

# Chapter I

## Introduction

### I.1 Background

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

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

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

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

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

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

In 2003, TDB III, the current third phase of the Project was started with an organisation and participation similar to the one adopted for TDB-II. Three reviews are contemplated: 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

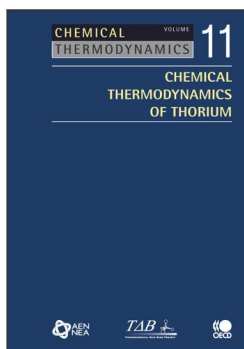
The objective of the present review is to present an assessment of the sources of published thermodynamic data in order to decide on the most reliable values and their uncertainties that can be recommended for modelling purposes. Experimental measurements published in the scientific literature are the 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  $\Delta_f G_m^\circ / RT$  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.



From:  
**Chemical Thermodynamics of Thorium, Volume 11**

Access the complete publication at:  
<https://doi.org/10.1787/9789264056688-en>

**Please cite this chapter as:**

OECD/Nuclear Energy Agency (2008), "Introduction", in *Chemical Thermodynamics of Thorium, Volume 11*, OECD Publishing, Paris.

DOI: <https://doi.org/10.1787/9789264056688-2-en>

This document, as well as any data and map included herein, are without prejudice to the status of or sovereignty over any territory, to the delimitation of international frontiers and boundaries and to the name of any territory, city or area. Extracts from publications may be subject to additional disclaimers, which are set out in the complete version of the publication, available at the link provided.

The use of this work, whether digital or print, is governed by the Terms and Conditions to be found at <http://www.oecd.org/termsandconditions>.