D* = $\log_{10}{}^*\beta^o$(C.16) − $\Delta\varepsilon\, m_k$, will yield the correct values for the intercept, $\log_{10}{}^*\beta^o$(C.16), and the slope, $\Delta\varepsilon$. In this case, m_k corresponds to the molality of ClO_4^-. *D* is the Debye-Hückel term, *cf.* Appendix B.

i	$m_{ClO_4^-,i}$	$\log_{10}{}^*\beta + 2D$	σ_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:

$$\text{intercept} = (1.837 \pm 0.054) = \log_{10}{}^*\beta^o\,(C.16)$$

$$\text{slope} = (0.029 \pm 0.036) = -\ \Delta\varepsilon$$

Calculation of the ion interaction coefficient $\varepsilon(UO_2F^+, ClO_4^-) = \Delta\varepsilon + \varepsilon(UO_2^{2+}, ClO_4^-) - \varepsilon(H^+, ClO_4^-)$: from $\varepsilon(UO_2^{2+}, ClO_4^-)$ = (0.46 ± 0.03) kg·mol^{-1}, $\varepsilon(H^+, ClO_4^-)$ = (0.14 ± 0.02) kg·mol^{-1} (see Appendix B) and the slope of the linear regression, $\Delta\varepsilon = -(0.03 \pm 0.04)$ kg·mol^{-1}, it follows that $\varepsilon(\mathrm{UO_2F^+}, \mathrm{ClO_4^-})$ = (0.29 ± 0.05) kg·mol^{-1}. Note that the uncertainty (± 0 05) kg·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:

$$\log_{10} {}^*\beta^\circ\,(\mathrm{C.16}) = (1.84 \pm 0.05)$$

$$\varepsilon(\mathrm{UO_2F^+}, \mathrm{ClO_4^-}) = (0.29 \pm 0.05)\ \mathrm{kg{\cdot}mol^{-1}}.$$

C.5.1 Discrepancies or insufficient number of data points

Discrepancies are principally treated as described in Section B.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 point obtained by this procedure, and its uncertainty must cover the entire range of expectancy of the two values, analogous to Case I in Section B.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 B.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:

$$\mathrm{UO_2^{2+} + SCN^- \rightleftharpoons UO_2SCN^+} \qquad \text{(C.17)}$$

are available in different electrolyte media:

$I_c = 0.1$ M (KNO$_3$) $\log_{10}\beta$ (C.17) = (1.19 ± 0.03)

$I_c = 0.33$ M (KNO$_3$) $\log_{10}\beta$ (C.17) = (0.90 ± 0.10)

$I_c = 1.0$ M (NaClO$_4$) $\log_{10}\beta$ (C.17) = (0.75 ± 0.03)

$I_c = 1.0$ M (NaClO$_4$) $\log_{10}\beta$ (C.17) = (0.76 ± 0.03)

$I_c = 1.0$ M (NaClO$_4$) $\log_{10}\beta$ (C.17) = (0.93 ± 0.03)

$I_c = 2.5$ M (NaNO$_3$) $\log_{10}\beta$ (C.17) = (0.72 ± 0.03)

The uncertainties are assumed to represent the 95% confidence level. From the values at $I_c = 1$ 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 ε 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 ε values.

A reaction of the same charge type as Reaction (C.17), and for which $\Delta\varepsilon$ is well known, is:

$$\mathrm{UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+}\,. \qquad \text{(C.18)}$$

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 M and I_c = 3 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 $\log_{10}\beta$ (C.17) to $I_c = 0$ is done using the specific ion interaction equation, *cf.* TDB-2, which uses molal units:

$$\log_{10}\beta + 4D = \log_{10}\beta^{\circ} - \Delta\varepsilon\, I_m. \qquad \text{(C.19)}$$

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 B.6.2.

Table C-1: Details of the calculation of equilibrium constant 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_3	(1.19 ± 0.03)	0.438	– 0.025	(1.68 ± 0.03)[a]
0.335	KNO_3	(0.90 ± 0.10)	0.617	– 0.084	(1.65 ± 0.10)[a]
1.050	$NaClO_4$	(0.75 ± 0.03)	0.822	– 0.263	(1.31 ± 0.04)
1.050	$NaClO_4$	(0.76 ± 0.03)	0.822	– 0.263	(1.32 ± 0.04)
1.050	$NaClO_4$	(0.93 ± 0.03)	0.822	– 0.263	(1.49 ± 0.04)
2.714	$NaNO_3$	(0.72 ± 0.03)	0.968	– 0.679	(1.82 ± 0.13)[a]

a: These values were corrected for the formation of the nitrate complex, $UO_2NO_3^+$, by using $\log_{10} K(UO_2NO_3^+) = (0.30 \pm 0.15)$ [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 B.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 is 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 ε 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^3 of solution (molar, M) and has to be converted to moles per kg H_2O (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:

$$M^{3+} + 2\,H_2O(l) \rightleftharpoons M(OH)_2^+ + 2\,H^+, \qquad (C.20)$$

only one credible determination in 3 M $NaClO_4$ solution is known to be, $\log_{10}{}^*\beta$ (C.20) = – 6.31, to which an uncertainty of ± 0.12 has been assigned. The ion interaction coefficients are as follows:

$$\varepsilon(M^{3+}, ClO_4^-) = (0.56 \pm 0.03)\ kg{\cdot}mol^{-1},$$

$$\varepsilon(M(OH)_2^+, ClO_4^-) = (0.26 \pm 0.11)\ kg{\cdot}mol^{-1},$$

$$\varepsilon(H^+, ClO_4^-) = (0.14 \pm 0.02)\ kg{\cdot}mol^{-1}.$$

The values of $\Delta\varepsilon$ and $\sigma_{\Delta\varepsilon}$ can be obtained readily (*cf.* Eq. (C.22)):

$$\Delta\varepsilon = \varepsilon(M(OH)_2^+, ClO_4^-) + 2\varepsilon(H^+, ClO_4^-) - \varepsilon(M^{3+}, ClO_4^-) = -\,0.22\ kg{\cdot}mol^{-1},$$

$$\sigma_{\Delta\varepsilon} = \sqrt{(0.11)^2 + (2\times 0.02)^2 + (0.03)^2} = 0.12\ kg\cdot mol^{-1}.$$

The two variables are thus:

$$\log_{10}{}^*\beta\,(C.20) = -\,(6.31 \pm 0.12),$$

$$\Delta\varepsilon = -\,(0.02 \pm 0.12)\ kg{\cdot}mol^{-1}.$$

According to the specific ion interaction model the following equation is used to correct for ionic strength for the reaction considered here:

$$\log_{10}{}^*\beta\,(C.20) + 6D = \log_{10}{}^*\beta^\circ\,(C.20) - \Delta\varepsilon\, m_{ClO_4^-}$$

D is the Debye-Hückel term:

$$D = \frac{0.509\sqrt{I_m}}{(1 + 1.5\sqrt{I_m})}.$$

The ionic strength, I_m, and the molality, $m_{ClO_4^-}$ ($I_m \approx m_{ClO_4^-}$), have to be expressed in molal units, 3 M $NaClO_4$ corresponding to 3.5 *m* $NaClO_4$ (see Section II.2), giving $D = 0.25$. This results in:

$$\log_{10}{}^*\beta^\circ\,(C.20) = -\,4.88.$$

The uncertainty in $\log_{10}{}^*\beta^\circ$ is calculated from the uncertainties in $\log_{10}{}^*\beta$ and $\Delta\varepsilon$ (*cf.* Eq. (C.22)):

$$\sigma_{\log_{10} {}^*\beta^\circ} = \sqrt{\sigma^2_{\log_{10} {}^*\beta} + (m_{\mathrm{ClO_4^-}}\sigma_{\Delta\varepsilon})^2} = \sqrt{(0.12)^2 + (3.5\times 0.12)^2} = 0.44$$

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,…,Y_N .

$$\sigma_X^2 = \sum_{i=1}^{N}\left(\frac{\partial X}{\partial Y_i}\sigma_{Y_i}\right)^2 \qquad \text{(C.21)}$$

Eq. (C.21) can be used only if the variables, Y_1, Y_2,…,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 formulas for a number of frequently encountered algebraic expressions, where c, c_1, c_2 are constants.

$$X = c_1Y_1 \pm c_2Y_2: \qquad \sigma_X^2 = (c_1\sigma_{Y_1})^2 + (c_2\sigma_{Y_2})^2 \qquad \text{(C.22)}$$

$$X = \pm\, cY_1Y_2 \text{ and } X = \pm\frac{cY_1}{Y_2}: \qquad \left(\frac{\sigma_X}{X}\right)^2 = \left(\frac{\sigma_{Y_1}}{Y_1}\right)^2 + \left(\frac{\sigma_{Y_2}}{Y_2}\right)^2 \qquad \text{(C.23)}$$

$$X = c_1Y^{\pm c_2}: \qquad \frac{\sigma_X}{X} = c_2\frac{\sigma_Y}{Y} \qquad \text{(C.24)}$$

$$X = c_1e^{\pm c_2Y}: \qquad \frac{\sigma_X}{X} = c_2\sigma_Y \qquad \text{(C.25)}$$

$$X = c_1\ln(\pm c_2Y): \qquad \sigma_X = c_1\frac{\sigma_Y}{Y} \qquad \text{(C.26)}$$

Example C.7:

A few simple calculations illustrate how these formulas are used. The values have not been rounded.

$$\text{Eq. (C.22)}: \quad \Delta_{\mathrm{r}}G_{\mathrm{m}} = 2\cdot[\,-(277.4 \pm 4.9)]\ \mathrm{kJ\cdot mol^{-1}} - [\,-(467.3 \pm 6.2)]\ \mathrm{kJ\cdot mol^{-1}}$$

$$= -\,(87.5 \pm 11.6)\ \mathrm{kJ\cdot mol^{-1}}.$$

$$\text{Eq. (C.23)}: \quad K = \frac{(0.038 \pm 0.002)}{(0.0047 \pm 0.0005)} = (8.09 \pm 0.96)$$

Eq. (C.24) : $K = 4\cdot(3.75 \pm 0.12)^3 = (210.9 \pm 20.3)$

Eq. (C.25) : $K^{\circ} = e^{\frac{-\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}}{\mathrm{R}T}}$; $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}} = -\,(2.7 \pm 0.3)\ \mathrm{kJ\cdot mol^{-1}}$

$\mathrm{R} = 8.3145\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

$T = 298.15\ \mathrm{K}$

$K^{\circ} = (2.97 \pm 0.36)$.

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.*,

$$\log_{10} K = (2.45 \pm 0.10);\ K = 10^{\log_{10} K} = e^{(\ln(10)\cdot\log_{10} K)} = (282 \pm 65).$$

Eq. (C.26) : $\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}} = -\mathrm{R}T\ln K^{\circ}$; $K^{\circ} = (8.2 \pm 1.2) \times 10^{6}$

$\mathrm{R} = 8.3145\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$

$T = 298.15\ \mathrm{K}$

$\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}} = -\,(39.46 \pm 0.36)\ \mathrm{kJ\cdot mol^{-1}}$

$\ln K^{\circ} = (15.92 \pm 0.15)$

$\log_{10} K^{\circ} = \ln K^{\circ} / \ln(10) = (6.91 \pm 0.06)$.

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 ± 0.008)

(3.48 ± 0.01)

(2.8 ± 0.4)

(10 ± 1)

(105 ± 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 ± 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.

Appendix D

The Gibbs energy minimisation and optimisation program, NONLINT-SIT

D.1 Introduction

A SIT fitting code, NONLINT-SIT (Personal communication, September 2004. A. R. Felmy, Pacific Northwest National Laboratory, Richland, WA, USA), was used in some systems to optimise $\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\mathrm{o}} / \mathrm{R}T$ values of different solid and aqueous species and SIT ion-interaction parameters, using solubility, ion-exchange, and solvent extraction data. From these, the optimised values of the different quantities can be compared with the other reported values. The program NONLINT-SIT is an extended version of the parameter optimisation programs (NONLIN and NONLINT) developed by A. R. Felmy using the MINPACK nonlinear least-squares programs, in conjunction with a Gibbs energy minimisation program (GMIN, [1990FEL] and [1995FEL]). The mathematical development of the latter is based on the formulations described in [1981HAR], [1987HAR/GRE] and [1985GRE/WEA]. GMIN and NONLIN have also been the bases for the development of the related parameter optimisation code INSIGHT, [1997STE/FEL], which uses the same algorithms as NONLINT, but deals with fewer types of experimental data.

In this Appendix, no attempt will be made to present details of all the equations involved in calculations; we restrict ourselves to a very general description of the formulation of Gibbs-energy minimisation problem and the optimisation procedure, illustrated by an example. Readers interested in the details of the programs and the detailed equations involved should consult [1995FEL] and the very detailed user manual of INSIGHT, [1997STE/FEL].

The program can be used to analyse different types of experimental data (*e.g.*, solvent extraction, ion-exchange, potentiometric, solubility of pure phases, solubility of solid solutions) involving aqueous, solid, and gaseous phases at different temperatures.

The experimental data analysed in this review using the NONLINT-SIT program included solubility, solvent extraction and ion exchange measurements. Optimisation is carried out by minimising the penalty function, *viz.* the standard deviation, (σ), of the set of *N* experimental data points defined by:

$$\sigma^2 = \sum\nolimits_{i=1}^{N} \left[\mu_i(\text{other}) - \mu_i(\text{aq})\right]^2 / N$$

where

- μ_i(other) is the iteratively-fitted dimensionless Gibbs energy $(\Delta_\text{f} G^\circ_\text{m} / \text{R}T)$ of the solid, organic phase, or exchange complex
- μ_i(aq) is the dimensionless Gibbs energy calculated from the experimental aqueous phase data and the associated ion-interaction parameters (or equivalently, the chemical potential of the corresponding second phase).

The user can select different models (Pitzer, Davies, and SIT) for calculating the activity coefficients of aqueous solutions. All of the input data are user-defined. The code can be used just as a calculational tool where all of the inputs are defined and solution equilibria calculated, or as a tool to optimise values of chemical potentials for different species and/or ion-interaction parameters, based on best fits to given experimental data. Multiple data sets of a specific chemical system (*e.g.*, solubility of a solid phase) in different media can be evaluated simultaneously.

The inputs required include:

1. the analytical total concentration of the different components, *e.g.* thorium and sulphate, considered in modelling. The total concentration of a certain component is arbitrarily assigned to *one* of the species considered in the chemical model tested, *e.g.* Th^{4+} or $\text{Th(SO}_4)^{2+}$. The program then automatically calculates the speciation, that is the actual concentrations of all the species based on the modelling parameters (equilibrium constants and total concentrations of all components).
2. dimensionless Gibbs energies of formation $(\Delta_\text{f} G^\circ_\text{m} / \text{R}T)$ of all of the species,
3. ion-interaction parameters, and
4. indication of the parameters to be varied.

The outputs include:

1. the new values of the parameters,
2. the molalities and activities of all of the species considered in modelling, based on the defined aqueous phase model,
3. the calculated differences in chemical potentials $[(\Delta_\text{f} G_\text{m} / \text{R}T)_\text{predicted}) - (\Delta_\text{f} G_\text{m} / \text{R}T)_\text{experimental}]$ for each data point, where $(\Delta_\text{f} G_\text{m} / \text{R}T)_\text{predicted})$ is the fitted/predicted chemical potential of the solid phase and $(\Delta_\text{f} G_\text{m} / \text{R}T)_\text{experimental}$ is the value calculated by the program for the aqueous phase from the experimental

data (or equivalently also the chemical potential of the solid phase). From the fitted chemical potentials the user can calculate the corresponding equilibrium constants.

4. the standard deviation (one sigma) in the predicted and experimental chemical potentials for the entire data set, and from these the uncertainties in the various equilibrium constants (the uncertainties quoted in text and appendices are two sigma).
5. In addition one can obtain the molalities and activities of all of the species in accordance with the aqueous phase model and in equilibrium with the solid phase or the other phases involved (solid, organic or ion exchanger).

D.2 Uncertainties in NONLINT-SIT calculations

There are three different types of uncertainties: those based in 1) the experimental data, 2) the ion-interaction parameters used in the SIT model, and 3) the Gibbs energies of the species which are not optimised. These uncertainties are briefly discussed below.

D.2.1 Uncertainties in experimental data

The NONLINT-SIT program has been used to interpret the available experimental data in order to find the "best" chemical model, including the most important species and their equilibrium constants based on the fixed values of the Gibbs energies of other participating species and values of the ion-interaction parameters. The latter were only varied in the optimisation in a few cases. The program provides uncertainty values for the fitted equilibrium constants based solely on the uncertainties in the experimental data. These are the values reported in the text of the review.

D.2.2 Accounting for uncertainties in ion-interaction parameters

The uncertainty values quoted from NONLINT-SIT calculations are based on the average values of the selected interaction parameters, but without taking into consideration their uncertainty. The most rigorous method of determining how these errors influence the uncertainty in $\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}/\mathrm{R}T$ of the different species and the equilibrium constants of the different reactions would be to describe the error in interaction parameters with a probability distribution function and then make a large number of Monte Carlo samplings to calculate $\Delta_{\mathrm{f}}G^{\mathrm{o}}_{\mathrm{m}}/\mathrm{R}T$ values. The average of these and their associated statistical uncertainty would provide the effects of uncertainties in the interaction parameters. Such calculations are time consuming and beyond the scope of this review. Thus for the uncertainties values quoted from the NONLINT-SIT calculations this review has not been able to implement strictly the procedures implied in Appendix C. However, to estimate the maximum effects of the interaction uncertainties for a few important species/reactions in the sulphate system, this review has made sample NONLINT-SIT calculations using maximum and minimum values for all interaction parameters.

The calculated uncertainties in $\Delta_f G_m^o / RT$ will increase with the uncertainty in the interaction parameters and with increasing ionic strength. We have used the studies of [1963ALL/MCD] and the solubility investigations of many sulphate solids (see Section IX.1.3.3) to explore this effect, because the chemical system is simple, with $Th(SO_4)_3^{2-}$ as the dominant species. The solvent extraction data of [1963ALL/MCD], where the ionic strength varies from a very low value up to 4.5 m, were used as a first test of the impact of uncertainties in interaction parameters on the fitted values of $\Delta_f G_m^o / RT$ ($Th(SO_4)_3^{2-}$), as it is expected that this system will provide maximum variability in the calculated values. The values of all of the ion-interaction parameters involved in this system are listed in Table D-1 and the $\Delta_f G_m^o / RT$ values of all of the species considered in interpretation are listed in Table D-2. The fitted $\Delta_f G_m^o / RT$ ($Th(SO_4)_3^{2-}$) value was found to be $-(1209.511 \pm 0.086)$ when maximum values of all the ion interaction parameters, based on the uncertainties reported in Table D-1, were used and $-(1209.348 \pm 0.088)$ when the minimum values were used. These compare with the value of $\Delta_f G_m^o / RT$ ($Th(SO_4)_3^{2-}$) $= -(1209.432 \pm 0.086)$ found when the mean values of the ion interaction parameters were used (see Section IX.1.3.2).

The mean and uncertainty based on the mean of the maximum and minimum values are $\Delta_f G_m^o / RT$ ($Th(SO_4)_3^{2-}$) $= -(1209.430 \pm 0.123)$.

Thus the optimised value is not significantly different from the value based on the mean epsilon values, but the uncertainty is slightly larger. The value including the uncertainty in the epsilon values would translate into $\log_{10} K^o$ (D.1) = (10.748 ± 0.053) for Reaction (D.1) as compared to $\log_{10} K^o$ (D.1) = (10.748 ± 0.038) based only on the mean epsilon values (Table IX-6).

$$Th^{4+} + 3\,SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-} \qquad (D.1)$$

Table D-1: Ion interaction parameters used in calculations involving $Th(SO_4)_3^{2-}$.

Species	SIT ion interaction parameters (kg·mol^{-1})		Reference
	ε_1	ε_2	
H^+- HSO_4^-	0.14 ± 0.02	0.00	This review [a]
H^+- $Th(SO_4)_3^{2-}$	– 0.068 ± 0.003	0.093 ± 0.007	This review [b]
Na^+- SO_4^{2-}	– 0.184 ± 0.002	0.139 ± 0.006	Table B-6
Na^+- HSO_4^-	– 0.01 ± 0.02	0.00	Table B-5
Na^+- $Th(SO_4)_3^{2-}$	– 0.091 ± 0.038	0.00	This review [c]
Th^{4+}- HSO_4^-	0.70 ± 0.10	0.00	This review [d]

a: Assumed to be identical to that for H^+- ClO_4^- (Table B-4).

b: Assumed to be identical to that for Li^+- SO_4^{2-} (Table B-6).

c: Based on experimental data interpretations (see Section IX.1.3.2 for details).

d: Assumed to be identical to that for Th^{4+}- ClO_4^-.

Table D-2: Dimensionless molar Gibbs energies of formation at 298.15 K used in calculations involving $\mathrm{Th(SO_4)_3^{2-}}$.

Species	$\Delta_f G_m^o / RT$
$H_2O(l)$	– 95.6607
H^+	0
Na^+	– 105.67
Th^{4+}	– 284.305
SO_4^{2-}	– 300.126
HSO_4^-	– 304.689
$ThSO_4^{2+}$	– 598.638
$Th(SO_4)_2(aq)$	– 906.869

In a similar fashion, the solubility data for $\mathrm{Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O(cr)}$ and the parameters listed in Table D-3 and Table D-4 were used to explore how the optimised value of $\Delta_f G_m^o / RT$ for $\mathrm{Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O(cr)}$ and the solubility product for Reaction (D.2) varied for changes in the ion interaction parameters. The fitted $\Delta_f G_m^o / RT$ ($\mathrm{Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O}$, cr) values were found to be – (2006.078 ± 0.460) when the maximum values of all of the ion interaction parameters, based on the uncertainties reported in Table D-3 were used and – (2006.184 ± 0.348) when the minimum values were used, compared with the value of – (2006.131 ± 0.402) found when the mean values of the ion interaction parameters were used (see Sections IX.1.3.3.3 and IX.1.3.4). The average and uncertainties based on the maximum and minimum values of ion-interaction parameters are $\Delta_f G_m^o / RT$ ($\mathrm{Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O}$, cr) = – (2006.131 ± 0.577)**,** where the calculated $\Delta_f G_m^o / RT$ is identical to that from the value based on the average epsilon values – (2006.131 ± 0.402) (Table IX-5). The uncertainty based on maximum and minimum epsilon values is slightly larger than that calculated from the average epsilon values. Thus, the calculated solubility product for Reaction (D.2) is unchanged from that reported in Table IX-6.

$$\mathrm{Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O(cr) \rightleftharpoons Th^{4+} + 3SO_4^{2-} + 2Na^+ + 6H_2O(l)} \qquad (D.2)$$

Table D-3: Ion interaction parameters used in calculations involving $\mathrm{Th(SO_4)_2.Na_2SO_4.6H_2O(cr)}$.

Species	SIT ion interaction parameters (kg·mol⁻¹)		Reference
	ε_1	ε_2	
Na^+- SO_4^{2-}	– 0.184 ± 0.002	0.139 ± 0.006	Table B-6
Na^+- $\mathrm{Th(SO_4)_3^{2-}}$	– 0.091 ± 0.038	0.00	This review [a]

a: Based on experimental data interpretations (see Section IX.1.3.2 for details).

Table D-4: Dimensionless molar Gibbs free energies of formation at 298.15 K, unless otherwise identified, used in calculations involving $Th(SO_4)_2{\cdot}Na_2SO_4{\cdot}6H_2O(cr)$.

Species	$\Delta_f G_m^o / RT$
$H_2O(l)$	– 96.375 [a]
H^+	0
Na^+	– 105.670
Th^{4+}	– 284.305
SO_4^{2-}	– 300.126
HSO_4^-	– 304.689
$ThSO_4^{2+}$	– 598.638
$Th(SO_4)_2(aq)$	– 906.869
$Th(SO_4)_3^{2-}$	– 1209.432

a: Value at 16ºC.

Based on the analyses of these two cases discussed above, it is expected that the additional uncertainties in $\Delta_f G_m^o / RT$ of different species and in the calculated equilibrium constants due to uncertainties in the epsilon values will not be large.

D.2.3 Accounting for uncertainties in $\Delta_f G_m^o / RT$ values of auxiliary input data

The NONLINT-SIT and most other chemical equilibrium programs fix the chemical potential of the basal species ("master species") of the various components (in this review the master species for thorium is always the aquo-ion, $Th^{4+}(aq)$), and the chemical potentials of all other thorium species are calculated relative to these. For the example discussed in this Appendix, the values of $\Delta_f G_m^o / RT$ for Th^{4+}, H^+, Na^+, H_2O, HSO_4^- and SO_4^{2-} were fixed to the selected values given in Table D-4 and the values calculated by NONLINT-SIT for other species are referred to these values when calculating the equilibrium constant for a given reaction and its uncertainty. Note that the uncertainty in the Gibbs energy data for different species must not be included in the calculation of the equilibrium constants, because the Gibbs energies of both sides of such a reaction 'float' by exactly the same amount. To exemplify, we may use the results from the optimisation of the data [1963ALL/MCD] as discussed above. Based on a value of $\Delta_f G_m^o / RT\,(Th^{4+}) = -284.305$, an optimised value of $\Delta_f G_m^o / RT\,(Th(SO_4)_3^{2-}) = -(1209.432 \pm 0.086)$ was obtained. If $\Delta_f G_m^o / RT\,(Th^{4+})$ values of -282.168 or -286.442 (corresponding to the upper and lower limit of the uncertainties selected for Th^{4+}) were used, the optimised $\Delta_f G_m^o / RT\,(Th(SO_4)_3^{2-})$ values would have changed by the same amounts to $-(1207.295 \pm 0.086)$ and $-(1211.569 \pm 0.086)$. Hence the calculated value and uncertainty of $-\ln K^o$ (D.1) = $-(24.749 \pm 0.086)$ would not change at all as is clear from Equation (D.3):

$$Th^{4+} + 3\,SO_4^{2-} \rightleftharpoons Th(SO_4)_3^{2-} \qquad (D.1)$$

$$-\ln K^o = \Delta_f G_m^o / RT\,(Th(SO_4)_3^{2-}) - \Delta_f G_m^o / RT\,(Th^{4+}) - 3\,[\Delta_f G_m^o / RT\,(SO_4^{2-})] \qquad (D.3)$$

In this respect, one may also regard the optimisation program as a convenient means of fitting equilibrium constants, through the formal use of equations such as (D.3).

To conclude: the derived values of $\log_{10} K^o$ and their associated uncertainties are based only on the aqueous phase model and the experimental data, and not on the selected values or uncertainties of the $\Delta_f G_m^o / RT$ values of Th^{4+} or other auxiliary species used in the modelling. This holds true for all the other cases where values of equilibrium constants are determined directly from the experimental data. NONLIN-SIT is a comprehensive program that uses ion interaction parameters and chemical potentials of all of the species expected in a given system, but it may be regarded as a method to optimise equilibrium constants, even if it operates *via* $\Delta_f G_m^o / RT$ values.

To avoid the disparities discussed in this Section, when analysing a system with NONLINT-SIT, this review has selected some well studied equilibrium values of $\log_{10} K^o$. The uncertainties associated with these $\log_{10} K^o$ values have been estimated from the uncertainty of the Gibbs energy of relevant reaction calculated from the combined uncertainties of $\Delta_f G_m^o / RT$ for the species and compounds involved in the corresponding equilibria as reported or used by NONLINT-SIT, not by following the error propagation rules for the formal calculation leading from to $\Delta_f G_m^o$ to $\log_{10} K^o$. Hence the inherent uncertainties in the auxiliary data, including that of Th^{4+}, are not included in the uncertainties of the $\log_{10} K^o$ values.

D.3 Example: Determining the $\Delta_f G_m^o /RT$ value of Th(SO$_4$)$_2$·9H$_2$O(cr) from its solubility in H$_2$SO$_4$ solutions [1912BAR]

D.3.1 General equations and schematic approach to calculations

The experimental data consists of measured thorium concentrations at different given H_2SO_4 concentrations in equilibrium with $Th(SO_4)_2 \cdot 9H_2O(cr)$. The total measured aqueous thorium concentration is the sum of all the major aqueous thorium species (D.4) and the total experimental sulphate concentration is the sum of all the aqueous sulphate species (D.5).

$$m_{\text{Th, total}} = m_{\text{Th}^{4+}} + m_{\text{ThSO}_4^{2-}} + m_{\text{Th(SO}_4)_2\text{(aq)}} + m_{\text{Th(SO}_4)_3^{2-}} \quad \text{(D.4)}$$

$$m_{\text{SO}_4^{2-},\text{total}} = m_{\text{SO}_4^{2-}} + m_{\text{HSO}_4^-} + m_{\text{ThSO}_4^{2-}} + 2\, m_{\text{Th(SO}_4)_2\text{(aq)}} + 3m_{\text{Th(SO}_4)_3^{2-}} \quad \text{(D.5)}$$

The $\Delta_f G_m^o /RT$ values of all the aqueous species in this system are known (Table D-6). The $\Delta_f G_m^o /RT$ value of $Th(SO_4)_2 \cdot 9H_2O(cr)$ is the unknown which we need to optimise. The NONLINT-SIT program starts out with an estimated $\Delta_f G_m^o / RT$ ($Th(SO_4)_2 \cdot 9H_2O$, cr) value and calculates the total $\Delta_f G_m / RT$ of the solution phase (D.6) and the concentrations and activities of all of the species defined in the problem (Table D-6). Multiple iterations with different $\Delta_f G_m^o /RT$ ($Th(SO_4)_2 \cdot 9H_2O$, cr) estimates are done in order to minimise the differences between the total chemical potential of $Th(SO_4)_2\cdot9H_2O(cr)$ ($\Delta_f G_m / RT$) and the total chemical potential of the solution phase while meeting the mass and charge balance constraints,

$$(\Delta_f G_m / \mathrm{R}T)_{\mathrm{solution}} = \Sigma_j\, n_j(\Delta_f G_m / \mathrm{R}T)_j \qquad \text{(D.6)}$$

where n_j is the number of moles of solute and solvent species j [relevant species in this case are H_2O, H^+, Th^{4+}, SO_4^{2-}, $ThSO_4^{2+}$, $Th(SO_4)_2$ and $Th(SO_4)_3^{2-}$]. On a molality basis, the $\Delta_f G_m / \mathrm{R}T$ of different phase species is related to molalities and activity coefficients (γ) as depicted in Table D-5. For example:

$$\Delta_f G_m / \mathrm{R}T = \Delta_f G^o_m / \mathrm{R}T + \ln m_i + \ln \gamma_i$$

for solute species, where m_i is the molality of the species calculated by the program from model inputs and solution composition, and γ_i is the activity coefficients based on SIT ion-interaction parameters (for details see Appendix B).

The actual quantity minimised by NONLINT-SIT for this example is the penalty function:

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

where $f(x)$ is given by the phase equilibrium condition as:

$$f(x) = [\Delta_f G_m /\mathrm{R}T]_{\mathrm{solid}} - [\Delta_f G_m /\mathrm{R}T]_{\mathrm{solution}}$$

where $[\Delta_f G_m /\mathrm{R}T]_{\mathrm{solution}}$ is the sum of the contributions of all the relevant species in the aqueous phase. This quantity can also be regarded as the chemical potential of the solid, calculated from the current set of parameters.

Table D-5: General equations for different phase species.

Phase	Equation
Aqueous phase	
Solvent (H_2O)	$\Delta_f G_m / \mathrm{R}T = (\Delta_f G^o_m / \mathrm{R}T) - (\mathrm{R}T\cdot W/1000)(\sum_{i=1}^{ns} m_i)\,\varphi$
Solute species	$\Delta_f G_m / \mathrm{R}T = (\Delta_f G^o_m / \mathrm{R}T) + \ln m_i + \ln \gamma_i$
Pure solid phase	$\Delta_f G_m / \mathrm{R}T = \Delta_f G^o_m / \mathrm{R}T$
Solid-solution species	$\Delta_f G_m / \mathrm{R}T = (\Delta_f G^o_m / \mathrm{R}T) + \ln x_i + \ln \gamma_i$
Gaseous species	$\Delta_f G_m / \mathrm{R}T = (\Delta_f G^o_m / \mathrm{R}T) + \ln f_i$

W = molecular weight of water (18.016 $g\cdot mol^{-1}$),

γ_i = activity coefficient of species i,

φ = osmotic coefficient of the solution

x_i = mole fraction of species i,

f_i = fugacity of species i.

D.3.2 Input data

The input $\Delta_f G^\circ_m /RT$ values are reported in Table D-6 and SIT ion-interaction parameters in Table D-7. The raw experimental data for the solubility of $Th(SO_4)_2 \cdot 9H_2O(cr)$ in H_2SO_4 solutions given by [1912BAR] and summarised in [1965LIN2] are listed in Table D-8. These experimental data were used to calculate the total molalities of H^+, sulphate, and thorium, and are listed in Table D-9 as the experimental data used as a part of the input to the NONLINT-SIT program. The species used in the model were: H^+, Th^{4+}, $ThSO_4^{2+}$, $Th(SO_4)_2(aq)$, $Th(SO_4)_3^{2-}$, SO_4^{2-}, HSO_4^-, and $H_2O(l)$. The input molalities of H^+, Th^{4+}, and SO_4^{2-} were assigned equal to the analytical total concentrations. The input values of the other species were set to a very low value (1.0×10^{-9}).

Table D-6: Dimensionless molar Gibbs energies of formation at 25°C used in calculations.

Species	$\Delta_f G^\circ_m / RT$	Reference
$H_2O(l)$	– 95.661	Table VI-1
SO_4^{2-}	– 300.126	Table VI-1
HSO_4^-	– 304.689	Table VI-1
H^+	0.00	Table VI-1
OH^-	63.421	Table VI-1
Th^{4+}	– 284.305	This Review
$ThSO_4^{2+}$	– 598.638 ± 0.737	This Review
$Th(SO_4)_2(aq)$	– 906.869 ± 0.622	This Review
$Th(SO_4)_3^{2-}$	– 1209.432 ± 0.086	This Review
$Th(SO_4)_2 \cdot 9H_2O$	– 1745.5	Estimated, input[a]
	– 1771.410 ± 0.232	Optimised value

a: Sum of $\Delta_f G^\circ_m / RT$ values of constituent species.

Table D-7: SIT ion interaction parameters used in calculations.

Species	Ion interaction coefficients (kg·mol^{-1})		References
	ε_1	ε_2	
$H^+ - Th(SO_4)_3^{2-}$	– 0.068 ± 0.003	0.093 ± 0.007	This review[a]
$Th^{4+} - HSO_4^-$	0.70 ± 0.10	0.00	This review[b]
$H^+ - HSO_4^-$	0.14 ± 0.02	0.00	This review[c]

a: It is assumed that the values for $Li^+ - SO_4^{2-}$ (Table B-6) are applicable to this interaction.

b: It is assumed that the values for $Th^{4+} - ClO_4^-$ (this review) are applicable to this interaction.

c: It is assumed that the values for $H^+ - ClO_4^-$ (Table B-4) are applicable to this interaction.

Table D-8: The solubility of $Th(SO_4)_2{\cdot}9H_2O(cr)$ in aqueous solutions of sulphuric acid [1912BAR].

Concentrations (g per 100 g H_2O)		Molarities [a]	
H_2SO_4	Total Th	H_2SO_4	Total Th
0.00	1.722	0.000	0.041
1.072	1.919	0.109	0.045
1.941	2.017	0.198	0.047
2.821	2.060	0.288	0.0486
3.843	2.061	0.392	0.0486
5.212	2.035	0.532	0.0480

a: Calculated from columns 1 and 2.

D.3.3 Outputs

An optimised value of $\Delta_f G^o_m/RT = -(1771.410 \pm 0.232)$ was obtained for $Th(SO_4)_2{\cdot}9H_2O(cr)$. Using this fitted value and other inputs (chemical potentials, ion-interaction parameters, and analytical molalities of different species) described above, the program calculates:

1. the equilibrium aqueous concentrations for all of the species included in the model, as listed in Table D-9 and plotted in Figure IX-6,
2. the uncertainty (0.232, two sigma) for the optimised parameter from the data set used in these calculations. The fitted $\Delta_f G^o_m/RT$ value of $-(1771.410 \pm 0.232)$ for $Th(SO_4)_2{\cdot}9H_2O(cr)$ when combined with the $\Delta_f G^o_m/RT$ values of other species given in Table D-6 gives a $\log_{10} K^o$ value of $-(11.250 \pm 0.096)$ for the following solubility reaction:

$$Th(SO_4)_2{\cdot}9H_2O(cr) \rightleftharpoons Th^{4+} + 2SO_4^{2-} + 9H_2O(l)$$

Table D-9: Experimental [1912BAR] and predicted concentrations for the solubility of $Th(SO_4)_2{\cdot}9H_2O(cr)$ in H_2SO_4 solutions.

Experimental data			Predicted concentrations							
Concentrations of species (m)			Concentrations of species (m)							
H^+	Total SO_4^{2-}	Total Th	Total Th	Th^{4+}	$ThSO_4^{2+}$	$Th(SO_4)_2aq$	$Th(SO_4)_3^{2-}$	SO_4^{2-}	HSO_4^-	H^+
$1.000{\cdot}10^{-9}$	$8.200{\cdot}10^{-2}$	$4.100{\cdot}10^{-2}$	$3.515{\cdot}10^{-2}$	$9.393{\cdot}10^{-6}$	$5.979{\cdot}10^{-3}$	$2.772{\cdot}10^{-2}$	$1.445{\cdot}10^{-3}$	$4.553{\cdot}10^{-3}$	$3.897{\cdot}10^{-10}$	$1.610{\cdot}10^{-9}$
0.220	$2.000{\cdot}10^{-1}$	$4.500{\cdot}10^{-2}$	$4.072{\cdot}10^{-2}$	$1.490{\cdot}10^{-5}$	$4.396{\cdot}10^{-3}$	$2.867{\cdot}10^{-2}$	$7.636{\cdot}10^{-3}$	$2.229{\cdot}10^{-2}$	$8.450{\cdot}10^{-2}$	$1.355{\cdot}10^{-1}$
0.440	$2.940{\cdot}10^{-1}$	$4.700{\cdot}10^{-2}$	$4.508{\cdot}10^{-2}$	$2.247{\cdot}10^{-5}$	$4.840{\cdot}10^{-3}$	$2.941{\cdot}10^{-2}$	$1.081{\cdot}10^{-2}$	$3.013{\cdot}10^{-2}$	$1.639{\cdot}10^{-1}$	$2.361{\cdot}10^{-1}$
0.580	$3.870{\cdot}10^{-1}$	$4.860{\cdot}10^{-2}$	$4.900{\cdot}10^{-2}$	$2.927{\cdot}10^{-5}$	$5.282{\cdot}10^{-3}$	$3.015{\cdot}10^{-2}$	$1.354{\cdot}10^{-2}$	$3.620{\cdot}10^{-2}$	$2.454{\cdot}10^{-1}$	$3.346{\cdot}10^{-1}$
0.780	$4.870{\cdot}10^{-1}$	$4.860{\cdot}10^{-2}$	$5.310{\cdot}10^{-2}$	$3.551{\cdot}10^{-5}$	$5.743{\cdot}10^{-3}$	$3.099{\cdot}10^{-2}$	$1.633{\cdot}10^{-2}$	$4.186{\cdot}10^{-2}$	$3.374{\cdot}10^{-1}$	$4.426{\cdot}10^{-1}$
1.060	$6.260{\cdot}10^{-1}$	$4.800{\cdot}10^{-2}$	$5.855{\cdot}10^{-2}$	$4.189{\cdot}10^{-5}$	$6.351{\cdot}10^{-3}$	$3.217{\cdot}10^{-2}$	$1.999{\cdot}10^{-2}$	$4.856{\cdot}10^{-2}$	$4.679{\cdot}10^{-1}$	$5.921{\cdot}10^{-1}$

Appendix E

Spectroscopic constants and statistical mechanics calculations for gaseous species

In most cases, the thermal functions for gaseous species have been calculated by well-known statistical-mechanical relations (see for example Chapter 27 of [1961LEW/RAN]).

The parameters defining the vibrational and rotational energy levels of the molecule in terms of the rotational (J) and vibrational (v) quantum numbers, and thus many of its thermodynamic properties, are:

- for diatomic molecules (non-rigid rotator, anharmonic oscillator approximation): ω (vibrational frequency in wavenumber units), x (anharmonicity constant), B (rotational constant for equilibrium position), D (centrifugal distortion constant), α (rotational constant correction for excited vibrational states), and σ (symmetry number), where the energy levels with quantum numbers v and J are given by:

$$\begin{aligned} \mathrm{E}_{(v,J)}/\mathrm{h\,c} = {} & \omega\,(v+1/2)-\omega\,x(v+1/2)^2+B\,J(J+1) \\ & -D\,J^2\,(J+1)^2-\alpha\,(v+1/2)\,J\,(J+1) \end{aligned} \qquad \text{(E.1)}$$

- for linear polyatomic molecules, the parameters are the same as those for diatomic molecules, except that the contributions for anharmonicity are usually neglected.

- for non-linear polyatomic molecules (rigid rotator, harmonic oscillator approximation): $I_x\,I_y\,I_z$, the product of the principal moments of inertia (readily calculated from the geometrical structure of the molecule), v(i), the vibration frequencies and σ, the symmetry number. While the vibrational energy levels for polyatomic molecules are given approximately by the first term of Equation (E.1) for each of the normal vibrations, the rotational energy levels cannot be expressed as a simple general formula. However, the required rotational partition function can be expressed with sufficient accuracy simply in terms of the product of the principal moments of inertia. As for linear polyatomic molecules, anharmonic contributions are usually neglected.

In each case, the symmetry number σ, the number of indistinguishable positions into which the molecule can be turned by simple rotations, is required to calculate the correct entropy.

The relations for calculating the thermal functions from the partition function defined by the energy levels are well-known – again, see Chapter 27 of [1961LEW/RAN], for a simple description. In each case, the relevant translational and electronic contributions (calculated from the molar mass and the electronic energy levels and degeneracies) must be added. Except where accurate spectroscopic data exist, the geometry and parameters of the excited states are assumed to be the same as those for the ground state.

Table E-1 gives the molecular parameters of all the gaseous thorium species for which data are selected. Part A gives the selected parameters of the ground states of diatomic molecules, where r is the interatomic distance, and the remaining symbols are described above; higher electronic levels were included only for ThO(g) and ThS(g). The parameters for the excited states of ThO(g) are given in detail in Table VII-1; the energy levels assumed for ThS(g) are included below.

Table E-1: Molecular parameters of gaseous thorium species

Part A: diatomic species.

	r (Å)	ω (cm^{-1})	ωx (cm^{-1})	B (cm^{-1})	$10^3\,\alpha$ (cm^{-1})	$10^7\,D$ (cm^{-1})	Ground-state degeneracy
Th$_2$	3.3	92.2	0	0.01334	0	0	2
ThO	1.8403	895.77	2.39	0.332644	1.302	1.833	1
ThH	1.985	1485.2	30	4.2636	150	2000	2
ThF	2.05	489	4.0	0.2284	2.0386	1.9931	4
ThCl	2.48	292	2.0	0.089124	0.60992	0.33206	4
ThBr	2.65	194	2.0	0.040388	0.30458	0.070029	4
ThI	2.85	151	1	0.025299	0.13447	0.02841	4
ThS	2.34	480	2.39	0.1093	0	0	1
ThN	1.93	775	3.0	0.3426	0	0	2
ThP	2.67	360	0.0	0.08654	0	0	4
Additional electronic levels (cm^{-1}) (degeneracy)							
ThO(g)	see Table VII-1						
ThS(g)	4200(2) 4700(2) 5200(2)						

(Continued on next page)

Table E-1: (continued)

Part B: polyatomic species.

Species	Point group (Symmetry number)	Interatomic distance (Å)	Angle (deg)	Vibration frequencies (multiplicities) (cm^{-1})	Product of moments of inertia ($g^3 \cdot cm^{-6}$)
ThO_2	C_{2v} (2)	1.82	122.5	787(1) 220(1) 735(1)	$8.28 \cdot 10^{-115}$
ThF_2	C_{2v} (2)	2.10	130	483(1) 130(1) 447(1)	$2.65 \cdot 10^{-114}$
ThF_3	C_{3v} (3)	2.10	110	484(2) 156(2) 480(1) 140(1)	$1.84 \cdot 10^{-113}$
ThF_4	T_d(12)	2.14	109.5	581.6(1) 109.3(2) 520.0(3) 116.0(3)	$5.72 \cdot 10^{-113}$
ThOF	C_{2v} (2)	Th-O 1.80 Th-F 2.10	110	750(1) 500(1) 150(1)	$1.98\ 10^{-114}$
$ThCl_2$	C_{2v} (2)	2.53	130	308(1) 84(1) 315(1)	$4.61 \cdot 10^{-113}$
$ThCl_3$	C_{3v} (3)	2.53	110	320(1) 100(1) 333(2) 105(2)	$3.49 \cdot 10^{-112}$
$ThCl_4$	T_d(12)	2.567	109.5	340.3(1) 62.0(1) 335.0(3) 61.8(3)	$1.11 \cdot 10^{-111}$
$ThBr_2$	C_{2v} (2)	2.70	130	196(1) 60(1) 232(1)	$5.83 \cdot 10^{-112}$
$ThBr_3$	C_{3v} (3)	2.70	110	200(1) 68(1) 223(2) 66(2)	$5.45 \cdot 10^{-111}$
$ThBr_4$	T_d(12)	2.73	109.5	297.8(1) 40.4(2) 230 (3) 44.6(3)	$1.83 \cdot 10^{-110}$
ThI_2	C_{2v} (2)	2.90	130	140(1) 45(1) 176(1)	$2.83 \cdot 10^{-111}$
ThI_3	C_{3v} (3)	2.90	110	144(1) 53(1) 170(2) 48(2)	$3.19 \cdot 10^{-110}$
ThI_4	T_d(12)	2.91	109.5	147.6(1) 29.0(2) 179.6(3) 33.9(3)	$1.08 \cdot 10^{-109}$
ThC_2	C_∞(2)		180	see Table VII-1	$I_x = 2.44 \cdot 10^{-38}\ g \cdot cm^{-2}$
ThC_4	C_∞(2)		180	761(1) 1836(1) 734(1) 1771(1) 101(2) 494(2) 437(2)	$I_x = 5.35 \cdot 10^{-38}\ g \cdot cm^{-2}$

Electronic levels (cm^{-1}) (degeneracy)	
Th_2	0(2)
ThO_2	0(1) 20000(2) 21000(2) 22000(2) 23000(2) 26000(2) 28000(2)
ThF_2	0(1)
ThF_3	0(6)
ThF_4	0(1)
$ThCl_2$	0(1)
$ThCl_3$	0(6)
$ThCl_4$	0(1)
$ThBr_2$	0(1)
$ThBr_3$	0(6)
$ThBr_4$	0(1)
ThI_2	0(1)
ThI_3	0(6)
ThI_4	0(1)
ThC_2	0(1) 5321(2) 106256(1) 11156(2) 14520(2) 15975(2) 16354(1) 18038(2) 18337.6(1) 19586(2)
ThC_4	see Table VII-1

Appendix F

Comment on the data for ZrO(g) and ZrO_2(g)

There may be some problems with the data for ZrO(g) and ZrO_2(g) selected in the NEA-TDB review of zirconium by Brown *et al.* [2005BRO/CUR]. The values given by Brown *et al.* are based on the assessment in the third edition of the Janaf tables [1985CHA/DAV], modified for the slightly different values of $\Delta_f H_m^\circ$ (ZrO_2, cr, 298.15 K) used in the two reviews. However, the assessments in [1985CHA/DAV] for these species were made in December 1965 and thus predate a number of detailed experimental studies made in 1970s. Indeed, their values of the Gibbs energies of formation of both ZrO(g) and ZrO_2(g) are based solely on an early mass-spectrometric study by Chupka *et al.* [1957CHU/BER].

The later assessment of [1982GLU/GUR] quotes seven studies of the thermodynamics of ZrO(g) and six for ZrO_2(g), in both cases dating from 1957 to 1979. There seem to be no more recent experimental data on the vaporisation of these species. The values of $\Delta_f H_m^\circ$ (ZrO, g, 298.15 K) derived by [1982GLU/GUR] vary from 45.9 to 108.9 $kJ \cdot mol^{-1}$ (selected value (83.89 ± 11.00) $kJ \cdot mol^{-1}$), and those for $\Delta_f H_m^\circ$ (ZrO_2, g, 298.15 K) vary from -298 to -349 $kJ \cdot mol^{-1}$ (selected value $-(318.31 \pm 15.00)$ $kJ \cdot mol^{-1}$). These selected values, especially that for ZrO(g), are appreciably different from the values in [1985CHA/DAV] and [2005BRO/CUR], as shown in Table F-1, which summarises the data for ZrO(g), ZrO_2(cr) and ZrO_2(g) from the three assessments.

Because of the considerable uncertainty in the value of $\Delta_f H_m^\circ$ (ZrO, g, 298.15 K), this review has not utilised the data for the gaseous reaction Th(g) + ZrO(g) $\rightleftharpoons$ ThO(g) + Zr(g) given by Ackermann and Rauh [1974ACK/RAU], as noted in Section VII.1.1.2.

Table F-1: Comparison of assessed data for ZrO(g), ZrO$_2$(cr) and ZrO$_2$(g)

Property	[1982GLU/GUR]	[1985CHA/DAV]	[2005BRO/CUR]
ZrO(g)			
$\Delta_f H_m^o$ (298.15 K) (kJ·mol^{-1})	83.89 ± 11.00	58.6 ± 50.2	56.200 ± 27.008
S_m^o (298.15 K) (J·K^{-1}·mol^{-1})	228.184	227.6 ± 8.4	227.6 ± 8.4
$C_{p,m}^o$ (298.15 K) (J·K^{-1}·mol^{-1})	34.374	30.845	30.8 ± 1.0
ZrO$_2$(cr)			
$\Delta_f H_m^o$ (298.15 K) (kJ·mol^{-1})	− 1100.3 ± 1.3	− 1097.463 ± 1.700	− 1100.6 ± 1.3
S_m^o (298.15 K) (J·K^{-1}·mol^{-1})	50.39	50.359 ± 0.330	50.19 ± 0.62
$C_{p,m}^o$ (298.15 K) (J·K^{-1}·mol^{-1})	55.92	56.191	55.96 ± 0.79
ZrO$_2$(g)			
$\Delta_f H_m^o$ (298.15 K) (kJ·mol^{-1})	− 318.31 ± 15.00	− 305.4 ± 12.6	− 289.600 ± 47.018
S_m^o (298.15 K) (J·K^{-1}·mol^{-1})	264.631	260.48 ± 4.2	273.7 ± 5.0
$C_{p,m}^o$ (298.15 K) (J·K^{-1}·mol^{-1})	42.487	46.061	46.1 ± 1.0

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Livet, J.	[1985LIV/MUS] , [1987CHA/CHE]
Lofgren, N. L.	[1950EAS/BRE] , [1964LOF/KRI]
Lohr, H. R.	[1954LOH/OSB]
Lonsdale, H. K.	[1963LON/GRA]
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Maggio, F.	[1967MAG/ROM] , [1974MAG/ROM]
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Manoravi, P.	[2002JOS/SIV]
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Pettersson, O.	[1880NIL/PET]
Pialoux, A.	[1976PIA/ZAU]
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Pichot, E.	[1998BRA/DAC]
Pickett, G. R.	[1966GOR/MON]
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Porto, R.	[1987CIA/IUL]
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Preis, W.	[2005GAM/BUG]
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