CHEMICAL THERMODYNAMICS OF AMERICIUM

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NUCLEAR ENERGY AGENCY
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

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The mission of the NEA is:

- to assist its member countries in maintaining and further developing, through international co-operation, the scientific, technological and legal bases required for a safe, environmentally friendly and economical use of nuclear energy for peaceful purposes, as well as
- to provide authoritative assessments and to forge common understandings on key issues, as input to government decisions on nuclear energy policy and to broader OECD policy analyses in areas such as energy and sustainable development.

Specific areas of competence of the NEA include safety and regulation of nuclear activities, radioactive waste management, radiological protection, nuclear science, economic and technical analyses of the nuclear fuel cycle, nuclear law and liability, and public information. The NEA Data Bank provides nuclear data and computer program services for participating countries.

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.

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Editor's note to the 2004 reprint

The present volume is a reprint of the 1995 edition of *Chemical Thermodynamics of Americium* by Robert J. Silva, Giovanni Bidoglio, Malcolm H. Rand, Piotr B. Robouch, Hans Wanner and Ignasi Puigdomenech, which also contains an Appendix on the *Chemical Thermodynamics of Uranium* by Ingmar Grenthe, M. C. Amaia Sandino, Ignasi Puigdomenech and Malcolm H. Rand. The book was edited at the NEA Data Bank and published by Elsevier under the North-Holland imprint.

As part of Phase II of the NEA Thermochemical Database Project (TDB), a new publication entitled *Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium* and authored by Robert Guillaumont, Thomas Fanghänel, Jean Fuger, Ingmar Grenthe, Volker Neck, Donald A. Palmer and Malcolm H. Rand, was published by Elsevier in 2003. For americium (and for the topics dealt with in the 1995 Appendix on uranium), this *Update* contains a review of the literature published since the cut-off date for the literature reviewed in the 1995 edition cited above. As a consequence of this new TDB Review, some of the values selected in the earlier publication have been superseded while others have retained their validity. The 2003 *Update* is self-contained with respect to any new data selections, but the discussions leading to the retained selections can in most cases only be found in the 1995 publication. Since the latter is no longer available from its original publisher, the NEA is making the present reprint available to the scientific community. ***Consequently, it is important to note that the Tables of Selected Values contained in this reprint ARE OUTDATED AND SHOULD NOT BE USED. The updated Tables and the rationale behind the new and updated selections can be consulted in the above-mentioned 2003*** **Update.**

This reprint has been prepared at the NEA Data Bank by Federico Mompean, Myriam Illemassene and Jane Perrone by reprocessing the files employed in the production of the 1995 edition. Every effort has been made to preserve the original layout and page numbering. We are grateful to the many readers who have provided feedback and pointed out errors in the 1995 book. In an attempt to make this reprint as close a reproduction of the original publication as possible, we have not implemented any corrections – major issues having been dealt with in the 2003 *Update*.

Preface

This is the second volume in a series of critical reviews of the chemical thermodynamic data of those elements of particular importance in the safety assessment modeling of high-level radioactive waste storage and disposal facilities. The Nuclear Energy Agency (NEA) Thermodynamic Data Base (TDB) project was started in 1984 by the Organisation for Economic Co-operation and Development (OECD). The objective, as outlined in NEA-TDB report 0, was to develop a set of reliable thermodynamic data that could be used to describe the behaviour of these elements under conditions relevant for radioactive waste disposal systems and the geochemical environments. The initiation of this peer review of the thermodynamic data of americium resulted from discussions between Hans Wanner, the TDB project leader at that time, and the chairman that took place during the Workshop on Geochemical Modeling at Fallen Leaf Lake, California in September 1986. A meeting was held at the NEA Data Bank, Saclay, France, in September of 1987 where the initial review committee met for the first time and where review philosophy, assignments and commitments where discussed. Present at this meeting, in addition to the chairman, were Dr. B. Allard (Linköping, Sweden), Dr. G. Bidoglio (JRC Ispra, Italy) and Dr. M. Rand (AERE Harwell, U.K.). Representing the NEA TDB project were Drs. H. Wanner and I. Poirot. A second meeting was held at the NEA Data Bank, Saclay, in May of 1990. At this meeting, first draft reviews of some of the sections of the Am review were submitted and discussed. Because of his work schedule, Dr. Allard was unable to make contributions to the review and was replaced by Dr. P. Robouch (IRMM, Geel, Belgium). Dr. I. Puigdomenech became the TDB project director in 1992 and assumed oversight of the final stages of this review.

This is a review of experimental data reported in the literature for americium. On a few occasions, where no data existed, comparisons and estimates were made based on experimental data on analog lanthanide elements. The basic philosophy was to develop a minimum set of solid phases and solution species of americium that would fit all experimental data being reviewed.

Each committee participant contributed selected review sections. Giovanni Bidoglio contributed the sections on hydrolysis products, halogen complexes and hydroxide solids. Elemental Am, aqua ions, oxides and compounds of the halogens, sulphur, nitrogen, phosphorous, *etc.* were drafted by Malcolm Rand. The data on sulphate, nitrate, phosphate, carbonate and thiocyanate complexes were reviewed by the chairman, by Piotr Robouch and by Ignasi Puigdomenech in close collaboration. When the sections were completed and assembled into one volume, all the members of the

team critically reviewed the entire volume. The final step, before submission for publication, was a technical review by three independent reviewers, Drs. Charles Baes, Lester Morss and Arthur Martell, and was a judgement of the peer review according to methods outlined in NEA-TDB report 6.

This review has been a very long time in completion. It would not have been possible without the constant attention and prodding of Hans Wanner and, in the later stages, Ignasi Puigdomenech. My personal thanks to the members of the review team who remained dedicated and diligent to the end. On behalf of the review team, I would like to thank the many colleagues who have helped and supported us in the completion of this review.

Livermore, California, September 1994 Robert J. Silva, Chairman

Acknowledgements

The contributions of Robert J. Silva were prepared as a Yucca Mountain Site Characterization Project (YMSCP) participant as part of the Civilian Radioactive Waste Management Program. The YMSCP is managed by the Yucca Mountain Site Characterization Project Office of the U.S. Department of Energy. Yucca Mountain Site Characterization Project work is sponsored by the DOE Office of Civilian Radioactive Waste Management.

A substantial part of the review work carried out by M.H. Rand was funded by the Corporate Research Programme of AEA Technology, Harwell, while he was employed by the U. K. Atomic Energy Authority.

P.B. Robouch would like to thank the Lawrence Livermore National Laboratory for financial support during his postdoctoral stay.

The following three independent experts have reviewed the contents of the present book (excluding Appendix D) according to the peer review procedures (*cf.* [90WAN]) prepared for this purpose in the framework of the NEA Thermochemical Data Base project. They have viewed and approved the modifications made by the authors according to their comments. The peer review comment records may be obtained on request from the OECD Nuclear Energy Agency.

Dr. C.F. Baes, Jr.	Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA (Retired)
Prof. A.E. Martell	Texas A. and M. University, College Station, Texas, USA
Dr. L.R. Morss	Argonne National Laboratory, Argonne, Illinois, USA

We are grateful to the members of both the NEA Radioactive Waste Management Committee and its Performance Assessment Advisory Group for their guidance and assistance in seeking financial support for this review. We thank the support and encouragement of the following persons within the NEA: Dr. Kunihiko Uematsu, Director General; Dr. Philippe Savelli, Deputy Director, Science, Computing and Development; Mr. Jean-Pierre Olivier, Head of the Division for Radiation Protection and Radioactive Waste Management; Dr. Nigel Tubbs and Mr. Claes Nordborg, of the Data Bank; Dr. Edward Patera of the Division for Radiation Protection and Waste Management; and Mrs. Isabelle Forest and Mrs. Sacha Koo-Oshima of the

Data Bank. The NEA–TDB data base system (*cf.* Foreword and Section II.6) has been developed and maintained with enthusiasm by Dr. Pierre Nagel of the NEA Data Bank. Thanks are due to S. Girod and L. Morel for their formatting and editing help.

We are grateful to Prof. I. Grenthe Royal Institute of Technology, Stockholm, Sweden, for his engagement and interest in the NEA–TDB project, and for allowing us to reproduce the text in Appendix B of the uranium review [92GRE/FUG].

In addition, we thank the following for their technical comments and suggestions in the course of the project: E. Falk, WS Atkins Internat. Ltd., Berlin, Germany; J. Fuger, Commission of the European Communities, JRC, Karlsruhe, Germany; E. Giffaut, ANDRA, Fontenay-aux-Roses, France; C. Pescatore, NEA, Issy-les-Moulineaux, France; J. Rydberg, Radiochemistry Consultant Group AB, V. Frölunda, Sweden; K. Spahiu, MBT Tecnologia Ambiental, Cerdanyola, Spain; P. Vitorge, Commissariat a l'Energie Atomique, Fontenay-aux-Roses, France; M. Yui, Power Reactor and Nuclear Fuel Development Corporation, Tokai Mura, Japan.

This book has been prepared with the aid of the LaTeX computer typesetting software [86LAM]. Most of the graphs were produced with the GNUPLOT plotting program, originally written by T. Williams and C. Kelly (LaTeX output option written by D. Kotz and R. Lang). Weighted least-squares fitting was performed with either the Deming program by Rinard and Goldman [88RIN/GOL], the DNLS1E-subroutine of the SLATEC library [80HAS/VAN, 84BUZ], or the NLIN procedure of the SAS software package [88SAS].

The authors also thank the following for their permission to reproduce copyright material: The American Institute of Physics and D.D.Wagman (National Institute for Science and Technology) for their permision to reproduce Figure II.1; the Committee on Data for Science and Technology, CODATA, for their permision to reproduce a sentence in Chapter IV.

Foreword

This is the second volume of a series of expert reviews of the chemical thermodynamics of key chemical elements in nuclear technology and waste management. Volumes on technetium, neptunium and plutonium are currently in progress. The recommended thermodynamic data are the result of a critical assessment of published information.

The data base system developed at the Data Bank of the OECD Nuclear Energy Agency (NEA), *cf.* Section II.6, ensures consistency not only within the recommended data set on americium but also among all the data sets to be published in the series. The NEA's thermochemical data base (TDB) system takes advantage of the functionality of the LaTeX document preparation software [86LAM], and is designed to retrieve the data base and construct tables of selected data, authors, references *etc.* in LaTeX format, which then can be inserted in the computer files that constitute the books in this series.

The NEA Data Bank provides a number of services that may be useful to the reader of this book.

- The recommended data can be obtained on electronic media (PC diskettes, magnetic tape, or via computer networks) directly from the NEA Data Bank. The special formatting of the data allows conversion to any specific formats convenient to the user. The design and development of a computer program to perform such format conversion is however left to the user.

- The NEA Data Bank maintains a library of computer programs in various areas. This includes geochemical codes such as PHREEQE, EQ3/6, MINEQL, MINTEQ, PHRQPITZ, *etc.*, in which chemical thermodynamic data like those presented in this book are required as the basic input data. These computer codes can be obtained on request from the NEA Data Bank.

For requests of data, computer programs, on-line access, and for further information, please write to:

OECD Nuclear Energy Agency, Data Bank
Le Seine St. Germain
12, boulevard des Iles
F-92130 Issy-les-Moulineaux, FRANCE

or send electronic mail through INTERNET to "tdb@nea.fr". Some information on the NEA is also available on the World-Wide Web at "http://www.nea.fr".

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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 factor is therefore the quantitative prediction of the reactions that are likely to occur between hazardous waste dissolved or suspended in groundwater, 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 provided by speciation calculations using chemical thermodynamic data. The local conditions, such as groundwater 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 a 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. 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.

The International Atomic Energy Agency (IAEA) in Vienna published between 1966 and 1983 special issues with compilations of physico-chemical properties of compounds and alloys of elements important in reactor technology: Pu, Nb, Ta, Be, Th, Zr, Mo, Hf and Ti. In 1976, 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 several parts, each concerning the thermodynamic properties of a given type of compounds for the entire actinide series. These reviews cover the literature approximately up to 1984. The latest volume in this series appeared in 1992, under Part 12: The Actinide Aqueous Inorganic Complexes [92FUG/KHO]. Unfortunately, data of importance for radioactive waste management (for example, Part 10: The Actinide Oxides) are lacking in the IAEA series.

The Radioactive Waste Management Committee (RWMC) of the OECD Nuclear Energy Agency recognised the need for an internationally acknowledged, high-quality thermochemical data base for the application in the safety assessment of radioactive waste disposal, and undertook the development of the NEA Thermochemical Data Base (TDB) project [85MUL4, 88WAN, 91WAN2]. 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. After the book on chemical thermodynamics of uranium [92GRE/FUG], the present report on americium thermodynamics is the second volume in the series.

Simultaneously with the NEA's TDB project, other reviews on the physical and chemical properties of actinides have appeared, including the book by Cordfunke *et al.* [90COR/KON], the series edited by Freeman *et al.* [84FRE/LAN, 85FRE/LAN, 85FRE/KEL, 86FRE/KEL, 87FRE/LAN, 91FRE/KEL], the two volumes edited by Katz *et al.* [86KAT/SEA], which include a chapter on americium [86SCH/PEN], and Part 12 by Fuger *et al.* [92FUG/KHO] within the IAEA reviews mentioned above. These compilations 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.

I.2. Focus of the review

As outlined in the previous section, the focus of the critical review presented in this report is on the thermodynamic data of americium 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 groundwaters and porewaters 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 puts much weight on the assessment of the low-temperature thermodynamics of americium in *aqueous solution* and makes independent analyses of the available literature in this area. There is little data available above room temperature. The standard method used for the analysis of ionic interactions between components dissolved in water (see Appendix B) allows the general and consistent use of the selected data for modelling purposes, regardless of the type and composition

of the groundwater, within the ionic strength limits given by the experimental data used for the data analyses in the present review.

This book contains a summary and a critical review (*cf.* Chapter V) of the thermodynamic data on compounds and aqueous complexes containing americium, as reported in the available chemical literature up to 1992, but a few more recent references are also included. A comparatively large number of primary references are discussed separately in Appendix A. Owing to the focus of this review, this report does not include data on the following items:

- Gaseous ions. A review on this subject, published by the IAEA [85HIL/GUR], will be useful for persons interested in gaseous ions of americium.
- Alloys and intermetallic compounds. Again, a review published by the IAEA [81CHI/AKH] can be used as initial source of information on this subject.
- Data on non-aqueous solutions (molten salts, organic solvents, *etc.*).
- Compounds or aqueous complexes containing organic ligands. This class of compounds is planned to be the subject of a later review in the NEA-TDB series.

Although the focus of this review is on americium, it is necessary to use data on a number of other species during the evaluation process that lead to the recommended data. These so-called auxiliary data are taken both from the publication of CODATA Key Values [89COX/WAG] and from the evaluation of additional auxiliary data in the uranium volume of this series [92GRE/FUG], 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, a 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 americium compounds and complexes.

I.3. Isotopes of americium

Although there are fourteen known isotopes of americium, only three have half-lives longer than a few days and would be of any concern in nuclear waste. The isotopes, their half-lives, modes of decay and specific activities are given in Table I.1 [78LED/SHI]. The isotope ^{242}Am is never present in spent reactor fuel in excess of a very small fraction of the total percent of americium radioactivity, while ^{241}Am dominates during the first few thousand years of decay and ^{243}Am dominates thereafter [80CRO].

Owing to the fact that americium is a synthetic element, all thermodynamic properties reviewed in this report have been obtained from measurements on either ^{241}Am or ^{243}Am.

Table I.1: Isotopes of americium in nuclear waste.

Isotope	Half-life	Mode of decay	Specific activity (GBq/g)
^{241}Am	433 years	alpha	128
^{242}Am	16 hours	82.7% beta 17.3% electron capture	2.99×10^{7}
^{242m}Am	152 years	internal transition 0.5% alpha	360
^{243}Am	7370 years	alpha	7.40

I.4. 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 that can be recommended. Experimental measurements published in the scientific literature are the main source for the selection of recommended data. Previous reviews are not neglected but 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 more realistic than those used by the original author, or which are consistent with side-reactions discussed in another section of the review (for example, data on carbonate complex formation might need to be reinterpreted to take into account consistent values for hydrolysis reactions). 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 interaction equations (*cf.* Appendix B).

In order to ensure that consistent procedures are used for the evaluation of primary data, a number of guidelines have been developed, *e.g.*, assignment of uncertainties. They have been updated and improved since 1987, and their most recent versions are available at the NEA [91WAN2, 91WAN3, 92GRE/WAN, 93PUI/RAR, 92WAN, 90WAN, 94WAN]. Some of these procedures are also outlined in this volume, *cf.* Chapter II, Appendix B, and Appendix C. These sections, which were also published in the uranium book [92GRE/FUG], have been revised in this review. For example, in Chapter II, the Section on "Redox equilibria" has been revised, a new Section on "pH" has been included, Table II.5 has been expanded, and two Sections (II.6 and II.7) have been moved from Chapter I. The most prominent changes in Appendix B are in Table B.1, Eq. (B.11) and Section B.1.4. Some minor errors have also been

removed from Appendix C.

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 [90WAN]. The purpose of the additional peer review is to receive 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 personnel having technical expertise in the subject matter to be reviewed, to a degree at least equivalent to that needed for the original review.

The thermodynamic data selected in the present review (see Chapters III and IV) 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. This review uses the approximate specific ion interaction method 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, this method, as described in Appendix B, should always be used in conjunction with the selected data presented in this review.

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 they are based on. 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 consider that the selected data set presented in this review (Chapter III) may not be "complete" with respect to all the conceivable systems and conditions; there are gaps in the information, particularly concerning aqueous species that contain more than one kind of ligands. The gaps are pointed out in the various sections of Chapter V, and this information may be used as a basis for the assignment of research priorities.

† It should be noted that Appendix D has not been included in the peer-review described here.

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 kept to a maximum of three characters (except for composed symbols) and are listed in Table II.1.

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 [79WHI2, 88MIL/CVI]. They are summarised in Table II.2.

II.1.3. Chemical formulae and nomenclature

This review follows the recommendations made by IUPAC [71JEN, 77FER, 90LEI] on the nomenclature of inorganic compounds and complexes, except for the following items:

Table II.1: Abbreviations for experimental methods.

aix	anion exchange
cal	calorimetry
chr	chromatography
cix	cation exchange
col	colorimetry
con	conductivity
cor	corrected
cou	coulometry
cry	cryoscopy
dis	distribution between two phases
em	electromigration
emf	electromotive force, not specified
gl	glass electrode
ise-X	ion selective electrode with ion X stated
ix	ion exchange
kin	rate of reaction
mvd	mole volume determination
nmr	nuclear magnetic resonance
pol	polarography
pot	potentiometry
prx	proton relaxation
qh	quinhydrone electrode
red	emf with redox electrode
rev	review
sp	spectrophotometry
sol	solubility
tc	transient conductivity
tls	thermal lensing spectrophotometry
vlt	voltammetry
?	method unknown to the reviewers

Table II.2: Symbols and terminology.

length	l
height	h
radius	r
diameter	d
volume	V
mass	m
density (mass divided by volume)	ρ
time	t
frequency	ν
wavelength	λ
internal transmittance (transmittance of the medium itself, disregarding boundary or container influence)	T
internal transmission density, (decadic absorbance): $\log_{10}(1/T)$	A
molar (decadic) absorption coefficient: $A/c_{\mathrm{B}}l$	ϵ
relaxation time	τ
Avogadro constant	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	$C_{p,\mathrm{m}}$
(molar) enthalpy	H_{m}
(molar) Gibbs energy	G_{m}
chemical potential of substance B	μ_{B}
pressure	p
partial pressure of substance B: $x_{\mathrm{B}}p$	p_{B}
fugacity of substance B	f_{B}
fugacity coefficient: $f_{\mathrm{B}}/p_{\mathrm{B}}$	$\gamma_{\mathrm{f,B}}$
amount of substance [(b)]	n
mole fraction of substance B: $n_{\mathrm{B}}/\sum_i n_i$	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}
mean ionic molality [(e)], $m_{\pm}^{(\nu_+ + \nu_-)} = m_+^{\nu_+} m_-^{\nu_-}$	$m_{\pm}$

Table II.2 (continued)

activity of substance B	a_{B}
activity coefficient, molality basis: $a_{\mathrm{B}}/m_{\mathrm{B}}$	γ_{B}
activity coefficient, concentration basis: $a_{\mathrm{B}}/c_{\mathrm{B}}$	y_{B}
mean ionic activity [(e)], $a_{\pm}^{(\nu_+ + \nu_-)} = a_{\mathrm{B}} = a_+^{\nu_+} a_-^{\nu_-}$	$a_{\pm}$
mean ionic activity coefficient [(e)], $\gamma_{\pm}^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$	$\gamma_{\pm}$
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
ion interaction coefficient between substance B_1 and substance B_2	$\varepsilon_{(\mathrm{B}_1,\mathrm{B}_2)}$
stoichiometric coefficient of substance B (negative for reactants, positive for products)	ν_{B}
general equation for a chemical reaction	$0 = \sum_{\mathrm{B}} \nu_{\mathrm{B}} \mathrm{B}$
equilibrium constant [(f)]	K
rate constant	k
Faraday constant	F
charge number of an ion B (positive for cations, negative for anions)	z_{B}
charge number of a cell reaction	n
electromotive force	E
$\mathrm{pH} = -\log_{10}[a_{\mathrm{H}^+}/(\mathrm{mol}\cdot\mathrm{kg}^{-1})]$, *cf.* Section II.1.7	pH
electrolytic conductivity	κ
superscript for standard state [(g)]	$^{\circ}$

(a) The ratio of the average mass per formula unit of a substance to $\frac{1}{12}$ of the mass of an atom of nuclide $^{12}\mathrm{C}$.

(b) *cf.* Sections 1.2 and 3.6 of the IUPAC manual [79WHI2].

(c) This quantity is called "amount-of-substance concentration" in the IUPAC manual [79WHI2]. A solution with a concentration equal to $0.1\,\mathrm{mol}\cdot\mathrm{dm}^{-3}$ is called a 0.1 molar solution or a 0.1 M solution.

(d) A solution having a molality equal to $0.1\,\mathrm{mol}\cdot\mathrm{kg}^{-1}$ is called a 0.1 molal solution or a 0.1 m solution.

(e) For an electrolyte $\mathrm{N}_{\nu_+}\mathrm{X}_{\nu_-}$ which dissociates into $\nu_{\pm}(=\nu_+ + \nu_-)$ inons, in an aqueous solution with concentration 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 1.2. 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 "Standard conditions".

i) The formulae of coordination compounds and complexes are not enclosed in square brackets [71JEN, Rule 7.21]. No brackets or parentheses are used at all to denote coordination compounds.

ii) 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 [71JEN, 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 [71JEN, Rules 2.163 and 7.21] is recalled here: the order of arranging ligands in coordination 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 ligating atoms determines the sequence of the ligands. For example, $(UO_2)_2CO_3(OH)_3^2$ is standard, $(UO_2)_2(OH)_3CO_3^-$ is non-standard and is not used.

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 a 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).

Examples:

$$\mathrm{UOCl_2(cr) + 2\,HBr(sln)} \rightleftharpoons \mathrm{UOBr_2(cr) + 2\,HCl(sln)} \tag{II.1}$$
$$\mathrm{UO_2Cl_2 \cdot 3H_2O(cr)} \rightleftharpoons \mathrm{UO_2Cl_2 \cdot H_2O(cr) + 2\,H_2O(l)} \tag{II.2}$$
$$\mathrm{UO_3(\gamma) + 2\,HCl(sln)} \rightleftharpoons \mathrm{UO_2Cl_2(cr) + H_2O(sln)} \tag{II.3}$$

- 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 a thermodynamic quantity refers to. The notation is in this case the same as outlined above. In an extended notation (*cf.* [82LAF]) the reference temperature is usually given in addition to the state of aggregation of the composition of a mixture.

Examples:

$\Delta_f G^\circ_m(\mathrm{Na^+, aq}, 298.15\ \mathrm{K})$	standard molar Gibbs energy of formation of aqueous Na^+ at 298.15 K
$S^\circ_m(\mathrm{UO_2SO_4 \cdot 2.5H_2O, cr}, 298.15\ \mathrm{K})$	standard molar entropy of $UO_2SO_4 \cdot 2.5H_2O$(cr) at 298.15 K
$C^\circ_{p,m}(\mathrm{UO_3}, \alpha, 298.15\ \mathrm{K})$	standard molar heat capacity of α-UO_3 at 298.15 K
$\Delta_f H_m(\mathrm{HF, sln, HF \cdot 7.8H_2O})$	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 [82LAF]. An exception to this rule is the equilibrium constant, *cf.* Section II.1.6. The nature of the process is denoted by

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

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

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.

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. 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 [64SIL/MAR, 71SIL/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 the data refer to, especially in cases where several ligands are discussed that might be confused. For example, for the equilibrium

$$m\,\mathrm{M} + q\,\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q \qquad \text{(II.4)}$$

both $\beta_{q,m}$ and β(II.4) would be appropriate, and $\beta_{q,m}$(II.4) is accepted, too. Note that, in general, K is used for the consecutive or stepwise formation constant, and 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.1.6.1. Protonation of a ligand

$$\mathrm{H^+ + H_{r-1}L} \rightleftharpoons \mathrm{H_rL} \qquad K_{1,r} = \frac{[\mathrm{H_rL}]}{[\mathrm{H^+}][\mathrm{H_{r-1}L}]} \tag{II.5}$$

$$r\,\mathrm{H^+ + L} \rightleftharpoons \mathrm{H_rL} \qquad \beta_{1,r} = \frac{[\mathrm{H_rL}]}{[\mathrm{H^+}]^r[\mathrm{L}]} \tag{II.6}$$

This notation has been proposed and used by Sillén and Martell [64SIL/MAR], but it has been simplified later by the same authors [71SIL/MAR] from $K_{1,r}$ to K_r. This review retains, for the sake of consistency, *cf.* Eqs. (II.7) and (II.8), the older formulation of $K_{1,r}$.

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

$$\mathrm{HL_{q-1} + L} \rightleftharpoons \mathrm{HL_q} \qquad K_q = \frac{[\mathrm{HL_q}]}{[\mathrm{HL_{q-1}}][\mathrm{L}]} \tag{II.7}$$

Eq. (II.8) refers to the overall formation constant of the species $\mathrm{H_rL_q}$.

$$r\,\mathrm{H^+} + q\,\mathrm{L} \rightleftharpoons \mathrm{H_rL_q} \qquad \beta_{q,r} = \frac{[\mathrm{H_rL_q}]}{[\mathrm{H^+}]^r[\mathrm{L}]^q} \tag{II.8}$$

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

Example:

$$\mathrm{H^+ + PO_4^{3-}} \rightleftharpoons \mathrm{HPO_4^{2-}} \qquad \beta_{1,1} = \beta_1 = \frac{[\mathrm{HPO_4^{2-}}]}{[\mathrm{H^+}][\mathrm{PO_4^{3-}}]}$$

$$2\,\mathrm{H^+ + PO_4^{3-}} \rightleftharpoons \mathrm{H_2PO_4^-} \qquad \beta_{1,2} = \frac{[\mathrm{H_2PO_4^-}]}{[\mathrm{H^+}]^2[\mathrm{PO_4^{3-}}]}$$

II.1.6.2. Formation of metal ion complexes

$$\mathrm{ML_{q-1} + L} \rightleftharpoons \mathrm{ML_q} \qquad K_q = \frac{[\mathrm{ML_q}]}{[\mathrm{ML_{q-1}}][\mathrm{L}]} \tag{II.9}$$

$$\mathrm{M} + q\,\mathrm{L} \rightleftharpoons \mathrm{ML_q} \qquad \beta_q = \frac{[\mathrm{ML_q}]}{[\mathrm{M}][\mathrm{L}]^q} \tag{II.10}$$

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

$$\mathrm{M + M_{q-1}L} \rightleftharpoons \mathrm{M_qL} \qquad K_{1,q} = \frac{[\mathrm{M_qL}]}{[\mathrm{M}][\mathrm{M_{q-1}L}]} \tag{II.11}$$

Eq. (II.12) refers to the overall formation constant of a complex M_mL_q.

$$m\,M + q\,L \rightleftharpoons M_mL_q \qquad \beta_{q,m} = \frac{[M_mL_q]}{[M]^m[L]^q} \tag{II.12}$$

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 H_2O occurs as a reactant to form hydroxide complexes, H_2O is considered as a protonated ligand, HL, so that the reaction is treated as described below in Eqs. (II.13) to (II.15) using n as the index variable. For convenience, no general form is used for the stepwise constants for the formation of the complex $M_mL_qH_r$. In many experiments, the formation constants of metal ion complexes are determined by adding to a metal ion solution a ligand in its protonated form. The complex formation reactions thus involve a deprotonation reaction of the ligand. If this is the case, the equilibrium constant is supplied with an asterisk, as shown in Eqs. (II.13) and (II.14) for mononuclear and in Eq. (II.15) for polynuclear complexes.

$$ML_{q-1} + HL \rightleftharpoons ML_q + H^+ \qquad {}^*K_q = \frac{[ML_q][H^+]}{[ML_{q-1}][HL]} \tag{II.13}$$

$$M + q\,HL \rightleftharpoons ML_q + q\,H^+ \qquad {}^*\beta_q = \frac{[ML_q][H^+]^q}{[M][HL]^q} \tag{II.14}$$

$$m\,M + q\,HL \rightleftharpoons M_mL_q + q\,H^+ \qquad {}^*\beta_{q,m} = \frac{[M_mL_q][H^+]^q}{[M]^m[HL]^q} \tag{II.15}$$

Examples:

$$UO_2^{2+} + HF(aq) \rightleftharpoons UO_2F^+ + H^+ \qquad {}^*K_1 = {}^*\beta_1 = \frac{[UO_2F^+][H^+]}{[UO_2^{2+}][HF(aq)]}$$

$$3\,UO_2^{2+} + 5\,H_2O(l) \rightleftharpoons (UO_2)_3(OH)_5^+ + 5\,H^+ \qquad {}^*\beta_{5,3} = \frac{[(UO_2)_3(OH)_5^+][H^+]^5}{[UO_2^{2+}]^3}$$

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 coordinated as such to the metal ion, the asterisk is to be omitted, as shown in Eq. (II.16).

$$M + q\,H_rL \rightleftharpoons M(H_rL)_q \qquad \beta_q = \frac{[M(H_rL)_q]}{[M][H_rL]^q} \tag{II.16}$$

Example:

$$UO_2^{2+} + 3\,H_2PO_4^- \rightleftharpoons UO_2(H_2PO_4)_3^- \qquad \beta_3 = \frac{[UO_2(H_2PO_4)_3^-]}{[UO_2^{2+}][H_2PO_4^-]^3}$$

II.1.6.3. Solubility constants

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

$$\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) \rightleftharpoons a\,\mathrm{M} + b\,\mathrm{L} \qquad K_{\mathrm{s},0} = [\mathrm{M}]^a[\mathrm{L}]^b \tag{II.17}$$

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

$$\frac{m}{a}\,\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) \rightleftharpoons \mathrm{M}_m\mathrm{L}_q + \left(\frac{mb}{a} - q\right)\mathrm{L} \qquad K_{\mathrm{s},q,m} = [\mathrm{M}_m\mathrm{L}_q][\mathrm{L}]^{\left(\frac{mb}{a}-q\right)} \tag{II.18}$$

Example:

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

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

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

$$^*K_{\mathrm{s},q,m} = \frac{[\mathrm{M}_m\mathrm{L}_q][\mathrm{HL}]^{\left(\frac{mb}{a}-q\right)}}{[\mathrm{H}^+]^{\left(\frac{mb}{a}-q\right)}} \tag{II.19}$$

Example:

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

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

II.1.6.4. Equilibria involving the addition of a gaseous ligand

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

$$\mathrm{ML}_{q-1} + \mathrm{L(g)} \rightleftharpoons \mathrm{ML}_q \qquad K_{\mathrm{p},q} = \frac{[\mathrm{ML}_q]}{[\mathrm{ML}_{q-1}]p_{\mathrm{L}}} \tag{II.20}$$

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

Examples:

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

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

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

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

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

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.1.6.5. 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 †, in accordance with the "1953 Stockholm Convention" [88MIL/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 electrode potential is related to the Gibbs energy change $\Delta_\mathrm{r}G_\mathrm{m}$ and the equilibrium constant K as outlined in Eq. (II.21).

$$E = -\frac{1}{nF}\Delta_\mathrm{r}G_\mathrm{m} = \frac{RT}{nF}\ln K \qquad \text{(II.21)}$$

The symbol E° is used for the emf 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). Eq. (II.21) can then be written in terms of E°, $\Delta_\mathrm{r}G_\mathrm{m}^\circ$ and K°.

For example, for the hypothetical galvanic cell:

$$\mathrm{Pt} \;\Big|\; \mathrm{H_2}(\mathrm{g}, p = 1\mathrm{bar}) \;\Big|\; \mathrm{HCl}(\mathrm{aq}, a_\pm = 1) \;\Big\vdots\; \begin{matrix}\mathrm{Fe(ClO_4)_2}(\mathrm{aq}, a'_\pm)\\ \mathrm{Fe(ClO_4)_3}(\mathrm{aq}, a''_\pm)\end{matrix} \;\Big|\; \mathrm{Pt}, \qquad \text{(II.22)}$$

where "⋮" denotes a liquid junction and "|" a phase boundary, the cell reaction is:

$$\mathrm{Fe^{3+}} + \tfrac{1}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{Fe^{2+}} + \mathrm{H^+} \qquad \text{(II.23)}$$

† The definitions of SHE and NHE are given in Section II.1.1.

For convenience Reaction (II.23) can be represented by half cell reactions, each involving an equal number of "electrons", as shown in the following equations

$$\mathrm{Fe^{3+} + e^- \rightleftharpoons Fe^{2+}} \tag{II.24}$$

$$\tfrac{1}{2}\mathrm{H_2(g) \rightleftharpoons H^+ + e^-} \tag{II.25}$$

where "$\mathrm{e^-}$" is a symbol devoid of any physical or chemical significance, and therefore its name, "electron", might be misleading but this inconvenience is compensated by its usefulness.

Equilibrium constants may be written for these half cell reactions in the following way:

$$K^\circ(\mathrm{II.24}) = \frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}} \times a_{\mathrm{e^-}}} \tag{II.26}$$

$$K^\circ(\mathrm{II.25}) = \frac{a_{\mathrm{H^+}} \times a_{\mathrm{e^-}}}{\sqrt{p_{\mathrm{H_2}}}} = 1 \quad \text{(by definition)} \tag{II.27}$$

In addition, $\Delta_\mathrm{r}G^\circ_\mathrm{m}(\mathrm{II.25}) = \Delta_\mathrm{r}H^\circ_\mathrm{m}(\mathrm{II.25}) = \Delta_\mathrm{r}S^\circ_\mathrm{m}(\mathrm{II.25}) = 0$ by definition, at all temperatures, and therefore $\Delta_\mathrm{r}G^\circ_\mathrm{m}(\mathrm{II.24}) = \Delta_\mathrm{r}G^\circ_\mathrm{m}(\mathrm{II.23})$.

The following equations describe the change in the Gibbs energy and redox potential of Reaction (II.23), if $p_{\mathrm{H_2}}$ and $a_{\mathrm{H^+}}$ are equal to unity (*cf.* Eq. (II.21)):

$$\Delta_\mathrm{r}G_\mathrm{m}(\mathrm{II.23}) = \Delta_\mathrm{r}G^\circ_\mathrm{m}(\mathrm{II.23}) + RT\ln\left(\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}\right)$$

$$E(\mathrm{II.23}) = E^\circ(\mathrm{II.23}) - \frac{RT}{nF}\ln\left(\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}\right) \tag{II.28}$$

The "activity of electrons" in Eqs. (II.26) and (II.27) may be interpreted to represent the relative tendency for electrons to leave an aqueous solution. For the standard hydrogen electrode $a_{\mathrm{e^-}} = 1$ (by the convention expressed in Eq. (II.27)), while rearrangement of Eq. (II.26) for the half-cell containing the iron perchlorates in cell II.22 gives:

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

and by the convention in Eq. (II.27):

$$-\log_{10} a_{\mathrm{e^-}} = \log_{10} K^\circ(\mathrm{II.23}) - \log_{10}\left(\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}\right) \tag{II.29}$$

A comparison of Eqs. (II.28) and (II.29) taking into account Eq. (II.21) shows that for the right half-cell in II.22:

$$-\log_{10} a_{\mathrm{e^-}} = \frac{F}{RT\ln(10)}E(\mathrm{II.23}) \tag{II.30}$$

The splitting of redox reactions into two half cell reactions by introducing the symbol "e^-", which according to Eq. II.30 is related to the standard electrode potential, is

arbitrary but justified by the usefulness of the resulting equations. 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, "e^-" is void of chemical and physical significance, and its concentration must be set to zero during the calculations (arbitrary values, however, may be assigned to a_{e^-} which are then related to E by Eq. (II.30)).

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 [81STU/MOR, 82DRE, 84HOS, 86NOR/MUN]).

II.1.7. 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

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

can only be strictly used in the limiting range of the Debye-Hückel equation (that is, in extremely dilute solutions). In practice the use of pH values requires extra assumptions on the values for single ion activities. In this review values of pH are used to describe qualitatively 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 [69ROS, 73BAT]. 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):

$$\mathrm{Pt(s)} \,\Big|\, \mathrm{Ag(s)} \,\Big|\, \mathrm{AgCl(s)} \,\Big|\, \mathrm{HCl(aq)} \,\underset{a}{\vdots}\, \begin{matrix}\text{salt}\\ \text{bridge}\end{matrix} \,\underset{b}{\vdots}\, \begin{matrix}\text{test}\\ \text{solution}\end{matrix} \,\vdots\vdots\, \mathrm{HCl(aq)} \,\Big|\, \mathrm{AgCl(s)} \,\Big|\, \mathrm{Ag(s)} \,\Big|\, \mathrm{Pt(s)}, \qquad \text{(II.31)}$$

where "$\vdots\vdots$" stands for a glass membrane (permeable to hydrogen ions). The emf of such a cell is given by

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

where $E^{\circ\prime}$ is a constant, and E_j is the 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 † 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 $[ClO_4^-] = 0.1$ M as background electrolyte, the dependence of the liquid junction at "*b*" on acidity is $E_j \approx -440 \times [H^+]$ mV $\cdot$ dm^3 $\cdot$ mol^{-1} at 25°C [69ROS, *p*.110], which corresponds to an error at pH= 2 of ≥ 0.07 pH units.

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 [88MIL/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).

II.1.8. Order of formulae

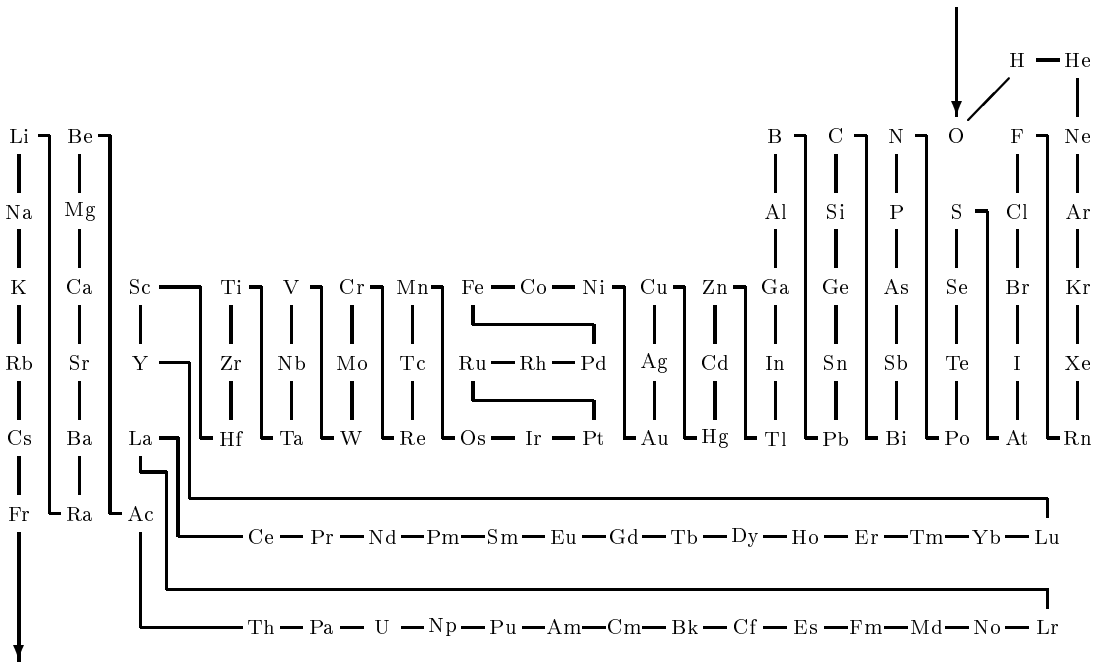
To be consistent with CODATA, the data tables are given in "Standard Order of Arrangement" [82WAG/EVA]. This scheme is presented in Figure II.1 below which shows the sequence of the ranks of the elements in this convention. The order follows the ranks of the elements. For uranium, this means that, after elemental uranium and its monoatomic ions (*e.g.*, U^{4+}), the uranium compounds and complexes with oxygen are 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.* Formulae with identical stoichiometry are in alphabetical order of their designators.

II.1.9. 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 [87GAR/PAR]. A reference code is made up of the final two digits of the year of appearance (if the publication is not from the 20th century, the year will be put in full). The year is followed by the first three letters of the first two authors, separated by a slash. If

† $KClO_4$(cr) has a solubility of ≈ 0.15 M in pure water at 25°C.

Figure II.1: Standard order of arrangement of the elements and compounds based on the periodic classification of the elements (from Ref. [82WAG/EVA]).



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.

The assignment of the reference codes is done automatically by the NEA updating programs for the TDB data base (*cf.* Section II.6). It is therefore possible that multiple reference codes in the TDB data base do not occur in multiple form in the present volume. The designators "2", "3", *etc.*, are nevertheless retained for reasons of compatibility with the TDB data base.

II.2. Units and conversion factors

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

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 "$\mathrm{mol \cdot dm^{-3}}$" for molarity, c, and "m" as an abbreviation of "$\mathrm{mol \cdot kg^{-1}}$" 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

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. $\triangleq$ cal $\cdot$ K^{-1} $\cdot$ mol^{-1})	J $\cdot$ K^{-1} $\cdot$ mol^{-1}	4.184 (exactly)

units (*cf.* Appendix B). This conversion is made in the following way. Molality is defined as m_{B} moles of substance B dissolved in 1000 grams of pure water. Molarity is defined as c_{B} moles of substance B dissolved in $(1000\rho - c_{\mathrm{B}}M)$ grams of pure water, where ρ is the density of the solution and M the molar weight of the solute. From this it follows that

$$m_{\mathrm{B}} = \frac{1000 c_{\mathrm{B}}}{1000\rho - c_{\mathrm{B}}M}$$

Baes and Mesmer [76BAE/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 [85SOH/NOV], are reported in Table II.5.

Examples:

$$\begin{aligned} 1.00\ \mathrm{M\ NaClO_4} &\triangleq 1.05\ \mathrm{m\ NaClO_4} \\ 1.00\ \mathrm{M\ NaCl} &\triangleq 1.02\ \mathrm{m\ NaCl} \\ 4.00\ \mathrm{M\ NaClO_4} &\triangleq 4.95\ \mathrm{m\ NaClO_4} \\ 6.00\ \mathrm{M\ NaNO_3} &\triangleq 7.55\ \mathrm{m\ NaNO_3} \end{aligned}$$

It should be noted that equilibrium constants, unless they are dimensionless, 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:

$$\begin{aligned} \log_{10} K_c &= \sum_{\mathrm{B}} \nu_{\mathrm{B}} \log_{10} c_{\mathrm{B}} \\ \log_{10} K_m &= \sum_{\mathrm{B}} \nu_{\mathrm{B}} \log_{10} m_{\mathrm{B}} \end{aligned}$$

With $(m_{\mathrm{B}}/c_{\mathrm{B}}) = \varrho$, or $(\log_{10} m_{\mathrm{B}} - \log_{10} c_{\mathrm{B}}) = \log_{10} \varrho$, the relationship between K_c and K_m becomes very simple, as shown in Eq. (II.32).

$$\log_{10} K_m = \log_{10} K_c + \sum_{\mathrm{B}} \nu_{\mathrm{B}} \log_{10} \varrho \qquad \text{(II.32)}$$

Table II.5: Factors ϱ 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 [85SOH/NOV]).

	$\varrho = m_B/c_B$ (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

$\sum_B \nu_B$ is the sum of the stoichiometric coefficients of the reaction, *cf.* Eq. (II.48), and the values of ϱ 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 [92GRE/FUG, *p*.23] are found at the highest concentrations, and are $\leq \pm 0.003 \mathrm{dm}^3/\mathrm{kg}$, reflecting the accuracy expected in this type of conversions. The uncertainty introduced by the use of Eq. (II.32) in the values of $\log_{10} K_m$ will then be $\leq \pm 0.001 \sum_B \nu_B$.

II.3. Standard and reference conditions

II.3.1. Standard state

A precise definition of the term "standard state" has been given by IUPAC [82LAF]. 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 [82LAF] definition of the standard state has been adopted in the NEA-TDB project. The standard state pressure, $p^\circ = 0.1\,\mathrm{MPa}$ (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 solution, at the standard state pressure, in which $m_B = m^\circ = 1\,\mathrm{mol} \cdot \mathrm{kg}^{-1}$, and in which the activity coefficient γ_B is unity.

It should be emphasised that the use of $^\circ$, *e.g.*, in $\Delta_f H^\circ_m$, 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.

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 [82LAF]. 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

Table II.6: Reference states for the elements at the reference temperature of 298.15 K [82WAG/EVA, 89COX/WAG].

O_2	gaseous	Pb	crystalline, cubic
H_2	gaseous	B	β, crystalline, rhombohedral
He	gaseous	Al	crystalline, cubic
Ne	gaseous	Zn	crystalline, hexagonal
Ar	gaseous	Cd	crystalline, hexagonal
Kr	gaseous	Hg	liquid
Xe	gaseous	Cu	crystalline, cubic
F_2	gaseous	Ag	crystalline, cubic
Cl_2	gaseous	Fe	crystalline, cubic
Br_2	liquid	V	crystalline, cubic
I_2	crystalline, orthorhombic	Ti	crystalline, hexagonal
S	crystalline, orthorhombic	U	crystalline, orthorhombic
Se	crystalline, hexagonal ("black")	Th	crystalline, cubic
Te	crystalline, hexagonal	Be	crystalline, hexagonal
N_2	gaseous	Mg	crystalline, hexagonal
P	crystalline, cubic ("white")	Ca	crystalline, cubic
As	crystalline, rhombohedral ("grey")	Sr	crystalline, cubic
Sb	crystalline, rhombohedral	Ba	crystalline, cubic
Bi	crystalline, rhombohedral	Li	crystalline, cubic
C	crystalline, hexagonal (graphite)	Na	crystalline, cubic
Si	crystalline, cubic	K	crystalline, cubic
Ge	crystalline, cubic	Rb	crystalline, cubic
Sn	crystalline, tetragonal ("white")	Cs	crystalline, cubic

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 parameters are affected significantly. A large part of the following discussion has been taken from the NBS tables of chemical thermodynamic properties [82WAG/EVA], see also Freeman [84FRE].

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

substances:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = V(1-\alpha T) \tag{II.33}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{II.34}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\alpha = -\left(\frac{\partial V}{\partial T}\right)_p \tag{II.35}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{II.36}$$

$$\text{where} \qquad \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{II.37}$$

For ideal gases, $V = \frac{RT}{p}$ and $\alpha = \frac{R}{pV} = \frac{1}{T}$. The conversion equations listed below (Eqs. (II.38) to (II.45)) 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 $^{(\mathrm{atm})}$ here, the ones that refer to the new standard state pressure of 1 bar the superscript $^{(\mathrm{bar})}$.

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

$$\Delta_\mathrm{f} H^{(\mathrm{bar})}(T) - \Delta_\mathrm{f} H^{(\mathrm{atm})}(T) = 0 \tag{II.38}$$

$$C_p^{(\mathrm{bar})}(T) - C_p^{(\mathrm{atm})}(T) = 0 \tag{II.39}$$

For gaseous substances, the entropy difference is

$$\begin{aligned} S^{(\mathrm{bar})}(T) - S^{(\mathrm{atm})}(T) &= R\ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right) \\ &= R\ln 1.01325 \\ &= 0.1094\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}. \end{aligned} \tag{II.40}$$

This is exactly true for ideal gases, as follows from Eq. (II.35) with $\alpha = \frac{R}{pV}$. The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

$$\begin{aligned} \Delta_\mathrm{r} S^{(\mathrm{bar})} - \Delta_\mathrm{r} S^{(\mathrm{atm})} &= \delta \times R\ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right) \\ &= \delta \times 0.1094\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}, \end{aligned} \tag{II.41}$$

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

$$\begin{aligned} \Delta_\mathrm{r} G^{(\mathrm{bar})} - \Delta_\mathrm{r} G^{(\mathrm{atm})} &= -\delta \times RT\ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right) \\ &= -\delta \times 0.03263\,\mathrm{kJ\cdot mol^{-1}} \text{ at } 298.15\,\mathrm{K}. \end{aligned} \tag{II.42}$$

Eq. (II.42) applies also to $\Delta_f G^{(bar)} - \Delta_f G^{(atm)}$, since the Gibbs energy of formation describes the formation process of a compound or complex from the reference states of the elements involved:

$$\Delta_r G^{(bar)} - \Delta_r G^{(atm)} = -\delta \times 0.03263\,\mathrm{kJ \cdot mol^{-1}} \text{ at } 298.15\,\mathrm{K}. \tag{II.43}$$

The change 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.42):

$$\begin{aligned} \log_{10} K^{(bar)} - \log_{10} K^{(atm)} &= -\frac{\Delta_r G^{(bar)} - \Delta_r G^{(atm)}}{RT \ln 10} \\ &= \delta \times \frac{\ln\left(\frac{p^{(atm)}}{p^{(bar)}}\right)}{\ln 10} = \delta \times \log_{10}\left(\frac{p^{(atm)}}{p^{(bar)}}\right) \\ &= \delta \times 0.005717 \end{aligned} \tag{II.44}$$

$$\begin{aligned} E^{(bar)} - E^{(atm)} &= -\frac{\Delta_r G^{(bar)} - \Delta_r G^{(atm)}}{nF} \\ &= \delta \times \frac{RT \ln\left(\frac{p^{(atm)}}{p^{(bar)}}\right)}{nF} \\ &= \delta \times \frac{0.0003382}{n}\,\mathrm{V} \text{ at } 298.15\,\mathrm{K}. \end{aligned} \tag{II.45}$$

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

$$\mathrm{H^+ + e^-} \rightleftharpoons \tfrac{1}{2}\mathrm{H_2(g)} \qquad E^\circ \stackrel{\text{def}}{=} 0.00\,\mathrm{V} \tag{II.46}$$

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

$$\mathrm{Ag^+ + e^-} \rightleftharpoons \mathrm{Ag(cr)}$$

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

$$\mathrm{Ag^+} + \tfrac{1}{2}\mathrm{H_2(g)} \rightleftharpoons \mathrm{Ag(cr)} + \mathrm{H^+}.$$

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.

Examples:

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

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 [82LAF], 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 [69COM]. The relation between the absolute temperature T (K, kelvin) and the Celsius temperature t (°C) is defined by $t = (T - T_0)$ where $T_0 = 273.15$ K.

II.4. Fundamental physical constants

The fundamental physical constants are taken from a recent publication by CODATA [86COD]. Those relevant to this review are listed in Table II.7.

Table II.7: Fundamental physical constants. These values have been taken from CODATA [86COD]. 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	$\mu_\circ$	$4\pi \times 10^{-7}$	
		$= 12.566\,370\,614\ldots$	$10^{-7}\,\mathrm{N \cdot A^{-2}}$
permittivity of vacuum	$\epsilon_\circ$	$1/\mu_\circ c^2$	
		$= 8.854\,187\,817\ldots$	$10^{-12}\,\mathrm{C^2 \cdot J^{-1} \cdot m^{-1}}$
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, $N_\mathrm{A} \times e$	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, $(e/\mathrm{C})\,\mathrm{J}$	eV	1.602 177 33(49)	$10^{-19}\,\mathrm{J}$
atomic mass unit, $1\mathrm{u} = m_\mathrm{u} = \frac{1}{12} m(^{12}\mathrm{C})$	u	1.660 5402(10)	$10^{-27}\,\mathrm{kg}$

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 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 data base system has been developed at the NEA Data Bank that allows the storage of thermodynamic parameters for individual species as well as for reactions. A simplified schema of the NEA-TDB system is shown in Figure II.2. The structure of the data base 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 stored in the REFERENCES record, and each author name has a link to the AUTHORS record for direct retrieval of author names.

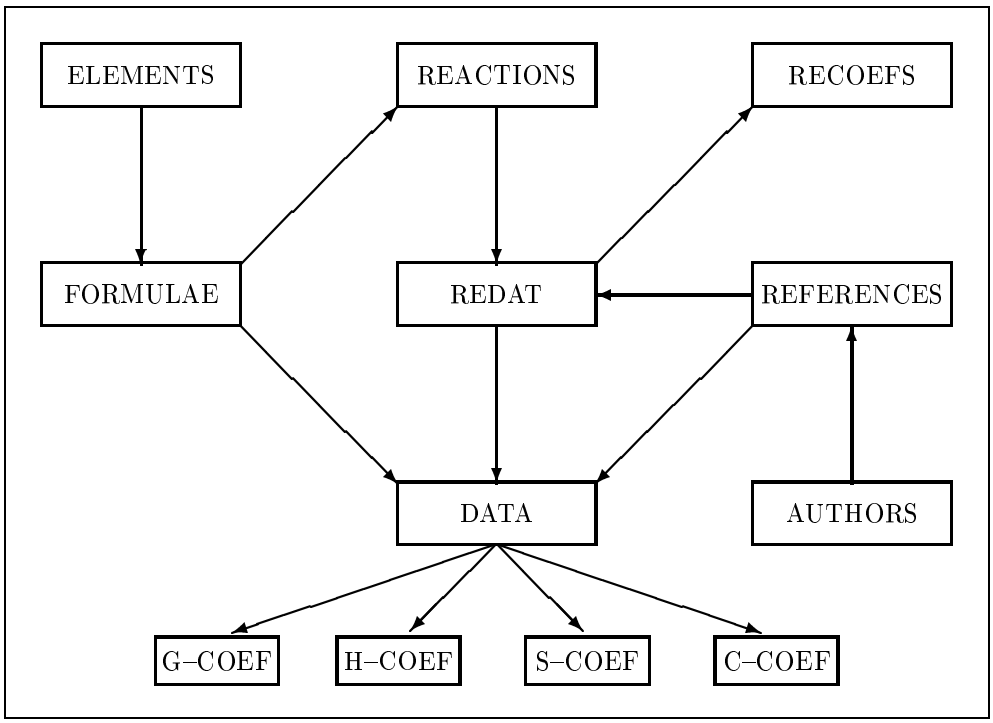
The thermodynamic data and their uncertainties selected for individual species are stored in the DATA record. The following parameters, valid at the reference temperature of 298.15 K and at the standard pressure of 1 bar, are considered:

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

For aqueous neutral species and ions, the values of $\Delta_f G^\circ_m$, $\Delta_f H^\circ_m$, S°_m and $C^\circ_{p,m}$ 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 [89COX/WAG] that $\Delta_f H^\circ_m(\mathrm{H^+, aq}, T) = 0$, and that $S^\circ_m(\mathrm{H^+, aq}, T) = 0$. Furthermore, for an *ionised solute* B containing any number of different cations and anions:

$$\begin{aligned}
\Delta_f H^\circ_m(\mathrm{B_\pm, aq}) &= \sum_+ \nu_+ \Delta_f H^\circ_m(\mathrm{cation, aq}) + \sum_- \nu_- \Delta_f H^\circ_m(\mathrm{anion, aq}) \\
S^\circ_m(\mathrm{B_\pm, aq}) &= \sum_+ \nu_+ S^\circ_m(\mathrm{cation, aq}) + \sum_- \nu_- S^\circ_m(\mathrm{anion, aq}).
\end{aligned}$$

Figure II.2: Principal schema of the NEA Thermochemical Data Base.



As the parameters in the DATA record vary as a function of temperature, provision is made to include the compilation of the coefficients of empirical temperature functions for these thermodynamic data in the records G-COEF, H-COEF, S-COEF and C-COEF, 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 non-linear regression method is used in this review to obtain the most significant coefficients of the following empirical function:

$$\begin{aligned} F(T) &= a + b \times T + c \times T^2 + d \times T^{-1} + e \times T^{-2} + f \times \ln T + g \times T \ln T \\ &\quad + h \times \sqrt{T} + \frac{i}{\sqrt{T}} + j \times T^3 + k \times T^{-3}. \end{aligned} \tag{II.47}$$

Most temperature variations can be described with three or four parameters, a, b and e being the ones most frequently used. In the present review, only $C^{\circ}_{p,\mathrm{m}}(T)$, *i.e.*, the thermal functions of the heat capacities of individual species, are considered and stored in the record C-COEF. They refer to the relation

$$C^{\circ}_{p,\mathrm{m}}(T) = a + b \times T + c \times T^2 + d \times T^{-1} + e \times T^{-2}$$

and are listed in Tables III.3 .

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.*, [82HAM, 84MAR/MES, 88SHO/HEL, 88TAN/HEL, 89SHO/HEL, 89SHO/HEL2, 90MON, 91AND/CAS].

Selected standard thermodynamic data referring to chemical reactions (which are stored in the REACTIONS record in alphanumeric notation) are compiled in the REDAT record (*cf.* Figure II.2). A chemical reaction "r", involving reactants and products "B", can be abbreviated as

$$0 \;=\; \sum_{\mathrm{B}} \nu_{\mathrm{B}}^{r}\,\mathrm{B} \tag{II.48}$$

where the stoichiometric coefficients ν_{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 in the record RECOEFS, according to Eq. (II.47).

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

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

and can be calculated from the individual values of $\Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{B})$ (for example, those given in Tables III.1 and IV.1) according to,

$$\log_{10} K_r^{\circ} \;=\; -\frac{1}{RT \ln(10)} \sum_{\mathrm{B}} \nu_{\mathrm{B}}^{r}\, \Delta_{\mathrm{f}} G_{\mathrm{m}}^{\circ}(\mathrm{B}). \tag{II.49}$$

II.7. Presentation of the selected data

The selected data are presented in Chapters III and IV. Unless otherwise indicated, they refer to standard conditions (*cf.* Section II.3) and 298.15 K (25.00°C) and are provided with an uncertainty which should correspond to the 95% confidence level (see Appendix C).

Chapter III contains a table of selected thermodynamic data for individual compounds and complexes of americium (Table III.1), a table of selected reaction data (Table III.2) for reactions concerning americium species, and a table containing selected thermal functions of the heat capacities of individual species of americium (Table III.3). The selection of these data is discussed in Chapter V.

Chapter IV contains, for auxiliary compounds and complexes that do not contain americium, 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 [89COX/WAG]. The selection of the remaining auxiliary data is discussed in Chapter VI of the uranium review [92GRE/FUG].

All the selected data presented in Tables III.1, III.2, IV.1 and 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 americium 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 Tables III.2 and IV.2 include only those species of which the primary selected data are reaction data. The formation data derived therefrom and listed in Table III.1 is 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 Tables III.2 and IV.2, rather than taking the derived values in Tables III.1 and IV.1 to calculate the reaction data with Eq. (II.49). 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 [93PUI/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:

$$\begin{aligned}\Delta_{\mathrm{r}}G^{\circ}_{\mathrm{m}}(T) &= \Delta_{\mathrm{r}}H^{\circ}_{\mathrm{m}}(T_0) + \int_{T_0}^{T} \Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}\mathrm{d}T \\ &\quad - T\left(\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}}(T_0) + \int_{T_0}^{T} \frac{\Delta_{\mathrm{r}}C^{\circ}_{p,\mathrm{m}}}{T}\mathrm{d}T\right),\end{aligned}$$

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

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

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 the disregard of the heat capacity contributions to the temperature correction. 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, Iuliano and Porto [87CIA/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. A guideline has therefore been developed at the NEA [93PUI/RAR] that gives the user some information on various procedures to estimate the temperature dependence of these thermodynamic parameters.

Chapter III

Selected americium data

This chapter presents the chemical thermodynamic data set for americium species which has been selected in this review. Table III.1 contains the recommended thermodynamic data of the americium compounds and complexes, Table III.2 the recommended thermodynamic data of chemical equilibrium reactions by which the americium 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 Tables III.1, III.2 and III.3 appear in the standard order of arrangement (*cf.* Figure II.1, *p*.21).

Table III.2 contains information only on those reactions for which primary data selections are made in this review. These selected reaction data are used, together with data for key americium species (for example Am^{3+}) and auxiliary data listed in Table IV.1, to derive the corresponding formation data in Table III.1. The uncertainties associated with values for key americium species (for example Am^{3+}) and for the auxiliary data are in most cases large, leading to comparatively large uncertainties in the formation data derived in this manner.

The uncertainties for auxiliary data given in Chapter IV differ slightly in significance depending on the source of the values (either CODATA [89COX/WAG] or the uranium NEA–TDB review [92GRE/FUG]). This difference in uncertainty definitions will have negligible effects in most of the practical uses of the values in Table III.1, because a larger part of the uncertainty given for most $\Delta_f G^\circ_m$ values in Table III.1 originates from the uncertainty in the value of $\Delta_f G^\circ_m(Am^{3+}, aq, 298.15\ K)$. There are however some instances where the $\pm$ terms listed by CODATA and reported in Table IV.1 have a clear influence in the confidence limits for $\Delta_f G^\circ_m$ of americium species in Table III.1 (for example, in the case of aqueous phosphate complexes like $AmHPO_4^+$, *etc.*). Therefore, the reader should be aware of the fact that equilibrium constants calculated from $\Delta_f G^\circ_m$ values in Table III.1 might result in confidence limits which perhaps do not correspond truly to the 95% confidence limit. The inclusion of a table for reaction data (Table III.2) in this report allows the use of equilibrium constants with total uncertainties which are directly based on the experimental accuracies. This is the main reason for including both the table for reaction data (Table III.2) and the table of $\Delta_f G^\circ_m$, $\Delta_f H^\circ_m$, S°_m and $C^\circ_{p,m}$values (Table III.1).

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

SUPERSEDED IN PART
Guillaumont et al., Update on the chemical thermodynamics of U, Np, Pu, Am and Tc. Elsevier, 2004.
Check the selected values in tables in:

the relation

$$C^{\circ}_{p,\mathrm{m}}(T) \;=\; a + b \times T + c \times T^2 + d \times T^{-1} + e \times T^{-2}. \qquad \text{(III.1)}$$

No references are given in these tables since the selected data are generally not directly attributable to a specific published source. A detailed discussion of the selection procedure is presented in Chapter V.

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, to a lesser degree, with the addition of gases and solids.

It should also be noted that the data set presented in this Chapter may not be "complete" for all the conceivable systems and conditions. Gaps are pointed out in the various sections of Chapter V.

SUPERSEDED IN PART
Check the Selected Value tables in:
Guillaumont et al.: Update on the Chemical Thermodynamics of
U, Np, Pu, Am and Tc, Elsevier, 2004.

Table III.1: Selected thermodynamic data for americium 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 Chapter V. 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 PC diskettes or other computer media from the OECD Nuclear Energy Agency.

Compound	$\Delta_f G^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^\circ_m$ ($kJ \cdot mol^{-1}$)	S°_m ($J \cdot K^{-1} \cdot mol^{-1}$)	$C^\circ_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
Am(cr)	0.000	0.000	55.400 ±2.000	26.500[c] ±1.500
β-Am [d]				
γ-Am [d]				
Am(l) [d]				
Am(g)	241.999[a] ±1.721	283.800 ±1.500	195.600 ±2.000	20.786[c] ±0.001
Am^{2+}	−376.780[b] ±15.236	−354.633[a] ±15.890	−1.000 ±15.000	
Am^{3+}	−598.698[a] ±4.755	−616.700 ±1.500	−201.000 ±15.000	
Am^{4+}	−346.358[a] ±8.692	−406.000 ±6.000	−406.000 ±21.000	
AmO_2(cr)	−874.492[a] ±4.271	−932.200 ±3.000	67.000 ±10.000	66.170[c] ±10.000

SUPERSEDED IN PART
Check the Selected Value tables in:
Guillaumont et al.: Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc, Elsevier, 2004.

Table III.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
AmO_2^+	−739.796[a] ±6.208	−804.260[b] ±5.413	−21.000 ±10.000	
AmO_2^{2+}	−585.801[a] ±5.715	−650.760[b] ±4.839	−88.000 ±10.000	
Am_2O_3(cr)	−1613.320[a] ±9.242	−1690.400 ±8.000	160.000 ±15.000	117.500[c] ±15.000
AmH_2(cr)	−134.661[a] ±15.055	−175.800 ±15.000	48.100 ±3.800	38.200[c] ±2.500
$AmOH^{2+}$	−799.307[b] ±6.211			
$Am(OH)_2^+$	−992.495[b] ±5.860			
$Am(OH)_3$(am)	−1213.082[b] ±5.861			
$Am(OH)_3$(aq)	−1163.422[b] ±5.547			
$Am(OH)_3$(cr)	−1223.356[b] ±5.861			
AmF^{2+}	−899.628[b] ±5.320			
AmF_2^+	−1194.851[b] ±5.082			
AmF_3(cr)	−1548.833[a] ±13.099	−1588.000 ±13.000	127.600 ±5.000	
AmF_3(g)	−1159.331[a] ±15.148	−1166.900[b] ±14.765	334.200[b] ±11.180	
AmF_4(cr)	−1616.833[a] ±20.064	−1710.000 ±20.000	148.500 ±5.000	
$AmCl^{2+}$	−735.909[b] ±4.768			

SUPERSEDED IN PART
Check the Selected Value tables in:
Guillaumont et al.: Update on the Chemical Thermodynamics of
U, Np, Pu, Am and Tc, Elsevier, 2004.

Table III.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
$AmCl_3$(cr)	−910.650[a] ±2.290	−977.800 ±1.300	164.800 ±6.000	103.000 ±10.000
AmOCl(cr)	−902.538[a] ±6.726	−949.800 ±6.000	111.000 ±10.000	70.400[c] ±10.000
$AmBr_3$(cr)	−786.531[a] ±11.228	−810.000 ±10.000	205.000 ±17.000	
AmOBr(cr)	−861.372[a] ±13.413	−893.000 ±12.000	128.000 ±20.000	
AmI_3(cr)	−613.309[a] ±9.216	−612.000 ±7.000	234.000 ±20.000	
AmS(cr)			92.000 ±14.000	
$AmSO_4^+$	−1364.678[b] ±4.776			
$Am(SO_4)_2^-$	−2117.530[b] ±6.267			
AmSe(cr)			109.000 ±12.000	
AmTe(cr)			121.000 ±12.000	
AmN_3^{2+}	−260.030[b] ±5.190			
$AmNO_2^{2+}$ [e]				
$AmNO_3^{2+}$	−717.083[b] ±4.908			
$AmPO_4$(am, hydr) [e]				
$AmH_2PO_4^{2+}$	−1752.974[b] ±5.763			

SUPERSEDED IN PART
Check the Selected Value tables in:
Guillaumont et al.: Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc, Elsevier, 2004.

Table III.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
Am_2C_3(cr)	−156.063[a] ±42.438	−151.000 ±42.000	145.000 ±20.000	
$AmCO_3^+$	−1171.120[b] ±5.069			
$Am(CO_3)_2^-$	−1724.706[b] ±5.332			
$Am(CO_3)_3^{3-}$	−2269.159[b] ±5.976			
$AmO_2(CO_3)_3^{4-}$ [e]				
$AmO_2(CO_3)_3^{5-}$ [e]				
$Am(CO_3)_5^{6-}$	−3210.227[b] ±7.919			
$Am_2(CO_3)_3$(cr)	−2971.743[b] ±15.795			
$AmCO_3OH$(cr)	−1404.828[b] ±9.307			
$AmSCN^{2+}$	−513.408[b] ±6.445			
$SrAmO_3$(cr)		−1539.000 ±4.100		
$BaAmO_3$(cr)		−1544.600 ±3.400		
$Cs_2NaAmCl_6$(cr)	−2164.816[a] ±4.864	−2315.800 ±1.800	440.000 ±15.000	260.000 ±15.000

(a) Value calculated internally with the Gibbs-Helmholtz equation, $\Delta_f G^\circ_m = \Delta_f H^\circ_m - T\Delta_f S^\circ_m$.
(b) Value calculated internally from reaction data (see Table III.2).
(c) Temperature coefficients of this function are listed in Table III.3.
(d) For this compound enthalpies of phase transformation are given in Section V.1, and a temperature function for the heat capacity is given in Table III.3.
(e) Only reaction data are selected for this compound, *cf.* Table III.2.

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Check the Selected Value tables in:
Guillaumont et al.: Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc, Elsevier, 2004.

Table III.2: Selected thermodynamic data for reactions involving americium 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.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapter V. 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 PC diskettes or other computer media from the OECD Nuclear Energy Agency.

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_r H^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_r S^\circ_m$ ($J \cdot K^{-1} \cdot mol^{-1}$)
Am(g)	$Am(cr) \rightleftharpoons Am(g)$			283.800 ±1.500	
Am^{2+}	$Am^{3+} + e^- \rightleftharpoons Am^{2+}$	−38.878[(b)] ±2.536	221.9[illegible] ±14.476		
AmO_2^+	$Am^{3+} + 2\ H_2O(l) \rightleftharpoons AmO_2^+ + 4\ H^+ + 2\ e^-$			384.100 ±5.200	
AmO_2^{2+}	$Am^{3+} + 2\ H_2O(l) \rightleftharpoons AmO_2^{2+} + 4\ H^+ + 3\ e^-$			537.600 ±4.600	
$AmOH^{2+}$	$Am^{3+} + H_2O(l) \rightleftharpoons AmOH^{2+} + H^+$	−6.400 ±0.700	36.531 ±3.996		
$Am(OH)_2^+$	$Am^{3+} + 2\ H_2O(l) \rightleftharpoons Am(OH)_2^+ + 2\ H^+$	−14.100 ±0.600	80.483 ±3.425		
$Am(OH)_3(am)$	$Am^{3+} + 3\ H_2O(l) \rightleftharpoons Am(OH)_3(am) + 3\ H^+$	−17.000 ±0.600	97.037 ±3.425		

SUPERSEDED IN PART
Check the Selected Value tables in:
Guillaumont et al.: Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc, Elsevier, 2004.

Table III.2 (continued)

Species	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})
$Am(OH)_3(aq)$	$Am^{3+} + 3\ H_2O(l) \rightleftharpoons Am(OH)_3(aq) + 3\ H^+$	−25.700	146.697		
		±0.500	±2.854		
$Am(OH)_3(cr)$	$Am^{3+} + 3\ H_2O(l) \rightleftharpoons Am(OH)_3(cr) + 3\ H^+$	−15.200	86.762		
		±0.600	±3.425		
AmF^{2+}	$Am^{3+} + F^- \rightleftharpoons AmF^{2+}$	3.400	−19.407		
		±0.400	±2.283		
AmF_2^+	$Am^{3+} + 2\ F^- \rightleftharpoons AmF_2^+$	5.800	−33.107		
		±0.200	±1.142		
$AmF_3(g)$	$AmF_3(cr) \rightleftharpoons AmF_3(g)$	−62.982[c]	359.502[c]	221.100	206.600
		±1.333	±7.609	±1.000	±10.000
$AmCl^{2+}$	$Am^{3+} + Cl^- \rightleftharpoons AmCl^{2+}$	1.050	−5.993		
		±0.060	±0.342		
$AmSO_4^+$	$Am^{3+} + SO_4^{2-} \rightleftharpoons AmSO_4^+$	3.850	−21.976		
		±0.030	±0.171		
$Am(SO_4)_2^-$	$Am^{3+} + 2\ SO_4^{2-} \rightleftharpoons Am(SO_4)_2^-$	5.400	−30.823		
		±0.800	±3.996		
AmN_3^{2+}	$Am^{3+} + N_3^- \rightleftharpoons AmN_3^{2+}$	1.670	−9.532		
		±0.100	±0.571		
$AmNO_2^{2+}$	$Am^{3+} + NO_2^- \rightleftharpoons AmNO_2^{2+}$	2.100	−11.987		
		±0.200	±1.142		
$AmNO_3^{2+}$	$Am^{3+} + NO_3^- \rightleftharpoons AmNO_3^{2+}$	1.330	−7.592		
		±0.200	±1.142		

SUPERSEDED IN PART
Guillaumont et al. Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc, Elsevier, 2004.
check the selected value tables in:

Table III.2 (continued)

Species	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})
$AmPO_4$(am, hydr)	$Am^{3+} + PO_4^{3-} \rightleftharpoons AmPO_4$(am, hydr)	24.790 ±0.600	−141.502 ±3.425		
$AmH_2PO_4^{2+}$	$Am^{3+} + H_2PO_4^- \rightleftharpoons AmH_2PO_4^{2+}$	3.000 ±0.500	−17.124 ±2.854		
$AmCO_3^+$	$Am^{3+} + CO_3^{2-} \rightleftharpoons AmCO_3^+$	7.800 ±0.300	−44.523 ±1.712		
$Am(CO_3)_2^-$	$Am^{3+} + 2\ CO_3^{2-} \rightleftharpoons Am(CO_3)_2^-$	12.300 ±0.400	−70.209 ±2.283		
$Am(CO_3)_3^{3-}$	$Am^{3+} + 3\ CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-}$	15.200 ±0.600	−86.722 ±3.425		
$AmO_2(CO_3)_3^{5-}$	$AmO_2(CO_3)_3^{4-} + e^- \rightleftharpoons AmO_2(CO_3)_3^{5-}$	13.100[b] ±0.600	−74.770 ±3.425		
$Am(CO_3)_5^{6-}$	$Am(CO_3)_3^{3-} + 2\ CO_3^{2-} \rightleftharpoons Am(CO_3)_5^{6-} + e^-$	−20.100[b] ±0.900	114.732 ±5.137		
$Am_2(CO_3)_3$(cr)	$Am^{3+} + 1.50\ CO_3^{2-} \rightleftharpoons 0.50\ Am_2(CO_3)_3$(cr)	16.700 ±1.100	−95.324 ±6.279		
$AmCO_3OH$(cr)	$Am^{3+} + CO_3^{2-} + OH^- \rightleftharpoons AmCO_3OH$(cr)	21.200 ±1.400	−121.010 ±7.991		
$AmSCN^{2+}$	$Am^{3+} + SCN^- \rightleftharpoons AmSCN^{2+}$	1.300 ±0.300	−7.420 ±1.712		

(a) Value calculated internally with the Gibbs-Helmholtz equation, $\Delta_r G_m^\circ = \Delta_r H_m^\circ - T\Delta_r S_m^\circ$.
(b) Value calculated from a selected standard potential.
(c) Value of $\log_{10} K^\circ$ calculated internally from $\Delta_r G_m^\circ$.

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Table III.3: Selected temperature coefficients for heat capacities functions for the values marked with [(c)] in Table III.1, according to the form

$$C^{\circ}_{p,\mathrm{m}}(T) = a + b\,T + c\,T^2 + e\,T^{-2}.$$

The functions are valid between the temperatures $T_{\min}$ and $T_{\max}$ (in K). The values in parentheses represent the power of 10. Units for $C^{\circ}_{p,\mathrm{m}}$are $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

Compound	a	b	c	e	$T_{\min}$	$T_{\max}$
Am(cr)	2.11868(+01)	1.11990(−02)	3.24620(−06)	6.08500(+04)	298	1042
β-Am	1.94406(+01)	1.08360(−02)	2.25140(−06)	5.20870(+05)	1042	1350
γ-Am	3.97480(+01)				1350	1449
Am(l)	4.18400(+01)				1449	3000
Am(g)	2.07861(+01)				298	1100
AmO_2(cr)	8.47390(+01)	1.07200(−02)	−8.15900(−07)	−1.92580(+06)	298	2000
Am_2O_3(cr)	1.13930(+02)	5.93700(−02)	−2.30100(−05)	−1.07100(+06)	298	1000
AmH_2(cr)	2.48000(+01)	4.50000(−02)			298	1200
AmOCl(cr)	6.12840(+01)	4.58933(−02)	−1.73065(−05)	−2.69380(+05)	298	1100

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Chapter IV

Selected auxiliary data

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

The values in the Tables of this Chapter are either CODATA Key Values, taken from Ref. [89COX/WAG], or were evaluated within the NEA's TDB project, as described in Chapter VI of the uranium review [92GRE/FUG].

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

All data in Tables IV.1 and 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 reference 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 [89COX/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 [92GRE/FUG], 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 [89COX/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 $\Delta_f H^\circ_m$ and S°_m the values of $\Delta_f G^\circ_m$ and,

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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-} and $H_2PO_4^-$, which were absent form the corresponding Table IV.2 in [92GRE/FUG], are included in this volume to provide the user of selected data for americium species (*cf.* Chapter III) with the data needed to obtain the lowest possible uncertainties on reaction properties.

Note that the values in Tables IV.1 and IV.2 may contain more digits than those listed in either [89COX/WAG] or in Chapter VI of [92GRE/FUG], 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.

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Table IV.1: Selected thermodynamic data for auxiliary compounds and complexes, including the CODATA Key Values [89COX/WAG] of species not containing uranium, as well as other data that were evaluated in Chapter VI of the uranium review [92GRE/FUG]. 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 in **bold** typeface are CODATA Key Values and are taken directly from Ref. [89COX/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 Chapter VI of Ref. [92GRE/FUG]. 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 PC diskettes or other computer media from the OECD Nuclear Energy Agency.

Compound	$\Delta_f G^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^\circ_m$ ($kJ \cdot mol^{-1}$)	S°_m ($J \cdot K^{-1} \cdot mol^{-1}$)	$C^\circ_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
O(g)	**231.743**[a] ±0.100	**249.180** ±0.100	**161.059** ±0.003	**21.912** ±0.001
O_2(g)	**0.000**	**0.000**	**205.152** ±0.005	**29.378** ±0.003
H(g)	**203.276**[a] ±0.006	**217.998** ±0.006	**114.717** ±0.002	**20.786** ±0.001
H^+	**0.000**	**0.000**	**0.000**	**0.000**
H_2(g)	**0.000**	**0.000**	**130.680** ±0.003	**28.836** ±0.002
OH^-	**−157.220**[a] ±0.072	**−230.015** ±0.040	**−10.900** ±0.200	
H_2O(g)	**−228.582**[a] ±0.040	**−241.826** ±0.040	**188.835** ±0.010	**33.609** ±0.030
H_2O(l)	**−237.140**[a] ±0.041	**−285.830** ±0.040	**69.950** ±0.030	**75.351** ±0.080
H_2O_2(aq)		−191.170[c] ±0.100		

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
He(g)	**0.000**	**0.000**	**126.153** ±0.002	**20.786** ±0.001
Ne(g)	**0.000**	**0.000**	**146.328** ±0.003	**20.786** ±0.001
Ar(g)	**0.000**	**0.000**	**154.846** ±0.003	**20.786** ±0.001
Kr(g)	**0.000**	**0.000**	**164.085** ±0.003	**20.786** ±0.001
Xe(g)	**0.000**	**0.000**	**169.685** ±0.003	**20.786** ±0.001
F(g)	**62.280**[a] ±0.300	**79.380** ±0.300	**158.751** ±0.004	**22.746** ±0.002
F^-	**−281.523**[a] ±0.692	**−335.350** ±0.650	**−13.800** ±0.800	
F_2(g)	**0.000**	**0.000**	**202.791** ±0.005	**31.304** ±0.002
HF(aq)	−299.675[b] ±0.702	−323.150[b] ±0.710	88.000[a] ±3.362	
HF(g)	**−275.400**[a] ±0.700	**−273.300** ±0.700	**173.779** ±0.003	**29.137** ±0.002
HF_2^-	−583.709[b] ±1.200	−655.500[b] ±2.221	92.683[a] ±8.469	
Cl(g)	**105.305**[a] ±0.008	**121.301** ±0.008	**165.190** ±0.004	**21.838** ±0.001
Cl^-	**−131.217**[a] ±0.117	**−167.080** ±0.100	**56.600** ±0.200	
Cl_2(g)	**0.000**	**0.000**	**223.081** ±0.010	**33.949** ±0.002
ClO^-	−37.670[b] ±0.962			

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
ClO_2^-	10.249[b] ±4.044			
ClO_3^-	−7.903[a] ±1.342	−104.000 ±1.000	162.300 ±3.000	
ClO_4^-	**−7.890**[a] **±0.600**	**−128.100** **±0.400**	**184.000** **±1.500**	
HCl(g)	**−95.298**[a] **±0.100**	**−92.310** **±0.100**	**186.902** **±0.005**	**29.136** **±0.002**
HClO(aq)	−80.024[b] ±0.613			
$HClO_2$(aq)	−0.939[b] ±4.043			
Br(g)	**82.379**[a] **±0.128**	**111.870** **±0.120**	**175.018** **±0.004**	**20.786** **±0.001**
Br^-	**−103.850**[a] **±0.167**	**−121.410** **±0.150**	**82.650** **±0.200**	
Br_2(aq)	4.900 ±1.000			
Br_2(g)	**3.105** **±0.142**	**30.910** **±0.110**	**245.468** **±0.005**	**36.057** **±0.002**
Br_2(l)	**0.000**	**0.000**	**152.210** **±0.300**	
BrO^-	−32.140[b] ±1.510			
BrO_3^-	19.070[a] ±0.634	−66.700 ±0.500	161.500 ±1.300	
HBr(g)	**−53.361**[a] **±0.166**	**−36.290** **±0.160**	**198.700** **±0.004**	**29.141** **±0.003**
HBrO(aq)	−81.356[b] ±1.527			

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
I(g)	**70.172**[a] **±0.060**	**106.760 ±0.040**	**180.787 ±0.004**	**20.786 ±0.001**
I^-	**−51.724**[a] **±0.112**	**−56.780 ±0.050**	**106.450 ±0.300**	
I_2(cr)	**0.000**	**0.000**	**116.140 ±0.300**	
I_2(g)	**19.323**[a] **±0.120**	**62.420 ±0.080**	**260.687 ±0.005**	**36.888 ±0.002**
IO_3^-	−126.338[a] ±0.779	−219.700 ±0.500	118.000 ±2.000	
HI(g)	**1.700**[a] **±0.110**	**26.500 ±0.100**	**206.590 ±0.004**	**29.157 ±0.003**
HIO_3(aq)	−130.836[b] ±0.797			
S(cr)[d]	**0.000**	**0.000**	**32.054 ±0.050**	**22.750 ±0.050**
S(g)	**236.689**[a] **±0.151**	**277.170 ±0.150**	**167.829 ±0.006**	**23.674 ±0.001**
S^{2-}	120.695[c] ±11.610			
S_2(g)	**79.686**[a] **±0.301**	**128.600 ±0.300**	**228.167 ±0.010**	**32.505 ±0.010**
SO_2(g)	**−300.695**[a] **±0.201**	**−296.810 ±0.200**	**248.223 ±0.050**	**39.842 ±0.020**
SO_3^{2-}	−487.473[b] ±4.020			
$S_2O_3^{2-}$	−519.293[b] ±11.345			
SO_4^{2-}	**−744.004**[a] **±0.418**	**−909.340 ±0.400**	**18.500 ±0.400**	

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
HS^-	**12.243**[a] **±2.115**	**−16.300** **±1.500**	**67.000** **±5.000**	
H_2S(aq)	**−27.648**[a] **±2.115**	**−38.600** **±1.500**	**126.000** **±5.000**	
H_2S(g)	**−33.443**[a] **±0.500**	**−20.600** **±0.500**	**205.810** **±0.050**	**34.248** **±0.010**
HSO_3^-	−528.685[b] ±4.046			
$HS_2O_3^-$	−528.369[b] ±11.377			
H_2SO_3(aq)	−539.188[b] ±4.072			
HSO_4^-	**−755.315**[a] **±1.342**	**−886.900** **±1.000**	**131.700** **±3.000**	
Se(cr)	0.000	0.000	42.270 ±0.050	25.030 ±0.050
SeO_2(cr)		−225.100 ±2.100		
SeO_3^{2-}	−361.570[b] ±1.410			
$HSeO_3^-$	−409.517[b] ±1.290			
H_2SeO_3(aq)	−425.527[b] ±0.736			
Te(cr)	0.000	0.000	49.221 ±0.050	25.550 ±0.100
N(g)	**455.537**[a] **±0.400**	**472.680** **±0.400**	**153.301** **±0.003**	**20.786** **±0.001**
N_2(g)	**0.000**	**0.000**	**191.609** **±0.004**	**29.124** **±0.001**

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
N_3^-	348.200 ±2.000	275.140 ±1.000	107.710[a] ±7.500	
NO_3^-	**−110.794**[a] **±0.417**	**−206.850** **±0.400**	**146.700** **±0.400**	
HN_3(aq)	321.372[b] ±2.051	260.140[b] ±10.050	147.381[b] ±34.403	
NH_3(aq)	−26.673[b] ±0.305	−81.170[b] ±0.326	109.040[b] ±0.913	
NH_3(g)	**−16.407**[a] **±0.350**	**−45.940** **±0.350**	**192.770** **±0.050**	**35.630** **±0.095**
NH_4^+	**−79.398**[a] **±0.278**	**−133.260** **±0.250**	**111.170** **±0.400**	
P(am)[e]		−7.500 ±2.000		
P(cr)[e]	**0.000**	**0.000**	**41.090** **±0.250**	**23.824** **±0.200**
P(g)	**280.093**[a] **±1.003**	**245.500** **±1.000**	**163.199** **±0.003**	**20.786** **±0.001**
P_2(g)	**103.469** **±2.006**	**144.000** **±2.000**	**218.123** **±0.004**	**32.032** **±0.002**
P_4(g)	**24.419**[a] **±0.448**	**58.900** **±0.300**	**280.010** **±0.500**	**67.081** **±1.500**
PO_4^{3-}	−1025.491[b] ±1.576	−1284.400[b] ±4.085	−220.970[b] ±12.846	
$P_2O_7^{4-}$	−1935.503[b] ±4.563			
HPO_4^{2-}	**−1095.985**[a] **±1.567**	**−1299.000** **±1.500**	**−33.500** **±1.500**	
$H_2PO_4^-$	**−1137.152**[a] **±1.567**	**−1302.600** **±1.500**	**92.500** **±1.500**	

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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_3PO_4(aq)	−1149.367[b] ±1.576	−1294.120[b] ±1.616	161.912[b] ±2.575	
$HP_2O_7^{3-}$	−1989.158[b] ±4.482			
$H_2P_2O_7^{2-}$	−2027.117[b] ±4.445			
$H_3P_2O_7^{-}$	−2039.960[b] ±4.362			
$H_4P_2O_7$(aq)	−2045.668[b] ±3.299	−2280.210[b] ±3.383	274.919[b] ±6.954	
As(cr)	0.000	0.000	35.100 ±0.600	24.640 ±0.500
AsO_2^-	−350.022[a] ±4.008	−429.030 ±4.000	40.600 ±0.600	
AsO_4^{3-}	−648.360[a] ±4.008	−888.14[illegible] ±4.000	−162.800 ±0.600	
As_2O_5(cr)	−782.449[a] ±8.016	−924.8[illegible] ±8.000	105.400 ±1.200	116.520 ±0.800
As_4O_6(cubi)[f]	−1152.4[illegible][a] ±16.032	−1313.94[illegible] ±16.000	214.200 ±2.400	191.290 ±0.800
As_4O_6(mono)[g]	−1154.008[a] ±16.041	−1309.600 ±16.000	234.000 ±3.000	
$HAsO_2$(aq)	−402.925[a] ±4.008	−456.500 ±4.000	125.900 ±0.600	
$H_2AsO_3^-$	−587.078[a] ±4.008	−714.790 ±4.000	110.500 ±0.600	
H_3AsO_3(aq)	−639.681[a] ±4.015	−742.200 ±4.000	195.000 ±1.000	
$HAsO_4^{2-}$	−714.592[a] ±4.008	−906.340 ±4.000	−1.700 ±0.600	

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
$H_2AsO_4^-$	−753.203[a] ±4.015	−909.560 ±4.000	117.000 ±1.000	
H_3AsO_4(aq)	−766.119[a] ±4.015	−902.500 ±4.000	184.000 ±1.000	
$(As_2O_5)_3 \cdot 5H_2O$(cr)		−4248.400 ±24.000		
Sb(cr)	0.000	0.000	45.520 ±0.210	25.260 ±0.200
C(cr)	**0.000**	**0.000**	**5.740 ±0.100**	**8.517 ±0.080**
C(g)	**671.254**[a] **±0.451**	**716.680 ±0.450**	**158.100 ±0.003**	**20.839 ±0.001**
CO(g)	**−137.168**[a] **±0.173**	**−110.530 ±0.170**	**197.660 ±0.004**	**29.141 ±0.002**
CO_2(aq)	**−385.970**[a] **±0.270**	**−413.260 ±0.200**	**119.360 ±0.600**	
CO_2(g)	**−394.373**[a] **±0.133**	**−393.510 ±0.130**	**213.785 ±0.010**	**37.135 ±0.002**
CO_3^{2-}	**−527.999**[a] **±0.390**	**−675.230 ±0.250**	**−50.000 ±1.000**	
HCO_3^-	**−586.845**[a] **±0.251**	**−689.930 ±0.200**	**98.400 ±0.500**	
SCN^-	92.700 ±4.000	76.400 ±4.000	144.268[a] ±18.974	
Si(cr)	**0.000**	**0.000**	**18.810 ±0.080**	**19.789 ±0.030**
Si(g)	**405.525**[a] **±8.000**	**450.000 ±8.000**	**167.981 ±0.004**	**22.251 ±0.001**
SiO_2(quar)[h]	**−856.287**[a] **±1.002**	**−910.700 ±1.000**	**41.460 ±0.200**	**44.602 ±0.300**

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
$SiO_2(OH)_2^{2-}$	−1175.651[b] ±1.265	−1381.960[b] ±15.330	−1.487[b] ±51.592	
$SiO(OH)_3^-$	−1251.740[b] ±1.162	−1431.360[b] ±3.743	88.026[b] ±13.144	
$Si(OH)_4$(aq)	−1307.735[b] ±1.156	−1456.960[b] ±3.163	189.973[a] ±10.245	
$Si_2O_3(OH)_4^{2-}$	−2269.878[b] ±2.878			
$Si_2O_2(OH)_5^-$	−2332.096[b] ±2.878			
$Si_3O_6(OH)_3^{3-}$	−3048.536[b] ±3.870			
$Si_3O_5(OH)_5^{3-}$	−3291.955[b] ±3.869			
$Si_4O_8(OH)_4^{4-}$	−4075.179[b] ±5.437			
$Si_4O_7(OH)_5^{3-}$	−4136.826[b] ±4.934			
SiF_4(g)	**−1572.772**[a] **±0.814**	**−1615.000** **±0.800**	**282.760** **±0.500**	**73.622** **±0.500**
Ge(cr)	**0.000**	**0.000**	**31.090** **±0.150**	**23.222** **±0.100**
Ge(g)	**331.209**[a] **±3.000**	**372.000** **±3.000**	**167.904** **±0.005**	**30.733** **±0.001**
GeO_2(tetr)[i]	**−521.404**[a] **±1.002**	**−580.000** **±1.000**	**39.710** **±0.150**	**50.166** **±0.300**
GeF_4(g)	**−1150.018**[a] **±0.584**	**−1190.200** **±0.500**	**301.900** **±1.000**	**81.602** **±1.000**
Sn(cr)	**0.000**	**0.000**	**51.180** **±0.080**	**27.112** **±0.030**

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
Sn(g)	**266.223**[a] ±1.500	**301.200** ±1.500	**168.492** ±0.004	**21.259** ±0.001
Sn^{2+}	**−27.624**[a] ±1.557	**−8.900** ±1.000	**−16.700** ±4.000	
SnO(tetr)[i]	**−251.913**[a] ±0.220	**−280.710** ±0.200	**57.170** ±0.300	**47.783** ±0.300
SnO_2(cass)[j]	**−515.826**[a] ±0.204	**−577.630** ±0.200	**49.040** ±0.100	**53.219** ±0.200
Pb(cr)	**0.000**	**0.000**	**64.800** ±0.300	**26.650** ±0.100
Pb(g)	**162.232**[a] ±0.805	**195.200** ±0.800	**175.375** ±0.005	**20.786** ±0.001
Pb^{2+}	**−24.238**[a] ±0.399	**0.920** ±0.250	**18.500** ±4.000	
$PbSO_4$(cr)	**−813.036**[a] ±0.447	**−919.970** ±0.400	**148.500** ±0.680	
B(cr)	**0.000**	**0.000**	**5.900** ±0.080	**11.087** ±0.100
B(g)	**521.012**[a] ±5.000	**565.000** ±5.000	**153.436** ±0.015	**20.796** ±0.005
B_2O_3(cr)	**−1194.324**[a] ±1.404	**−1273.500** ±1.400	**53.970** ±0.300	**62.761** ±0.300
$B(OH)_3$(aq)	**−969.268**[a] ±0.820	**−1072.800** ±0.800	**162.400** ±0.600	
$B(OH)_3$(cr)	**−969.667**[a] ±0.820	**−1094.800** ±0.800	**89.950** ±0.600	**86.060** ±0.400
BF_3(g)	**−1119.403**[a] ±0.803	**−1136.000** ±0.800	**254.420** ±0.200	**50.463** ±0.100
Al(cr)	**0.000**	**0.000**	**28.300** ±0.100	**24.200** ±0.070

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
Al(g)	**289.376**[a] ±4.000	**330.000** ±4.000	**164.554** ±0.004	**21.391** ±0.001
Al^{3+}	**−491.507**[a] ±3.338	**−538.400** ±1.500	**−325.000** ±10.000	
Al_2O_3(coru)[k]	**−1582.257**[a] ±1.302	**−1675.700** ±1.300	**50.920** ±0.100	**79.033** ±0.200
AlF_3(cr)	**−1431.096**[a] ±1.309	**−1510.400** ±1.300	**66.500** ±0.500	**75.122** ±0.400
Zn(cr)	**0.000**	**0.000**	**41.630** ±0.150	**25.390** ±0.040
Zn(g)	**94.813**[a] ±0.402	**130.400** ±0.400	**160.990** ±0.004	**20.786** ±0.001
Zn^{2+}	**−147.203**[a] ±0.254	**−153.390** ±0.200	**−109.800** ±0.500	
ZnO(cr)	**−320.479**[a] ±0.299	**−350.460** ±0.270	**43.650** ±0.400	
Cd(cr)	**0.000**	**0.000**	**51.800** ±0.150	**26.020** ±0.040
Cd(g)	**77.230**[a] ±0.203	**112.300** ±0.200	**167.749** ±0.004	**20.786** ±0.001
Cd^{2+}	**−77.733**[a] ±0.750	**−75.920** ±0.600	**−72.800** ±1.500	
CdO(cr)	**−228.661**[a] ±0.602	**−258.350** ±0.400	**54.800** ±1.500	
$CdSO_4 \cdot 2.667H_2O$(cr)	**−1464.959**[a] ±0.810	**−1729.300** ±0.800	**229.650** ±0.400	
Hg(g)	**31.842**[a] ±0.054	**61.380** ±0.040	**174.971** ±0.005	**20.786** ±0.001
Hg(l)	**0.000**	**0.000**	**75.900** ±0.120	

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
Hg^{2+}	**164.667**[a] ±0.313	**170.210** ±0.200	**−36.190** ±0.800	
Hg_2^{2+}	**153.567**[a] ±0.559	**166.870** ±0.500	**65.740** ±0.800	
HgO(mont)[l]	**−58.523**[a] ±0.154	**−90.790** ±0.120	**70.250** ±0.300	
Hg_2Cl_2(cr)	**−210.725**[a] ±0.471	**−265.370** ±0.400	**191.600** ±0.800	
Hg_2SO_4(cr)	**−625.780**[a] ±0.411	**−743.090** ±0.400	**200.700** ±0.200	
Cu(cr)	**0.000**	**0.000**	**33.150** ±0.080	**24.440** ±0.050
Cu(g)	**297.672**[a] ±1.200	**337.400** ±1.200	**166.398** ±0.004	**20.786** ±0.001
Cu^{2+}	**65.040**[a] ±1.557	**64.900** ±1.000	**−98.000** ±4.000	
$CuSO_4$(cr)	**−662.185**[a] ±1.206	**−771.400** ±1.200	**109.200** ±0.400	
Ag(cr)	**0.000**	**0.000**	**42.550** ±0.200	**25.350** ±0.100
Ag(g)	**246.007**[a] ±0.802	**284.900** ±0.800	**172.997** ±0.004	**20.786** ±0.001
Ag^+	**77.096**[a] ±0.156	**105.790** ±0.080	**73.450** ±0.400	
AgCl(cr)	**−109.765**[a] ±0.098	**−127.010** ±0.050	**96.250** ±0.200	
Ti(cr)	**0.000**	**0.000**	**30.720** ±0.100	**25.060** ±0.080
Ti(g)	**428.403**[a] ±3.000	**473.000** ±3.000	**180.298** ±0.010	**24.430** ±0.030

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
TiO_2(ruti)$^{(m)}$	**−888.767**$^{(a)}$ ±0.806	**−944.000** ±0.800	**50.620** ±0.300	**55.080** ±0.300
$TiCl_4$(g)	**−726.324**$^{(a)}$ ±3.229	**−763.200** ±3.000	**353.200** ±4.000	**95.408** ±1.000
Th(cr)	**0.000**	**0.000**	**51.800** ±0.500	**26.230** ±0.050
Th(g)	**560.745**$^{(a)}$ ±6.002	**602.000** ±6.000	**190.170** ±0.050	**20.789** ±0.100
ThO_2(cr)	**−1169.238**$^{(a)}$ ±3.504	**−1226.400** ±3.500	**65.230** ±0.200	
Be(cr)	**0.000**	**0.000**	**9.500** ±0.080	**16.443** ±0.060
Be(g)	**286.202**$^{(a)}$ ±5.000	**324.000** ±5.000	**136.375** ±0.003	**20.786** ±0.001
BeO(brom)$^{(n)}$	**−580.090**$^{(a)}$ ±2.500	**−609.400** ±2.500	**13.770** ±0.040	**25.565** ±0.100
Mg(cr)	**0.000**	**0.000**	**32.670** ±0.100	**24.869** ±0.020
Mg(g)	**112.521**$^{(a)}$ ±0.801	**147.100** ±0.800	**148.648** ±0.003	**20.786** ±0.001
Mg^{2+}	**−455.375**$^{(a)}$ ±1.335	**467.000** ±0.600	**−137.000** ±4.000	
MgO(cr)	**−569.312**$^{(a)}$ ±0.305	**−601.600** ±0.300	**26.950** ±0.150	**37.237** ±0.200
MgF_2(cr)	**−1071.051**$^{(a)}$ ±1.210	**−1124.200** ±1.200	**57.200** ±0.500	**61.512** ±0.300
Ca(cr)	**0.000**	**0.000**	**41.590** ±0.400	**25.929** ±0.300
Ca(g)	**144.021**$^{(a)}$ ±0.809	**177.800** ±0.800	**154.887** ±0.004	**20.786** ±0.001

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
Ca^{2+}	**−552.806**[a] **±1.050**	**−543.000** **±1.000**	**−56.200** **±1.000**	
CaO(cr)	**−603.296**[a] **±0.916**	**−634.920** **±0.900**	**38.100** **±0.400**	**42.049** **±0.400**
Sr(cr)	0.000	0.000	55.700 ±0.210	
Sr^{2+}	−563.864[a] ±0.781	−550.900 ±0.500	−31.500 ±2.000	
SrO(cr)	−559.939[a] ±0.914	−590.600 ±0.900	55.440 ±0.500	
$SrCl_2$(cr)	−784.974[a] ±0.714	−833.850 ±0.700	114.850 ±0.420	
$Sr(NO_3)_2$(cr)	−783.146[a] ±1.018	−982.360 ±0.800	294.600 ±2.000	
Ba(cr)	0.000	0.000	62.420 ±0.840	
Ba^{2+}	−557.656[a] ±2.582	−537.800 ±2.500	8.400 ±2.000	
BaO(cr)	−520.394[a] ±2.515	−548.100 ±2.500	72.070 ±0.380	
$BaCl_2$(cr)	−806.953[a] ±2.514	−855.200 ±2.500	123.680 ±0.250	
Li(cr)	**0.000**	**0.000**	**29.120** **±0.200**	**24.860** **±0.200**
Li(g)	**126.604**[a] **±1.002**	**159.300** **±1.000**	**138.782** **±0.010**	**20.786** **±0.001**
Li^+	**−292.918**[a] **±0.109**	**−278.470** **±0.080**	**12.240** **±0.150**	
Na(cr)	**0.000**	**0.000**	**51.300** **±0.200**	**28.230** **±0.200**

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Table IV.1 (continued)

Compound	$\Delta_f G^\circ_m$ (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})
Na(g)	**76.964**[a] ±0.703	**107.500** ±0.700	**153.718** ±0.003	**20.786** ±0.001
Na^+	**−261.953**[a] ±0.096	**−240.340** ±0.060	**58.450** ±0.150	
K(cr)	**0.000**	**0.000**	**64.680** ±0.200	**29.600** ±0.100
K(g)	**60.479**[a] ±0.802	**89.000** ±0.800	**160.341** ±0.003	**20.786** ±0.001
K^+	**−282.510**[a] ±0.116	**−252.140** ±0.080	**101.200** ±0.200	
Rb(cr)	**0.000**	**0.000**	**76.780** ±0.300	**31.060** ±0.100
Rb(g)	**53.078**[a] ±0.805	**80.900** ±0.800	**170.094** ±0.003	**20.786** ±0.001
Rb^+	**−284.009**[a] ±0.153	**−251.020** ±0.100	**121.750** ±0.250	
Cs(cr)	**0.000**	**0.000**	**85.230** ±0.400	**32.210** ±0.200
Cs(g)	**49.556**[a] ±1.007	**76.500** ±1.000	**175.601** ±0.003	**20.786** ±0.001
Cs^+	**−291.456**[a] ±0.535	**−258.000** ±0.500	**132.100** ±0.500	

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Footnotes to Table IV.1:

(a) Value calculated internally with the equation $\Delta_f G^\circ_m = \Delta_f H^\circ_m - T\Delta_f S^\circ_m$.

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

(c) From [82WAG/EVA], uncertainty estimated in the uranium review [92GRE/FUG].

(d) Orthorhombic.

(e) P(cr) refers to white, crystalline (cubic) phosphorus and is the reference state for the element phosphorus. P(am) refers to red, amorphous phosphorus.

(f) Cubic.

(g) Monoclinic.

(h) α-Quartz.

(i) Tetragonal.

(j) Cassiterite, tetragonal.

(k) Corundum.

(l) Montroydite, red.

(m) Rutile.

(n) Bromellite.

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Table IV.2: Selected thermodynamic data for reactions involving auxiliary compounds and complexes used in the evaluation of the selected americium data. All ionic species listed in this table are aqueous species. The selection of these data is described in Chapter VI. Reactions are listed only if they were used for primary data selection. The thermodynamic data of formation (see Table IV.1) are derived therefrom. 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.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapter VI. 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 PC diskettes or other computer media from the OECD Nuclear Energy Agency.

Species	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})
HF(aq)	$F^- + H^+ \rightleftharpoons HF(aq)$				
		3.180	−18.152	12.200	101.800[a]
		±0.020	±0.114	±0.300	±1.077
HF_2^-	$F^- + HF(aq) \rightleftharpoons HF_2^-$				
		0.440	−2.512	3.000	18.486[a]
		±0.120	±0.685	±2.000	±7.091
ClO^-	$HClO(aq) \rightleftharpoons ClO^- + H^+$				
		−7.420	42.354	19.000	−78.329[a]
		±0.130	±0.742	±9.000	±30.289
ClO_2^-	$HClO_2(aq) \rightleftharpoons ClO_2^- + H^+$				
		−1.950	11.188		
		±0.020	±0.114		
HClO(aq)	$Cl_2(g) + H_2O(l) \rightleftharpoons Cl^- + H^+ + HClO(aq)$				
		−4.537[c]	25.900		
		±0.105	±0.600		
$HClO_2(aq)$	$H_2O(l) + HClO(aq) \rightleftharpoons 2\ H^+ + HClO_2(aq) + 2\ e^-$				
		−55.400[b]	316.226		
		±0.700	±3.996		
BrO^-	$HBrO(aq) \rightleftharpoons BrO^- + H^+$				
		−8.630	49.260	30.000	−64.600[a]
		±0.030	±0.171	±3.000	±10.078

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Table IV.2 (continued)

Species	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})
HBrO(aq)	$Br_2(aq) + H_2O(l) \rightleftharpoons Br^- + H^+ + HBrO(aq)$				
		−8.240	47.034		
		±0.200	±1.142		
$HIO_3(aq)$	$H^+ + IO_3^- \rightleftharpoons HIO_3(aq)$				
		0.788	−4.498		
		±0.029	±0.166		
S^{2-}	$HS^- \rightleftharpoons H^+ + S^{2-}$				
		−19.000	108.453		
		±2.000	±11.416		
SO_3^{2-}	$H_2O(l) + SO_4^{2-} + 2\ e^- \rightleftharpoons 2\ OH^- + SO_3^{2-}$				
		−31.400[b]	179.233		
		±0.700	±3.996		
$S_2O_3^{2-}$	$3\ H_2O(l) + 2\ SO_3^{2-} + 4\ e^- \rightleftharpoons 6\ OH^- + S_2O_3^{2-}$				
		−39.200[b]	223.755		
		±1.400	±7.991		
$H_2S(aq)$	$H_2S(aq) \rightleftharpoons H^+ + HS^-$				
		−6.990	39.890		
		±0.170	±0.970		
HSO_3^-	$H^+ + SO_3^{2-} \rightleftharpoons HSO_3^-$				
		7.220	−41.212	66.000	359.591[a]
		±0.080	±0.457	±30.000	±100.632
$HS_2O_3^-$	$H^+ + S_2O_3^{2-} \rightleftharpoons HS_2O_3^-$				
		1.590	−9.076		
		±0.150	±0.856		
$H_2SO_3(aq)$	$H^+ + HSO_3^- \rightleftharpoons H_2SO_3(aq)$				
		1.840	−10.503	16.000	88.891[a]
		±0.080	±0.457	±5.000	±16.840
HSO_4^-	$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$				
		1.980	−11.302		
		±0.050	±0.285		
SeO_3^{2-}	$HSeO_3^- \rightleftharpoons H^+ + SeO_3^{2-}$				
		−8.400	47.948	−5.020	−177.654[a]
		±0.100	±0.571	±0.500	±2.545

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Table IV.2 (continued)

Species	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})
$H_2Se(aq)$	$H^+ + HSe^- \rightleftharpoons H_2Se(aq)$				
		3.800	−21.691		
		±0.300	±1.712		
$HSeO_3^-$	$H_2SeO_3(aq) \rightleftharpoons H^+ + HSeO_3^-$				
		−2.800	15.983	−7.070	−77.319[a]
		±0.200	±1.142	±0.500	±4.180
$H_2SeO_3(aq)$	$3\ H_2O(l) + 2\ I_2(cr) + Se(cr) \rightleftharpoons 4\ H^+ + H_2SeO_3(aq) + 4\ I^-$				
		−13.840	78.999		
		±0.100	±0.571		
$HSeO_4^-$	$H^+ + SeO_4^{2-} \rightleftharpoons HSeO_4^-$				
		1.800	−10.274	23.800	114.286[a]
		±0.140	±0.799	±5.000	±16.983
$HN_3(aq)$	$H^+ + N_3^- \rightleftharpoons HN_3(aq)$				
		4.700	−26.828	−16.000	39.671[a]
		±0.080	±0.457	±10.000	±33.575
$NH_3(aq)$	$NH_4^+ \rightleftharpoons H^+ + NH_3(aq)$				
		−9.237	52.723	52.090	−2.130[a]
		±0.022	±0.126	±0.210	±0.821
$HNO_2(aq)$	$H^+ + NO_2^- \rightleftharpoons HNO_2(aq)$				
		3.210	−18.323	−11.400	23.219[a]
		±0.160	±0.913	±3.000	±10.518
PO_4^{3-}	$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$				
		−12.350	70.494	14.600	−187.470[a]
		±0.030	±0.171	±3.800	±12.758
$P_2O_7^{4-}$	$HP_2O_7^{3-} \rightleftharpoons H^+ + P_2O_7^{4-}$				
		−9.400	53.656		
		±0.150	±0.856		
$H_2PO_4^-$	$H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^-$				
		7.212	−41.166	−3.600	125.998[a]
		±0.013	±0.074	±1.000	±3.363
$H_3PO_4(aq)$	$H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4(aq)$				
		2.140	−12.215	8.480	69.412[a]
		±0.030	±0.171	±0.600	±2.093

SUPERSEDED IN PART
Check the selected value tables in:
Guillaumont et al. Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc, Elsevier, 2004.

Table IV.2 (continued)

Species	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})
$HP_2O_7^{3-}$	$H_2P_2O_7^{2-} \rightleftharpoons H^+ + HP_2O_7^{3-}$	−6.650 ±0.100	37.958 ±0.571		
$H_2P_2O_7^{2-}$	$H_3P_2O_7^- \rightleftharpoons H^+ + H_2P_2O_7^{2-}$	−2.250 ±0.150	12.843 ±0.856		
$H_3P_2O_7^-$	$H_4P_2O_7(aq) \rightleftharpoons H^+ + H_3P_2O_7^-$	−1.000 ±0.500	5.708 ±2.854		
$H_4P_2O_7(aq)$	$2\ H_3PO_4(aq) \rightleftharpoons H_2O(l) + H_4P_2O_7(aq)$	−2.790 ±0.170	15.925 ±0.970	22.200 ±1.000	21.045[a] ±4.674
$CO_2(g)$	$CO_2(aq) \rightleftharpoons CO_2(g)$	1.472 ±0.020	−8.391 ±0.114		
HCO_3^-	$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$	10.329 ±0.020	58.964 ±0.114		
HCO_3^-	$H^+ + HCO_3^- \rightleftharpoons CO_2(aq) + H_2O(l)$	6.354 ±0.020	−36.246 ±0.114		
$SiO_2(OH)_2^{2-}$	$Si(OH)_4(aq) \rightleftharpoons 2\ H^+ + SiO_2(OH)_2^{2-}$	−23.140 ±0.090	132.084 ±0.514	75.000 ±15.000	−191.461[a] ±50.340
$SiO(OH)_3^-$	$Si(OH)_4(aq) \rightleftharpoons H^+ + SiO(OH)_3^-$	−9.810 ±0.020	55.996 ±0.114	25.600 ±2.000	−101.948[a] ±6.719
$Si(OH)_4(aq)$	$2\ H_2O(l) + SiO_2(quar) \rightleftharpoons Si(OH)_4(aq)$	−4.000 ±0.100	22.832 ±0.571	25.400 ±3.000	8.613[a] ±10.243
$Si_2O_3(OH)_4^{2-}$	$2\ Si(OH)_4(aq) \rightleftharpoons 2\ H^+ + H_2O(l) + Si_2O_3(OH)_4^{2-}$	−19.000 ±0.300	108.453 ±1.712		

SUPERSEDED IN PART
Guillaumont et al., Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc, Elsevier, 2004.
Check the selected value tables in:

Table IV.2 (continued)

Species	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})
$Si_2O_2(OH)_5^-$	$2\ Si(OH)_4(aq) \rightleftharpoons H^+ + H_2O(l) + Si_2O_2(OH)_5^-$	−8.100 ±0.300	46.235 ±1.712		
$Si_3O_6(OH)_3^{3-}$	$3\ Si(OH)_4(aq) \rightleftharpoons 3\ H^+ + 3\ H_2O(l) + Si_3O_6(OH)_3^{3-}$	−28.600 ±0.300	163.250 ±1.712		
$Si_3O_5(OH)_5^{3-}$	$3\ Si(OH)_4(aq) \rightleftharpoons 3\ H^+ + 2\ H_2O(l) + Si_3O_5(OH)_5^{3-}$	−27.500 ±0.300	156.971 ±1.712		
$Si_4O_8(OH)_4^{4-}$	$4\ Si(OH)_4(aq) \rightleftharpoons 4\ H^+ + 4\ H_2O(l) + Si_4O_8(OH)_4^{4-}$	−36.300 ±0.500	207.202 ±2.854		
$Si_4O_7(OH)_5^{3-}$	$4\ Si(OH)_4(aq) \rightleftharpoons 3\ H^+ + 4\ H_2O(l) + Si_4O_7(OH)_5^{3-}$	−25.500 ±0.300	145.555 ±1.712		

(a) Value calculated internally with the equation $\Delta_r G_m^\circ = \Delta_r H_m^\circ - T\Delta_r S_m^\circ$.
(b) Value calculated from a selected standard potential.
(c) Value of $\log_{10} K^\circ$ calculated internally from $\Delta_r G_m^\circ$.

SUPERSEDED IN PART
Check the Selected Value tables in Guillaumont et al.: Update on the Chemical Thermodynamics of U, Np, Pu, Am and Tc, Elsevier, 2004.

Chapter V

Discussion of data selection

V.1. Elemental americium†

V.1.1. Americium metal

V.1.1.1. Allotropy and crystal structure

Americium is the first 5f element to resemble the early lanthanide elements. McWhan, Cunningham and Wallmann [62MCW/CUN] showed that at room temperature americium has a double hexagonal close-(dhcp) structure, confirming the early work of Graf *et al.* [56GRA/CUN], whose lattice parameters were appreciably larger. McWhan, Cunningham and Wallmann also observed an fcc phase formed by condensing americium on to tantalum or quartz fibres, and suggested a melting point of 1267 K for Am(cr). Wade and Wolf [67WAD/WOL] (essentially differential thermal analysis, DTA, measurements) and Stephens, Stromberg and Lilley [68STE/STR] (also DTA studies) both found solid-solid transformations at 1350 K and melting at 1448 K, later confirmed by Sari, Müller and Benedict [72SAR/MUE] and Seleznev *et al.* [77SEL/KOS]. Sari, Müller and Benedict were unable to observe any indications, in quenched samples, of a transition below 1273 K. However, recent work by Seleznev and his colleagues by DTA and high temperature X-ray diffraction [77SEL/KOS, 78SEL/SHU, 83SHU/SEL] has clarified the allotropy of Am by unambiguously identifying a dhcp to fcc transition at (1042 ± 30) K. This transition is easily missed, since it is very sluggish, has a small associated enthalpy, and the principal X-ray diffraction lines of the dhcp and fcc structures essentially overlap. The allotropy is summarised in Table V.1. The structure of the γ-phase formed at 1347 K has not been established, but is almost certainly bcc, the phase from which many metals, particularly the lanthanide metals, melt.

† An earlier version of this Section was published in the volume edited by Cordfunke and Konings [90COR/KON]. This, however, contained a number of misprints which have been corrected in the current version.

Table V.1: Allotropy of Am(cr).

Phase	Structure	Lattice parameters	$T_{\max}$ (K)	Reference
α	dhcp	$a = 0.347$, $c = 1.125$ nm	1042	[62MCW/CUN] [72SAR/MUE] [83SHU/SEL]
β	fcc	$a = 0.4894$ nm	1350	[83SHU/SEL]
γ	bcc?	?	1449	

V.1.1.2. Low-temperature heat capacity and standard entropy

The first measurements of the low-temperature heat capacity of two samples of ^{241}Am by Hall *et al.* [76HAL/MOR] were supplemented by further measurements on a sample of ^{243}Am by Hall *et al.* [80HAL/LEE]. The high self-heat of these samples, together with the relatively small masses of pure Am metal available, leads to severe problems in low-temperature thermal measurements. The heat capacity values for ^{243}Am(cr) are appreciably different from those of ^{241}Am(cr). Given these problems, the composite values given by Hall *et al.* [80HAL/LEE] are accepted, leading to

$$\begin{aligned} C^{\circ}_{p,\mathrm{m}}(\mathrm{Am}, \alpha, 298.15\,\mathrm{K}) &= (25.5 \pm 1.5)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}, \\ S^{\circ}_{\mathrm{m}}(\mathrm{Am}, \alpha, 298.15\,\mathrm{K}) &= (55.4 \pm 2.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}. \end{aligned}$$

V.1.1.3. High-temperature heat capacity and transformation data

There are no experimental measurements on the high-temperature heat capacity of Am(cr), but both Oetting, Rand and Ackermann [76OET/RAN] and Ward, Kleinschmidt and Peterson [86WAR/KLE] have given very similar estimated values. Since the latter's transition temperatures (see below) are probably more accurate, their values for $C^{\circ}_{p,\mathrm{m}}$(Am, cr) above 400 K, based on those of praseodymium, with a correction for the mass difference, are used, in order to avoid too many essentially equivalent tables of thermal functions.

However, the tabulated values of Ward, Kleinschmidt and Peterson [86WAR/KLE] do not merge smoothly at 298.15 K, and their value of $C^{\circ}_{p,\mathrm{m}}(298.15\,\mathrm{K})$ is somewhat smaller than the experimental value given by Hall *et al.* [80HAL/LEE]. The estimates of Ward, Kleinschmidt and Peterson [86WAR/KLE] from 298.15 K to 400 K are thus amended slightly to provide a smooth join at 298.15 K.

These expressions are closely fitted by equations of the form

$$C^{\circ}_{p,\mathrm{m}}(T) = (a + bT + cT^2 + eT^{-2})\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \qquad \text{(V.1)}$$

Table V.2: Heat capacity coefficients and transformation data.

Phase	Heat capacity coefficients a	$b \times 10^3$	$c \times 10^6$	$e \times 10^{-5}$	$T_{\min}$ (K)	$T_{\max}$ (K)	T_{trs} (K)	$\Delta_{\text{trs}}H_{\text{m}}$ ($\text{J} \cdot \text{mol}^{-1}$)
α	21.1868	11.199	3.2462	0.6085	298.15	1042	1042 ± 30	870
β	19.4406	10.836	2.2514	5.2087	1042	1350	1350 ± 5	5862
γ	39.748	0	0	0	1350	1449	1449 ± 5	14393
liq	41.840	0	0	0	1449	3000		
gas	20.7861	0	0	0	298.15	1100		
	25.2809	-4.96394	1.54658	-10.9495	1100	1700		
	62.3915	-33.5329	7.76400	-199.137	1700	3000		

with the coefficients given in Table V.2.

The enthalpies of transition are deduced from DTA traces by Wade and Wolf [67WAD/WOL] ($\beta \rightarrow \gamma$, $\gamma \rightarrow$ liquid) and by Seleznev *et al.* [77SEL/KOS]. The earlier values, which are 50% larger than those by Seleznev *et al.* [77SEL/KOS], are preferred, since they were obtained on a massive sample of quite pure Am(cr). An approximate value for $\Delta_{\text{trs}}S_{\text{m}}(\alpha \rightarrow \beta)$ can be calculated from the pressure required to stabilise the fcc phase at room temperature, which is taken to be (6 ± 1) GPa [79AKE/JOH, 81ROO]. With $\Delta_{\text{trs}}V(\alpha \rightarrow \beta) = -(1.08 \pm 0.24) \times 10^{-7}\,\text{m}^3 \cdot \text{mol}^{-1}$ [83SHU/SEL], one finds $\Delta_{\text{trs}}S = (0.87 \pm 0.24)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, assuming $(\text{d}T/\text{d}p)$ is constant from 298.15 K to 1042 K. We therefore retain the entropy of transition estimated by Oetting, Rand and Ackermann [76OET/RAN] (and used by Ward, Kleinschmidt and Peterson [86WAR/KLE]), $\Delta_{\text{trs}}S = 0.837\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. This is larger than the value $\Delta_{\text{trs}}S = 0.32\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ estimated from DTA traces by Seleznev *et al.* [77SEL/KOS], which is not surprising in view of the sluggishness of this transition.

V.1.2. Americium ideal monoatomic gas

V.1.2.1. Heat capacity and entropy

Feber and Herrick [65FEB/HER], Oetting, Rand and Ackermann [76OET/RAN] and Ward, Kleinschmidt and Peterson [86WAR/KLE] calculated the thermal functions of Am(g) based on observed and estimated spectroscopic energy levels. The most recent values of Ward, Kleinschmidt and Peterson [86WAR/KLE], however, are calculated for the ^{243}Am isotope, using the 33 spectroscopic levels up to 18000 cm^{-1} given by Brewer [84BRE]. This isotope is not the one of major importance for most studies, so we recalculate the thermal functions for the ^{241}Am isotope, adding as well 18 more spectroscopic levels between 18000 and 30000 cm^{-1}, previously communicated by

Fred [75FRE] to Oetting, Rand and Ackermann [76OET/RAN]. The Gibbs energy function $-(G-H(298.15\,\mathrm{K}))/\mathrm{T}$ at 3000 K is 0.003 and 0.0150 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ greater than those given by Ward, Kleinschmidt and Peterson [86WAR/KLE] and Oetting, Rand and Ackermann [76OET/RAN], respectively.

The recommended standard heat capacity and entropy are

$$\begin{aligned} C^{\circ}_{p,\mathrm{m}}(\mathrm{Am,g},298.15\,\mathrm{K}) &= (20.786 \pm 0.001)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}, \\ S^{\circ}_{\mathrm{m}}(\mathrm{Am,g},298.15\,\mathrm{K}) &= (195.6 \pm 2.0)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}. \end{aligned}$$

The heat capacity as a function of temperature is closely fitted by Eq. (V.1) with the coefficients given in Table V.2.

V.1.2.2. Enthalpy of vaporization

Precise vapour pressure measurements were made in two separate studies by Ward, Müller and Kramer [76WAR/MUE] (^{243}Am, 990 to 1358 K) and by Ward and Kleinschmidt [79WAR/KLE] (^{243}Am, 1200 to 1595 K). These are preferred to the earlier work by Erway and Simpson [50ERW/SIM] and Carniglia and Cunningham [55CAR/CUN], using much less pure materials. The vapour pressure equations from the three studies are:

$$\mathrm{Am(s)}: \quad \log_{10}(p/\mathrm{atm}) = 6.578 - 143.15/T \qquad \text{(V.2)}$$

990 to 1358 K [76WAR/MUE]

$$\mathrm{Am(s)}: \quad \log_{10}(p/\mathrm{atm}) = 6.296 - 13983/T \qquad \text{(V.3)}$$

1200 to 1415 K [79WAR/KLE]

$$\mathrm{Am(l)}: \quad \log_{10}(p/\mathrm{atm}) = 6.279 - 13935/T \qquad \text{(V.4)}$$

1469 to 1595 K [79WAR/KLE].

The uncertainty in the values of $\log_{10} p$ obtained from Eqs. (V.2) and (V.3) is probably ± 0.10, increasing to ± 0.15 for Eq. (V.4).

The enthalpy of sublimation at 298.15 K is calculated by both the second- and third-law methods using the thermal functions assessed in the present work, with the results shown in Table V.3.

The selected value is

$$\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}(\mathrm{Am,g},298.15\,\mathrm{K}) = (283.8 \pm 1.5)\ \mathrm{kJ \cdot mol^{-1}}$$

based on the third-law heat from all the studies (this is automatically weighted towards the more complete study of Ward, Müller and Kramer [76WAR/MUE] which has excellent agreement between the second- and third-law enthalpies).

It may be noted that the values for $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}}(\mathrm{Am,g},298.15\,\mathrm{K})$ given by Ward, Kleinschmidt and Peterson [86WAR/KLE] are identical with those given by Ward and Kleinschmidt [79WAR/KLE], obtained using different thermal functions for both Am(s, l) and Am(g) and are thus not quite consistent with the thermal functions given in Ward, Kleinschmidt and Peterson [86WAR/KLE]. Nevertheless, the selected value is very close to that selected by both Ward, Kleinschmidt and Peterson [86WAR/KLE] and Oetting, Rand and Ackermann [76OET/RAN], $\Delta_{\mathrm{f}} H^{\circ}_{\mathrm{m}} = (284.1 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$.

Table V.3: $\Delta_f H^\circ_m(\mathrm{Am, g}, 298.15\,\mathrm{K})$ derived from vaporisation measurements.

Equation	$\Delta_f H^\circ_m$ (298.15 K, second-law) ($\mathrm{kJ \cdot mol^{-1}}$)	$\Delta_f H^\circ_m$ (298.15 K, third-law) ($\mathrm{kJ \cdot mol^{-1}}$)
(V.2)	284.0	283.7 ± 1.2
(V.3)	279.8	284.2 ± 1.0
(V.4)	303.2	283.0 ± 1.6

The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy:

$$\Delta_f G^\circ_m(\mathrm{Am, g}, 298.15\,\mathrm{K}) \quad = \quad (242.0 \pm 1.7)\ \mathrm{kJ \cdot mol^{-1}}.$$

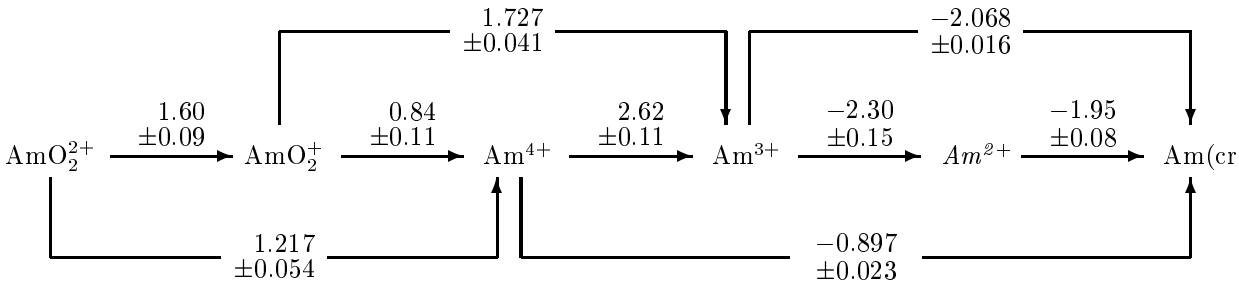
V.2. Simple americium aqua ions

In aqueous media, americium exists as the trivalent ion except under strongly oxidising conditions, where the five- and six-valent dioxoamericium ions AmO_2^+ and AmO_2^{2+} are formed. In acid solutions, the former slowly disproportionates to AmO_2^{2+} and Am^{3+}. The free radicals produced from α-particles in water readily reduce these dioxoamericium ions back to Am^{3+}. Tetravalent americium is only stable in the presence of strongly complexing agents such as carbonate, fluoride, phosphate and phosphotungstate ions.

There are no solubility or other data from which the Gibbs energies of any of the americium ions can be related to any of the condensed phase compounds, although there are emf data relating one ion to another. The Gibbs energies and related properties of the ions therefore depend on estimates of the entropies of the aqua ions, based on comparisons with other actinide and lanthanide ions.

Fuger and Oetting [76FUG/OET] reviewed the thermodynamic properties of the aqua ions, and except for the tetravalent ion, no further relevant data have been published, so their careful evaluation is accepted with minor changes for the more stable ions. A later review of the thermochemistry of the simple aqua ions has been given by Martinot and Fuger [85MAR/FUG]. The discussion in the following sections summarizes the original works from which the selected data are derived and the potential diagram in Figure V.1 outlines the selected values which are given in Table III.1. The current values of the thermodynamic data for the aqua ions will be re-examined for overall consistency within the actinide series by the reviewers of the Np and Pu volumes when their selections for the aqueous data for the ions of these elements have been finalised.

Figure V.1: Electrode potentials (in units of V) for some americium redox couples. The species Am^{2+} is italicized to stress the fact that it is only a transient species, *cf.* Section V.2.1.



Fuger and Oetting [76FUG/OET] and Martinot and Fuger [85MAR/FUG] have discussed the evidence for the formation of the heptavalent aquaion in 3 to 5 M NaOH by oxidising Am(VI) solutions using γ-irradiation in the presence of N_2O or $K_2S_2O_8$. It is also claimed (Nikolaevskii *et al.* [75NIK/SHI]) that AmO_2^{2+} disproportionates to Am(VII) and Am(V) in alkaline solutions with concentrations above 10 M NaOH. There are no quantitative thermodynamic data for the Am(VII) aquaion, and the species will not be considered further.

V.2.1. Am^{2+}

As discussed by Martinot and Fuger [85MAR/FUG], there is evidence for the transient formation of Am^{2+} in aqueous perchlorate media in pulse radiolysis experiments [76SUL/GOR, 78GOR/MUL] the half life was reported to be approximately 5μs. Radiopolarography (*cf.* the review by David *et al.* [90DAV/MAS]) shows fairly unambiguosly that Am^{2+} is *not* an intermediate species in the reduction of Am^{3+} to the metal in non-complexing media, although its formation has been suggested in molten salts [83MIK] and organic solvents [69MUS/MJA, 76FRI/STO, 92KUL/KAM]. Nugent *et at.* [73NUG/BAY] estimated the Am^{3+}/Am^{2+} potential to be −2.3 V from a systematic study of the properties of the lathanide and actinide chlorocomplexes in relation to their M(II)/M(III) potentials. A similar value of −2.4 V has been estimated by Bratsch and Lagowski [86BRA/LAG]. The value of $E^\circ = -(2.3 \pm 0.15)$ V, and the standard Gibbs energy of formation of Am^{3+} selected below gives

$$\Delta_f G^\circ_m(Am^{2+}, aq, 298.15\,K) \;=\; -(377 \pm 15)\ kJ \cdot mol^{-1}.$$

Morss and Morss and McCue [76MOR, 76MOR/MCC] and David [86DAV] have suggested two similar equations expressing $S^\circ_m(M^{2+}, aq, 298.15\,K)$ in terms of the relative atomic mass, charge, ionic radius and total angular momentum quantum number. These equations give the same estimated value,

$$S^\circ_m(Am^{2+}, aq, 298.15\,K) \;=\; -(1 \pm 15)\ J \cdot K^{-1} \cdot mol^{-1}$$

where the uncertainty is estimated in this review (the slightly earlier estimate of $-9.3\ J \cdot K^{-1} \cdot mol^{-1}$ [85DAV/FOU] was presumably superseded by that of [86DAV]).

Combination with the standard Gibbs energy of formation gives the following estimated standard enthalpy of formation:

$$\Delta_f H^\circ_m(Am^{2+}, aq, 298.15\,K) \quad = \quad -(355 \pm 16)\ kJ \cdot mol^{-1}.$$

V.2.2. *Am^{3+}*

The first values of the enthalpy of solution of americium in hydrochloric acid, reported by Lohr and Cunningham [51LOH/CUN] and Westrum and Eyring [51WES/EYR], were carried out before the details of the allotropy were well defined, and the crystalline structure of the metal used in these investigations is not known. Both these values correspond to a value of $\Delta_f H^\circ_m(Am^{3+}, aq, 298.15K) = -670$ to -680 kJ·mol^{-1} for the standard enthalpy of formation of Am^{3+} with an uncertainty of about 15 kJ · mol^{-1}. Later, Morss [69MOR] made some preliminary measurements which indicated an appreciably more positive value of about -625 kJ · mol^{-1}. Subsequently, Fuger, Spirlet and Müller [72FUG/SPI] measured the enthalpy of solution of two samples of Am(α, dhcp) in hydrogen-saturated 1 M, 1.5 M and 6 M HCl solutions. Their americium samples, which contained mainly ^{241}Am, were characterised for non-metallic (H, N, O) and metallic elements. Their values for $\Delta_f H^\circ_m(Am^{3+}, aq, 298.15\,K)$ in 1 M, 1.5 M and 6 M HCl were $-(616.1\pm0.8)$, $-(615.4\pm0.8)$ and $-(613.1\pm1.4)$ kJ·mol^{-1}, respectively. More recently, Mondal *et al.* [87MON/RAS] have found the enthalpy of dissolution of essentially isotopically pure ^{243}Am(α, dhcp), containing < 50 ppm by weight of metallic impurities, in hydrogen saturated 1 M HCl to be $-(620.6 \pm 1.3)$ kJ · mol^{-1}. Since the samples used by Fuger *et al.* [72FUG/SPI] were characterised for both metallic and non-metallic impurities, and since Fuger *et al.* carried out consistent measurements in 1, 1.5 and 6 M HCl, their values are preferred in the present assessment. Extrapolation of these values to zero ionic strength leads to the selected value of

$$\Delta_f H^\circ_m(Am^{3+}, aq, 298.15\,K) \quad = \quad -(616.7 \pm 1.5)\ kJ \cdot mol^{-1}.$$

The reason for the large discrepancy with the early measurements is not clear. It is too large to be attributable to the presence of β- or γ-phases of americium in the earlier material. Undetected impurities in the rather small samples used could of course be a contributing factor. The close agreement of the value by [87MON/RAS] based on dissolution of ^{243}Am suggests that the effect of the radioactivity of americium (such as radiation damage of the metal) is probably negligible. It may be noted that similar discrepancies have been found in the enthalpies of solution of uranium and (to a lesser extent) plutonium metals; for these elements, however, there are problems of the formation of unwanted oxidation states (U^{3+} and Pu^{4+}, respectively), which is not the case with americium. Some Am(V) is slowly formed by radiolysis in Am^{3+} solutions in the presence of Cl^-, *cf.* Sections V.3.1.2 and V.3.2.5, but this effect will not be significant in the short time ($\sim$ 1 h) taken for the calorimetric dissolution, in the presence of both dissolved and evolving hydrogen.

However, the careful measurements of Fuger, Spirlet and Müller [72FUG/SPI] are confirmed by the study in Ref. [87MON/RAS], as well as the earlier preliminary

work of Morss [69MOR] already mentioned. The systematic relationships between the enthalpies of formation of the aqua ions and the enthalpy of sublimation of the monoatomic gas in actinide and lanthanide metals noted by Nugent, Burnett and Morss [73NUG/BUR] also suggest the enthalpy of formation of Am^{3+} is close to the value selected here.

As noted previously, the entropy of Am^{3+} was estimated by Fuger and Oetting [76FUG/OET] from the interrelationship of the ionic radii and the known thermodynamic properties of lanthanide and actinide ions. Their value of

$$S^\circ_{\mathrm{m}}(\mathrm{Am}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) \quad = \quad -(201 \pm 15)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

is accepted. David [85DAV/FOU, 86DAV] has estimated the very similar value of $-199\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$.

The Gibbs energy of formation is calculated from the selected values for the enthalpy of formation and the entropy.

$$\Delta_{\mathrm{f}} G^\circ_{\mathrm{m}}(\mathrm{Am}^{3+}, \mathrm{aq}, 298.15\,\mathrm{K}) \quad = \quad -(598.7 \pm 4.8)\ \mathrm{kJ \cdot mol^{-1}}.$$

V.2.3. Am^{4+}

As noted in Section V.2, this species is never found in any appreciable amount in tetravalent americium solutions, which are only stable in the presence of strongly complexing anions. Nevertheless, good estimates of its thermodynamic properties are of interest.

A fairly precise estimate of its enthalpy of formation was given by Morss and Fuger [81MOR/FUG]. They pointed out that the enthalpy of the hypothetical solution process,

$$M\mathrm{O_2(cr)} + 4\,\mathrm{H^+} \quad \rightleftharpoons \quad M^{4+} + 2\,\mathrm{H_2O(l)} \tag{V.5}$$

is an excellent linear function of the lattice parameter of the dioxide where M is a lanthanide (Ce and Pr) or actinide (Th, U, Np, Pu) element. Only the values for terbium are discrepant. In the same paper, Morss and Fuger [81MOR/FUG] present a careful calorimetric determination of the enthalpy of formation of two samples of AmO_2(cr), one containing ^{241}Am, the other ^{243}Am. With a lattice parameter of $a = 0.53743$ nm for AmO_2(cr), the correlation noted above indicates that the enthalpy of the above hypothetical reaction for $M = \mathrm{Am}$ is $-(45 \pm 5)\ \mathrm{kJ \cdot mol^{-1}}$, which combined with $\Delta_{\mathrm{f}} H^\circ_{\mathrm{m}}(\mathrm{AmO_2}, \mathrm{cr}, 298.15\,\mathrm{K})$ (*cf.* Section V.3.2.3) finally gives

$$\Delta_{\mathrm{f}} H^\circ_{\mathrm{m}}(\mathrm{Am}^{4+}, \mathrm{aq}, 298.15\,\mathrm{K}) \quad = \quad -(406 \pm 6)\ \mathrm{kJ \cdot mol^{-1}}$$

Although there have been a number of estimates for the electrode potential of the Am^{3+}/Am^{4+} couple, the most reliable value for this is probably from an estimate of $S^\circ_{\mathrm{m}}(\mathrm{Am}^{4+}, \mathrm{aq})$. Following Fuger and Oetting [76FUG/OET], we take the difference in entropy of Am^{4+} and Am^{3+} to be the same as that for the plutonium ions, namely $-(205 \pm 21)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, giving for Am^{4+}

$$S^\circ_{\mathrm{m}}(\mathrm{Am}^{4+}, \mathrm{aq}, 298.15\,\mathrm{K}) \quad = \quad -(406 \pm 21)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

in agreement with the estimate of David [85DAV/FOU, 86DAV] of $-402\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. When combined with the enthalpy of formation, the selected value of the entropy gives

$$\Delta_f G^\circ_m(\mathrm{Am^{4+}, aq}, 298.15\,\mathrm{K}) \quad = \quad -(346 \pm 9)\ \mathrm{kJ \cdot mol^{-1}}.$$

The assessed values for the Gibbs energies of formation of Am^{3+} and Am^{4+} correspond to a reduction potential of $E^\circ = (2.62 \pm 0.11)$ V. This is in reasonable agreement with the following values extrapolated from measurements in phosphate and carbonate solutions:

- $E^\circ = (2.50 \pm 0.06)$ V calculated by Marcus *et al.* [72MAR/YAN] from the measured value of $E^\circ = (1.75 \pm 0.03)$ V in 11.5 M phosphoric acid [70YAN/GIV]. However, given the uncertainties in the speciation in such concentrated solutions, the uncertainty of ± 0.06 V in the inferred E° value is almost certainly too low.

- $E^\circ = (2.6 \pm 0.1)$ V from measurements in carbonate solutions by Hobart, Samhoun and Peterson [82HOB/SAM].

- $E^\circ = (2.34 \pm 0.22)$ V extrapolated by Nugent*et al.* [71NUG/BAY] from their value of $E = 1.78$ V measured in 10 M H_3PO_4.

- $E^\circ = 2.4$ V, with an unknown uncertainty, estimated by Bratsch and Lagowski [86BRA/LAG].

These measurements are discussed in more detail in Sections V.6.2.1.2, *p.*142, and V.7.1.2.1.d, *p.*157. The correlation with spectroscopic values proposed by Nugent *et al.* [73NUG/BAY] leads to the appreciably lower value of $E^\circ = (2.2 \pm 0.2)$ V.

V.2.4. AmO_2^+

The enthalpy of reduction of AmO_2^+ to Am^{3+} by the Fe^{2+} ion

$$\mathrm{AmO_2^+ + 2\,Fe^{2+} + 4\,H^+ \rightleftharpoons Am^{3+} + 2\,Fe^{3+} + 2\,H_2O(l)}, \qquad \text{(V.6)}$$

was measured by Gunn and Cunningham [57GUN/CUN] in 1 M $HClO_4$ to be $\Delta_r H^\circ_m(\mathrm{V.6}, 298.15\mathrm{K}, 1\,\mathrm{M\,HClO_4}) = -(302.1 \pm 4.0)\ \mathrm{kJ \cdot mol^{-1}}$. If this value is assumed to hold at infinite dilution (since the correction will be both small and uncertain), combination with the current best CODATA compatible value for the enthalpy of the Fe^{3+}/Fe^{2+} reduction [95PAR/KHO], $(41.0 \pm 1.5)\ \mathrm{kJ \cdot mol^{-1}}$, gives a value of

$$\Delta_r H^\circ_m(\mathrm{V.7}, 298.15\,\mathrm{K}) \quad = \quad (384.1 \pm 5.2)\ \mathrm{kJ \cdot mol^{-1}}$$

for the reaction

$$\mathrm{Am^{3+} + 2\,H_2O(l) \rightleftharpoons AmO_2^+ + 4\,H^+ + 2\,e^-}. \qquad \text{(V.7)}$$

From this and the previously assigned enthalpy of formation of Am^{3+}, the selected enthalpy of formation is obtained:

$$\Delta_f H^\circ_m(AmO_2^+, aq, 298.15\,K) = -(804.3 \pm 5.4)\ kJ \cdot mol^{-1}.$$

Following Fuger and Oetting [76FUG/OET] this review accepts

$$S^\circ_m(AmO_2^+, aq, 298.15\,K) = -(21 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1},$$

based on the same value for NpO_2^+ from the (corrected) work of Brand and Cobble [70BRA/COB]. Corrections could be made in an attempt to take account of the differing magnetic contributions to the entropies of these ions, but since the overall sign of these (small) corrections is not known with certainty, they are ignored and deemed to be included in the (increased) overall uncertainty.

Hence, the following Gibbs energy value is obtained:

$$\Delta_f G^\circ_m(AmO_2^+, aq, 298.15\,K) = -(739.8 \pm 6.2)\ kJ \cdot mol^{-1}.$$

V.2.5. AmO_2^{2+}

The enthalpy of reduction of AmO_2^{2+} to Am^{3+} by the Fe^{2+} ion in 1 M $HClO_4$ was also measured by Gunn and Cunningham [57GUN/CUN]. For the reaction

$$AmO_2^{2+} + 3\,Fe^{2+} + 4\,H^+ \rightleftharpoons Am^{3+} + 3\,Fe^{3+} + 2\,H_2O(l) \qquad (V.8)$$

they obtained $\Delta_r H^\circ_m(V.8, 298.15\,K,\ 1\,M\ HClO_4) = -(414.6 \pm 1.0)\ kJ \cdot mol^{-1}$. If this value is assumed to hold at infinite dilution (since the correction will be both small and uncertain), combination with the current best CODATA compatible value for the enthalpy of the Fe^{3+}/Fe^{2+} reduction [95PAR/KHO], $(41.0 \pm 1.5)\ kJ \cdot mol^{-1}$, gives a value of

$$\Delta_r H^\circ_m(V.9, 298.15\,K) = (537.6 \pm 4.6)\ kJ \cdot mol^{-1}$$

for the reaction

$$Am^{3+} + 2\,H_2O(l) \rightleftharpoons AmO_2^{2+} + 4\,H^+ + 3\,e^-. \qquad (V.9)$$

From this, the selected enthalpy of formation is obtained:

$$\Delta_f H^\circ_m(AmO_2^{2+}, aq, 298.15\,K) = -(650.8 \pm 4.8)\ kJ \cdot mol^{-1}.$$

Penneman and Asprey [50PEN/ASP] measured the potentials of the AmO_2^{2+}/AmO_2^+ couple to be $E(1M\ HClO_4) = (1.600 \pm 0.0005)$ V and $E(0.3M\ HClO_4) = (1.614 \pm 0.001)$ V. Brand and Cobble [70BRA/COB] suggested that the difference of 0.100 V they found between the potential of the NpO_2^+/NpO_2^{2+} couple in 1 M $HClO_4$ and the value extrapolated to infinite dilution should also be applied to the similar couples in other actinides. However, it is now clear from more recent data for the dioxoneptunium ions (see Fuger and Oetting [76FUG/OET]) and the dioxouranium

ions (see Grenthe *et al.* [92GRE/FUG]) that this correction is far too large. Following Fuger and Oetting, we do not apply any correction to the "formal" potentials of Penneman and Asprey [50PEN/ASP], but increase somewhat the uncertainty limits. The small change in the potential due to the change in standard state pressure from 1 atm to 1 bar is entirely negligible in the present case. Thus, for the reaction

$$AmO_2^+ + H^+ \rightleftharpoons AmO_2^{2+} + 0.5\,H_2(g) \qquad (V.10)$$

this review obtains $\Delta_r G_m^\circ(V.10, 298.15\,K) = (154.3 \pm 5.0)$ kJ·mol^{-1}. When combined with the enthalpy of the same reaction $\Delta_f H_m^\circ(AmO_2^{2+}) - \Delta_f H_m^\circ(AmO_2^+) = (153 \pm 2.5)$ kJ·mol^{-1} and the standard entropy of AmO_2^+ selected in Section V.2.4, this gives $S_m^\circ(AmO_2^{2+}, aq, 298.15\,K) = -(91 \pm 20)$ J·K^{-1}·mol^{-1}. This is in excellent agreement with the value estimated from the entropy NpO_2^{2+} from the (corrected) work of Brand and Cobble [70BRA/COB]. According to the method used to correct for the difference in the magnetic contributions to the entropy of these ions, the estimate for the entropy of AmO_2^{2+} is −86.2 or −88.7 J·K^{-1}·mol^{-1}, with uncertainties of ≈ 10 J·K^{-1}·mol^{-1}.

The selected value is

$$S_m^\circ(AmO_2^{2+}, aq, 298.15\,K) = -(88 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}$$

from which one obtains

$$\Delta_f G_m^\circ(AmO_2^{2+}, aq, 298.15\,K) = -(585.8 \pm 5.7)\ kJ \cdot mol^{-1}.$$

V.3. Oxygen and hydrogen compounds and complexes

V.3.1. Aqueous americium hydroxide complexes

V.3.1.1. Aqueous Am(III) hydroxide complexes

Thermodynamic data on Am(III) hydrolysis have been compiled or reviewed by a number of authors [76SCH, 78RAI/SER, 80BEN/TEA, 82ALL, 84KER, 85PHI/PHI, 86KER/SIL, 86KIM, 88MOU/ROB, 89ROB, 92FUG/KHO, 94JUN/EDE]. Only a few of them, however, attempted a critical examination of the existing information [86KER/SIL, 89ROB, 92FUG/KHO, 94JUN/EDE]. Table V.4 shows the wide variability and uncertainties of the reported values of Am(III) hydrolysis constants. They refer to the reaction

$$Am^{3+} + n\,H_2O(l) \rightleftharpoons Am(OH)_n^{(3-n)} + n\,H^+. \qquad (V.11)$$

A re-evaluation of the published data is made by this review in cases where discrepancies or results of doubtful interpretation were reported. In general, there is no unique statistical procedure for selecting the best regression equation of experimental data. A great deal of personal judgement is often a necessary part of the method. Possibilities of bias in the estimates may arise in the case of very high intercorrelation among the predictor variables. This review has used the *same* procedure to select the best hydrolysis model from *all* sets of experimental data reported by the different

authors. The procedure first involved the fitting of all possible hydrolysis models using the nonlinear regression programme NLIN of the SAS/STAT software package [88SAS] on a mainframe computer. This was then followed by a series of internal comparisons to find the best cutoff point for the number of predictor variables. The partial F-test and the residual mean square were used as criteria for the assessment. The values of the hydrolysis constants recalculated by this review from the original experimental data are given in Table V.5, where the reported error limits represent this review's estimate of the 95% confidence level.

Major difficulties in the experimental determination of equilibrium constants for Am(III) hydroxide complexes generally come from its great ease of adsorption and precipitation. Most of the experimental work was carried out in the pH region where the first and the second hydroxo species are present, while only a few data have been reported on the neutral $Am(OH)_3(aq)$. By analogy with neodymium [76BAE/MES], Allard [82ALL] and Phillips *et al.* [85PHI/PHI] proposed also the existence of $Am(OH)_4^-$. The formation of this negatively charged species would increase the Am(III) solubility in the high pH region. A number of experimental studies [83RAI/STR, 84BER/KIM, 84KIM/BER, 88STA/KIM, 88STA/KIM2] have shown that such a solubility increase does not occur at pH $\leq$ 13. The observations by Vitorge and Tran The [91VIT/TRA] are not considered because of the great variation of the ionic strength during their experiments. Thus, there is no experimental evidence for anionic hydrolysis complexes of Am(III). Although polynuclear hydroxo- or oxo-complexes could be formed in the region immediately before precipitation, there is no evidence of their existence. Spectroscopic results [84BER/KIM, 84KIM/BER, 88STA/KIM] suggesting the absence of polynuclear complexes were inconclusive since these species are not expected to appreciably affect spectral shapes. This review has excluded the presence of polynuclear species on a statistical basis during the computer refinement of experimental data [82SIL, 84BER/KIM, 84KIM/BER].

No systematic studies have been made with the ionic strength varied to allow extrapolation to thermodynamic conditions. Corrections for activity coefficients should be possible with the equation derived from the specific ion interaction equations (see Appendix B, Eqs. (B.5) and (B.8)). Eq. (B.5) predicts a linear ionic strength dependence. Figures V.2 and V.3 show, however, that the equilibrium data from Table V.4, rearranged according to Eq. (B.5), cluster in two distinct regions of the graphs. According to Korotkin [73KOR2, 74KOR], the contradictory data might be explained with a different effect of the cations H^+, Li^+, Na^+,K^+ and NH_4^+ of the background electrolyte on Am(III) hydrolysis. However, the difference between the $\log_{10}{}^*\beta_n^\circ$ values, obtained using the specific ion interaction equations (Eq. (B.5) in Appendix B), is too large to be accounted for by a medium effect.

A kinetic method of analysis was used in Refs. [69MAR/KIK, 72SHA/STE, 73KOR2], with Am species moving in the solution either under the influence of an electric field or because of the solvent flow. Assuming a slow rate of equilibration between the various Am species, the formation of distinct Am peaks was entirely attributed to hydrolysis reactions. This review rejects this assumption because the rate of hydrolysis reactions, which involve only dissociation of protons from bound water molecules is expected to be rapid. Furthermore, it is likely that adsorption-

Table V.4: Literature values of equilibrium constants (in logarithmic units) for the reactions

$$Am(OH)_3(s) + 3\,H^+ \rightleftharpoons Am^{3+} + 3\,H_2O(l)$$

and

$$Am^{3+} + n\,H_2O(l) \rightleftharpoons Am(OH)_n^{(3-n)} + n\,H^+.$$

$Am(OH)_3(s)$	$AmOH^{2+}$	$Am(OH)_2^+$	$Am(OH)_3(aq)$	t (°C)	Medium	Method	Reference
	-5.92 ± 0.11			23	0.1 M (H, Li) ClO_4	dis	[69DES/HUS]
	-3.05 ± 0.05			15	5×10^{-3} M (H,K)Cl	em	[69MAR/KIK]
	-3.13 ± 0.1	-6.76		25	5×10^{-3} M NH_4ClO_4	em	[72SHA/STE]
	-5.3 ± 0.1			?	0.1 M (H, Li) ClO_4	dis	[73HUS/HUB, 76HUB/HUS]
	-2.5	-6.6		19	0.1 M $LiNO_3$	chr, em	[73KOR2]
		-14.7		25	0.2 M $NaClO_4$	dis	[82BID]
	-7.5 ± 0.3			25	1 M $NaClO_4$	dis	[82LUN]
	-7.03 ± 0.04			25	1 M $NaClO_4$	pot	[82NAI/CHA]
16.6 ± 0.4	-7.7 ± 0.3[a]	-16.7 ± 0.7	-25.0 ± 0.3[b]	25	0.1 M $NaClO_4$	sol	[82SIL]
	-7.54 ± 0.2			21	0.7 M NaCl	dis	[83CAC/CHO]
17.5 ± 0.3				25	0.1 M $NaClO_4$	sol	[83EDE/BUC]
17.5 ± 0.3	≤ -8.2	-17.1 ± 0.5	≤ -27.0	22	corr. to 0	sol	[83RAI/STR]
13.85 ± 0.11	-7.93 ± 0.35	-14.77 ± 0.25	-24.71 ± 0.11	25?	0.1 M $NaClO_4$	sol	[84BER/KIM]
(c)	-7.93 ± 0.13	-14.95 ± 0.13	-24.82 ± 0.11				
14.18 ± 0.47	-6.34 ± 0.83	-13.64 ± 0.63	-22.87 ± 0.52	25?	0.1 M $NaClO_4$	sol	[84KIM/BER]
(c)	-4.96	-12.88	-22.34				
	-6.8 ± 0.3			25	0.5 M $NaClO_4$	dis	[87RAO/MAH]
15.6 ± 0.3	-7.5 ± 0.3	-15.4 ± 0.4	-26.9 ± 0.5	25	0.1 M $NaClO_4$ ($\leq$ 3.7 GBq/l)	sol	[88STA/KIM, 88STA/KIM2]
16.3 ± 0.3	-7.5 ± 0.2	-15.4 ± 0.3	-26.9 ± 0.2	25	0.1 M $NaClO_4$ (44 - 185 GBq/l)		
16.2 ± 0.5	-7.8 ± 0.4	-15.4 ± 0.5	-26.9 ± 0.5	25	0.1 M NaCl (74 - 185 GBq/l)		
16.1 ± 0.1	-8.1 ± 0.3	-15.8 ± 0.4	-27.0 ± 0.5	25	0.6 M NaCl (74 - 185 GBq/l)		
-25.0[d]			14.4[e]	25	5 M $NaClO_4$		
14.60 ± 0.11	-6.40 ± 0.11	-13.40 ± 0.16	-20.31 ± 0.17	25	3 M $NaClO_4$	sol	[89PAZ/KOC]
	-6.9 ± 0.2		-23.8 ± 0.9[f]	25	0.1 M ClO_4^-	em	[89ROS/REI]

Table V.4 (continued)

$Am(OH)_3(s)$	$AmOH^{2+}$	$Am(OH)_2^+$	$Am(OH)_3(aq)$	t (°C)	Medium	Method	Reference
			≤ -28.6	?	corr. to 0	sol	[90FEL/RAI]
$-27.35^{(d)}$				?	diluted	pot	[90PER/SAP]
			$-11.1^{(g,h)}$	?	diluted	sol	[91VIT/TRA]

(a) Silva kept $\log_{10}{}^*\beta_1$ constant ($= -7.7$) in the least-squares fitting of his solubility data. The value of $\log_{10}{}^*\beta_1$ was taken from a previous work, [83EDE/BUC] where the first hydrolysis constant of Cm(III) was measured by potentiometry (*cf.* Appendix A).
(b) For $Am(OH)_4^-$, Silva reported $\log_{10}{}^*\beta_4 < -34.9$.
(c) Data obtained from solubility measurements of $AmO_2(s)$.
(d) Equilibrium constant $\log_{10}K_{s,0}$ for the reaction: $Am(OH)_3(s) \rightleftharpoons Am^{3+} + 3\,OH^-$.
(e) Stability constant $\log_{10}\beta_3$ for the reaction: $Am^{3+} + 3\,OH^- \rightleftharpoons Am(OH)_3(aq)$.
(f) For $Am(OH)_4^-$, Rösch *et al.* reported $\log_{10}{}^*\beta_4 \leq -38 \pm 1$.
(g) Equilibrium constant $\log_{10}K_{s,3}$ for the reaction: $Am(OH)_3(s) \rightleftharpoons Am(OH)_3(aq)$.
(h) Vitorge and Tran The reported $\log_{10} K_4 = -0.2$ for the equilibrium: $Am(OH)_3(aq) + OH^- \rightleftharpoons Am(OH)_4^-$.

desorption processes of americium species on the stationary phase interfered with the measurements.

Americium hydrolysis equilibria were studied using a solvent extraction technique by both Désiré, Hussonnois and Guillaumont [69DES/HUS] and Hussonnois *et al.* [73HUS/HUB] below pH 5.9 in 0.1 M $LiClO_4$ solutions. They assumed the presence of $AmOH^{2+}$ in quantities large enough to produce measurable deviations from the pH dependence of distribution coefficients expected in the presence of Am^{3+} only. Reanalysis of the data by this review excluded this for statistical reasons.

The values of $\log_{10}{}^*\beta_n$ for $n = 1$ and 2 at 0.1 M ionic strength reported by the same research group for distinct solubility experiments [84BER/KIM, 84KIM/BER, 88STA/KIM] cover nearly three orders of magnitude (see Figures V.2 and V.3). However, a reanalysis of the data [84BER/KIM, 84KIM/BER] made by this review indicated that a major disagreement exists only for $\log_{10}{}^*\beta_3$. This discrepancy appears to be related to a change of the solid phase with pH, *cf.* Appendix A. Model calculations below pH 8 were insensitive to ${}^*\beta_1$, suggesting a small concentration of $AmOH^{2+}$ overwhelmed with the predominant $Am(OH)_2^+$ (*cf.* Table V.5). Solubility measurements using $AmO_2(s)$ cannot be used for a quantitative evaluation of hydrolysis constants because the dissolution reactions could not be identified.

Silva [82SIL] analysed the pH dependence of $Am(OH)_3(cr)$ solubility in 0.1 M $NaClO_4$ in terms of four hydroxide complexes. The claim for the species $Am(OH)_3(aq)$ and $Am(OH)_4^-$ is refuted by this review because the experimental points above pH 8.5, influential in fitting the chosen model, were improperly overweighted.

The publication by Stadler and Kim [88STA/KIM] is the major contribution to the study of $^{241}Am(OH)_3(s)$ solubility at high pH. Measurements were made in various

Table V.5: Values of equilibrium constants (logarithmic units) for the reactions

$$Am(OH)_3(s) + 3\,H^+ \rightleftharpoons Am^{3+} + 3\,H_2O$$

and

$$Am^{3+} + n\,H_2O(l) \rightleftharpoons Am(OH)_n^{(3-n)} + n\,H^+$$

as recalculated by this review from the original experimental data (see Appendix A).

$Am(OH)_3(s)$ (phase)	$AmOH^{2+}$	$Am(OH)_2^+$	$Am(OH)_3(aq)$	t (°C)	Medium	Reference
	-7.3 ± 0.4	-15.0 ± 0.2		25	1 M ($NaClO_4$)	[82LUN]
	-7.2 ± 0.2	-15.0 ± 0.3		25	1 M ($NaClO_4$)	[82NAI/CHA]
17.5 ± 0.6(am)				22	corr. to 0	[83RAI/STR]
15.9 ± 0.6(cr)	-6.9 ± 0.6	-15.1 ± 0.6		25	0.1 M ($NaClO_4$)	[82SIL]
13.7 ± 0.2(?)		-14.7 ± 0.2		25?	0.1 M ($NaClO_4$)	[84BER/KIM]
13.9 ± 0.2(?)		-14.3 ± 0.3		25?	0.1 M ($NaClO_4$)	[84KIM/BER]
15.5 ± 0.4(?)	-7.0 ± 0.4	-15.1 ± 0.4	-26.4 ± 0.5	25	0.1 M ($NaClO_4$)	[88STA/KIM]

ionic media (0.1 M and 5 M $NaClO_4$; 0.1 M, 0.6 M and 3 M NaCl), and at increasing radiation fields. The α-radiation damage affected the particle size of the precipitates without changing the chemical nature of the solution species. Formation of Am(V) only occurred in 3 M NaCl because of the presence of oxidising radicals. The analysis of the data obtained in 0.1 M $NaClO_4$ used $^*\beta_1$, $^*\beta_2$, and $^*\beta_3$ as best predictor variables (Table V.5).

Rai *et al.* [83RAI/STR], working with an amorphous solid in 1.5×10^{-3} M $CaCl_2$, reported a much higher americium solubility. Although the curve fitting analysis was insensitive to the first hydrolysis constant, an upper limit was assigned to the value of $^*\beta_1$. The proposed values for $^*\beta_2$ and $^*\beta_3$ are lower than selected in this review. The difference may be attributed to a pH dependent change of the solubility controlling solid phase in Ref. [83RAI/STR].

Values for $^*\beta_1$ in 0.7 M NaCl [83CAC/CHO] and in 0.5 M $NaClO_4$ [87RAO/MAH], and for $^*\beta_2$ in 0.2 M $NaClO_4$ [82BID] were obtained by solvent extraction. Although they are of the correct order of magnitude, they have not been included in the set of data used to calculate thermodynamic constants, because of experimental shortcomings (*cf.* Appendix A on discussion of selected references).

Hydrolysis equilibria in 1 M $NaClO_4$ were investigated by Lundqvist [82LUN] and by Nair, Chander and Joshi [82NAI/CHA] using, respectively, solvent extraction and potentiometry. In both cases, model calculations assumed only the formation of $AmOH^{2+}$. However, reinterpretation of the data by this review finds statistically significant evidence also for $Am(OH)_2^+$ (*cf.* Table V.5).

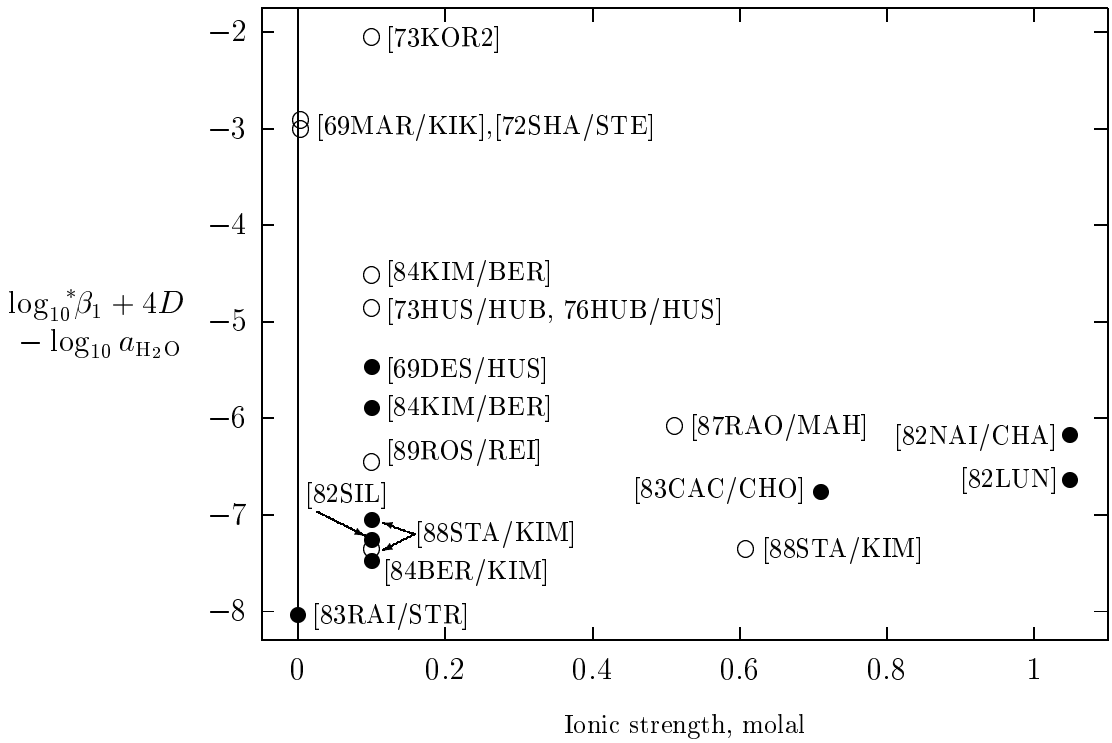
The results of Pazukhin and Kochergin [89PAZ/KOC] are not considered in this review for the reasons specified in Appendix A.

Thermodynamic data can be derived from the selected set of hydrolysis constants

Figure V.2: Literature data (*cf.* Table V.4) for the equilibrium

$$Am^{3+} + H_2O(l) \rightleftharpoons AmOH^{2+} + H^+$$

plotted according to Eq. (B.5). Filled circles denote the original equilibrium constants in experimental studies that are re-evaluated in the present review as described in the text and in Appendix A. For the sake of clarity, the constant from [89PAZ/KOC] at 3.5 m $NaClO_4$ ($\log_{10}{}^*\beta_1 + 4D - \log_{10} a_{H_2O} = -5.28$) is not presented in this graph.



at 0.1 M and 1 M ionic strength (Table V.5) on behalf of Eq. (B.5) in Appendix B. However, the data are too sparse to allow an accurate least-square extrapolation to zero ionic strength. To this purpose, experimental measurements should be undertaken at other ionic strengths. Consequently, equilibrium constants in Table V.5 are separately extrapolated to infinite dilution. Since there are no interaction coefficient data for Am^{3+}, $AmOH^{2+}$ and $Am(OH)_2^+$, the correction has been made by taking the data for trivalent lanthanides, and for typical di- and monovalent ions, *cf.* Appendix B, Section B.1.4, together with the value for $\varepsilon_{(H^+,\ ClO_4^-)}$. This gives the following estimated values in sodium perchlorate media:

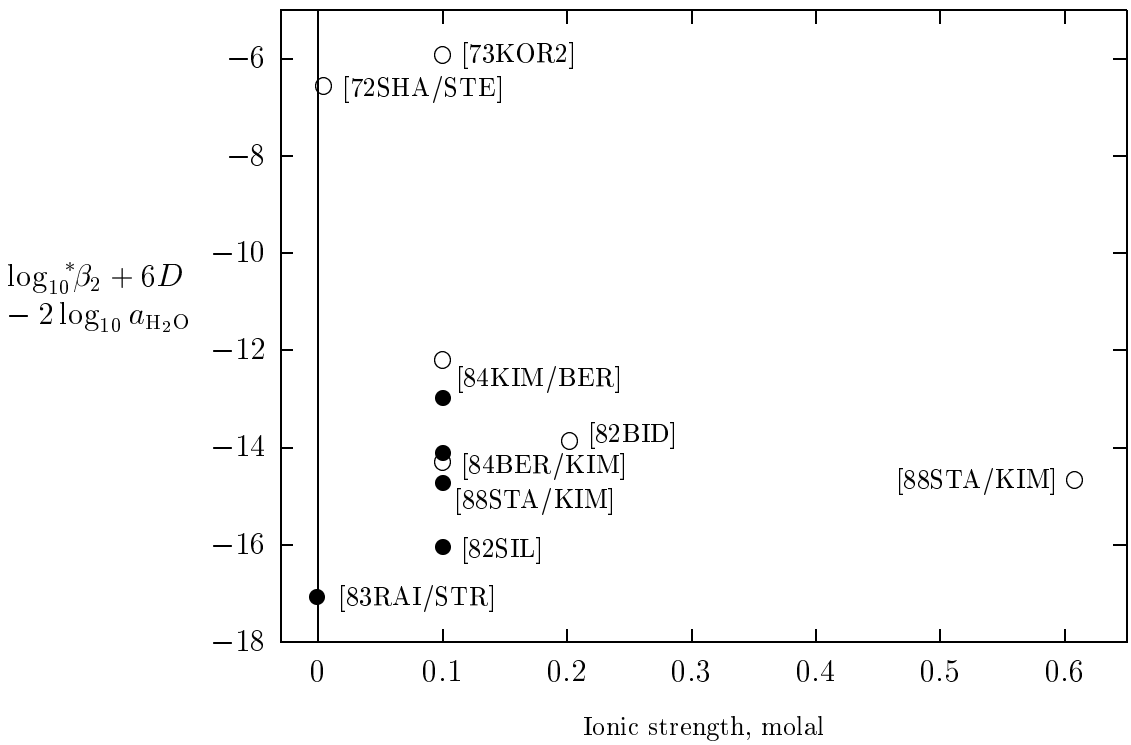
$$\begin{aligned}
\Delta\varepsilon_1(\text{V.11}, n=1) &= (0.04 \pm 0.05)\ \text{kg}\cdot\text{mol}^{-1} \\
\Delta\varepsilon_2(\text{V.11}, n=2) &= -(0.04 \pm 0.07)\ \text{kg}\cdot\text{mol}^{-1} \\
\Delta\varepsilon_3(\text{V.11}, n=3) &= -(0.07 \pm 0.07)\ \text{kg}\cdot\text{mol}^{-1}
\end{aligned}$$

A weighted average of the recalculated and then extrapolated values of ${}^*\beta_n^\circ$ gives $\log_{10}{}^*\beta_1^\circ = -(6.4 \pm 0.2)$ and $\log_{10}{}^*\beta_2^\circ = -(13.9 \pm 0.1)$. Although the calculated uncertainties are statistically correct, it is possible that the actual uncertainties are much

Figure V.3: Literature data (*cf.* Table V.4) for the equilibrium

$$Am^{3+} + 2\,H_2O(l) \rightleftharpoons Am(OH)_2^+ + 2\,H^+$$

plotted according to Eq. (B.5). Filled circles denote the original equilibrium constants in experimental studies that are re-evaluated in the present review as described in the text and in Appendix A. For the sake of clarity, the constant from [89PAZ/KOC] at 3.5 m $NaClO_4$ ($\log_{10}{}^*\beta_2 + 6D - 2\log_{10} a_{H_2O} = -11.66$) is not presented in this graph.



larger.

The value for the first hydrolysis constant implies a higher stability for $Am(OH)^{2+}$ than reported in previous reviews on americium and lanthanide hydrolysis. For example, values of $\log_{10}{}^*\beta_1^\circ = -(7.1 \pm 0.5)$, -7.5 and -6.6 have been selected, respectively, by Fuger [92FUG], Allard, Olofsson and Torstenfelt [84ALL/OLO] and Moulin *et al.* [88MOU/ROB]. Baes and Mesmer [76BAE/MES] assigned a value of $\log_{10}{}^*\beta_1^\circ = -8.0$ to Nd(III) (a chemical analogue of Am(III)), while Rard [85RAR3] selected a value of -8.25 for Eu(III). Moreover, $AmOH^{2+}$ was rejected on statistical grounds in the re-evaluation of the experimental data of Refs. [84BER/KIM, 84KIM/BER], suggesting that $AmOH^{2+}$ was not an important species in these experiments, *i.e.*, that $\log_{10}{}^*\beta_1 \leq \log_{10}{}^*K_2 = (\log_{10}{}^*\beta_2 - \log_{10}{}^*\beta_1)$. This result also favors a lower stability for $AmOH^{2+}$ and a value for $\log_{10}{}^*\beta_1^\circ$ near -7.0. The reason for the apparent discrepancy is unknown and may be due to unrecognised systematic errors in some of the experimental data. Furthermore, different procedures exist to calculate confidence intervals of predictor variables in non-linear regression analysis. Indeed, slightly different uncertainties have been obtained using different statistical computer packages. Therefore, it was felt that it would be more realistic to select the unweighted av-

erage of the values extrapolated to $I = 0$, *i.e.*, $\log_{10}{}^*\beta_1^\circ = -(6.4 \pm 0.7)$, where the uncertainty has been assigned to cover the maximum range of expectancy.

It is difficult to decide whether the values of $\log_{10}{}^*\beta_2^\circ$ belong to different parent distributions. A discrepancy may exist between the data in Ref. [82SIL] and [88STA/KIM], and the remaining values. A weighted average of $\log_{10}{}^*\beta_2^\circ = -(14.4 \pm 0.3)$ and $-(13.8 \pm 0.1)$ can be calculated, respectively, from the first and the second set of data. The unweighted average of the two values gives $\log_{10}{}^*\beta_2^\circ = -(14.1 \pm 0.6)$ where the uncertainty has been assigned to cover the maximum range of expectancy.

There are not many equilibrium data for $Am(OH)_3(aq)$. The value selected by this review is that recalculated from solubility data reported by Stadler and Kim [88STA/KIM] and extrapolated to infinite dilution. More accurate determinations of hydrolysis equilibria in the alkaline pH region are recommended.

This review selects the following standard equilibrium constants (*cf.* Table III.2):

$$\begin{aligned}
\log_{10}{}^*\beta_1^\circ\ (\mathrm{V.11}, n = 1, 298.15\,\mathrm{K}) &= -6.4 \pm 0.7 \\
\log_{10}{}^*\beta_2^\circ\ (\mathrm{V.11}, n = 2, 298.15\,\mathrm{K}) &= -14.1 \pm 0.6 \\
\log_{10}{}^*\beta_3^\circ\ (\mathrm{V.11}, n = 3, 298.15\,\mathrm{K}) &= -25.7 \pm 0.5
\end{aligned}$$

The standard Gibbs energies of formation have been calculated to be

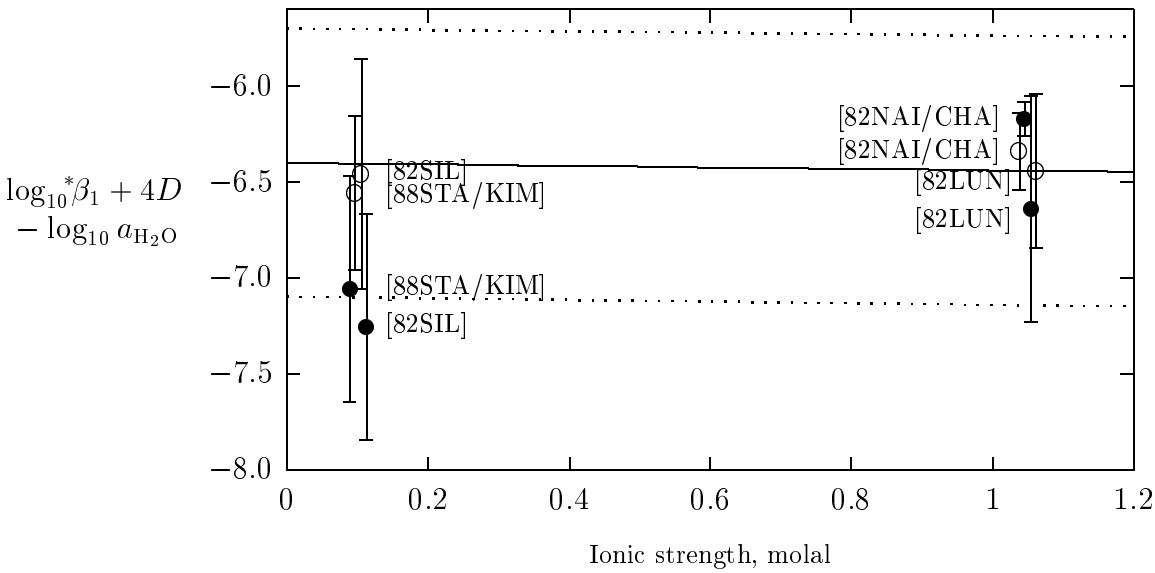
$$\begin{aligned}
\Delta_f G_m^\circ(AmOH^{2+}, aq, 298.15\,\mathrm{K}) &= -(799.3 \pm 6.2)\ \mathrm{kJ \cdot mol^{-1}} \\
\Delta_f G_m^\circ(Am(OH)_2^+, aq, 298.15\,\mathrm{K}) &= -(992.5 \pm 5.9)\ \mathrm{kJ \cdot mol^{-1}} \\
\Delta_f G_m^\circ(Am(OH)_3, aq, 298.15\,\mathrm{K}) &= -(1163.4 \pm 5.5)\ \mathrm{kJ \cdot mol^{-1}}
\end{aligned}$$

Figure V.4 shows the ionic strength dependence of the re-evaluated and original literature values of $\log_{10}{}^*\beta_1$ (*cf.* Tables V.5 and V.4) according to the specific ion interaction principles described in Appendix B, *cf.* Eq. (B.5). Although this Figure does not illustrate the selection procedure for the value of the equilibrium constant, ${}^*\beta_1^\circ$, at $I = 0$, it shows nevertheless that the recalculated values of ${}^*\beta_1$ given in Table V.5 do follow the ionic strength dependence predicted by the estimated specific interaction parameters in Section B.1.4. A linear fit of the original literature values (filled circles in Figure V.4) would instead require a value of $\varepsilon_{(AmOH^{2+}, ClO_4^-)} \approx -0.4\,\mathrm{kg \cdot mol^{-1}}$, which would be inconsistent with the values of specific ion interaction coefficients for divalent ions, which are in the range $+0.09 \leq \varepsilon \leq +0.89$, *cf.* Table B.3 and Section B.1.4.

The distribution of dissolved species in the americium(III) hydroxide system in standard aqueous solutions (*i.e.*, at $I = 0$) at 298.15 K is illustrated in Figure V.5 for the range $6 \leq \mathrm{pH} \leq 12$. This diagram shows that $AmOH^{2+}$ is a relatively minor species predominating only in a pH range of about one unit, contrary to the other species in this system. Furthermore, increasing ionic strength reduces the acidity range in which $AmOH^{2+}$ predominates, as shown in Figure V.6. A distribution diagram for the hydrolysis of Am(III) in 0.1 M $NaClO_4$ solutions is presented in the lower part of Figure V.8.

The values for the second and third hydrolysis constants of americium(III) selected here fall in the range of values selected in other reviews for Am(III), and lanthanide(III) hydrolysis. For example, for $Am(OH)_2^+$ and $Am(OH)_3(aq)$ Fuger

Figure V.4: Equilibrium constants for reaction: $Am^{3+} + H_2O(l) \rightleftharpoons AmOH^{2+} + H^+$ at 25°C in $NaClO_4$ solutions plotted according to Eq. (B.5). Open circles correspond to the values re-evaluated in this review and given in Table V.5, while filled circles correspond to the original values reported in the literature, *cf.* Table V.4 (with the uncertainties increased by a factor of 1.96 in order to approximate the 95% uncertainty level). For increased readability, the symbols are arbitrarily shifted ($\leq \pm 0.014$ mol/kg) along the X-axis. The solid line represents Eq. (B.5) with $\log_{10}{}^*\beta_1^\circ = -(6.4 \pm 0.2)$ and $\Delta\varepsilon = (0.04 \pm 0.05)\,\mathrm{kg \cdot mol^{-1}}$. The associated uncertainties are given by the dotted lines.



[92FUG] recommended $\log_{10}{}^*\beta_2^\circ = -(14.8 \pm 0.5)$ and suggested, by analogy with Nd(III), a value of $\log_{10}{}^*\beta_3^\circ = -26.5$ for Am(III). For the same equilibrium constants Allard, Olofsson and Torstenfelt [84ALL/OLO] selected −16.5 and −26.5 respectively, while Moulin *et al.* [88MOU/ROB] preferred −14.6 and −23.6. It must be pointed out, however, that these constants extend over a range of a few logarithmic units.

Hubbert *et al.* [76HUB/HUS] report $\Delta_r H_m(\mathrm{V.11}, n = 1, 298.15\,\mathrm{K}) = 65\ \mathrm{kJ \cdot mol^{-1}}$. However, due to the scarcity of the experimental data and the narrow pH range used (*cf.* Appendix A) this review does not consider the values reported by Hubbert *et al.* as reliable.

V.3.1.2. Aqueous Am(V) and Am(VI) hydroxide complexes

Cohen has described the instability of Am(VI) solutions [72COH]. The formation of $AmO_2OH(aq)$ was assumed by Kim *et al.* [85MAG/CAR, 86BUP/MAG, 88KIM/BUC, 88STA/KIM, 88STA/KIM2] in their interpretation of americium solubility measurements in aqueous solutions containing significant chloride concentrations. This is discussed in Section V.3.2.5. Tananaev proposed the existence

Figure V.5: Calculated distribution diagram of americium species at 25°C in standard aqueous solutions ($I = 0$) in the range $6 \leq \text{pH} \leq 12$. The precipitation of solid phases is not considered. The dotted curves represent the uncertainty range of each calculated fraction according to the rules of error propagation, *cf.* Eq. (C.18).

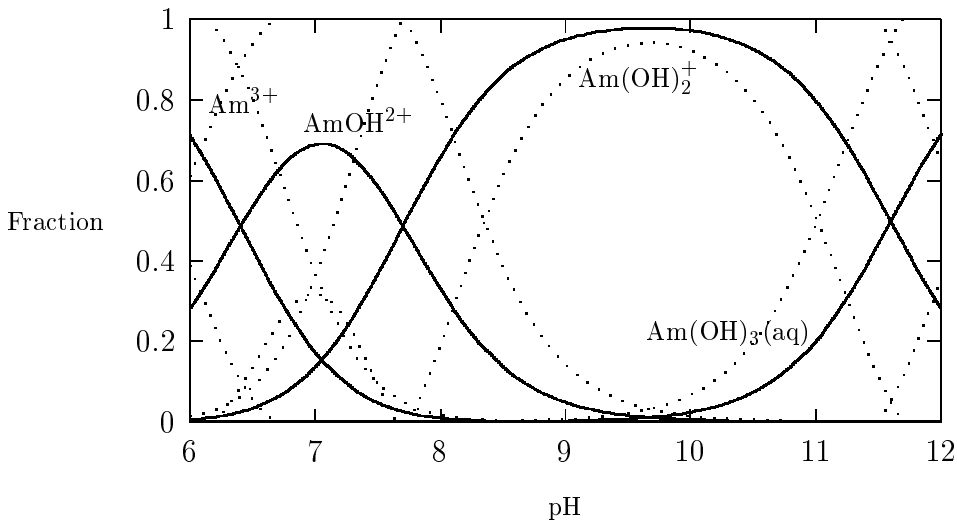
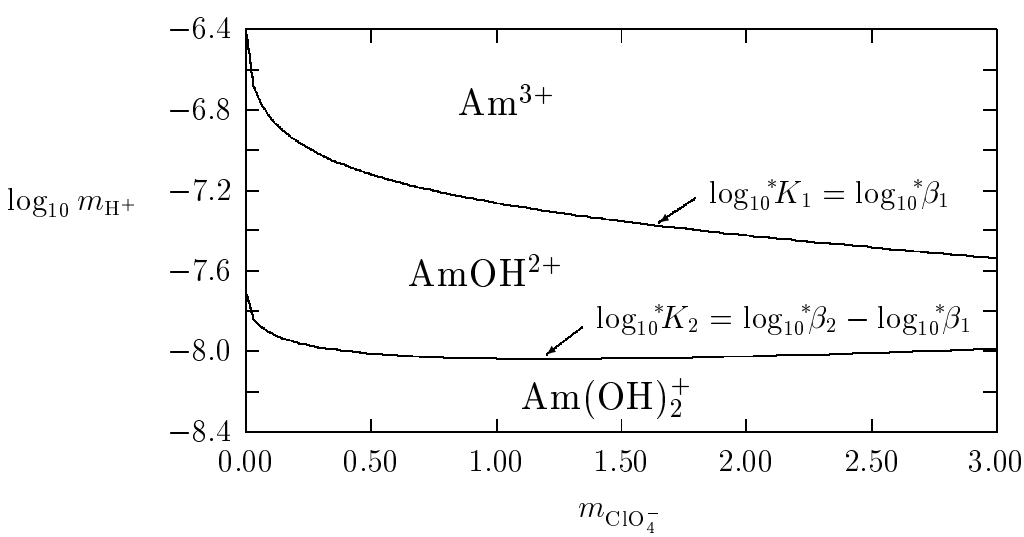


Figure V.6: Calculated ionic strength dependence of the distribution of Am^{3+}, $AmOH^{2+}$ and $Am(OH)_2^+$, at 25°C in $NaClO_4$ solutions. The precipitation of solid phases is suppressed. The curves represent the acidity at which two aqueous americium species have the same concentration, and are calculated with the specific ion interaction equations of Appendix B. For clarity, neither uncertainties nor the curve for $\log_{10}{}^*K_3$ are plotted in this diagram.



of $AmO_2(OH)_n^{(1-n)}$ with $n = 1 \ldots 4$ [90TAN2] and of $AmO_2(OH)_n^{(2-n)}$ also with $n = 1 \ldots 4$ [89TAN] based on spectrophotometric measurements in strongly alkaline solutions. No thermodynamic data can be recommended for any of these complexes.

V.3.2. Solid americium oxides and hydroxides†

V.3.2.1. The americium-oxygen system

It is still not possible to give a definite phase diagram for the Am–O system, since the principal studies are far from consistent. Chikalla and Eyring have investigated the system using room- and high-temperature X-ray techniques [68CHI/EYR] and have also measured the oxygen dissociation pressures and derived partial enthalpies and entropies for $1.8 < O/Am < 1.99$ from 1139 to 1445 K [67CHI/EYR], while Sari and Zamorani [70SAR/ZAM] have made DTA measurements for $1.67 < O/Am < 2.00$ and examined ceramographs for a wider range of compositions. However, since it is impossible to quench the hypostoichiometric fluorite phase, while the reactions involving oxides at lower O/Am are very sluggish, room-temperature X-ray patterns and ceramographs are difficult to interpret. In addition, the relatively short half-life of ^{241}Am, used in all these studies, means that any subtly ordered phases similar to those in the corresponding lanthanide oxide systems are unlikely to be observed due to the radiation self-damage (but see below). A possible phase diagram consistent with many of the observations of the major studies and with known behaviour of the Pu–O and Ln–O systems is shown in Figure V.7.

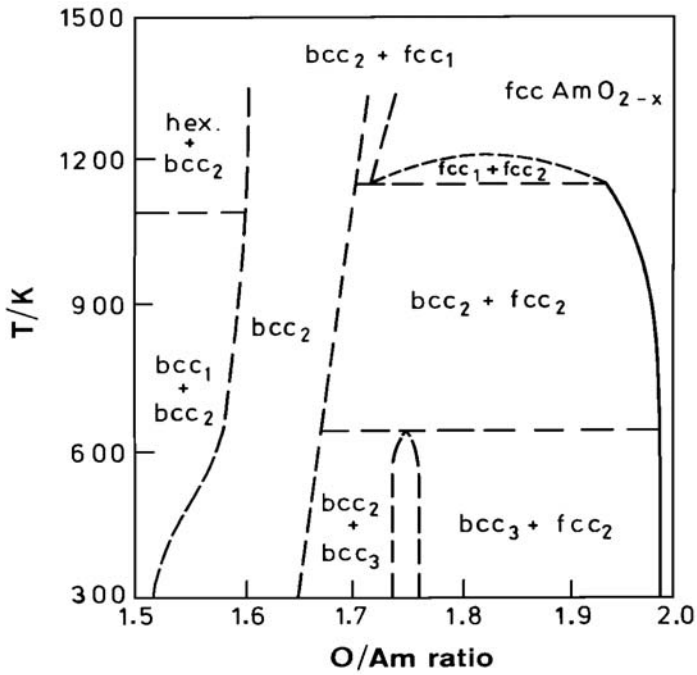
The major features are a broad fcc fluorite phase AmO_{2-x}(cr) which certainly above 1300 K [70SAR/ZAM], and possibly above 1150 K [67CHI/EYR], extends from $\sim AmO_{1.65}$(cr) to AmO_2(cr). At lower temperatures, there is probably a bcc phase with a range of homogeneity around $AmO_{1.6}$(cr), but the phase relationships in this region are very far from clear. The stoichiometric sesquioxide can exist in two and possibly three of the crystal structures adopted by the lanthanide oxides, see Section V.3.2.2.

Lyalyushkin *et al.* [86LYA/SUD] have shown that when heated in a closed capillary with finely-powdered SiO_2(s), AmO_2(cr) starts to decompose to lower oxides at temperatures appreciably lower than for pure AmO_2(cr) under the same conditions. This was attributed to the formation of reducing gases such as H_2(g) from radiolytic decomposition of vapours outgassed from the silica. The same authors also suggest that an intermediate phase formed under these conditions was a rhombohedral oxide $AmO_{1.71}$(cr), based on splitting of the 220 reflections of the fundamental fcc structure, but this conclusion needs to be confirmed.

Akimoto [67AKI] claims to have prepared AmO(s) by heating "tens of micrograms" of americium metal in a sealed quartz capillary with the stoichiometric amount of (separately heated) Ag_2O(s). Although it was intended to heat the Am(cr) to ~850°C, the actual reaction temperature was much higher, since the quartz capillary

† Earlier versions of Sections V.3.2.1, V.3.2.2 and V.3.2.3 were published in the volume edited by Cordfunke and Konings [90COR/KON]. This, however, contained a number of misprints which have been corrected in the current version.

Figure V.7: Tentative americium-oxygen phase diagram (revised from [90COR/KON]).



had recrystallised. A grey brittle product was found to have an fcc structure, with $a = 5.045 \times 10^{-10}$ m. No further analysis of the product was possible. AmN(cr) has a similar NaCl(cr) structure with $a = 5.00 \times 10^{-10}$ m. It seems likely that this was an Am(O,N)(cr) solid solution, similar to the so-called plutonium monoxide which is now known to be a Pu(C,O,N)(cr) phase. Other reports of a phase with the NaCl(cr) structure and a lattice parameter around 5×10^{-10} m had previously been given by Zachariasen [49ZAC2] who examined material of unknown provenance, and McWhan [61MCW], during his attempts to prepare americium metal.

Since none of these studies show convincing evidence that AmO(cr) is stable as a pure bulk phase, it is not considered further.

V.3.2.2. Americium sesquioxide

At low temperatures, the stoichiometric sesquioxide, Am_2O_3(cr), has the cubic bcc rare-earth type-C Mn_2O_3 structure, space group Ia3, with $a = 11.03 \times 10^{-10}$ m around 300 K, [53TEM/DAU, 68CHI/EYR]. It transforms at a temperature between 973 and 1173 K [64WAL2, 75KEL/BER] to the rare-earth type-A La_2O_3(cr) hexagonal

structure, space group P3m1, with $a = 3.817 \times 10^{-10}$ and $c = 5.971 \times 10^{-10}$ m. The monoclinic B-form of the sesquioxide may be stable between the C and A forms, but it is probably a metastable phase stabilised by minor impurities, particularly Sm and other lanthanide elements [68CHI/EYR, 73MAI, 74BER/TAN, 75KEL/BER]. Hexagonal Am_2O_3(cr) melts at (2478 ± 15) K [73CHI/MCN].

The enthalpy of formation of hexagonal Am_2O_3(cr) was recently measured by dissolution in hydrochloric acid in a microcalorimeter [85MOR/SON].

$$\Delta_f H^\circ_m(Am_2O_3, cr, 298.15\,K) = -(1690.4 \pm 8.0)\ kJ \cdot mol^{-1}$$

There are no experimental heat capacity data, and all the values are estimated from the values for Ce_2O_3(cr) and Pu_2O_3(cr), the latter at 298.15 K only.

$$\begin{aligned} C^\circ_{p,m}(298.15 \text{ to } 1000\,K) &= [113.93 + 5.937 \times 10^{-2}(T/K) - 2.301 \times 10^{-5}(T/K)^2 \\ &\quad - 1.071 \times 10^6 (T/K)^{-2}]\ J \cdot K^{-1} \cdot mol^{-1} \\ C^\circ_{p,m}(1000 \text{ to } 2000\,K) &= [153.13 + 3.573 \times 10^{-3}(T/K) + 2.372 \times 10^{-6}(T/K)^2 \\ &\quad - 9.8742 \times 10^6 (T/K)^{-2}]\ J \cdot K^{-1} \cdot mol^{-1} \end{aligned}$$

Thus

$$C^\circ_{p,m}(Am_2O_3, cr, 298.15\,K) = (117.5 \pm 15.0)\ J \cdot K^{-1} \cdot mol^{-1}$$

Since there are no experimental values of heat capacities, this review estimates

$$S^\circ_m(Am_2O_3, cr, 298.15\,K) = (160 \pm 15)\ J \cdot K^{-1} \cdot mol^{-1}$$

from the value for the Pu_2O_3(cr), 163.0 $J \cdot K^{-1} \cdot mol^{-1}$ [81FLO/TET]. Preliminary calculations of a revised treatment of the vaporisation data for americium oxides dissolved in plutonium oxides [66ACK/FAI2] suggest the value may be somewhat lower (150 $J \cdot K^{-1} \cdot mol^{-1}$).

The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy.

$$\Delta_f G^\circ_m(Am_2O_3, cr, 298.15\,K) = -(1613.3 \pm 9.2)\ kJ \cdot mol^{-1}.$$

V.3.2.3. Americium dioxide

The dioxide, AmO_2(cr), crystallises in the fcc fluorite structure, space group Fm3m, with $a = 5.377 \times 10^{-10}$ m [68CHI/EYR]. Like many other fluorite oxides it can exist with a large deficit of oxygen, the lattice parameter increasing with decrease in oxygen content.

The enthalpy of dissolution of AmO_2(cr) in 0.5 M H_2SO_4 - 0.1 M KI solution has been measured by Morss and Fuger [81MOR/FUG]. They combined this value with their measured enthalpies of mixing of aqueous $AmCl_3$, HCl and H_2SO_4 solutions to correct for the effects of the medium, to obtain finally the enthalpy of dissolution of AmO_2(cr) in a 0.55 M HCl solution. Following Morss and Fuger [81MOR/FUG],

we use the infinite dilution values for aqueous I^- and I_3^-, since the effects of the extrapolation to infinite dilution will be similar. With $\Delta_f H_m^\circ(I^-, aq, 298.15\,K) = -(56.78 \pm 0.05)\ kJ \cdot mol^{-1}$ [89COX/WAG], and $\Delta_r H_m^\circ = -(5.0 \pm 0.5)\ kJ \cdot mol^{-1}$ for the reaction

$$I^- + I_2(cr) \rightleftharpoons I_3^-$$

at infinite dilution [76PAR/WAG], we find $\Delta_f H_m^\circ(I_3^-, aq, 298.15K) = -(51.8 \pm 0.5)\ kJ \cdot mol^{-1}$, which with the enthalpy of formation of Am^{3+} in 0.55 M hydrochloric acid solution at 298.15 K: $-(616.5 \pm 1.3)\ kJ \cdot mol^{-1}$ interpolated from the data of [72FUG/SPI], *cf.* Section V.2.2, gives

$$\Delta_f H_m^\circ(AmO_2, cr, 298.15\,K) = -(932.3 \pm 3.0)\ kJ \cdot mol^{-1}$$

where the uncertainty has been increased to allow for the uncertainty in the enthalpy of transfer of Am^{3+} from sulphuric to hydrochloric acid solutions in the presence of I^-.

There are no experimental heat capacity data and the values are estimated from the values from $CeO_2(cr)$ and $PuO_2(cr)$. The estimated heat capacity is given by the relation

$$\begin{aligned} C_{p,m}^\circ(298.15 \text{ to } 2000\,K) &= [84.739 + 1.072 \times 10^{-2}(T/K) - 8.159 \times 10^{-7}(T/K)^2 \\ &\quad - 19.285 \times 10^5 (T/K)^{-2}]\ J \cdot K^{-1} \cdot mol^{-1}. \end{aligned}$$

Thus

$$C_{p,m}^\circ(AmO_2, cr, 298.15\,K) = (66.17 \pm 10.0)\ J \cdot K^{-1} \cdot mol^{-1}$$

The estimate of the standard entropy by Westrum and Grønvold [62WES/GRO] ($83.7\ J \cdot K^{-1} \cdot mol^{-1}$) is almost certainly too high. Their estimate for $PuO_2(cr)$, before the heat capacity was measured, was $82.4\ J \cdot K^{-1} \cdot mol^{-1}$ compared with the experimental value of $66.1\ J \cdot K^{-1} \cdot mol^{-1}$. We estimate

$$S_m^\circ(AmO_2, cr, 298.15\,K) = (67 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}$$

from the values for the other measured actinide dioxides. This value is also consistent with preliminary calculations of the vaporisation data for americium oxides dissolved in plutonium oxides [66ACK/FAI].

The Gibbs energy of formation is derived from the selected enthalpy of formation and entropy.

$$\Delta_f G_m^\circ(AmO_2, cr, 298.15\,K) = -(874.5 \pm 4.3)\ kJ \cdot mol^{-1}.$$

V.3.2.4. Solid Am(III) hydroxides

A number of solubility studies have been reported for precipitated $Am(OH)_3(s)$. Conflicting data are, however, proposed for the following reaction (*cf.* Table V.4):

$$Am(OH)_3(s) + 3\,H^+ \rightleftharpoons Am^{3+} + 3\,H_2O(l). \qquad (V.12)$$

The difference in $\log_{10} {}^{*}K_{s,0}$ (V.12) values can be rationalised by particle size considerations and possible changes in the solid hydroxide phase.

$Am(OH)_3(s)$ is generally prepared by addition of basic reagents to Am(III) solutions. The amorphous hydroxide formed initially at room temperature and atmospheric pressure then transforms to a crystalline phase. The rate of this transformation depends on solution composition and acidity, temperature, radiolysis, details of preparation and pretreatment of the precipitate.

Milligan *et al.* [68MIL/BEA] and Haire *et al.* [77HAI/LLO] found that rapid drying of freshly precipitated $^{241}Am(OH)_3(s)$ at room temperature yields a stable amorphous solid consisting of very small particles (1.5 to 2 nm). Ageing under water after an initial heating at 80°C for 90 minutes leads instead to a crystalline structure, as indicated by electron diffraction of 5-week aged suspensions [68MIL/BEA]. Electron microscopy observations showed, however, that crystalline rod-like particles already exist in a fluid sol aged only for 2 hours at 25°C [77HAI/LLO]. The ageing processes continue for weeks and are accelerated at higher temperatures. Silva [82SIL] reported that complete conversion required 3 weeks boiling in 5 M NaOH under reflux conditions. The crystallisation time was reduced to 3 to 4 days if the suspension was evaporated to near dryness. Rod-like structures of approximately 1μm diameter and 10μm length were formed. In a paper still in press at the moment that the the final draft of this book was completed, Morss and Williams [94MOR/WIL] reported on the preparation and characterisation of a more crystalline $^{243}Am(OH)_3(s)$ than found by Silva [82SIL]. A precipitate of Am(III) oxalate first calcined to $AmO_2(s)$ in air, was then reduced to $Am_2O_3(s)$ under $H_2(g)$ at 800°C and finally hydrated in the presence of steam at 225°C. Rai *et al.* [83RAI/STR] reported that an increase of pH accelerates the transformation rate of $Am(OH)_3(am)$ at room temperature.

The destruction of crystallinity by self-irradiation was studied by Haire *et al.* [77HAI/LLO]. The rate of this process depended on the specific activity of the isotope used. In pure water, the complete degradation required 1 day with $^{244}Cm(III)$ (specific activity 3×10^3 MBq/mg) and 5 months with $^{241}Am(III)$ (specific activity 120 MBq/mg). In the latter case crystal damage was evident already after two weeks. Unlike the fresh amorphous precipitate, the product of degradation did not regenerate crystallinity upon heating. A hydrous oxide phase was suggested to form.

The distinction between amorphous and crystalline $Am(OH)_3(s)$ may be ambiguous. Rather than a continuous network of polynuclear species, the freshly precipitated amorphous body of $Am(OH)_3(s)$ can be considered an agglomerate of very small crystals too minute to give diffraction lines but visible by electron microscopy (the 1.5 to 2 nm particles seen by Milligan *et al.* [68MIL/BEA]). The ageing processes allow aggregation to larger rods and the appearance of diffraction patterns [82SIL]. The various studies in the literature cannot describe the dissolution process (V.12) with a unique solubility constant (*cf.* Table V.4), because of the complex ageing behaviour of $Am(OH)_3(s)$ suspensions. Although americium trihydroxide appears to be formed in all cases, it is difficult to explain why so different values were obtained. Possible reasons for the lower values of ${}^{*}K_{s,0}$ reported in Refs. [84BER/KIM, 84KIM/BER] are that the equilibrium was not attained during the measurements or that a different phase involving formation of oxo bridges was present. The value found by Stadler and

Kim [88STA/KIM] is in agreement with that obtained by Silva [82SIL] for crystalline material, but no characterisation of the final precipitated product was accomplished. Based on calorimetric measurements of the enthalpy of solution of $^{243}Am(OH)_3(cr)$ in 6 M HCl, and on entropy values estimated by analogy with rare earth hydroxides, Morss and Williams [94MOR/WIL] calculated a solubility constant ${}^*K^\circ_{s,0}$ nearly three orders of magnitude lower than reported by Silva [82SIL]. This may reflect the different behaviour of well-crystallised and microcrystalline $Am(OH)_3(s)$.

The studies of Pazukhin and Kochergin [89PAZ/KOC] and of Pershin and Sapozhnikova [90PER/SAP] are discarded by this review for the reasons specified in Appendix A.

When a single solid phase is in equilibrium with the aqueous solution, the solubility of $Am(OH)_3(s)$ can be expressed as,

$$\begin{aligned}
[\mathrm{Am}]_{TOT} &= [\mathrm{Am}^{3+}] + [\mathrm{AmOH}^{2+}] + [\mathrm{Am(OH)}_2^+] + [\mathrm{Am(OH)}_3(\mathrm{aq})] \\
&= {}^*K_{\mathrm{s},0}[\mathrm{H}^+]^3 + {}^*K_{\mathrm{s},1}[\mathrm{H}^+]^2 + {}^*K_{\mathrm{s},2}[\mathrm{H}^+] + {}^*K_{\mathrm{s},3} \\
&= {}^*K_{\mathrm{s},0}\left([\mathrm{H}^+]^3 + {}^*\beta_1[\mathrm{H}^+]^2 + {}^*\beta_2[\mathrm{H}^+] + {}^*\beta_3\right)
\end{aligned}$$

and therefore,

$$\begin{aligned}
[\mathrm{Am}]_{TOT}/\,{}^*K_{\mathrm{s},0} &= \left([\mathrm{H}^+]^3 + {}^*\beta_1[\mathrm{H}^+]^2 + {}^*\beta_2[\mathrm{H}^+] + {}^*\beta_3\right) \qquad \text{(V.13)} \\
&= \Bigg([\mathrm{H}^+]^3 + {}^*\beta_1^\circ \frac{a_{\mathrm{H_2O}}\gamma_{\mathrm{Am^{3+}}}}{\gamma_{\mathrm{AmOH^{2+}}}\gamma_{\mathrm{H^+}}}[\mathrm{H}^+]^2 \\
&\quad + {}^*\beta_2^\circ \frac{a^2_{\mathrm{H_2O}}\gamma_{\mathrm{Am^{3+}}}}{\gamma_{\mathrm{Am(OH)_2^+}}\gamma^2_{\mathrm{H^+}}}[\mathrm{H}^+] + {}^*\beta_3^\circ \frac{a^3_{\mathrm{H_2O}}\gamma_{\mathrm{Am^{3+}}}}{\gamma_{\mathrm{Am(OH)_3(aq)}}\gamma^3_{\mathrm{H^+}}}\Bigg)
\end{aligned}$$

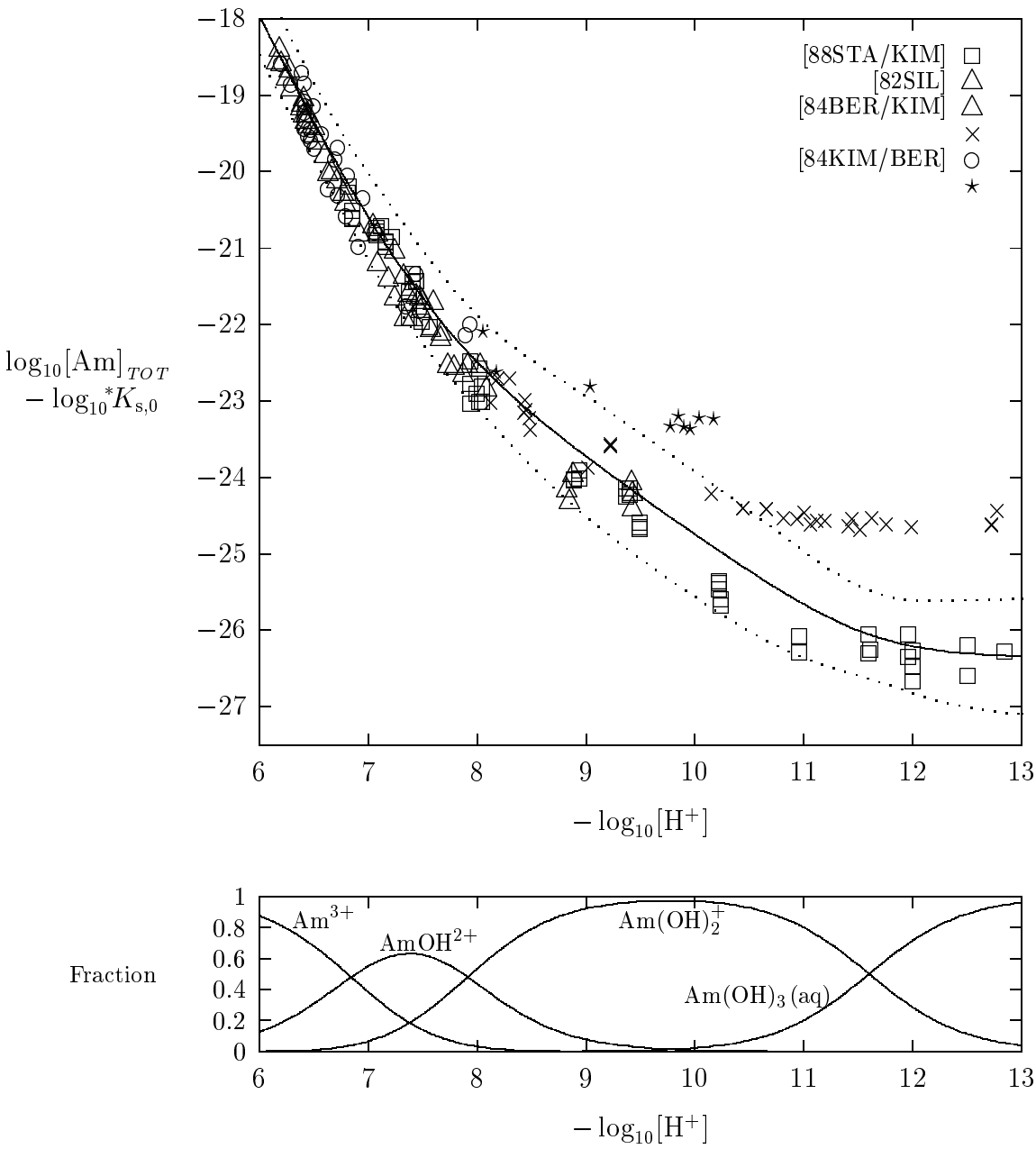
This implies that solubility curves obtained in the presence of $Am(OH)_3(s)$ of different solubility products should be expressed as the same function of $[H^+]$ as long as the same aqueous speciation of americium occurs in the different solutions. In Figure V.8 the solubility data of americium(III) hydroxide in 0.1 M $NaClO_4$ [82SIL, 84BER/KIM, 84KIM/BER, 88STA/KIM] are plotted according to Eq. (V.13), using the recalculated values of ${}^*K_{s,0}$ taken from Table V.5. It can be seen that all data points fall on the same curve. Deviation of the data at pH $\geq$ 8 from Refs. [84BER/KIM, 84KIM/BER] indicates that either equilibrium is not reached, or there is a conversion of the solid to a different phase. The solid line in Figure V.8 was calculated with the selected set of standard equilibrium constants (*cf.* Table III.2), extrapolated to 0.1 M $NaClO_4$ using the specific ion interaction equations described in Appendix B, as well as the associated uncertainty.

In principle, all the solubility constants in Table V.5 could be used for the purpose of thermodynamic calculations. However, this review prefers to evaluate the Gibbs energy of formation of $Am(OH)_3(cr)$ from the data of Silva [82SIL]. Only this author conducted a careful characterisation of the solid phase.

The selected solubility constant for $Am(OH)_3(cr)$, *cf.* Table V.5 and Appendix A, is thus

$$\log_{10} {}^*K^\circ_{\mathrm{s},0}(\mathrm{V.12}, \mathrm{Am(OH)_3}, \mathrm{cr}, 298.15\,\mathrm{K}) \;=\; 15.2 \pm 0.6.$$

Figure V.8: Solubility measurements of Am(III) hydroxide in 0.1 M $NaClO_4$ solutions at 25°C from Refs. [82SIL, 84BER/KIM, 84KIM/BER, 88STA/KIM] plotted as "$\log_{10}[\mathrm{Am}]_{TOT} - \log_{10}{}^{*}K_{\mathrm{s},0}$" *vs.* $-\log_{10}[\mathrm{H}^+]$, where for each experimental study the corresponding value of ${}^{*}K_{\mathrm{s},0}$ is taken from Table V.5. The continuous curve represents the values calculated with the selected set of equilibrium constants (*cf.* Table III.2) extrapolated to 0.1 M $NaClO_4$ using the specific ion interaction equations described in Appendix B, and the dotted curves show the associated uncertainties. The bottom diagram shows the calculated acidity ranges of predominance for each Am(III) species under the same conditions as described above.



The value proposed by Morss and Williams [94MOR/WIL], nearly three orders of magnitude lower than that selected here, was in disagreement with their predictions based on the relative basicity of actinide and lanthanide hydroxides as a function of ionic size. For this reason, Morss and Williams [94MOR/WIL] recommended a working value for $\log_{10} {}^*K^\circ_{s,0}$ of (14.5 ± 2), which differs slightly from but is consistent with the value recommended by this review.

The two studies using a well characterised amorphous americium hydroxide [83RAI/STR, 85NIT/EDE2] reported similar solubilities at pH ≈ 7. Although there are some difficulties in interpreting the data by Rai *et al.* in the full pH range (*cf.* Appendix A), this review selects

$$\log_{10} {}^*K^\circ_{s,0}(\text{V.12}, \text{Am(OH)}_3, \text{am}, 298.15\,\text{K}) \quad = \quad 17.0 \pm 0.6.$$

From the solubility constants for Am(OH)_3(cr) and Am(OH)_3(am), the following Gibbs energies of formation are derived:

$$\begin{aligned} \Delta_f G^\circ_m(\text{Am(OH)}_3, \text{am}, 298.15\,\text{K}) &= -(1213.1 \pm 5.9)\ \text{kJ} \cdot \text{mol}^{-1} \\ \Delta_f G^\circ_m(\text{Am(OH)}_3, \text{cr}, 298.15\,\text{K}) &= -(1223.4 \pm 5.9)\ \text{kJ} \cdot \text{mol}^{-1}. \end{aligned}$$

The only experimental data on the enthalpy of formation of Am(OH)_3(s) has been reported in the paper by Morss and Williams [94MOR/WIL] still in press at the moment that the final draft of this book was completed. The authors gave a value of $\Delta_f H^\circ_m(\text{Am(OH)}_3, \text{cr}, 298.15\,\text{K}) = -(1371.2 \pm 7.9)\ \text{kJ} \cdot \text{mol}^{-1}$. It has to be stressed however that this value refers to a solid which may exhibit a degree of crystallinity different than that of the Am(OH)_3(s) used by Silva [82SIL] and recommended by this review.

V.3.2.5. Am(IV) and Am(V) hydroxides

There are very few studies of americium hydroxides of oxidation states higher than (III). Procedures for the preparation of Am(IV) and Am(V) precipitates in alkaline solutions with attempts to characterise the corresponding aqueous species were reported by Penneman, Coleman and Keenan [61PEN/COL], by Cohen [72COH] and by Tananaev [90TAN]. Kim *et al.* [85MAG/CAR, 86BUP/MAG, 88KIM/BUC, 88STA/KIM, 88STA/KIM2] measured the solubility of $^{241}\text{Am(OH)}_3$(s) in 3 and 5 M NaCl. The high dose rates of α-radiation produced the oxidation of Am(III) to Am(V), as evidenced by spectroscopic techniques. For the reaction

$$\text{AmO}_2\text{OH(s)} \rightleftharpoons \text{AmO}_2^+ + \text{OH}^- \qquad \text{(V.14)}$$

the value of $\log_{10} K_{s,0} = -(9.3 \pm 0.5)$ was obtained both in 3 M and 5 M NaCl. In alkaline solutions, the following equilibrium was assumed

$$\text{AmO}_2^+ + \text{OH}^- \rightleftharpoons \text{AmO}_2\text{OH(aq)} \qquad \text{(V.15)}$$

for which $\log_{10} \beta_1$(V.15, 3 M NaCl) $= (1.5 \pm 0.5)$ [85MAG/CAR] and $\log_{10} \beta_1$(V.15, 5 M NaCl)$= (1.7 \pm 0.6)$ [88KIM/BUC, 88STA/KIM] were proposed. However, according to these values, very little $\text{AmO}_2\text{OH(aq)}$ should be present in the solutions. This

review does not accept these values because of the lack of structural characterisation of the solid and other experimental shortcomings, *cf.* Appendix A.

No data are selected for Am(IV), (V) and (VI) hydroxides. Estimates may be made by analogy with other actinides.

V.3.2.6. Ternary and quaternary americium oxides

a) Crystallographic data

Schulz and Penneman [86SCH/PEN] have summarised the crystallographic structures of the numerous ternary and quaternary oxide phases containing Am(IV), Am(V) and Am(VI), and Table V.6 has been abstracted from their Table 8.3. Further details of the preparation and properties of these oxides can be obtained from the original references quoted by [86SCH/PEN].

b) Thermodynamic data

The only thermodynamic data for the ternary oxides are the enthalpies of formation of the perovskite-type compounds $BaAmO_3$(cr) and $SrAmO_3$(cr), measured by Goudiakas *et al.* [90GOU/HAI]. $BaAmO_3$(cr) was prepared from $BaCO_3$(s) and AmO_2(s) at temperatures up to 1350 K and its X-ray pattern was indexed as a pseudo-cubic cell with $a = 4.367 \times 10^{-10}$ m, although it probably has a distorted structure. $SrAmO_3$(cr) was formed from the co-precipitated oxalates at 1100 K, and its X-ray pattern was indexed as an orthorhombic cell – compare the idealised cubic structures given in Table V.6. For the calorimetric measurements, the ternary oxides were dissolved in an aqueous mixture of 1 M HCl and 0.1 M KI. Using auxiliary data consistent with those used in the present work, Goudiakas *et al.* [90GOU/HAI] derived the following values for the enthalpies of formation of the perovskite-type oxides:

$$\begin{aligned} \Delta_f H^\circ_m(SrAmO_3, cr, 298.15\,K) &= -(1539.0 \pm 4.1)\ kJ \cdot mol^{-1} \\ \Delta_f H^\circ_m(BaAmO_3, cr, 298.15\,K) &= -(1544.6 \pm 3.4)\ kJ \cdot mol^{-1} \end{aligned}$$

These values correspond to the following enthalpies of reaction from AmO_2(cr) and MO(cr): $-(64 \pm 5)$ kJ · mol^{-1} for M = Ba, and $-(16 \pm 5)$ kJ · mol^{-1} for M = Sr. The appreciably lower stability of the Sr compound oxide follows similar behaviour for the analogous perovskite oxides of BaO(s) and SrO(s) with ZrO_2(s) and CeO_2(s).

V.3.3. Americium hydrides

No new data have been published since Flotow *et al.* [84FLO/HAS] reviewed the phase diagram and thermodynamic data for the Am-H system and our assessment has utilised some of the data estimated therein.

Table V.6: Crystallographic data for ternary and quaternary oxide phases (adapted from [86SCH/PEN, Table 8.3]).

Phase	Crystal Symmetry	Space Group and Structural Type	Lattice parameters $\times 10^{10}$/m a	b	c	angle
$AmGeO_4$(cr)	tetragonal	$I4_1/a$	5.04		11.03	
$AmAlO_3$(cr)	hexagonal	$R\overline{3}m$, $LaAlO_3$	5.336		12.91	
α-$Am_2(MoO_4)_3$	tetragonal	$I4_1/a$	5.24		11.52	
β-$Am_2(MoO_4)_3$	orthorhombic		9.095	10.527	10.820	
$Am_2(WO_4)_3$(cr)	tetragonal	$I4_1/a$				
$AmVO_3$(cr)	orthorhombic	Pbnm, $GdFeO_3$	5.45	5.58	7.76	
$AmVO_4$(cr)	tetragonal	zircon	7.31		6.42	
$Am_{0.33}NbO_3$(cr)	pseudo-tetragonal	P4/mm, $La_{0.33}TaO_3$	3.819		7.835	
α-$AmNbO_4$	monoclinic	I2	5.444	11.25	5.141	β=94.95°
β-$AmNbO_4$	tetragonal	$I4_1/a$	5.30		11.34	
$Am_{0.33}TaO_3$(cr)	tetragonal	$I4_1/a$	3.889		7.820	
$AmTaO_4$(cr)	monoclinic	I2	5.489	11.21	5.115	β=95.37°
$AmNbTiO_6$(cr)	orthorhombic	Pnam	5.34	11.00	7.53	
$AmTaTiO_6$(cr)	orthorhombic	Pnam	5.33	10.95	7.49	
$AmScO_3$(cr)	orthorhombic	P6mm, $GdFeO_3$	5.540	5.785	8.005	
$AmPaO_4$(cr)	fcc	Fm3m	5.458			
$SrAmO_3$(cr)	cubic	perovskite	4.23	*(see text)*		
Sr_3AmO_6(cr)	cubic	Ba_3WO_6				
$SrAm_2O_4$(s)[(a)]						
$BaAmO_3$(cr)	cubic	perovskite	4.356	*(see text)*		
Ba_3AmO_6(cr)	cubic	$F\overline{4}3m$	8.81			
$BaAm_2O_4$(s)[(a)]						
Ba_2AmNbO_6(cr)	cubic	$F\overline{4}3m$	8.520			
Ba_2AmTaO_6(cr)	cubic	$F\overline{4}3m$	8.518			
Ba_2AmPaO_6(cr)	cubic	$F\overline{4}3m$	8.793			
$LiAmO_2$(s)[(a)]						
Li_2AmO_3(s)[(a)]						
Li_3AmO_4(cr)	tetragonal	Li_3UO_4	4.459		8.355	
Li_4AmO_5(cr)	tetragonal	I4/m	6.666		4.415	
Li_6AmO_6(cr)	hexagonal	Li_6ReO_6	5.174		14.59	
Li_7AmO_6(cr)	hexagonal	$R\overline{3}$	5.54		15.65	
Li_8AmO_6(cr)	hexagonal	Li_8PbO_6	5.62		15.96	
$LiAm(MoO_4)_2$(cr)	tetragonal	$I4_1/a$, $LiGd(MoO_4)_2$	5.20		11.39	
Na_2AmO_3(cr)	monoclinic	C2/c	5.92	10.26	11.23	β=100.12°
Na_3AmO_4(cr)	fcc	Fm3m	4.757			
Na_4AmO_5(cr)	fcc	Fm3m	4.70			
Na_6AmO_6(cr)	hexagonal	Li_6ReO_6	4.76		16.10	
$NaAm(MoO_4)_2$(cr)	tetragonal	scheelite	5.25		11.55	
$Na_5Am(MoO_4)_4$(cr)		$Na_5La(WO_4)_4$	11.515		11.429	
K_2AmO_4(cr)	tetragonal	I_4/mmm	4.286		13.05	
$K_2Am_2(MoO_4)_4$(s)[(a)]						
$K_{10}Am_2(MoO_4)_8$(s)[(a)]						

(a) Structure not known.

V.3.3.1. The americium-hydrogen system

Olson and Mulford [66OLS/MUL] and Roddy [73ROD] have shown that there are two solid hydrides of americium, $AmH_{2\pm x}$(cr), with a very wide range of homogeneity from a hydrogen stoichiometry slightly less than 2 to at least 2.7, and AmH_3(cr). Above 700 K Am(cr, α) begins to dissolve appreciable amounts of hydrogen, as does the fcc Am(cr, β) at higher temperatures. In the two studies mentioned, hydrogen pressures were measured as a function of r = H/Am (r = 0 to 3) and temperature (773 to 1073 K for [66OLS/MUL] using ^{241}Am, and 748 to 1152 K for [73ROD] using ^{243}Am). In both studies, an invariant diphasic field was found between Am with dissolved hydrogen and AmH_{2-x}(cr). From H/Am $=\sim$ 1.9 to 2.7, the single-phase AmH_{2+x}(cr) is stable. In both these fields, equilibrium was easily established. Above H/Am = 2.7, AmH_3(cr) exists in equilibrium with hydrogen saturated AmH_{2+x}(cr); the hydrogen pressures in this region suffer from considerable hysteresis, and no reliable pressures can be given. Flotow *et al.* [84FLO/HAS] have presented a schematic phase diagram based in these results.

V.3.3.2. Americium dihydride

a) Crystal structure

$AmH_{2\pm x}$(cr) crystallises in the fcc CaF_2 fluorite structure, space group Fm3m, with a lattice parameter which decreases as H/Am increases. The quoted values are

H/Am	$a \times 10^{10}$/m	Reference
Lower Phase Boundary	5.349	[66OLS/MUL]
1.96	5.344 ± 0.0015	[73ROD]
2.34	5.341 ± 0.0022	[73ROD]
2.67	5.338 ± 0.004	[66OLS/MUL]

b) Thermodynamic properties

The assessed thermodynamic properties for AmH_2(cr) are calculated from the hydrogen pressures for the diphasic region Am(cr, saturated with hydrogen) + AmH_{2-x}(cr), which are assumed to apply to the reaction Am(cr)+H_2(g) $\rightleftharpoons$ AmH_2(cr). The uncertainty in the experimental pressures, particularly at low pressures, does not warrant a more complete analysis.

The experimental pressures for the diphasic region Am(cr) + AmH_{2-x}(cr) measured by Olson and Mulford [66OLS/MUL], using ^{241}Am, and by Roddy [73ROD] agree well at temperatures around 1100 K, but the earlier measurements are about a factor of two higher at 773 K, for an unknown reason. In analysing these data, we have accepted the values for the standard entropy and heat capacity for AmH_2(cr)

estimated by Flotow *et al.* [84FLO/HAS], but rounded them in Joule units:

$$\begin{aligned} S^\circ_{\mathrm{m}}(\mathrm{AmH_2, cr}, 298.15\,\mathrm{K}) &= (48.1 \pm 3.8)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \\ C^\circ_{p,\mathrm{m}}(\mathrm{AmH_2, cr}) &= (24.8 + 4.5 \times 10^{-2} T/\mathrm{K})\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \\ &\quad (298.15 \text{ to } 1200\,\mathrm{K}) \\ C^\circ_{p,\mathrm{m}}(\mathrm{AmH_2, cr}, 298.15\,\mathrm{K}) &= (38.2 \pm 2.5)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \end{aligned}$$

These give $\Delta_{\mathrm{f}} S^\circ_{\mathrm{m}}(\mathrm{AmH_2, cr}, 950\,\mathrm{K}) = 147.3\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, as compared to the values of 137.7 and 156.2 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ calculated from the studies by Olson and Mulford [66OLS/MUL] and Roddy [73ROD] respectively.

The enthalpy of formation of $\mathrm{AmH_2(cr)}$

$$\Delta_{\mathrm{f}} H^\circ_{\mathrm{m}}(\mathrm{AmH_2, cr}, 298.15\,\mathrm{K}) = -(175.8 \pm 15.0)\ \mathrm{kJ \cdot mol^{-1}}$$

is then derived from the Gibbs energy of formation at 1165 K

$$\Delta_{\mathrm{f}} G^\circ_{\mathrm{m}}(\mathrm{AmH_2, cr}, 1165\,\mathrm{K}) = -8.340\ \mathrm{kJ \cdot mol^{-1}}$$

derived from the concordant values (at this temperature) for the equilibrium hydrogen pressure in the diphasic region obtained from the equations given in the two studies noted above.

Most of the uncertainty in the enthalpy of formation arises from the uncertainty of $\Delta_{\mathrm{f}} S^\circ_{\mathrm{m}}(\mathrm{AmH_2, cr})$. The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy.

$$\Delta_{\mathrm{f}} G^\circ_{\mathrm{m}}(\mathrm{AmH_2, cr}, 298.15\,\mathrm{K}) = -(135 \pm 15)\ \mathrm{kJ \cdot mol^{-1}}$$

V.3.3.3. Americium trihydride

a) Crystal structure

$\mathrm{AmH_3}$ crystallises with a hexagonal structure. Since at close to ambient pressures, it is only stable at low temperatures, the X-ray patterns are not good enough to define the complete structure, but it is presumably the same as $\mathrm{PuH_3(cr)}$, space group $\mathrm{P6_3/mmc}$, $\mathrm{AsNa_3(cr)}$ type. The lattice parameters are $a = (3.764 \pm 0.0044) \times 10^{-10}$, $c = (6.763 \pm 0.0073) \times 10^{-10}$m [73ROD].

b) Thermodynamic properties

$\mathrm{AmH_3(cr)}$ is formed only sluggishly at low temperatures (*e.g.* > 200 h at 125°C and 0.92 bar), and neither Olson and Mulford [66OLS/MUL] nor Roddy [73ROD] could obtain any equilibrium pressures pertaining to this phase. No reliable thermodynamic data can therefore be given.

Table V.7: Literature values of equilibrium constants for the formation of $AmF_n^{(3-n)}$ complexes.

Method	Medium	t(°C)	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	Reference
sol	0.1 M $HClO_4$	23			(a)	[54FEA]
dis	0.5 M $NaClO_4$	25	3.39 ± 0.01	6.11 ± 0.03	9.0	[69AZI/LYL]
dis	1 M $NaClO_4$	25	2.93 ± 0.10			[69JON/CHO]
emf	0.1 M $NaClO_4$	25 ± 0.5	3.32 ± 0.06			[73MAK/STE]
dis	1 M $NaClO_4$	25	2.93 ± 0.10			[75DEG/CHO]
dis	1 M $NaClO_4$	10	2.39 ± 0.01			[76CHO/UNR]
		25	2.49 ± 0.02			
		40	2.57 ± 0.02			
		55	2.71 ± 0.03			
ix	0.1 M $NaClO_4$	25	2.59 ± 0.01	4.75 ± 0.04		[84NAS/CLE2]

(a) For the reaction: $AmF_2^+ + F^- \rightleftharpoons AmF_3(aq)$, Feay reports $\log_{10} K_3^\circ = (3.11 \pm 0.07)$.

V.4. Group 17 (halogen) compounds and complexes

As procedures for the estimation of the enthalpies of formation and standard entropies for americium halide compounds are used extensively in this review, and since these estimation procedures are the same for all the halide compounds, data selection for all the aqueous halide complexes is discussed first in Section V.4.1, while the discussion of the data selection for all the halide compounds is postponed to Section V.4.2.

V.4.1. Aqueous group 17 (halogen) complexes

V.4.1.1. Aqueous Am(III) fluorides

The number of experimental studies on Am(III) complexation with fluoride ions is relatively limited. They were mainly designed to determine possible correlations with analogous complexes of 4f elements. The equilibrium constants for the reactions

$$Am^{3+} + n\,F^- \rightleftharpoons AmF_n^{(3-n)} \tag{V.16}$$

reported in Table V.7 are considerably larger than for the corresponding aqueous complexes with chloride ions (*cf.* Table V.8). The values reported by Choppin *et al.* in Refs. [69JON/CHO, 75DEG/CHO] are disregarded in this review because they refer to preliminary work. The reactions (V.16) are characterised by a positive enthalpy term. These are indications that the $AmF_n^{(3-n)}$ complexes are predominantly inner-sphere, in contrast to the other Am(III) halide complex species.

Conclusive evidence exists for the formation of the first two fluoride complexes. Aziz and Lyle [69AZI/LYL] reported equilibrium data for AmF^{2+}, AmF_2^+ and

AmF_3(aq), at $I = 0.5$ M. A liquid-liquid partition technique was used in the range of F^- concentration from 1×10^{-4} to 4×10^{-3} M. Nash and Cleveland [84NAS/CLE2] found no evidence for the existence of the third complex up to a F^- concentration of 8×10^{-3} M in a 0.1 M perchlorate medium. Ionic strength effects alone cannot explain the observed difference. Corrections to thermodynamic conditions still yield very discordant values of β_1° and β_2°. The data of Ref. [69AZI/LYL] are rejected by this review, because the extraction mechanism of Am(III) species in the organic phase was not well characterised.

The experimental data of Choppin and Unrein [76CHO/UNR] and Nash and Cleveland [84NAS/CLE2] are used to calculate the thermodynamic value of $\log_{10}\beta_1^\circ$. The first stability constant determined by Makarova, Stepanov and Shestakov [73MAK/STE] is not included in the selected data set because the electromigration method used does not appear to be sufficiently accurate for quantitative measurements of this type.

Extrapolation to infinite dilution is performed by using estimated values of ion interaction coefficients (*cf.* Appendix B, Section B.1.4), obtaining $\Delta\varepsilon_{(\mathrm{V.16},n=1)} = -(0.12 \pm 0.1)\,\mathrm{kg \cdot mol^{-1}}$ and $\Delta\varepsilon_{(\mathrm{V.16},n=2)} = -(0.36 \pm 0.1)\,\mathrm{kg \cdot mol^{-1}}$, which results in

$$\log_{10}\beta_1^\circ(\mathrm{V.16}, n = 1, 298.15\,\mathrm{K}) \quad = \quad 3.4 \pm 0.4,$$

calculated as the unweighted average of the two accepted values [76CHO/UNR, 84NAS/CLE2].

For the second formation reaction, this review selects the equilibrium constant proposed by Nash and Cleveland [84NAS/CLE2], obtaining

$$\log\beta_2^\circ(\mathrm{V.16}, n = 2, 298.15\,\mathrm{K}) \quad = \quad 5.8 \pm 0.2.$$

Contrary to the selection in the IAEA review [92FUG/KHO], no values are recommended for the formation of AmF_3(aq) because the only existing data by [54FEA] and [69AZI/LYL] are rejected by the present review as explained previously and in Appendix A.

The Gibbs energies of formation calculated using the auxiliary data for Am^{3+} and F^- are

$$\begin{aligned} \Delta_\mathrm{f}G_\mathrm{m}^\circ(\mathrm{AmF^{2+}}, \mathrm{aq}, 298.15\,\mathrm{K}) &= -(899.6 \pm 5.3)\ \mathrm{kJ \cdot mol^{-1}} \\ \Delta_\mathrm{f}G_\mathrm{m}^\circ(\mathrm{AmF_2^+}, \mathrm{aq}, 298.15\,\mathrm{K}) &= -(1194.9 \pm 5.1)\ \mathrm{kJ \cdot mol^{-1}}. \end{aligned}$$

Choppin and Unrein [76CHO/UNR] determined $\Delta_\mathrm{r}H_\mathrm{m}(\mathrm{V.16}, n = 1) = (27.6 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$ at $I = 1$ M. The values determined by Nash and Cleveland [84NAS/CLE2] at $I = 0.1$ M are $\Delta_\mathrm{r}H_\mathrm{m}(\mathrm{V.16}, n = 1) = (22.9 \pm 1.6)\ \mathrm{kJ \cdot mol^{-1}}$ and $\Delta_\mathrm{r}H_\mathrm{m}(\mathrm{V.16}, n = 2) = (24 \pm 5)\ \mathrm{kJ \cdot mol^{-1}}$. Although no major shortcomings can be identified in the experimental procedures of Refs. [76CHO/UNR, 84NAS/CLE2] this review does not recommend any enthalpy value because of the uncertainty in the influence of temperature on activity coefficients.

V.4.1.2. Aqueous Am(III) chlorine complexes

V.4.1.2.1. Aqueous Am(III) chlorides

Most of the available data on complex formation of Am(III) with chloride ions were published in the sixties. Since this time a number of reviews have appeared, but they are restricted mainly to data compilations. Recent evaluations of literature data are reported in Refs. [92FUG/KHO, 88CHA/ROB].

Equilibrium data for the complexation reactions

$$\mathrm{Am}^{3+} + n\,\mathrm{Cl}^- \rightleftharpoons \mathrm{AmCl}_n^{(3-n)} \qquad \text{(V.17)}$$

are given in Table V.8. The existence of the species AmCl^{2+} and AmCl_2^+ is well established. Anion exchange measurements in very highly concentrated media indicated the presence of negatively charged species, probably AmCl_4^- [56WAR/WEL, 66MAR]. On the basis of spectrophotometric studies, higher order complexes were claimed to be stable only in non-aqueous solvents [67RYA, 70MAR/BOM, 72BAR/KOT]. Marcus and Bomse [70MAR/BOM] calculated the stepwise formation constant of AmCl_6^{3-} both in propylene carbonate and in acetonitrile-succinonitrile mixtures. However, these are constants for non-aqueous media and therefore of limited use in this review.

The Am(III) chloride complexes are so weak that relatively high concentrations of complexing ligand are required to get a measurable variation of the intensive properties monitored throughout the experiments. The ratio of water to salt in concentrated media is far lower than in dilute solutions. Under these circumstances, the replacement of a water molecule in the inner coordination sphere of the metal ion by a chloride ion should be enhanced. According to Marcus and Shiloh [69MAR/SHI], outer-sphere interactions have very little effect on the absorption bands in the Am(III)/chloride system. On this basis, the spectral changes observed at high ligand concentrations were ascribed to the presence of inner-sphere complexes [64SHI/MAR, 69MAR/SHI, 69BAR/MIK]. However, because of the extensive change of ionic strength, it is difficult to distinguish unambiguously between complexation effects and activity effects. This consideration applies also to the NMR investigation by Vdovenko, Kolokl'tsov and Stebunov [66VDO/KOL] and Vdovenko and Stebunov [69VDO/STE], to the solubility study of Marcus [67MAR] and to the electrophoresis measurements of Marin [69MAR2].

The temperatures at which the experiments were carried out vary between 20° and 30°C, *cf.* Table V.8. No enthalpy measurements are available to correct $\log_{10}\beta_1$ to 25°C. However, by analogy with EuCl^{2+} [63CHO/UNR], the temperature dependence of $\log_{10}\beta_1$ is expected to be negligible within the investigated range. The conversion to molality units is not straightforward because of the continuous variation of the ionic media at fixed ionic strength. For example, the numerical value of molality in the 4 M $\mathrm{Na(ClO_4,Cl)}$ medium used by Sekine [64SEK, 65SEK] changes from 4.95 m in the absence of complexing ligands to 4.37 m in the NaCl solution. Moreover, the concentration dependence of interaction coefficients cannot be neglected at such high ionic strengths. Therefore, no data from experiments at $I = 3$ M [82FUK/KAW,

Table V.8: Literature values of equilibrium constants for the reaction
$$Am^{3+} + n\,Cl^- \rightleftharpoons AmCl_n^{(3-n)}.$$

Method	Medium	t(°C)	$\log_{10}\beta_1$	$\log_{10}\beta_2$	Reference
ix	0.206 M HCl	?	0.35		[56WAR/WEL]
ix	0.5 M HCl	?	0.24		
ix	4 M H(ClO_4,Cl)	20	−0.16±0.02	−0.74±0.1	[62GRE]
dis	1 M H(ClO_4,Cl)	22 ± 1	−0.05 ± 0.1		[62PEP/MAS]
ix	1 M H(ClO_4,Cl)	26 ± 1	−0.05 ± 0.05		[64BAN/PAT]
ix	1 M Na(ClO_4,Cl)	26 ± 1	0.15 ± 0.03		
dis	4 M Na(ClO_4,Cl)	25	−0.15 ± 0.07	−0.69 ± 0.10	[64SEK, 65SEK]
prx	LiCl, var	?	0.032	−0.97	[66VDO/KOL]
sol	0	25 ± 1 and 40 ± 1		−0.45 ± 0.04[(a)]	[67MAR]
sp	(H,Li)Cl, var	25 ± 1	−1.99 ± 0.05		[69BAR/MIK]
em	HCl, var	15	1.0	0.34	[69MAR2]
sp	LiCl, var	?	−2.2 ± 0.1	−4.70 ± 0.06	[64SHI/MAR, 69MAR/SHI]
prx	LiCl, var	?	0.26 ± 0.12	−0.05 ± 0.29	[69VDO/STE]
dis	1 M H(ClO_4,Cl)	30±0.1	−0.14±0.02	−0.52±0.04	[71KHO/NAR]
	1 M Li(ClO_4,Cl)		−0.25±0.02		
	1 M Na(ClO_4,Cl)		0.02 ± 0.02	−0.37 ± 0.05	
	1 M NH_4(ClO_4,Cl)		0.12±0.02	0.03 ± 0.02	
dis	3 M (Li,H)(ClO_4,Cl)	20	−0.26±0.02	−0.66±0.04	[82FUK/KAW, 85SAT/MIT]

(a) This constant refers to the solubility process $AmCl_3 \cdot x H_2O(s) \rightleftharpoons AmCl_2^+ + Cl^- + x\,H_2O(l)$.

85SAT/MIT] and at $I = 4$ M [62GRE, 64SEK, 65SEK] are used in the present analysis. For the remaining data, the plot of $(\log_{10}\beta_1 + 6D)$ according to the specific ion interaction theory shows no obvious trend with ionic strength. Although a medium effect on stability constants was sometimes observed [64BAN/PAT, 71KHO/NAR], these differences are smaller than the scatter in the data obtained in H^+ or Na^+ containing media. This set of data [56WAR/WEL, 62PEP/MAS, 64BAN/PAT, 71KHO/NAR] is used to calculate $\log_{10}\beta_1^\circ$. Extrapolation to infinite dilution with a weighted linear regression procedure is inappropriate. This review corrects the data at different ionic strengths using an estimated value of $\Delta\varepsilon$. By combining experimental and estimated interaction coefficients (*cf.* Appendix B), this review obtains $\Delta\varepsilon = -(0.22 \pm 0.1)\,\mathrm{kg \cdot mol^{-1}}$ and $-(0.13 \pm 0.1)\,\mathrm{kg \cdot mol^{-1}}$ for the H(ClO_4,Cl) and the Na(ClO_4,Cl) media, respectively. The uncertainty is increased to ±0.1 because of the approximation concerning $\varepsilon_{(AmCl^{2+},ClO_4^-)}$. The derived set of thermodynamic

values for Reaction V.17 appears to belong to the same parent distribution. Thus, the weighted average is accepted:

$$\log_{10} \beta_1^\circ(\text{V.17}, n = 1, 298.15\,\text{K}) \quad = \quad 1.05 \pm 0.06.$$

The recommended value of the standard Gibbs energy of formation is calculated to be

$$\Delta_\text{f} G_\text{m}^\circ(\text{AmCl}^{2+}, \text{aq}, 298.15\,\text{K}) \quad = \quad -(735.9 \pm 4.8)\ \text{kJ} \cdot \text{mol}^{-1}.$$

No values for $\log_{10} \beta_2^\circ$ are selected. The interpretation of the solvent extraction measurements made by Khopkar and Narayanankutty [71KHO/NAR] cannot be taken as definitive (*cf.* Appendix A). Although Grenthe [62GRE] and Sekine [64SEK, 65SEK] found evidence for the formation of very weak AmCl_2^+ species, this review prefers not to use the reported values of $\log_{10} \beta_2$, because their correction to $I = 0$ from a mixed ionic medium of high ionic strength is not sufficiently accurate.

V.4.1.2.2. Aqueous Am(III) perchlorates

Stability constant data are available for perchlorate complexes of Am(III) only. Solvent extraction measurements apparently indicated that weak AmClO_4^{2+} species form below 2 M ClO_4^-, with equilibrium constants $\beta_1 = (0.86 \pm 0.06)$ at ionic strength 2 M fixed with HBF_4 [72BAI/CHO], and $\beta_1^\circ = (4 \pm 0.9)$ as estimated by Lebedev and Mazur in NaClO_4 media of variable concentrations [81LEB/MAZ]. Celeda, Holub and Smirous [74CEL/HOL] found no significant effect of ClO_4^- on electromigration velocity measurements.

The formation of the aqueous outer-sphere complex $\text{Am}(\text{ClO}_4)_2^+$ was reported in the presence of excess perchlorate ions up to 8 m [81LEB/MAZ]. The reported thermodynamic constant at 25°C is $\beta_2^\circ = (2.0 \pm 0.1)$. The positive enthalpy and entropy values derived from experiments in the temperature range 25 to 55°C would suggest, however, that the perchlorate complexes are predominantly inner-sphere.

The large change of ionic strength necessary to investigate complex formation makes the extrapolation to infinite dilution extremely susceptible to error. Thus, no clear distinction can be made between very weak complexation effects and large variations of activity coefficients. Because of these considerations, this review does not recommend equilibrium constants for any of the americium perchlorates.

V.4.1.3. Aqueous Am(III) bromides and iodides

Only a few studies addressed complex formation of Am(III) with bromide and iodide ions. Shiloh *et al.* [64SHI/MAR, 69SHI/GIV] showed by spectrophotometry the formation of the first two halide complexes in highly concentrated solutions. The equilibrium constant for the formation of the inner-sphere complex AmBr^{2+} was reported to be $\log_{10}\beta_1 = -(3.3 \pm 0.1)$. As discussed in Appendix A, it is difficult to distinguish between complexation and activity effects in such concentrated media ([LiBr] $\geq$ 8.7 M). Fukusawa *et al.* [82FUK/KAW] and Sato *et al.* [85SAT/MIT]

reported $\log_{10}\beta_1 = -(0.52 \pm 0.04)$ and $\log_{10}\beta_2 = -(0.55 \pm 0.03)$ for the bromide complexes of americium(III) in 3 M $Li(ClO_4,Br)$ at 220°C. Extrapolation to $I = 0$ is hampered by the variation of the anionic composition of the medium during the experiments. Therefore, no values are selected.

V.4.1.4. Higher oxidation states of americium

No thermodynamic data are available on the formation of Am(IV), (V) and (VI) halide complexes.

High concentrations of fluorides ions were found to stabilise Am(IV) in aqueous solutions [61ASP/PEN, 73VAR/BAY]. The close correspondence between the absorption spectrum of these soluble Am species and that of solid AmF_4 suggests the existence of AmF_4(aq). Similar observations were made for Am(VI) [82KEL]. However, no thermodynamic data are available.

Dioxoamericium(V) was found to be present in 3 M and 5 M NaCl solutions because of radiolytic oxidation of Am(III), but no complex formation was observed [85MAG/CAR, 88STA/KIM]. The outer-sphere complex between AmO_2^{2+} and Br^- was postulated to be an intermediate in the reduction process of Am(VI) to Am(V) by bromide ions [77COO/WOO]. However, no equilibrium data were reported.

V.4.2. Americium halide compounds

V.4.2.1. Introduction

There are rather few experimental studies from which accurate thermodynamic data for americium halides can be derived:

1. The enthalpy of solution of $AmCl_3$(cr) [63FUG/CUN]
2. The vapour pressure of AmF_3(cr) [55CAR/CUN]
3. The equilibrium $AmOCl(cr)+2\,HCl(g) \rightleftharpoons AmCl_3(cr)+H_2O(g)$ [54KOC/CUN, 76WEI/WIS]
4. The equilibrium $AmOBr(cr)+2\,HBr(g) \rightleftharpoons AmBr_3(cr)+H_2O(g)$ [82WEI/WIS]

However, because of the systematic trends in the thermodynamic behaviour of the actinide elements, reliable values of both the enthalpy of formation and the entropy of many americium halides have been developed, particularly by Fuger *et al.* [83FUG/PAR] in the most recent review of the thermochemistry of the actinide halides. Since very little thermodynamic information on americium halides has been published since that review, the present values are derived predominantly from this work, with some amplification of the high-temperature properties, and consideration of some additional compounds.

Since the procedures [83FUG/PAR] for the estimation of the enthalpies of formation and standard entropies of the halides are the same for all the halides, the details and relevant data used are given here, and only the derived values given in the later text.

Table V.9: Data used to estimate $\Delta_f H^\circ_m(AmX_3, cr, 298.15K)$. Values are in $kJ \cdot mol^{-1}$ and refer to 298.15 K.

	M = U	M = Np	M = Pu	Reference
$r(M^{3+})/(10^{-10}$ m)	1.025	1.010	1.000	[76SHA]
$\Delta_f H^\circ_m(M^{3+}, aq)$	-489.1 ± 3.8	-527.2 ± 2.1	-592.0 ± 2.1	[76FUG/OET]
$\Delta_f H^\circ_m(MF_3, cr)$	-1502.1 ± 5.0		-1585.7 ± 3.0	[83FUG/PAR]
$\Delta_f H^\circ_m(MCl_3, cr)$	-866.0 ± 3.8		-959.8 ± 1.7	[83FUG/PAR]
$\Delta_f H^\circ_m(MBr_3, cr)$	-698.7 ± 4.2	-730.5 ± 2.1	-792.9 ± 2.1	[83FUG/PAR]
$\Delta_f H^\circ_m(MI_3, cr)$	-467.4 ± 4.2	-513.0 ± 2.1	-579.9 ± 2.5	[83FUG/PAR]

V.4.2.1.1. Estimation of enthalpies of formation

Consideration of thermodynamic data for the actinide halides shows that plots of the enthalpy difference $(\Delta_f H^\circ_m(MX_3, cr, 298.15\,K) - \Delta_f H^\circ_m(M^{3+}, aq, 298.15\,K))$ (where M = U, Np, Pu and X = F, Cl, Br, I), as a function of the ionic radius of the M^{3+} ion, are very close to linear — see for example Figure 2 in the earlier review by Fuger [82FUG]. It is therefore assumed that this linear function can be extended to include americium. This assumption can be tested for $AmCl_3(cr)$, for which a reliable enthalpy of formation is available. The estimated value is $\Delta_f H^\circ_m(AmCl_3, cr, 298.15K) = -(975 \pm 7)$ $kJ \cdot mol^{-1}$, as compared with the experimental value (see Section V.4.2.3.2) of $-(977.8 \pm 1.3)$ $kJ \cdot mol^{-1}$. The values estimated in the text are therefore judged to be quite reliable within rather conservative error limits based on the combined uncertainties of the data used in the estimation procedure. These data are summarised in Table V.9. Table V.10 summarizes the values used to estimate $\Delta_f H^\circ_m(AmF_4, cr, 298.15\,K)$ by similar procedures but using values for thorium in place of neptunium and dioxides as well as the aqueous ions. It may be noted that some of the values in Tables V.9 and V.10 for the Np and Pu species will not be identical with those to be selected in forthcoming NEA reviews, since the latter volumes are not finalized at this time. However the differences will not be large, and the effect on the estimated values for the Am species will be within the estimated uncertainties.

The values for the corresponding quantities of the americium species used in the estimations are: $r(Am^{3+}) = 0.975 \times 10^{-10}$ m, $r(Am^{4+}) = 0.850 \times 10^{-10}$ m [76SHA] and the following enthalpies of formation derived in this work:

$$\begin{aligned}
\Delta_f H^\circ_m(Am^{3+}, aq, 298.15\,K) &= -(616.7 \pm 1.5)\ kJ \cdot mol^{-1} \\
\Delta_f H^\circ_m(Am^{4+}, aq, 298.15\,K) &= -(406 \pm 6)\ kJ \cdot mol^{-1} \\
\Delta_f H^\circ_m(AmO_2, cr, 298.15\,K) &= -(932.2 \pm 3.0)\ kJ \cdot mol^{-1}.
\end{aligned}$$

Table V.10: Data used to estimate $\Delta_f H^\circ_m(AmF_4, cr, 298.15K)$. Values are in $kJ \cdot mol^{-1}$ and refer to 298.15 K.

	M = Th	M = U	M = Pu	Reference
$r(M^{4+})/(10^{-10}$ m)	0.94	0.89	0.86	[76SHA]
$\Delta_f H^\circ_m(M^{4+}, aq)$	-769.0 ± 2.5	-591.2 ± 3.3	-536.4 ± 3.3	[76FUG/OET]
$\Delta_f H^\circ_m(MF_4, cr)$	-2097.9 ± 8.4	-1914.2 ± 4.2	*−1846 ±21*[(a)]	[83FUG/PAR]
$\Delta_f H^\circ_m(MO_2, cr)$	-1226.4 ± 3.5	-1085.0 ± 1.0	-1055.8 ± 1.0	[89COX/WAG, 82GLU/GUR]

(a) This value is itself an estimate.

V.4.2.1.2. Estimation of standard entropies

There are no measured values of the entropies of any americium halide. These values are therefore all estimated, following [83FUG/PAR] and earlier workers, from the values for the halides of the other actinide elements, often by relating the difference in entropy to the number of unpaired electrons, assuming a spin-only contribution to the entropy.

V.4.2.2. Americium fluoride compounds

The trifluoride and tetrafluoride of americium and the six-valent $AmO_2F_2(cr)$ are well established compounds, and there is considerable evidence that the hexafluoride $AmF_6(cr)$ can be formed under strongly fluorinating conditions.

There are a number of complex fluorides containing three-, four- and five-valent americium, whose structures and methods of preparation have been summarised by Schulz and Penneman [86SCH/PEN]. Since there are no thermodynamic data for these ternary compounds, they are not considered further in this review.

V.4.2.2.1. Americium trifluoride

a) Crystal structure

Americium trifluoride has the hexagonal $LaF_3(cr)$ type crystal structure, the type in which all the earlier actinide and many lanthanide trifluorides crystallise. This structure was discussed in detail by Taylor [76TAY]. The real structure is a distortion of the idealised fully-capped trigonal prism, with two molecules per unit cell, space group $P6_3/mmc$. Subsequent work, discussed by Taylor [76TAY], indicates that the true cell contains six molecules; however, it is still not clear whether the space group is $P\overline{3}c1$ or $P6_3cm$, corresponding to slightly different distortions or the smaller cell. The refinement of the neutron diffraction data gives the same R-factors for each structure. The lattice parameters given by Asprey, Keenan and Kruse [65ASP/KEE]

have thus been converted to this larger cell (by multiplying the a parameter by $\sqrt{3}$), $a = (7.044 \pm 0.002) \times 10^{-10}$, $c = (7.225 \pm 0.002) \times 10^{-10}$ m.

b) Enthalpy of formation and entropy

A value for the standard enthalpy of formation of americium trifluoride was estimated by Fuger *et al.* [83FUG/PAR] by the procedure noted in Section V.4.2.1.1 to be:

$$\Delta_f H^\circ_m(AmF_3, cr, 298.15\,K) \;=\; -(1588 \pm 13)\ kJ \cdot mol^{-1}.$$

This value is preferred to that of $-1605\ kJ \cdot mol^{-1}$ estimated by Morss [86MOR] by a slightly different procedure from the systematics of the lanthanide as well as the actinide trihalides. However, as noted by Morss, the correlations involving the enthalpies of solution of the trihalides are rather irregular for the elements Nd to Eu, (which have similar molar volumes to AmF_3), whereas the correlation of Fuger *et al.* [83FUG/PAR], involving actinides only, gives excellent predictions in all cases (for NpX_3(cr) as well as AmX_3(cr)) where it has been tested.

The standard entropy is estimated (see Section V.4.2.1) to be:

$$S^\circ_m(AmF_3, cr, 298.15\,K) \;=\; (127.6 \pm 5.0)\ J \cdot K^{-1} \cdot mol^{-1}.$$

This value is very close to that estimated by assuming the entropy of formation of AmF_3(cr) is the same as that of PuF_3(cr) ($\Delta_f S^\circ_m = -232.5\ J \cdot K^{-1} \cdot mol^{-1}$ [83FUG/PAR]), namely $127.1\ J \cdot K^{-1} \cdot mol^{-1}$.

The Gibbs energy of formation is calculated from the selected enthalpy formation and entropy.

$$\Delta_f G^\circ_m(AmF_3, cr, 298.15\,K) \;=\; -(1518.8 \pm 13.1)\ kJ \cdot mol^{-1}.$$

c) Vapour pressure

Carniglia and Cunningham [55CAR/CUN] measured the vapour pressure of americium trifluoride from 1126 to 1469 K by the effusion method, using tantalum cells, and target collection of the effusate. The mass of effusate was calculated from the α-radiometric assay of the targets using the half-life of ^{241}Am given by Hollander, Perlman and Seaborg [53HOL/PER]. These authors in fact gave values of 470 and 475 y for the half-life of ^{241}Am, so it is assumed that Carniglia and Cunningham [55CAR/CUN] used a value of 472.5 y. However, the preferred value today is (432.7 ± 0.5) y, [86VAN, *p.*127], so all the pressures of AmF_3(g) given by [55CAR/CUN] are reduced by a factor of $(432.7/472.5) = 0.916$.

In one series of experiments, twin effusion cells were used to compare the vapour pressures of PuF_3(cr) and AmF_3(cr). The measured pressures of PuF_3(cr) were close to those determined by Phipps *et al.* [50PHI/SEA], which agree with currently accepted values [83FUG/PAR], indicating that the general calibration of the measuring system was not seriously in error.

It should be noted that despite the great care taken to exclude oxygen from the apparatus, the samples of PuF_3(cr) after the effusion experiments were invariably found

to contain some oxyfluoride; however, Carniglia and Cunningham [55CAR/CUN] noted that this was unlikely to affect the vapour pressure measurements appreciably.

The experimental values for the vaporisation of AmF_3(cr) for the assumed process

$$AmF_3(cr) \rightleftharpoons AmF_3(g) \qquad (V.18)$$

can be fitted by the linear expression between 1140 and 1469 K to

$$\log_{10} p(\text{bar}) = -20813/T + 9.071,$$

giving

$$\Delta_r G^\circ_m(\text{V.18, 1140 to 1469 K}) = (398462 - 173.663\ T)\ \text{J} \cdot \text{mol}^{-1}.$$

The experimental point at the lowest temperature (1126 K) deviates noticeably from this and has been omitted from the fitting.

Carniglia and Cunningham [55CAR/CUN] noted that the derived entropy of sublimation is consistent with the monomeric sublimation assumed, rather than a more complicated vaporisation process, though small amounts of dimer molecules could be present in the vapour.

The entropy of sublimation for the corresponding vaporisation of UF_3(cr) at 1300 K, the mean temperature of the measurements, calculated from the thermal functions given by Glushko *et al.* [82GLU/GUR], is 191.0 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. However, it would be expected that the entropy of AmF_3(g) would be appreciably smaller than that of UF_3(g) owing to smaller electronic contributions, so this is consistent with the entropy of vaporisation obtained from the study by Carniglia and Cunningham. In order to correct the measurements of Carniglia and Cunningham [55CAR/CUN] to room temperature, it is therefore assumed that the enthalpy and entropy corrections to 298.15 K are the same as those for the vaporisation of UF_3(cr) [82GLU/GUR]:

$$\begin{aligned} \Delta_r H^\circ_m(\text{V.18}, 1300\ \text{K}) - \Delta_r H^\circ_m(\text{V.18}, 298.15\ \text{K}) &= -22.65\ \text{kJ} \cdot \text{mol}^{-1} \\ \Delta_r S^\circ_m(\text{V.18}, 1300\ \text{K}) - \Delta_r S^\circ_m(\text{V.18}, 298.15\ \text{K}) &= -32.94\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}. \end{aligned}$$

The values for the sublimation of AmF_3(cr) to AmF_3(g) at 298.15 K are thus

$$\begin{aligned} \Delta_r H^\circ_m(\text{V.18}, 298.15\ \text{K}) &= (421.1 \pm 7.0)\ \text{kJ} \cdot \text{mol}^{-1} \\ \Delta_r S^\circ_m(\text{V.18}, 298.15\ \text{K}) &= (206.6 \pm 10.0)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}. \end{aligned}$$

The derived enthalpy of formation and entropy are:

$$\begin{aligned} \Delta_f H^\circ_m(AmF_3, g, 298.15\ \text{K}) &= -(1167 \pm 15)\ \text{kJ} \cdot \text{mol}^{-1} \\ S^\circ_m(AmF_3, g, 298.15\ \text{K}) &= (334 \pm 11)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

The latter value is consistent with a gaseous molecule with similar molecular parameters as those of UF_3(g) [82GLU/GUR] , but with a smaller electronic contribution to the entropy. The standard entropies at 298.15 K (for 1 bar standard state pressure) for UF_3(g) and PuF_3(g) are 347.4 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [82GLU/GUR, 85HIL/GUR] and 336.2 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [85HIL/GUR], respectively.

The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy.

$$\Delta_f G^\circ_m(AmF_3, g, 298.15\,K) \quad = \quad -(1159.3 \pm 15.1)\ kJ \cdot mol^{-1}$$

d) Melting point

Burnett [66BUR] reported the melting point of a sample of AmF_3(cr), prepared by reacting the hydrate of AmF_3 precipitated from concentrated HF solution with $NH_4 \cdot HF_2$ at 400 K, to be (1666 ± 20) K, when supported on a molybdenum holder in a graphite furnace.

e) Solubility in aqueous solutions

The solubility product obtained with the selected value of $\Delta_f G^\circ_m(AmF_3, cr, 298.15\,K)$ is

$$AmF_3(cr) \quad \rightleftharpoons \quad Am^{3+} + 3\,F^- \qquad\qquad \log_{10} K_{s,0}(298.15\,K) = -13.3 \pm 2.5$$

As discussed above, this value is derived from the estimated values of the selected enthalpy of formation and the entropy of the solid phase. The americium solubilities calculated with this selected value for $K_{s,0}$ are orders of magnitude higher than the americium concentrations reported by Feay [54FEA] and by Nash and Cleveland [84NAS/CLE2] for fluoride solutions having $[ClO_4^-] \approx 0.1$ M. However, it is not certain that these solutions were indeed in equilibrium with crystalline americium trifluoride rather than an amorphous (or even hydrated) trifluoride (*cf.* Appendix A). Therefore the selection made by this review can not be confirmed with solubility data.

V.4.2.2.2. Americium tetrafluoride

a) Crystal structure

Americium tetrafluoride has the monoclinic UF_4 type crystal structure, space group C2/c, $a = 12.538 \times 10^{-10}$ m, $b = 10.516 \times 10^{-10}$ m, $c = 8.204 \times 10^{-10}$ m, $\beta = 126.18°$ [73ASP/HAI].

b) Thermodynamic data

The standard enthalpy of formation of AmF_4(cr) has been estimated by two (related) correlations: Fuger and Parker [83FUG/PAR] used the same procedure as used for the trihalides, namely correlating $\Delta_f H_m(MF_4, cr) - \Delta_f H_m(M^{4+}, aq)$ with the atomic radius of the metal ion, for M = Th, U, Pu, which, with the values noted in the introduction, Section V.4.2.1.1, gives a value of $-(1720 \pm 25)$ kJ $\cdot$ mol^{-1} for the enthalpy of formation of AmF_4(cr). The extrapolation is less satisfactory in this

case, since $\Delta_f H^\circ_m(Am^{4+}, aq, 298.15\,K)$ is not experimentally well defined. A related correlation is to plot $\Delta_f H^\circ_m(MF_4, cr) - \Delta_f H^\circ_m(MO_2, cr)$ also against the ionic radius of the M^{4+} ion, which gives a value of $-(1705 \pm 15)$ kJ · mol^{-1}. The selected value is

$$\Delta_f H^\circ_m(AmF_4, cr, 298.15\,K) \quad = \quad -(1710 \pm 21)\ \text{kJ} \cdot \text{mol}^{-1},$$

which is consistent with the semi-quantitative decomposition measurements discussed below.

The value of the standard entropy estimated by Fuger *et al.* [83FUG/PAR] by the procedure noted in Section V.4.2.1,

$$S^\circ_m(AmF_4, cr, 298.15\,K) \quad = \quad (148.5 \pm 5.0)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1},$$

is essentially identical to that estimated by assuming the entropy of formation of AmF_4 is the same as that of $PuF_4(-312.7\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$ [83FUG/PAR], namely $148.2\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$.

The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy.

$$\Delta_f G^\circ_m(AmF_4, cr, 298.15\,K) \quad = \quad -(1617 \pm 20)\ \text{kJ} \cdot \text{mol}^{-1}$$

c) Vapour pressure

Chudinov and Choporov [70CHU/CHO] measured the vapour pressure of AmF_4(cr) by the effusion method from a nickel cell. However, their AmF_4(cr) was prepared in situ by the reaction of F_2(g) with AmO_2(cr) at a pressure of < 1 atm for 4 days at 673 K. This reaction is known to give AmF_4(cr) [54ASP] in agreement with the relevant thermodynamic data. The results from a first run in the apparatus gave pressures which above 800 K were lower than expected from the normal extrapolation from lower temperatures. After a further fluorination, however, the total vapour pressure gave a satisfactorily linear relation between $\log_{10} p$ and $1/T$ up to ~925 K. Above this temperature, the vapour decreased with increasing temperature, indicating decomposition (or reaction) of the AmF_4(cr). AmF_4(cr) is indeed now known to start to dissociate appreciably at about this temperature, as discussed more fully below.

Their [70CHU/CHO] equation for the vapour pressure under these conditions is

$$\log_{10} p(\text{bar}) \quad = \quad -11911/T + 6.564, \qquad \text{from 729 to 908 K}$$

corresponding to the Gibbs energy of sublimation of

$$\Delta_{sub}\, G^\circ_m(\text{V.19, 729 to 908 K}) \quad = \quad (228000 - 125.7\ T)\ \text{J} \cdot \text{mol}^{-1}$$

for the assumed process

$$AmF_4(cr) \quad \rightleftharpoons \quad AmF_4(g). \qquad \text{(V.19)}$$

There are no reliable thermal functions for either AmF_4(cr) or AmF_4(g) with which the entropy of sublimation of $\sim 126\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ can be compared, but $\Delta_{vap} S$ for

the corresponding reaction involving uranium (which is certainly predominantly a simple evaporation) is about 192 $J \cdot K^{-1} \cdot mol^{-1}$, using the thermal functions given by Fuger *et al.* [83FUG/PAR] for UF_4(cr) and Glushko *et al.* [82GLU/GUR] for UF_4(g) (C_{2v} symmetry). It is unlikely that the entropy of vaporisation of AmF_4(cr) would differ by more than 20 $J \cdot K^{-1} \cdot mol^{-1}$ from this value, so it may be that the reaction measured by Chudinov and Choporov [70CHU/CHO] was more complicated than the simple vaporisation to AmF_4(g).

In fact, the reaction

$$3\,AmF_4(cr) + AmO_2(cr) \rightleftharpoons 4\,AmF_3(cr) + O_2(g)$$

considered by Chudinov and Choporov [70CHU/CHO] to account for the decomposition above 950 K is thermodynamically favourable even at low temperatures, so could have led to some reduction in the vapour pressure of AmF_4(cr), particularly on the first run, when some unreacted AmO_2(cr) could have been present. Moreover, Gibson and Haire [88GIB/HAI] suggested that nickel cells react with the fluorine evolved from AmF_4(cr), equivalent to the reduction of AmF_4(cr) by Ni(cr), which is of course thermodynamically favourable at all temperatures. Thus nickel could lose its passivity at these temperatures, perhaps by reaction of the nickel fluoride film with AmF_3(cr) or AmF_4(cr).

Since the properties of AmF_4(g) are of minimal importance for the present purposes, this species is not considered further in this compilation.

d) Decomposition of AmF_4

The suggestion of Chudinov and Choporov [70CHU/CHO] that AmF_4(cr) loses fluorine at temperatures above $\sim$ 1000 K according to the reaction

$$2\,AmF_4(cr) \rightleftharpoons 2\,AmF_3(cr) + F_2(g),$$

has recently been confirmed semi-quantitatively by Gibson and Haire [88GIB/HAI]. These authors heated $\sim$ 5mg of AmF_4(cr) in a (leaking) LaF_3(cr) effusion cell in a tantalum furnace leading to a quadrupole mass-spectrometer. Fluorine gas was identified in the vapour, even at the lowest temperature of the study ($\sim$ 850 K). On heating to $\sim$ 1000 K the F_2(g) signal disappeared. The mass-spectrometer employed could not detect species with mass numbers as high as those for americium fluorides. AmF_3(cr) (identified by X-ray diffraction) was found to be present in the Knudsen cell after the experiments, in an amount approximately equal to the starting amount.

From the details of the experiments, in which all the AmF_4(cr) was converted into AmF_3(cr) in a few minutes at 1000 K, it is estimated that the pressure of F_2(g) in their (leaking) effusion cell was 3×10^{-5} to 5×10^{-5} bar; the $p(F_2)$ calculated from the selected data at 298.15 K, extrapolated to 1000 K without any $C_{p,m}$ correction is 5×10^{-5} bar.

In their experiments, Chudinov and Choporov [70CHU/CHO] used a larger sample of AmF_4(cr), and an appreciably smaller effusion orifice, so they would have converted only part of their sample to AmF_3(cr), leading to a lower pressure of AmF_4(g) (due

to lack of saturation in the Knudsen cell), but not to complete decomposition to americium trifluoride, as in the experiments of Gibson and Haire [88GIB/HAI].

If the study of Chudinov and Choporov [70CHU/CHO] represents, even approximately, the vapour pressure of AmF_4(cr), the F_2/AmF_4 ratio in the vapour over AmF_3(cr) + AmF_4(cr) is about 10, suggesting that AmF_4(cr) certainly vaporizes mainly by decomposition.

Jouniaux [79JOU] has studied the vaporisation and redeposition of americium fluorides in gaseous fluorine in a nickel tube with a temperature gradient at $p_{F_2(g)} = 1$ and 5 bar. The volatilization was assumed to occur *via* the tetrafluoride. They report enthalpies of adsorption of 251 and 349 $kJ \cdot mol^{-1}$ at the two pressures, but it is far from clear to which precise process or processes these values refer.

V.4.2.2.3. Americium pentafluoride

Fargeas *et al.* [86FAR/FRE] have studied the vaporisation of americium compounds in atmospheres of HF(g), F_2(g) (both of these with and without O_2(g)) and $BF_3 + F_2$ gases, followed by deposition in a tube with a temperature gradient running from 1073 to 123 K. The position of deposition of any volatile compounds along the temperature gradient tube was identified radiometrically. Fargeas *et al.* [86FAR/FRE] noted that the position (and thus temperature) of deposition is strongly correlated with the type of volatile species (MF_5, MO_2F_2, *etc.*), depending little on the metal M. From their experiments, they suggest that americium is deposited as both AmF_5(s) and AmF_6(s). More definitive identification of the formation of AmF_5(g) would be very welcome.

V.4.2.2.4. Americium hexafluoride

Drobichevski *et al.* [80DRO/PRU] suggested that AmF_6 can be formed in both the condensed and gaseous states by the reaction of KrF_2 with AmF_3 in anhydrous HF at 313 to 333 K. They were not able to isolate any pure americium fluoride from this reaction, but found that ^{241}Am, identified by its γ-spectrum, was present in the vapour, that when the solvent was evaporated, a dark brown solid vaporised to give a vapour with a symmetric infra-red active absorption peak at (604 ± 3) cm^{-1} (the similar peaks of UF_6(s) and PuF_6(s) lie at 624 and 615 cm^{-1}, respectively), and that on hydrolysis this solid yielded AmO_2^{2+} in solution, all of which, they suggest, indicates that a volatile higher americium fluoride, probably AmF_6, can be formed under strongly fluorinating conditions. The temperature gradient experiments of Fargeas *et al.* [86FAR/FRE], which also suggest that 0.04% AmF_6(g) can be formed in an atmosphere of BF_3(g) + F_2(g), have been discussed in Section V.4.2.2.3. However more recently Gibson and Haire [92GIB/HAI] were unable to detect the formation of a volatile americium fluoride either by mass-spectrometric or radiometric analysis when AmO_2(cr), AmF_4(cr) or Am(cr) were heated in fluorinating agents such as F_2(g), F_2(g) + BF_3(g) and ClF_3(g) + BF_3(g).

Drobichevski *et al.* [80DRO/PRU] have estimated the enthalpy of the reaction

$$AmF_4(cr) + F_2(g) \rightleftharpoons AmF_6(g)$$

at 298.15 K to be $+(67 \pm 21)$ kJ·mol^{-1}, by analogy with ruthenium, and Gibson and Haire [92GIB/HAI] give the same estimated value, without an uncertainty. This is probably not a totally independent estimate, since [92GIB/HAI] merely refer to the methods used by [80DRO/PRU] and [86MOR] in describing their own assessment procedure. With this enthalpy of reaction, the fraction of $AmF_6(g)$ in equilibrium with $AmF_4(cr)$ and $F_2(g)$ at 1 bar would be 10^{-10} to 10^{-8} at 300 to 400 K, but would, of course, be higher in more strongly fluorinating atmospheres. The balance of evidence probably points to $AmF_6(g)$ being formed, at least transiently, in such atmospheres. A repetition of the experiments of [80DRO/PRU], but using ^{243}Am, with its lower irradiation flux, would be valuable.

V.4.2.2.5. Dioxoamericium(VI) fluoride

Dioxoamericium(VI) fluoride, $AmO_2F_2(cr)$, was characterised by Keenan [68KEE]. It is formed by the action of an HF/F_2 mixture on sodium americyl(VI) acetate, initially at liquid N_2 temperature, but finally at room temperature. X-ray patterns of the product after evaporation of the solvent indicated the presence of a phase with a hexagonal structure, space group $R\overline{3}m$, UO_2F_2 type, with $a = 4.136 \times 10^{-10}$ m, $c = 15.85 \times 10^{-10}$ m, isostructural with the other actinide(VI) oxyfluorides.

No further information is available on this compound.

V.4.2.2.6. Ternary fluorides

a) Li and Na compounds

Penneman *et al.* [67PEN/KEE] have prepared the compounds $LiF \cdot AmF_4(cr)$ and $7NaF \cdot 6AmF_4(cr)$ by heating chlorides with the appropriate cation ratio in elemental fluorine at 350°C for ~ 16 h. The structures and lattice parameters of these phases are:

- $LiAmF_5(cr)$, tetragonal, $LiUF_5$-type, space group $I4_1/a$, $a = (14.63 \pm 0.02) \times 10^{-10}$ m, $c = (6.449 \pm 0.005) \times 10^{-10}$ m.
- $Na_7Am_6F_{31}(cr)$, hexagonal, $Na_7Zr_6F_{31}$-type [68BUR/ELL], space group $R\overline{3}$ $a = (14.48 \pm 0.02) \times 10^{-10}$ m, $c = (9.665 \pm 0.003) \times 10^{-10}$ m.

b) Rb compounds

Kruse and Asprey [62KRU/ASP] have prepared the Am(IV) complex fluoride $Rb_2AmF_6(cr)$ by treating Am(IV) hydroxide or Am(V) carbonates with concentrated RbF – HF solutions. Orange pink crystals of $Rb_2AmF_6(cr)$ were found to

have an orthorhombic cell with lattice parameters $a = (6.98 \pm 0.02) \times 10^{-10}$ m, $b = (12.09 \pm 0.02) \times 10^{-10}$ m, $c = (7.56 \pm 0.02) \times 10^{-10}$ m.

The corresponding Na and K compounds of U and Th have hexagonal symmetry, but the larger Rb^+ ion causes a slight distortion to the overall orthorhombic symmetry, but the distorting influence is so weak that the crystals tend to revert to higher symmetry by twinning.

V.4.2.3. Americium chlorides

Americium is the first actinide element for which common truly divalent compounds are stable, and both the dichloride and the trichloride of americium, as well as the trivalent oxychloride AmOCl(cr), have been well characterised.

V.4.2.3.1. Americium dichloride

a) Crystal structure

Americium dichloride, prepared (together with $AmCl_3$(cr)) by the reaction of americium metal with $HgCl_2$(s) has the orthorhombic $PbCl_2$(cr) type crystal structure, space group Pnma, $a = 8.963 \times 10^{-10}$ m, $b = 7.573 \times 10^{-10}$ m, $c = 4.532 \times 10^{-10}$ m, Baybarz [73BAY].

b) Enthalpy of formation

Morss [86MOR] estimated the enthalpy of formation of $AmCl_2$(cr) to be -654 kJ $\cdot$ mol^{-1}, with an unknown uncertainty, based on the assumption that the hypothetical enthalpy of solution is similar to that of $SmCl_2$(cr), the lanthanide dichloride with the same ionic radius of the cation as americium in americium dichloride. However, since this involves the highly uncertain value of the enthalpy of formation of Am^{2+}(aq), the most that can probably be said of the enthalpy of formation of $AmCl_2$ is that it is likely to be more negative than $2\Delta_f H^\circ_m(AmCl_3, cr)/3$, namely -652 kJ $\cdot$ mol^{-1}.

V.4.2.3.2. Americium trichloride

a) Crystal structure

Americium trichloride has the hexagonal UCl_3(cr) type crystal structure, space group $P6_3/m$, $a = 7.382 \times 10^{-10}$ m, $c = 4.214 \times 10^{-10}$ m, as determined from single crystal X-ray diffraction data by Burns and Peterson [70BUR/PET]. This is the structural type in which all the known actinide trichlorides crystallise.

b) Thermodynamic data

The enthalpy of solution of $AmCl_3$(cr) in 0.001 and 1.5 M HCl solutions was measured by Fuger and Cunningham [63FUG/CUN]. When combined with the enthalpy of

solution of α-Am(cr) in the same solutions (where the infinite dilution value has been used for the 0.001 M HCl solution), and the enthalpies of formation of the chloride ion [89COX/WAG] and Parker, Wagman and Garvin [76PAR/WAG], the derived values for the enthalpy of formation of $AmCl_3$ are $-(978.2 \pm 1.7)$ and $-(977.8 \pm 1.3)$ kJ $\cdot$ mol^{-1}, respectively (see [83FUG/PAR] for details). Following [83FUG/PAR] the value accepted is

$$\Delta_f H^\circ_m(AmCl_3, cr, 298.15\,K) \quad = \quad -(977.8 \pm 1.3)\ kJ \cdot mol^{-1}.$$

The standard entropy is estimated (see Section V.4.2.1) to be

$$S^\circ_m(AmCl_3, cr, 298.15\,K) \quad = \quad (164.8 \pm 6.0)\ J \cdot K^{-1} \cdot mol^{-1}.$$

This value is close to that estimated by assuming the entropy of formation of $AmCl_3$(cr) is the same as that of UCl_3(cr) ($\Delta_f S^\circ_m = -225.8$ J$\cdot$K$^{-1}\cdot$mol^{-1} [83FUG/PAR]), namely 164.2 J $\cdot$ K^{-1} $\cdot$ mol^{-1}.

The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy.

$$\Delta_f G^\circ_m(AmCl_3, cr, 298.15\,K) \quad = \quad -(910.7 \pm 2.3)\ kJ \cdot mol^{-1}$$

The heat capacity at 298.15 K is estimated to be similar to that of UCl_3(cr) [89COR/KON] † :

$$C^\circ_{p,m}(AmCl_3, cr, 298.15\,K) \quad = \quad (103 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1}.$$

c) Melting data

Weigel and Kohl [85WEI/KOH] measured the melting point, $T_{fus} = (991 \pm 5)$ K and the enthalpy of fusion of $AmCl_3$(cr) using a commercial DTA apparatus.

$$AmCl_3(cr) \quad \rightleftharpoons \quad AmCl_3(l) \qquad (V.20)$$

Their values are accepted, but with increased uncertainties.

$$\Delta_{fus} H^\circ_m(AmCl_3, 911\,K) \quad = \quad (48.1 \pm 4.0)\ kJ \cdot mol^{-1}.$$

There is too much uncertainty in the heat capacities of solid and liquid $AmCl_3$ to attempt a meaningful extrapolation of this value to 298.15 K.

d) Vapour pressure

Weigel and Shuster [85WEI/SCH] attempted to measure the vapour pressure of $AmCl_3$(cr) by a variant of the static boiling-point method, using very small amounts of americium trichloride trapped under a molybdenum cup floating in a bath of liquid

† The value of $C^\circ_{p,m}(UCl_3, cr, 298.15$ K) in Table III.1 of the uranium NEA-TDB review [92GRE/FUG, *p.*36] is erroneous, *cf.* the discussion in Appendix D, *p.*348

tin. Their description of the experimental difficulties, plus the numerous quite appreciable corrections which have to be applied to the measured static pressure, suggest that this technique is certainly difficult to use on a micro-scale. This is borne out by the extreme variation in the resulting pressures. The authors carried out seven runs; within runs, individual points deviated from a linear $\log_{10}p$ *vs.* $1/T$ plot by up to a factor of two in the pressure, and between runs, the pressures at the same temperature differed by up to a factor of ten. Moreover, with amounts of 100 to 200 μg of americium trichloride (prepared from americium dioxide) under a Mo cup, in contact with hydrogen-reduced Sn(l) at temperatures up to 1343 K, there can be no guarantee that volatile reaction products such as H_2O, HCl or molybdenum oxychlorides do not form a part, if not the major part, of the measured pressures.

Given these problems, and that the pressures derived by Weigel and Schuster; $\log_{10}p(1098 \text{ to } 1343\text{ K}) = 7.8 - 11826/T(\text{bar})$ are about two orders of magnitude higher than those of plutonium trichloride, it seems unlikely that these represent the vapour pressure of americium trichloride, and no further treatment of the results is attempted.

V.4.2.3.3. Americium oxychloride

a) Crystal structure

Americium oxychloride AmOCl(cr) has the tetragonal PbFCl type crystal structure, space group P4/nmm, $a = 3.99 \times 10^{-10}$ m, $c = 6.77 \times 10^{-10}$ m [54KOC/CUN]. This is the structural type in which all the known MOX actinide oxyhalides crystallise.

b) Thermodynamic data

The equilibrium constant of the reaction

$$\mathrm{AmCl_3(cr) + H_2O(g)} \rightleftharpoons \mathrm{AmOCl(cr) + 2\,HCl(g)} \qquad \text{(V.21)}$$

was studied by Koch and Cunningham [54KOC/CUN] from 682 to 880 K, and by Weigel and Wishnewsky [76WEI/WIS], using both $^{241}\mathrm{AmCl_3(cr)}$ (from 767 to 864 K) and $^{243}\mathrm{AmCl_3(cr)}$ (from 752 to 854 K). The results of these three studies are in excellent agreement, and all the equilibrium constants are fitted to one linear expression

$$\log_{10} K_p(\text{V.21, 682 to 880 K}) = 6.676 - 4360/T(\text{bar}),$$

corresponding to

$$\Delta_r G^\circ_m(\text{V.21, 682 to 880 K}) = (83472 - 127.81T)\ \mathrm{kJ \cdot mol^{-1}}$$

for the Gibbs energy for the above reaction.

To utilise this expression to calculate the standard properties of AmOCl(cr) at 298.15 K, the heat capacity change for this reaction must be estimated. For this, the

heat capacity of $AmCl_3$(cr) is assumed to be the same as that of UCl_3(cr) and that of AmOCl(cr) is taken to be a smooth curve, between 298.15 and 1100 K,

$$\begin{aligned} C^\circ_{p,\mathrm{m}} &= (61.284 + 4.58933 \times 10^{-2}\ T \\ &\quad -1.730645 \times 10^{-5} T^2 - 269380/T^2)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \end{aligned}$$

based on values calculated from $C^\circ_{p,\mathrm{m}}(3UO_2 + U + 2UCl_3)/6$.

If the enthalpy and entropy of the hydrolysis reaction are taken to be those at the mean temperature of the two studies 781 K, the corrections to 298.15 K are:

$$\begin{aligned} \Delta_\mathrm{r} H^\circ_\mathrm{m}(\mathrm{V.21}, 781\,\mathrm{K}) - \Delta_\mathrm{r} H^\circ_\mathrm{m}(\mathrm{V.21}, 298.15\,\mathrm{K}) &= -1741\,\mathrm{J \cdot mol^{-1}} \\ \Delta_\mathrm{r} S^\circ_\mathrm{m}(V.21, 781\,\mathrm{K}) - \Delta_\mathrm{r} S^\circ_\mathrm{m}(\mathrm{V.21}, 298.15\,\mathrm{K}) &= -3.57\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}. \end{aligned}$$

With the values given above for $AmCl_3$(cr) and the CODATA Key Values [89COX/WAG] for H_2O(g) and HCl(g), the final values for AmOCl(cr) are

$$\begin{aligned} \Delta_\mathrm{f} H^\circ_\mathrm{m}(\mathrm{AmOCl, cr}, 298.15\,\mathrm{K}) &= -(949.8 \pm 6.0)\ \mathrm{kJ \cdot mol^{-1}} \\ S^\circ_\mathrm{m}(\mathrm{AmOCl, cr}, 298.15\,\mathrm{K}) &= (111 \pm 10)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}. \end{aligned}$$

These values are slightly different from those given by Fuger *et al.* [83FUG/PAR] who used a constant heat capacity difference of 6.3 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for the hydrolysis reaction (V.21). The major uncertainties in the enthalpy of formation and entropy indeed come from the heat capacity correction.

The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy.

$$\Delta_\mathrm{f} G^\circ_\mathrm{m}(\mathrm{AmOCl, cr}, 298.15\,\mathrm{K}) = -(902.5 \pm 6.7)\ \mathrm{kJ \cdot mol^{-1}}.$$

V.4.2.3.4. Ternary and quaternary chlorides

Complex chlorides of $AmCl_3$ with one and three moles of CsCl have been identified, together with a series of compounds M_2AmCl_5(s) (M = K, NH_4, Rb) and the quaternary halide $Cs_2NaAmCl_6$. Data for the enthalpy of formation of the latter compound are available.

V.4.2.3.4.1. Ternary chlorides $CsAmCl_4$, Cs_3AmCl_6, M_2AmCl_5 (M = K, NH_4, Rb)

$CsAmCl_4$(s) and Cs_3AmCl_6(s) were prepared by Bagnall, Laidler and Stewart [68BAG/LAI] from acidic aqueous solutions; their structures are not known. The pentachlorides have been described and characterised by Schleid *et al.* [87SCH/MOR]. Solutions of $^{243}AmCl_3$ in hydrochloric acid were mixed with the solid alkali chloride and evaporated to dryness at 200 – 300°C under a stream of HCl(g), to yield tan-yellow powders of the ternary chlorides. X-ray examination indicated they have an orthorhombic crystal structure, space group Pnma, isotypic with K_2PrCl_5(cr) and

Table V.11: Lattice parameters for americium ternary chlorides.

Compound	Lattice parameters $\times 10^{10}$/m a	b	c
K_2AmCl_5(cr)	12.6832	8.7038	7.9525
$(NH_4)_2AmCl_5$(cr)	13.0482	8.7939	8.1630
Rb_2AmCl_5(cr)	13.0854	8.8707	8.1629

many other similar lanthanide and actinide compounds. The lattice parameters of the americium compounds are given in Table V.11.

The ammonium compound forms a convenient intermediary for the synthesis of $AmCl_3$(cr).

V.4.2.3.4.2. Quaternary chloride $Cs_2NaAmCl_6$

Schoebrechts *et al.* [89SCH/GEN] have characterised $Cs_2NaAmCl_6$(cr) and measured its enthalpy of solution in 1 molal hydrochloric acid solution.

$Cs_2NaAmCl_6$(cr) was found to have the fcc ideal-cryolite structure, space group Fm3m, with $a = 10.8546 \times 10^{-10}$m for a sample containing ^{241}Am. This is significantly smaller than the parameter reported by Soderholm *et al.* [86SOD/EDE] for a sample containing ^{243}Am; the reason for this difference is not clear.

Schoebrechts *et al.* [89SCH/GEN] measured the enthalpy of solution of the ^{241}Am compound in an 1 M HCl solution to be $-(51.62 \pm 0.85)$ kJ $\cdot$ mol^{-1} at 298.15 K. We have accepted all the auxiliary data used by Schoebrechts *et al.*, except for $\Delta_f H^\circ_m(\mathrm{CsCl, cr, 298.15\,K})$, for which we prefer the value $-(442.31 \pm 0.16)$ kJ $\cdot$ mol^{-1} suggested by Glushko *et al.* [82GLU/GUR] rather than the value proposed by Parker [76PAR/WAG], $-(442.69 \pm 0.04)$ kJ $\cdot$ mol^{-1}, since the former value is essentially in agreement with all the experimental data considered by the CODATA Key Values Task Group, Cox *et al.* [89COX/WAG]. The derived enthalpy of formation of $Cs_2NaAmCl_6$(cr) is

$$\Delta_f H^\circ_m(\mathrm{Cs_2NaAmCl_6, cr, 298.15\,K}) = -(2315.8 \pm 1.8)\ \mathrm{kJ \cdot mol^{-1}}.$$

The standard entropy and heat capacity at 298.15 K have been estimated in this review by assuming that the differences from sums of the constituent chlorides are close to zero:

$$\begin{aligned} S^\circ_m(\mathrm{Cs_2NaAmCl_6, cr, 298.15\,K}) &= (440 \pm 15)\ \mathrm{kJ \cdot mol^{-1}} \\ C^\circ_{p,m}(\mathrm{Cs_2NaAmCl_6, cr, 298.15\,K}) &= (260 \pm 15)\ \mathrm{kJ \cdot mol^{-1}}. \end{aligned}$$

The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy.

$$\Delta_f G^\circ_m(Cs_2NaAmCl_6, cr, 298.15\,K) = -(2164.8 \pm 4.9)\ kJ \cdot mol^{-1}$$

V.4.2.3.5. Molten salt systems

There are a number of studies on the distribution of actinides in molten chlorides [74MAR/SPI, 91MAR] and on the electrochemical processing of actinides in molten Cd/KCl-LiCl eutectic mixtures [92KOY/JOH, 93ACK/SET] which contain data on partition coefficients. However these studies are outside the scope of this review and will not be considered further.

V.4.2.4. Americium bromides

Both the dibromide and tribromide of americium, as well as the trivalent oxybromide AmOBr(cr) have been well characterised. Baybarz [73BAY] reported that in the reaction of americium metal with sufficient $HgBr_2$(cr) to form approximately equal amounts of $AmBr_2$(cr) and $AmBr_3$(cr), the X-ray pattern of the product in fact contained no lines attributable to these compounds, but showed lines for an unidentified phase, similar to that obtained by the hydrogen reduction of $CfBr_3$(cr). This possible new phase clearly needs further investigation.

V.4.2.4.1. Americium dibromide

a) Crystal structure

Americium dibromide, prepared by the reaction of americium metal and $HgBr_2$(cr), has the tetragonal $EuBr_2$(cr) type crystal structure, space group P4/n, $a = 11.592 \times 10^{-10}$ m, $c = 7.121 \times 10^{-10}$ m [73BAY].

b) Thermodynamic data

There are no published thermodynamic data for this compound.

V.4.2.4.2. Americium tribromide

a) Crystal structure

Americium tribromide was first prepared on the microgramme scale by the action of $AlBr_3$(cr) on AmO_2(cr), and purified by sublimation [51FRI]. Milligramme amounts of the tribromide of the longer-lived ^{243}Am isotope were prepared by Asprey, Keenan and Kruse [65ASP/KEE] from $AmCl_3$(cr) and ammonium bromide at 672 to 723 K in a stream of hydrogen. Asprey *et al.* confirmed the crystal structure, first reported by Zachariasen [48ZAC], to be the orthorhombic $PuBr_3$(cr) type, space group Cmcm,

with $a = 4.064 \times 10^{-10}$ m, $b = 12.66 \times 10^{-10}$ m, $c = 9.144 \times 10^{-10}$ m.

b) Thermodynamic data

The standard enthalpy of formation and standard entropy were estimated by Fuger *et al.* [83FUG/PAR] by the procedure noted in the introduction (Section V.4.2.1.1) and are accepted in this review.

$$\begin{aligned} \Delta_f H^\circ_m(AmBr_3, cr, 298.15\,K) &= -(810\pm10)\ kJ \cdot mol^{-1} \\ S^\circ_m(AmBr_3, cr, 298.15\,K) &= (205\pm17)\ J \cdot K^{-1} \cdot mol^{-1}. \end{aligned}$$

The Gibbs energy of formation calculated from these values is

$$\Delta_f G^\circ_m(AmBr_3, cr, 298.15\,K) = -(787 \pm 11)\ kJ \cdot mol^{-1}.$$

V.4.2.4.3. Americium oxybromide

a) Crystal structure

Americium oxybromide AmOBr(cr) has the tetragonal PbFCl(cr) type crystal structure, space group P4/nmm, $a = 3.982 \times 10^{-10}$ m, $c = 7.644 \times 10^{-10}$ m [79WEI/WIS]. This is the structural type in which all the known MOX actinide oxyhalides crystallise.

b) Thermodynamic data

The equilibrium constant of the reaction

$$AmBr_3(cr) + H_2O(g) \rightleftharpoons AmOBr(cr) + 2\,HBr(g) \qquad (V.22)$$

was studied by Weigel, Wishnevsky and Guldner [82WEI/WIS] from 719 to 890 K. The equilibrium constants from this study are fitted to the linear expression,

$$\log_{10} K_p(V.22,\ 719 \text{ to } 890\,K) = 6.671 - 4408.3/T(bar)$$

corresponding to

$$\Delta_r G^\circ_m(V.22,\ 719 \text{ to } 890\,K) = (84396 + 127.72\ T)\ kJ \cdot mol^{-1}$$

for the Gibbs energy for the above reaction. It will be seen that the equilibrium constants for the bromide hydrolysis are almost identical with those for the corresponding reaction involving the chlorides, being on average about 15% lower in the temperature range studied.

The heat capacity change for this reaction is assumed to be the same as that estimated for the reaction involving chlorides, so the differences to convert to enthalpy and entropy values at 298.15 K are similar:

$$\Delta_r H^\circ_m(\text{V.22}, 805\,\text{K}) - \Delta_r H^\circ_m(\text{V.22}, 298.15\,\text{K}) = -1860 \quad \text{J} \cdot \text{mol}^{-1}$$
$$\Delta_r S^\circ_m(\text{V.22}, 805\,\text{K}) - \Delta_r S^\circ_m(\text{V.22}, 298.15\,\text{K}) = -3.71 \quad \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

With the values given above for $AmBr_3$(cr) and CODATA Key Values for H_2O(g) and HBr(g) [89COX/WAG] (*cf.* Table IV.1), the final values for AmOBr(cr) are

$$\Delta_f H^\circ_m(\text{AmOBr, cr}, 298.15\,\text{K}) = -(893 \pm 12)\ \text{kJ} \cdot \text{mol}^{-1}$$
$$S^\circ_m(\text{AmOBr, cr}, 298.15\,\text{K}) = (128 \pm 20)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

These values are slightly different from those selected in the review by Fuger *et al.* [83FUG/PAR] who used a constant heat capacity difference of 6.3 $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for the hydrolysis reaction (V.22). The major contribution to the uncertainties given is indeed the heat capacity correction.

The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy.

$$\Delta_f G^\circ_m(\text{AmOBr, cr}, 298.15\,\text{K}) = -(861 \pm 13)\ \text{kJ} \cdot \text{mol}^{-1}$$

V.4.2.5. Americium iodides

Both the diiodide and triiodide of americium, as well as the trivalent oxyiodide AmOI(cr) have been well characterised.

V.4.2.5.1. Americium diiodide

a) Crystal structure

Americium diiodide is prepared [72BAY/ASP] by the action of HgI_2(cr) on americium metal. The divalency of americium in this compound was confirmed by magnetic susceptibility measurements. It has the monoclinic EuI_2(cr) type crystal structure, space group Pc, P2/c or $P2_1/c$, $a = 7.677 \times 10^{-10}$ m, $b = 8.311 \times 10^{-10}$ m, $c = 7.925 \times 10^{-10}$ m, $\beta = 98.5°$.

b) Thermodynamic data

There are no published thermochemical data for this compound, but Baybarz *et al.* [72BAY/ASP] reported that it melts with decomposition at ~973 K.

V.4.2.5.2. Americium triiodide

a) Crystal structure

Based on microgramme samples of the strong γ-emitting ^{241}Am isotope, americium triiodide prepared by Fried [51FRI] from americium dioxide and AlI_3(cr) was first reported [48ZAC] to crystallise in the orthorhombic $PuBr_3$(cr) type structure. However, in more recent work using the more easily handled ^{243}Am isotope, Asprey, Keenan

and Kruse [64ASP/KEE, 65ASP/KEE] prepared AmI_3(cr) from $AmCl_3$(cr) and ammonium iodide at 672 to 723 K in a stream of hydrogen; its structure was found to be hexagonal BiI_3(cr) type. They were unable to convert this to an orthorhombic phase, at any temperature from 673 to 1173 K. More recently Haire *et al.* [83HAI/YOU] have shown that the triiodide prepared from the metal and iodine at 300°C has the orthorhombic $PuBr_3$(cr) structure, while samples prepared from $AmBr_3$(cr) or $AmCl_3$(cr) and HI(g) above 600°C had the hexagonal BiI_3(cr) structure. There is a reversible transition between the polymorphs at 673 ± 30 K, but the conversion of the high temperature hexagonal phase to the low temperature orthorhombic phase is very sluggish, so the hexagonal phase can easily be quenched to room temperature, *e.g.* from the melt. Subsequently Haire *et al.* [85HAI/BEN] showed that the conversion of the hexagonal structure to the orthorhombic also occurs by the imposition of a pressure of $\sim$ 2 GPa at ambient temperature, in accord with the considerably smaller molar volume of the latter.

The lattice parameters for the two phases given by [83HAI/YOU] are:

- low temperature phase, orthorhombic $PuBr_3$(cr) type, space group CmCm, $a = 4.28 \times 10^{-10}$ m, $b = 13.94 \times 10^{-10}$ m, $c = 9.974 \times 10^{-10}$ m.
- high temperature phase, hexagonal BiI_3(cr) type, space group $R\overline{3}$, $a = 7.637 \times 10^{-10}$ m, $c = 20.91 \times 10^{-10}$ m.

Their parameters for the orthorhombic phase agree with those reported by Zachariasen [48ZAC] within the rather large uncertainties of the latter; those of the hexagonal phase are appreciably greater (by 1.8 and 2.9%) than those reported by Asprey and co-workers [64ASP/KEE, 65ASP/KEE]. The reason for this discrepancy is not known – both studies utilized the longer-lived ^{243}Am isotope, so radiation damage is not likely to be the cause.

b) Enthalpy of formation and entropy

The standard enthalpy of formation and standard entropy were estimated by Fuger *et al.* [83FUG/PAR] by the procedure noted in the introduction and are selected in this review.

$$\begin{aligned} \Delta_f H^\circ_m(AmI_3, cr, 298.15\,K) &= -(612 \pm 7)\ kJ \cdot mol^{-1} \\ S^\circ_m(AmI_3, cr, 298.15\,K) &= (234 \pm 20)\ J \cdot K^{-1} \cdot mol^{-1}. \end{aligned}$$

The Gibbs energy of formation derived from these values is

$$\Delta_f G^\circ_m(AmI_3, cr, 298.15\,K) = -(613 \pm 9)\ kJ \cdot mol^{-1}.$$

V.4.2.5.3. Americium oxyiodide

a) Crystal structure

Baybarz *et al.* [72BAY/ASP] prepared americium oxyiodide by heating AmI_2(cr) in moist air at $\sim$673 K. AmOI(cr) has the tetragonal PbFCl(cr) type crystal structure,

space group P4/nmm, $a = 4.011 \times 10^{-10}$, $c = 9.204 \times 10^{-10}$ m [72BAY/ASP]. This is the structural type in which all the known MOX actinide oxyhalides crystallise.

b) Thermodynamic data

There are no published thermodynamic data for this compound.

V.5. Group 16 (chalcogen) compounds and complexes

There are no experimental studies involving the thermodynamic properties for americium chalcogenides, so this review summarizes the preparative and structural data for these phases, but includes a few estimated values for the entropies of the monochalcogenides.

V.5.1. Sulphur compounds and complexes

V.5.1.1. Americium sulphides

The monosulphide, a "substoichiometric sesquisulphide" (with a composition close to Am_3S_4(cr)), the true sesquisulphide and the substoichiometric disulphide are known. The so-called β-sesquisulphide is treated with the oxysulphides.

V.5.1.1.1. AmS(cr)

Damien [71DAM] obtained a phase with the fcc NaCl(cr) type structure, space group Fm3m, mixed with the Am_3S_4(cr) phase, (which Damien called γ-Am_2S_3), by heating the sesquisulphide in vacuum ($\sim 10^{-5}$ Torr) at 650°C. By analogy with other actinide elements, this was assumed to be the monosulphide, but the precise composition is not known. The lattice parameter of this presumably sulphur-saturated composition was 5.592×10^{-10} m.

The lattice parameter of the single-phase AmS(cr) prepared by Charvillat *et al.* [76CHA/BEN] from stoichiometric amounts of americium hydride and sulphur was 5.600×10^{-10} m. These authors also prepared the diphasic mixture of AmS(cr) + Am_3S_4(cr) after Damien, finding a lattice parameter increasing from 5.592×10^{-10} to 5.618×10^{-10} m as the annealing temperature was increased from 800°C to 1100°C. This may indicate an appreciable range of homogeneity for this phase.

During this heating, there was a continuous loss of weight, and at 1300°C, no monosulphide was present. This may be due to preferential loss of Am(g) from the monosulphide:

$$4\,\mathrm{AmS(cr)} \rightleftharpoons \mathrm{Am_3S_4(cr)} + \mathrm{Am(g)}$$

or loss of AmS(g). The former seems more likely, since as Damien [71DAM] noted, the decomposition of Am_2S_3(cr) at as low a temperature as 650°C implies that Am_2S_3(cr) is appreciably less stable than the corresponding Pu and Np compounds. This,

together with the higher volatility of elemental Am, could lead to the congruently vaporising composition in this system being near Am_3S_4(cr).

There are no experimental thermodynamic data for AmS(cr), but Grønvold, Drowart and Westrum [84GRO/DRO] estimated the standard entropy to be

$$S^\circ_m(\mathrm{AmS, cr}, 298.15\,\mathrm{K}) \quad = \quad (92 \pm 12)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}},$$

based on estimated lattice and magnetic contributions of 75.3 [62WES/GRO] and 16.7 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively.

V.5.1.1.2. Am_2S_3(cr)

Damien [71DAM] prepared Am_2S_3(cr) on the 50 mg scale by heating americium hydride with the stoichiometric amount of sulphur at 500°C. Reaction was complete in four days to give a black powder with an X-ray pattern which could be indexed as an orthorhombic cell, with $a = 7.39 \times 10^{-10}$, $b = 3.98 \times 10^{-10}$ and $c = 15.36 \times 10^{-10}$ m. The structure is assumed to be the same as that of Pu_2S_3(cr), namely the α-Ce_2S_3 type space group. The sample probably contained some Am_3S_4(cr).

There are no experimental thermodynamic data for Am_2S_3(cr), but Moskvin [73MOS, 73MOS2] has estimated the standard entropy and heat capacity of Am_2S_3(cr) to be 133 and 244 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively. These are appreciably different from the experimental values for U_2S_3(cr) [84GRO/DRO], 190 and 133.7 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and may not be very reliable.

V.5.1.1.3. Am_3S_4(cr)

This phase was first identified by Zachariasen [48ZAC, 49ZAC2]; it has the cubic Th_3P_4(cr) structure. More recently it has been prepared by Damien [71DAM] (who called it γ-Am_2S_3), by the decomposition of the sesquisulphide in vacuum. Further work by Charvillat *et al.* [76CHA/BEN] showed that the lattice parameter of this phase increases with the temperature of decomposition, suggesting that it probably has a range of composition. Even the highest lattice parameter found by [76CHA/BEN] (8.434×10^{-10} m by decomposition at 1300°C) is appreciably lower than found by Zachariasen (8.445×10^{-10} m).

V.5.1.1.4. AmS_2(cr)

When Damien and Jove [71DAM/JOV] heated americium hydride with excess sulphur in a Pyrex tube at 400°C for one week, they found a coarse black material which contained a tetragonal phase with $a = 3.938 \times 10^{-10}$ and $c = 7.981 \times 10^{-10}$ m. The intensities of the X-ray pattern suggest that this phase has a pseudo-cell of the Cu_2Sb(cr) type, space group P4/nmm similar to the substoichiometric plutonium disulphide, with the composition $MS_{1.9}$(cr). No analysis of the compound was made, so the exact composition is not known.

V.5.1.1.5. Americium Oxysulphides

There are two oxysulphides known, Am_2O_2S(cr), and a phase related to the sesquisulphide, $Am_{10}OS_{14}$(cr).

a) Am_2O_2S(cr)

This phase was prepared by Haire and Fahey [77HAI/FAH] by reducing Am(III) oxysulphate $Am_2O_2SO_4$(cr) in H_2/Ar at $\sim$ 800°C. Well-crystallised samples were obtained in as short a time as 2 h. Am_2O_2S(cr) is isostructural with hexagonal La_2O_2S(cr), space group $P\bar{3}m$, with $a = 3.910 \times 10^{-10}$ and $c = 6.772 \times 10^{-10}$ m.

b) $Am_{10}OS_{14}$(cr)

This compound was prepared by Damien, Marcon and Jove [72DAM/MAR] by heating Am_2S_3(cr) americium disulphide in vacuum in a platinum crucible. Am_2S_3(cr) is formed at 850°C; on further heating to 1100°C, a tetragonal phase with $a = 14.87 \times 10^{-10}$ and $c = 19.73 \times 10^{-10}$ m is formed. The similar plutonium and lanthanide phases were first thought to be polymorphs of the sesquisulphides, but Carre, Laruelle and Besançon [70CAR/LAR] showed that they were oxysulphides with the composition $M_{10}OS_{14}$(cr), with space group $I4_1/acd$. The americium compound is assumed to be similar.

V.5.1.2. Americium sulphates

V.5.1.2.1. Aqueous americium sulphates

Yakovlev and Kosyakov [56YAK/KOS] first reported some qualitative spectrophotometric observations on the formation of americium-sulphate complexes. There are few reliable quantitative studies available in the literature on the americium(III) sulphate system, and all of them refer to solutions of low pH (pH $\leq$ 3.6, *cf.* Table V.12). Only extraction techniques such as cation exchange [60LEB/PIR, 64BAN/PAT, 67NAI, 68AZI/LYL, 68NAI] and solvent extraction [64SEK, 65SEK2, 67CAR/CHO, 68AZI/LYL, 78RAO/BAG, 80KHO/MAT] as well as electromigration [90ROS/REI] were used to determine the composition and the stability constants of the complexes formed. No solubility measurements were reported. $Am(SO_4)_n^{(3-2n)}$ (n = 1 and 2) and $Am(HSO_4)_2^+$ species have been suggested to interpret the various experimental data.

The data listed in Table V.12 refer to equilibria of the type

$$Am^{3+} + n\,SO_4^{2-} \rightleftharpoons Am(SO_4)_n^{(3-2n)}. \qquad \text{(V.23)}$$

The cation-exchange experiments performed by Lebedev, Pirozhkov and Yakovlev [60LEB/PIR] at $I = 0.75$ and 1.5 M were interpreted assuming the formation of the $AmSO_4^+$ and $Am(SO_4)_2^-$ complexes. The scarceness of the experimental data and the narrow concentration range investigated at $I = 1.5$ M does not allow a reliable

Table V.12: Literature equilibrium constants for the americium(III) sulphate system.

Method	Medium	pH	t(°C)	$\log_{10}\beta_1$	$\log_{10}\beta_2$	Reference
cix	1.5 M $NH_4(X^{(a)},SO_4)$	~ 4	20–25	1.76	2.11	[60LEB/PIR]
	0.75 M $NH_4(X^{(a)},SO_4)$			1.78		
cix	1 M $H(ClO_4,HSO_4)$	0	26±1	1.18	1.38	[64BAN/PAT]
	1 M $Na(ClO_4,SO_4)$	3		1.49	2.48	
dis	1 M $Na(ClO_4,SO_4)$	3–4	25	1.57±0.09	2.66±0.08	[64SEK, 65SEK2]
dis	2 M $Na(ClO_4,SO_4)$	3	25±0.1	1.43±0.06	1.85±0.12	[67CAR/CHO, 67CAR/CHO2]
dis	2 M $Na(ClO_4,SO_4)$	3	0	1.11±0.07	1.73±0.10	[67CAR/CHO2]
			40	1.58±0.07	2.03±0.12	
			55	1.65±0.06	2.38±0.10	
cix	1 M $H(ClO_4,HSO_4)$	0	27	1.22±0.01	(b)	[67NAI, 68NAI]
	1 M $Na(ClO_4,SO_4)$	3		1.49±0.01	2.36±0.01	
dis	0.5 M $Na(ClO_4,SO_4)$	3.6	25±0.5	1.86±0.01	2.83±0.02	[68AZI/LYL]
cix				1.86±0.01	2.80±0.03	
dis	$I \longrightarrow 0$	3	25±0.1	3.76±0.11	5.64±0.10$^{(c)}$	[72MCD/COL]
dis	1 M $H(ClO_4,HSO_4)$	0	25±0.1	1.82±0.01$^{(d)}$	3.12±0.01$^{(d)}$	[78RAO/BAG]
	2 M $H(ClO_4,HSO_4)$	−0.3		$1.711 \pm 0.004^{(d)}$	$3.04 \pm 0.01^{(d)}$	
dis	1 M $NH_4(ClO_4,SO_4)$	3	30	1.72±0.02		[80KHO/MAT]
em	0.1 M $Na(ClO_4,SO_4)$	2.8	25	2.50±0.3	3.6±0.4	[90ROS/REI]
		5.5		2.50±0.2	3.1±0.7	

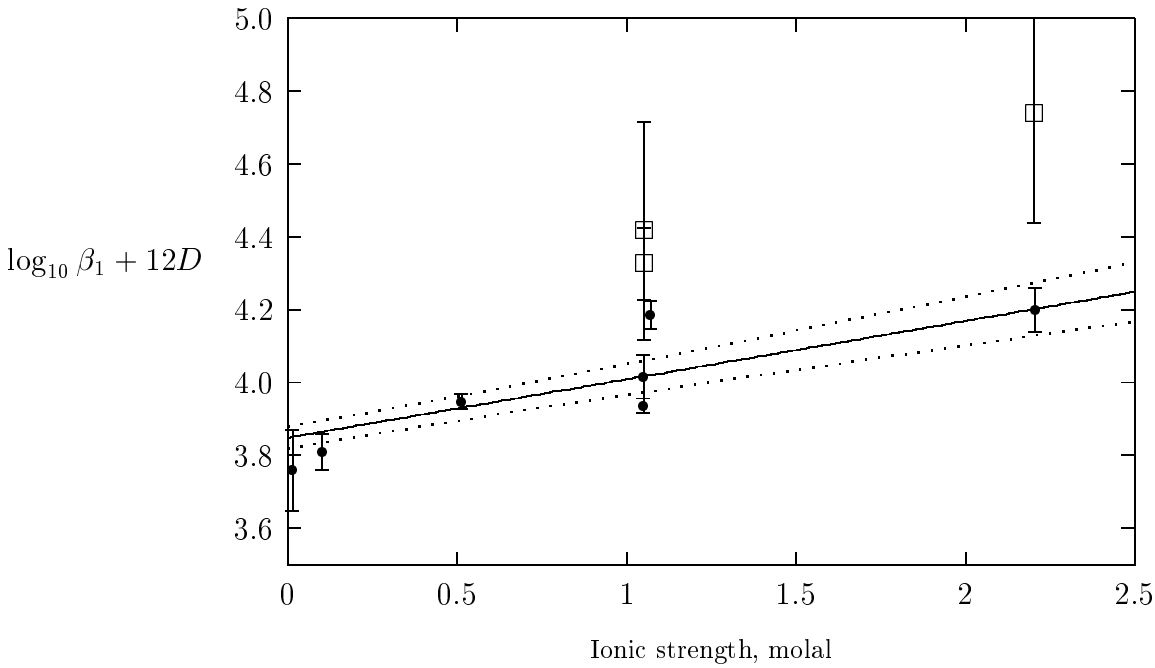
(a) Lebedev, Pirozhkov and Yakovlev [60LEB/PIR] report that the ionic strength was kept constant by addition of ammonium chloride or perchlorate.
(b) Nair reports $\log_{10} K = (0.54 \pm 0.03)$ for: $Am^{3+} + 2HSO_4^- = Am(H_2SO_4)_2^+$.
(c) McDowell and Coleman report $\log_{10}\beta_3^\circ = (5.29 \pm 0.05)$.
(d) The stability constants of Rao *et al.* [78RAO/BAG] for the reactions: $Am^{3+} + n\,HSO_4^- \rightleftharpoons Am(SO_4)_n^{(3-2n)} + n\,H^+$, were combined with the protonation constant of SO_4^{2-} used by Rao *et al.* ($\log_{10} K_1 = 1.18$ and 1.08 at $I = 1$ and 2 M respectively) to give the values presented in this Table.

determination of the the equilibrium constants which are therefore disregarded by this review. Furthermore, because the authors did not specify the composition of the ionic media used, the $\log_{10}\beta_1$ value at $I = 0.75$ M is not included in the extrapolation to $I = 0$ performed by this review.

Bansal, Patil and Sharma's results [64BAN/PAT] are not selected by this review, as the reported values refer to unpublished work by Nair and Welch.

Nair [67NAI, 68NAI] used a dissociation constant of HSO_4^- not consistent with the auxiliary data adopted in the NEA reviews, and therefore his experimental data are reinterpreted using $\log_{10} K_1 = (1.22 \pm 0.03)$ at $I = 1$ M. The results obtained at pH = 3 are not affected by the acid constant. At pH = 0, the dependence of the partition data with $[SO_4^{2-}]$ indicates the presence of $AmSO_4^+$. There is no evidence of $Am(HSO_4)_2^+$ formation; thus, this review does not support the existence of the americium hydrogen-sulphate complexes.

Figure V.9: Extrapolation to $I = 0$ of experimental data for the equilibrium constants of formation of $AmSO_4^+$, according to reaction (V.23), using the specific ion interaction equations (*cf.* Appendix B). Both experiments with $[H^+] \geq 1$ M (□) and $[H^+] \leq 1$ mM (•) are plotted. The result of the weighted linear regression for the experiments with $[H^+] \leq 1$ mM is shown as a straight line, and the dotted lines represent the uncertainty range.



Reinterpretation of the solvent extraction data of Rao *et al.* [78RAO/BAG] using an acid constant for HSO_4^- consistent with the data in Chapter IV, leads to slightly different formation constants (*cf.* Appendix A).

The re-evaluated values from Refs. [67NAI, 68NAI, 78RAO/BAG] and the equilibrium constants from all other references listed in Table V.12 except [60LEB/PIR, 64BAN/PAT] are converted to molal units to perform an extrapolation using the specific ion interaction equations of Appendix B. The corrected stability constants obtained at $[H^+] \geq 1$ M (□, Figure V.9) and $[H^+] \leq 1$ mM (•, Figure V.9) seem not to belong to the same parent distribution. The apparent discrepancy, between pH ≤ 0 and pH ≈ 3 data, may be attributed to the difference in ionic media used ($H^+/HSO_4^-/ClO_4^-$ and $Na^+/SO_4^{2-}/ClO_4^-$). The lack of data obtained in concentrated acid solutions does not allow a reliable estimate of the pH influence on the sum of ion interaction coefficients, $\Delta\varepsilon$, and even though the results of Rao *et al.* [78RAO/BAG] ($I = 1$ and 2 M $H^+/HSO_4^-/ClO_4^-$) are considered satisfactory by this review, they will not be included in the extrapolation to $I = 0$. The weighted linear regression, performed on pH ≥ 3 data, results in

$$\log_{10}\beta_1^\circ(\text{V.23}, 298.15\,\text{K}) \;=\; 3.85 \pm 0.03$$

and $\Delta\varepsilon_1 = (-0.16 \pm 0.03)\,\text{kg}\cdot\text{mol}^{-1}$. The selected value for $\log_{10}\beta_1^\circ$ is close to

Table V.13: Values of the formation constants for $Am(SO_4)_2^-$ obtained at pH$\approx$ 3 extrapolated to $I = 0$. The equilibrium constants, reported in Table V.12 in molar units, have been converted to molal units in accordance with Eq. (II.32). The $\pm$ terms correspond to a 95% uncertainty.

Reference	Medium	t/(°C)	$\log_{10}\beta_2$	$\log_{10}\beta_2^\circ$
[64SEK, 65SEK2]	1 M $Na(ClO_4,SO_4)$	25	2.62 ± 0.05	5.72 ± 0.10
[67CAR/CHO]	2 M $Na(ClO_4,SO_4)$	25	1.76 ± 0.12	4.92 ± 0.22
[67NAI, 68NAI]	1 M $Na(ClO_4,SO_4)$	27	2.32 ± 0.05	5.42 ± 0.10
[68AZI/LYL]	0.5 M $Na(ClO_4,SO_4)$	25	2.81 ± 0.04	5.57 ± 0.06

the value ($\log_{10}\beta_1^\circ = 3.82$) obtained by Bidoglio *et al.* [87BID/TAN] and to the equilibrium constant determined experimentally at $I \leq 0.1$ M by McDowell and Coleman [72MCD/COL]. The slight difference is due to the fact that Bidoglio performed the regression to $I = 0$ using molar (instead of molal) units for the ionic strength. From the determined value of $\Delta\varepsilon_1$ and the ion interaction coefficients $\varepsilon_{(Am^{3+},ClO_4^-)}$ and $\varepsilon_{(Na^+,SO_4^{2-})}$ given in Appendix B this review obtains: $\varepsilon_{(AmSO_4^+,ClO_4^-)} = (0.22 \pm 0.08)\,\mathrm{kg \cdot mol^{-1}}$, which is in good agreement with the selected estimate for ε-values for the interaction between perchlorate and complexes of americium with electric charge of +1 (*cf.* Section B.1.4).

No reliable extrapolation to $I = 0$ M can be obtained from the scattered $Am(SO_4)_2^-$ formation constants. Furthermore, no evidence of $Am(SO_4)_2^-$ was found in the pH$\approx$ 0 results reported in [68NAI], which is in contradiction with the study of [78RAO/BAG], performed under similar conditions, *cf.* Appendix A. As there is no apparent reason for such discrepancy, this review extrapolates to zero ionic strength only the values of $\log_{10}\beta_2$ obtained at pH ≈ 3, using the specific ion interaction equations of Appendix B, and $\Delta\varepsilon_2 = (-0.30 \pm 0.08)\,\mathrm{kg \cdot mol^{-1}}$. The results are presented in Table V.13. The values of Sekine [64SEK, 65SEK2], Nair [67NAI, 68NAI] and Khopkar and Mathur [80KHO/MAT] do not agree with the data by De Carvalho and Choppin [67CAR/CHO]. Because there is no apparent reason to prefer one set of data over the other, an unweighted average of all these equilibrium constants is selected, and the uncertainty assigned to cover the range of expectation of all selected values:

$$\log_{10}\beta_2^\circ(\mathrm{V.23}, 298.15\,\mathrm{K}) \quad = \quad 5.4 \pm 0.7.$$

which is in good agreement with the value experimentally determined by McDowell and Coleman [72MCD/COL].

It should be mentioned that the experimental data used for these calculations refer

to slightly different temperatures (*cf.* Table V.13). However, the study of De Carvalho and Choppin [67CAR/CHO2] shows that the temperature effects on the values of the equilibrium constants are not large in this temperature range.

The selected Gibbs energies of formation are calculated to be

$$\begin{aligned} \Delta_f G^\circ_m(AmSO_4^+, aq, 298.15\,K) &= -(1364.7 \pm 4.8)\ kJ \cdot mol^{-1} \\ \Delta_f G^\circ_m(Am(SO_4)_2^-, aq, 298.15\,K) &= -(2117.5 \pm 6.3)\ kJ \cdot mol^{-1}\ . \end{aligned}$$

The equilibrium constants reported by De Carvalho and Choppin [67CAR/CHO, 67CAR/CHO2] (*cf.* Table V.12) are used to determine the enthalpy and entropy changes. A weighted linear regression of "$\ln \beta_n$ *vs.* $1/T(K^{-1})$" leads to the following non-standard values:

$$\begin{aligned} \Delta_r H_m(V.23, n = 1, 298.15\,K) &= (17.0 \pm 3.2)\ kJ \cdot mol^{-1} \\ \Delta_r S_m(V.23, n = 1, 298.15\,K) &= (84 \pm 10)\ J \cdot K^{-1} \cdot mol^{-1} \\ \\ \Delta_r H_m(V.23, n = 2, 298.15\,K) &= (19.0 \pm 11)\ kJ \cdot mol^{-1} \\ \Delta_r S_m(V.23, n = 2, 298.15\,K) &= (102 \pm 36)\ J \cdot K^{-1} \cdot mol^{-1} \end{aligned}$$

at $I = 2$ M, pH = 3 and 298.15 K. The values for the formation of $AmSO_4^+$ agree with $\Delta_r H_{m,1} = (18.4 \pm 3.3)$ kJ·mol^{-1} and $\Delta_r S_{m,1} = (88 \pm 13)$ J·K^{-1}·mol^{-1} reported in Ref. [67CAR/CHO2].

V.5.1.2.2. Solid americium sulphates

Hydrated and anhydrous Am(III) sulphates, $Am_2(SO_4)_3 \cdot nH_2O(cr)$ ($n = 0, 5, 8$), and the trivalent oxysulphate $(AmO)_2SO_4(cr)$, have been prepared. Yellow-pink crystals of $Am_2(SO_4)_3 \cdot 8H_2O(cr)$ were obtained by evaporation of a 5 M solution; they crystallise in the monoclinic system, space group C2/c with $a = 13.619 \times 10^{-10}$ m, $b = 6.837 \times 10^{-10}$ m, $c = 18.405 \times 10^{-10}$ m, $\beta = 102.67°$ [72BUR/BAY]. On the basis of analyses for Am, SO_4^{2-} and water Yakovlev *et al.* [58YAK/GOR] suggested the precipitate obtained by the addition of ethanol to a solution of Am(III) in 0.5 M H_2SO_4 was the pentahydrate; no further characterization was made. Hall and Markin [57HAL/MAR] have reported thermogravimetric results for the dehydration of $Am_2(SO_4)_3$ hydrates, and showed that the sulphate content of the white product formed at 550 - 650°C corresponded to anhydrous Am(III) sulphate. The oxysulphate of Am(III), $(AmO)_2SO_4(cr)$, was obtained by Haire and Fahey [77HAI/FAH] by stopping the calcination of the Am(III) sulphate hydrates in air at $\sim$ 750°C; it has a body-centered orthorhombic crystal structure with $a = 4.225 \times 10^{-10}$ m, $b = 4.103 \times 10^{-10}$ m, $c = 13.328 \times 10^{-10}$ m. The precise space group has not been established.

Fedoseeva and Budantseva [89FED/BUD] suggest the product of nitrite reduction of Am(VI) sulphate solutions at unknown pH to be an unspecified hydrate of the Am(V) sulphate. However the X-ray diffraction pattern of this phase was quite distinct from the well-established Np(V) analogue, so this identification is far from certain.

Yakovlev and Kosyakov [58YAK/KOS] reported the existence of Am(III) double sulphates of type $M\mathrm{Am(SO_4)_2} \cdot x\mathrm{H_2O(s)}$ (with M = K, Rb, Cs and Tl) as well as $\mathrm{K_3Am(SO_4)_3} \cdot \mathrm{H_2O(s)}$, $\mathrm{K_8Am_2(SO_4)_7(s)}$ and $\mathrm{Tl_8Am_2(SO_4)_7(s)}$.

V.5.2. Selenium compounds

V.5.2.1. Selenides

The monoselenide, a "substoichiometric sesquiselenide" (with a composition close to $\mathrm{Am_3Se_4}$) and the substoichiometric diselenide are known.

V.5.2.1.1. AmSe(cr)

Damien and Wojakowski [75DAM/WOJ], and Charvillat *et al.* [76CHA/BEN] prepared a phase with the fcc NaCl(cr) type structure, space group Fm3m, mixed with the $\mathrm{Am_3Se_4(cr)}$ phase, by heating the hydride with selenium in equimolar ratio at 800°C in vacuum ($\sim 10^{-5}$ Torr) for 24 h, followed by annealing the products in alumina crucibles at 1100°C. By analogy with other actinide elements, this was assumed to be the monoselenide, but the precise composition is not known. The lattice parameter of this presumably selenium-saturated composition was 5.821×10^{-10} m. On further heating to 1250°C, the monoselenide was no longer observed.

There are no experimental thermodynamic data for AmSe(cr), but Grønvold, Drowart and Westrum [84GRO/DRO] estimated the standard entropy to be

$$S^{\circ}_{\mathrm{m}}(\mathrm{AmSe, cr}, 298.15\,\mathrm{K}) \quad = \quad (109 \pm 12)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}},$$

based on estimated lattice and magnetic contributions of 92.1 [62WES/GRO] and 16.7 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively.

V.5.2.1.2. Am_3Se_4(cr)

Mitchell and Lam [70MIT/LAM] first prepared this phase, mixed with another unidentified phase, from equimolar amounts of americium and selenium heated first to $\sim$ 200°C, and annealed at 1000 and then 800°C. The major phase had a bcc structure. $\mathrm{Th_3P_4}$-type, space group $\mathrm{I\bar{4}3}d$, $a = 8.782 \times 10^{-10}$ m, and was assumed to be $\mathrm{Am_3Se_4(cr)}$. Damien and Wojakowski [75DAM/WOJ], and Charvillat *et al.* [76CHA/BEN] also prepared this phase together with AmSe(cr) by reacting americium hydride with selenium and annealing at 1100°C. They report a somewhat larger lattice parameter of 8.799×10^{-10} m.

V.5.2.1.3. $AmSe_2$(cr)

When Damien and Jove [71DAM/JOV] heated americium hydride with excess selenium in a Pyrex tube at 673 K for one week they found a coarse black material which contained a tetragonal phase with $a = 4.096 \times 10^{-10}$ and $c = 8.347 \times 10^{-10}$ m.

The intensities of the X-ray pattern suggest that this phase has a pseudo-cell of the Cu_2Sb(cr) type, space group P4/nmm, similar to the substoichiometric plutonium diselenide, with the composition $MSe_{1.8}$(cr). No analysis of the compound was made, so the exact composition is not known.

V.5.3. Tellurium compounds

V.5.3.1. Tellurides

The monotelluride, Am_3Te_4(cr), the sesquitelluride, the substoichiometric ditelluride and the tritelluride have been identified.

V.5.3.1.1. AmTe(cr)

Damien and Wojakowski [75DAM/WOJ], and Charvillat *et al.* [76CHA/BEN] prepared a phase with the fcc NaCl(cr) type structure, space group Fm3m, mixed with the Am_3Te_4(cr) phase, by heating the hydride with tellurium in equimolar ratio at 800°C in vacuum ($\sim 10^{-5}$ Torr) for 24 h, followed by annealing the products in alumina crucibles at 1200°C. By analogy with other actinide elements, this was assumed to be the monotelluride, but the precise composition is not known. The lattice parameter of this presumably tellurium-saturated composition was 6.171×10^{-10} m.

There are no experimental thermodynamic data for AmTe(cr), but Grønvold, Drowart and Westrum [84GRO/DRO] estimated the standard entropy to be

$$S^\circ_{\mathrm{m}}(\mathrm{AmTe, cr}, 298.15\,\mathrm{K}) \quad = \quad (121 \pm 12)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}},$$

based on estimated lattice and magnetic contributions of 104.6 [62WES/GRO] and 16.7 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively.

V.5.3.1.2. Am_3Te_4(cr)

Mitchell and Lam [70MIT/LAM] first prepared this phase, mixed with another unidentified phase, from equimolar amounts of americium and tellurium heated first to $\approx$ 420°C, and annealed at 1000 and then 800°C. The major phase had a bcc structure, Th_3P_4-type, space group I$\bar{4}$3d, $a = 9.393 \times 10^{-10}$ m and was assumed to be Am_3Te_4(cr).

Damien and Wojakowski [75DAM/WOJ], Charvillat *et al.* [76CHA/BEN] also prepared this phase together with AmTe(cr) by reacting americium hydride with tellurium and annealing at 1100°C. They reported a rather larger lattice parameter of 9.404×10^{-10} m. This phase is also the decomposition product of higher americium tellurides above 900°C [72DAM/CHA]. They suggested that this phase has an appreciable range of homogeneity, since its lattice parameter increased with annealing temperature from 9.382×10^{-10} m at 900°C to 9.420×10^{-10} m at 1100°C.

V.5.3.1.3. $AmTe_2(cr)$

Damien [72DAM] obtained a tetragonal phase with $a = 4.366 \times 10^{-10}$ and $c = 8.969 \times 10^{-10}$ m by thermal dissociation of $AmTe_3$(cr) in vacuum at 400°C. The intensities of the X-ray pattern suggest that this phase has a pseudo-cell of the Cu_2Sb(cr) type, space group P4/nmm, similar to the substoichiometric plutonium ditelluride. No analysis of the compound was made, so the exact composition is not known, but by analogy with $PuTe_{2-x}$(cr) it was assumed to be substoichiometric. Subsequently Burns, Damien and Haire [79BUR/DAM] prepared $^{243}AmTe_{2-x}$(cr) from the elements at 550°C for 20 h and removing excess Te by distillation. Refinement of the crystal structure was consistent with 27% vacancies in one of the two Te lattices, suggesting the composition was $AmTe_{1.73}$(cr). The lattice parameters of the tetragonal cell were $a = 4.358 \times 10^{-10}$ and $c = 9.027 \times 10^{-10}$ m.

V.5.3.1.4. $AmTe_3(cr)$

Damien [72DAM] obtained a tetragonal phase with $a = 4.339 \times 10^{-10}$ and $c = 2.557 \times 10^{-9}$ m by vapour phase reaction of excess Te (Te/Am = 3.5) and americium hydride at 350°C for 5 d. After removal of unreacted Te by distillation, the weight increase corresponded to a composition of $AmTe_3$. However, the line intensities suggested that the phase is isostructural with $NdTe_3$(cr) (Norling and Steinfink [66NOR/STE]) and that its true symmetry is orthorhombic, space group Cmcm, with the a and b parameters essentially equal.

V.5.3.2. Americium oxytelluride

In their study of the thermal decomposition of $AmTe_2$(cr), Charvillat and Damien [72DAM/CHA] found that in the X-ray pattern of the major component Am_3Te_4(cr) obtained by heating to 900°C, there were four additional lines with d-spacings close to those of four of the strongest lines of Pu_2O_2Te(cr). It seems likely therefore that Am_2O_2Te(cr) was formed, presumably by reaction with silica, in this study.

V.6. Group 15 compounds and complexes

V.6.1. Nitrogen compounds and complexes

There are no experimental studies involving the thermodynamic properties for americium pnictides, so this review summarizes the preparative and structural data for these phases.

V.6.1.1. Americium nitrides

Only the mononitride has been identified. As noted below, even in the presence of ammonia/hydrogen mixtures, which correspond to quite high effective nitrogen pressures, no higher nitrides were found that correspond to those in the earlier actinide element-nitrogen systems.

Akimoto [67AKI] was the first to report the preparation of a phase with the NaCl(cr) structure, space group Fm3m, by heating, in sealed quartz tubes, either americium hydride and ammonia at 800°C for 30 minutes, or americium powder (obtained by decomposition of the hydride) with nitrogen at 750°C for 1 h. Since only 100μg of Am was used, no further analysis was possible. The lattice parameters of the black products, assumed to be AmN(cr), were 5.000×10^{-10} and 5.005×10^{-10} m respectively, with an uncertainty of 0.005×10^{-10} m.

Charvillat *et al.* [75CHA/BEN, 76CHA/BEN] repeated the preparation from nitrogen (600 Torr pressure, 550°C, 12 h) finding a phase with the slightly smaller lattice parameter of $(4.995 \pm 0.002) \times 10^{-10}$ m, as have Radchenko *et al.* [82RAD/RYA] using 70% N_2(g) + 30% H_2(g) at 800°C, who found $a = (4.991 \text{ to } 4.993) \times 10^{-10}$ m for the single phase products. In neither of these studies were any further analyses carried out.

It is clear from the method of preparation that these "mononitride" phases may well contain dissolved oxygen.

V.6.1.2. Americium azide complexes

A preliminary report by Cuillerdier, Musikas and Marteau [77CUI/MUS] on the complex formation between americium(III) and azide ions, was followed by Ph.D. thesis [81CUI] and the publications by Musikas *et al.* [80MUS/MAR, 83MUS/CUI], which report that solvent extraction experiments yielded $\log_{10}\beta_1 = 1.3$, $\log_{10}\beta_2 = 1.6$ and $\log_{10}\beta_3 = 1.4$, and absorption spectrophotometric measurements resulted in $\log_{10}\beta_1 = 1.0$ and $\log_{10}\beta_2 = 1.4$. The papers by Musikas *et al.* indicate that the spectrophotometric experiments were performed at $I = 5$ M, without stating clearly which background electrolyte was used, although Cuillerdier [81CUI] indicates that sodium perchlorate was employed.

Choppin and Barber [89CHO/BAR] performed a solvent extraction study at pH = 5.9 and $I = 0.5$ M $NaClO_4$, involving a few rare earths and actinides. For americium, they obtained $\log_{10}\beta_1 = (0.67 \pm 0.05)$ at 25°C. Choppin and Barber obtained $\Delta_r H_m(CmN_3^{2+}, I = 0.5) = (15.1 \pm 2.8)$ kJ · mol^{-1} from a temperature variation study involving Cm^{3+}.

The specific ion interaction equations (*cf.* Appendix B) are not appropriate to perform ionic strength extrapolations for the study reported in [80MUS/MAR, 81CUI, 83MUS/CUI], and the constant reported by Choppin and Barber [89CHO/BAR] is adopted. A value of $\Delta\varepsilon = -(0.1 \pm 0.1)$ kg · mol^{-1} is derived from the following estimates: $\varepsilon_{(AmN_3^{2+},ClO_4^-)} \approx \varepsilon_{(AmOH^{2+},ClO_4^-)} = (0.39 \pm 0.04)$ (*cf.* Section B.1.4), and $\varepsilon_{(N_3^-,Na^+)} = (0.0 \pm 0.1)$ [92GRE/FUG, *p*.267]. This review assumes that the uncertainties reported in [89CHO/BAR] are ±1 standard deviation. The ionic strength correction yields:

$$\log_{10}\beta_1^\circ(298.15\,\mathrm{K}) = 1.67 \pm 0.10$$

where the uncertainty has been increased to reflect the 95% confidence level. The Gibbs energy of formation is calculated to be:

$$\Delta_f G_m^\circ(AmN_3^{2+}, aq, 298.15\,\mathrm{K}) = -(260.0 \pm 5.2)\ \mathrm{kJ \cdot mol^{-1}}$$

V.6.1.3. Americium nitrite complexes

Rao, Kusumakumari and Patil [78RAO/KUS] performed a solvent extraction study on the complexation of Am(III) and Cm(III) by nitrite ions. For americium they report $\log_{10}\beta_1 = (0.96 \pm 0.03)$ at 1 M $NaClO_4$ and 25°C. The acid constant of nitrous acid was measured under the same conditions: $\log_{10} K_1 = 2.86$. When extrapolated to $I = 0$ using the equations in Appendix B, the acid constant ($\log_{10} K_1^\circ = 3.10$) agrees with the value selected by Grenthe *et al.* [92GRE/FUG], *cf.* Table IV.2. This review selects the formation constant for $AmNO_2^{2+}$ reported by Rao, Kusumakumari and Patil [78RAO/KUS] after extrapolation to $I = 0$ (again using the equations in Appendix B) and increasing the uncertainty to ±0.2:

$$\log_{10}\beta_1^\circ(298.15\,\mathrm{K}) \quad = \quad 2.1 \pm 0.2$$

No Gibbs energy of formation can be calculated because there is no selected value for the NO_2^- ion.

V.6.1.4. Americium nitrate compounds and complexes

V.6.1.4.1. Aqueous americium nitrates

The americium(III)-nitrate system has been investigated by solvent extraction, mainly in 1.0 M HNO_3-$XClO_4$ media (where X = H, Na, Li or NH_4), as presented in Table V.14. The experimental measurements were interpreted assuming the formation of $AmNO_3^{2+}$ and $Am(NO_3)_2^+$. The corresponding stability constants indicate that the nitrate complexes are weak. It is therefore difficult to distinguish between complex formation and changes in the activity factors of the solutes caused by the (often large) changes in solute concentration. Hence, this review relies only on the data obtained for the $AmNO_3^{2+}$ species according to

$$Am^{3+} + NO_3^- \quad \rightleftharpoons \quad AmNO_3^{2+}, \tag{V.24}$$

and considers that there is no clear evidence of the existence of higher complexes.

Early qualitative spectrophotometric observation by Yakovlev and Kosyakov [56YAK/KOS] evidenced the formation of americium-nitrate complexes, although the composition of the complexes was not reported. The cation-exchange data obtained by Lebedev, Pirozhkov and Yakovlev [60LEB/PIR] revealed the existence of the $AmNO_3^{2+}$ complex. Lahr and Knoch [70LAH/KNO] found evidence for the formation of $Am(NO_3)_n^{(3-n)}$ ($n = 1, 2, 3$). However, very large changes in the solution composition were made in this study (0 to 8 M HNO_3), and the data might perhaps also be explained by activity factor variations. The same reasoning can be applied to Refs. [66GIV, 69SHI/GIV]. Chiarizia, Danesi and Scibona studied the competitive complexation of Am(III) in $NH_4^+/SCN^-/NO_3^-$ media [73CHI/DAN] and interpreted their results assuming the formation of $Am(SCN)_n^{(3-n)}$ ($n = 1, 2, 3$) and $AmNO_3^{2+}$ complexes. The thiocyanate data contradict all previous observations, and this review rejects the corresponding equilibrium constants for the thiocyanate complexes (*cf.* Section V.7.1.4), and disregards the proposed $\log_{10}\beta_1(NO_3^-)$.

Table V.14: Literature equilibrium constants for the Americium(III)-nitrate system, according to the reactions

$$Am^{3+} + n\,NO_3^- \rightleftharpoons Am(NO_3)_n^{(3-n)}.$$

n	Method	Medium[a]	pH	t(°C)	$\log_{10}\beta_n$	Reference
1	cix	1.0 M NH_4X[b]	1.5	20–25	0.60	[60LEB/PIR]
1	dis	1.0 M $H(ClO_4, NO_3)$	0	22 ± 1	0.26 ±0.07	[62PEP/MAS]
1	dis	1.0 M (H,Na)ClO_4	0	26 ± 1	0.15±0.03	[64BAN/PAT]
1			0		0.27 ± 0.02[c]	
1			3		0.20 ± 0.03	
1			3		0.23 ± 0.03[c]	
1	dis	1.0 M $HClO_4$	0	25	0.26 ± 0.02	[65CHO/STR]
1	sp	1 – 15 M HNO_3	≤ 0	25	−1.30±0.09	[66GIV, 69SHI/GIV]
1	dis	8.0 M $H(ClO_4, NO_3)$	≤ 0	20 ± 1	−0.33	[70LAH/KNO]
2					−0.77	
3					−1.4	
1	dis	1.0 M $HClO_4$	0	30	0.29 ± 0.01	[71KHO/NAR]
1		1.0 M $LiClO_4$	2.5		0.30 ± 0.01	
1		1.0 M $NaClO_4$	2.5		0.26 ± 0.01	
1		1.0 M NH_4ClO_4	2.5		0.23 ± 0.01	
2					0.13 ± 0.06	
1	dis	2.0 M NH_4ClO_4	2.0	25	0.20 ± 0.03	[73CHI/DAN]

(a) A significant amount of the anion in the background electrolyte was substituted by NO_3^- in these studies.

(b) Lebedev, Pirozhkov and Yakovlev [60LEB/PIR] report that the ionic strength was kept constant by addition of ammonium chloride or perchlorate.

(c) Value obtained in this review by a reinterpretation of original data (*cf.* Appendix A).

The equilibrium constant from the reinterpretation of the solvent extraction data of Bansal, Patil and Sharma's [64BAN/PAT] (*cf.* Appendix A) are in agreement with the results of Peppard, Mason and Hucher [62PEP/MAS], those of Choppin and Strasik [65CHO/STR], and those of Khopkar and Narayanankutty [71KHO/NAR]. The corresponding values of $\log_{10}\beta_1$ are accepted by this review. These equilibrium constants are converted to molal units and extrapolated to zero ionic strength using the specific ion interaction equations (*cf.* Appendix B) with $\Delta\varepsilon = (-0.06 \pm 0.06)\,\mathrm{kg}\cdot\mathrm{mol}^{-1}$. An uncertainty of ± 0.1 has been assigned to all $\log_{10}\beta_1$ values in order to take into account the change of the anionic composition of the media. For the same reason, an unweighted average of the data corrected to $I = 0$ is performed, yielding:

$$\log_{10}\beta_1^\circ(\mathrm{V.24}, 298.15\,\mathrm{K}) \;=\; 1.33 \pm 0.20.$$

It should be mentioned that the experimental data used for this calculation refer to slightly different temperatures (*cf.* Table V.14). No reliable enthalpy data are available in the literature, and therefore this review considers that an increased uncertainty of ± 0.20 is representative of the eventual (minor) temperature effects on the equilibrium constants.

The Gibbs energy of formation is calculated to be

$$\Delta_\mathrm{f}G_\mathrm{m}^\circ(\mathrm{AmNO_3^{2+}}, \mathrm{aq}, 298.15\,\mathrm{K}) \;=\; -(717.1 \pm 4.9)\ \mathrm{kJ}\cdot\mathrm{mol}^{-1}.$$

Vasil'ev *et al.* [75VAS/AND] studied the Am(VI)–NO_3^- system in $0 \le [\mathrm{HNO_3}] \le 18$ M solutions using a spectrophotometric technique and suggested the formation of $\mathrm{AmO_2(NO_3)_n^{(2-n)}}$ ($n = 2, 3$). Vasil'ev *et al.* interpreted their measurements at $[\mathrm{HNO_3}] < 10$ M according to the following reaction

$$\mathrm{AmO_2(H_2O)_6^{2+}} + 2\,\mathrm{NO_3^-} \;\rightleftharpoons\; \mathrm{AmO_2(NO_3)_2(H_2O)_2(aq)} + 4\,\mathrm{H_2O(l)}$$

with $\log_{10}\beta_2 = (3.93 \pm 0.04)$. As it is not possible to extrapolate data from this high and varying ionic strength to $I = 0$ with the specific ion interaction approach, this equilibrium constant is not selected in this review.

No other investigations of Am(IV/V/VI)–NO_3^- are found in the literature.

V.6.1.4.2. Solid americium nitrates

Vasil'ev *et al.* [90VAS/KAL] prepared hydrated Am(III) nitrate by dissolving the oxide in 8 M HNO_3. The solution was first evaporated and then dried under He(g), to give a yellow-rose $\mathrm{Am(NO_3)_3}\cdot x\mathrm{H_2O}$ precipitate. The authors used different thermal analysis (DTA) to study the thermal decomposition of the prepared solid:

$$\mathrm{Am(NO_3)_3(s)} \;\longrightarrow\; \mathrm{AmO_2(s)}$$

which indicates that Am(III) is oxidised to Am(IV) during thermal decomposition. From the area of the DTA curve for the thermal decomposition, the authors estimated the standard heat of formation of the anhydrous crystalline Am(III) nitrate:

$$\Delta_\mathrm{f}H_\mathrm{m}^\circ(\mathrm{Am(NO_3)_3}, \mathrm{cr}, 298.15\,\mathrm{K}) \;=\; -(640 \pm 100)\ \mathrm{kJ}\cdot\mathrm{mol}^{-1}.$$

As not enough experimental and computational details are given in Ref. [90VAS/KAL], this value can not be recommended.

V.6.2. Phosphorus compounds and complexes

V.6.2.1. Aqueous americium phosphorus complexes

V.6.2.1.1. Aqueous americium(III)-phosphate complexes

There are few reliable studies available in the literature on americium complexation by phosphate anions, and most of these studies were performed on solutions of low pH and fairly high concentration of phosphoric acid. Experimental studies of equilibria in the americium phosphoric acid system are complicated by the presence of several competing ligands: H_3PO_4(aq), $H_2PO_4^-$, HPO_4^{2-} and PO_4^{3-}. Techniques such as cation exchange [66BOR/ELE, 71MOS2], spectrophotometry [79LEB/FRE2] and solvent extraction [86RAO/MAH, 88RAO/MAH] have been used to determine the composition and the stability constants of the americium(III)–phosphate complexes. The mono- and dihydrogen phosphate complexes $AmHPO_4^+$ and $Am(H_2PO_4)_n^{(3-n)}$ (n = 1 to 4) have been suggested to interpret the various experimental data (*cf.* Table V.15).

In order to reanalyze all the available literature data (Table V.15 and Appendix A) the free ligand concentration, $[H_pPO_4^{(p-3)}]$ was computed using the selected protonation constants of phosphate (Table IV.2) and the corresponding specific interaction coefficients (Table B.4). Equilibrium constants obtained in reinterpretations of experimental data given in selected references were analysed using the specific ion interaction equations (*cf.* Appendix B) and values of $\varepsilon_{(Am(H_pPO_4)_n^{3+n(p-3)},ClO_4^-)}$ estimated in Section B.1.4.

One of the limitations of the specific ion interaction method (*cf.* Appendix B) is that it only takes into account the interactions between ions of different charges while disregarding interactions with uncharged species. This assumption is sufficient in most of the experimental conditions encountered in the literature for $I \leq 4$ M. However, at higher concentration of a neutral species, in this case H_3PO_4(aq), the ion-neutral interaction should be considered [76PIT/SIL]. Because the appropriate ion-neutral interaction coefficients are not known for the americium phosphate system, it is not possible to make the proper corrections to zero ionic strength. This review nevertheless decides to consider the data collected at $[H_3PO_4] \geq 4$ M, but cannot include the resulting stability constants in the table of selected standard reaction data (Table III.2).

Borisov *et al.* [66BOR/ELE] studied the Am(III)-phosphate system, at $I = 0.2$ M NH_4ClO_4, using a cation exchange resin. The variation of the distribution coefficient *vs.* $[H_2PO_4^-]$, at pH = 2, 3 and 4, indicates the formation of $AmH_2PO_4^{2+}$. The same experimental technique was used by Moskvin [71MOS2] at 1.0 M NH_4Cl and at pH = 0.3 and 1.8, proposing the existence of the four complexes $Am(H_2PO_4)_n^{(3-n)}$, with n = 1 to 4. The cation exchange technique appears however inadequate to study this system where several potential ligands (PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$) may form various cationic complexes. Hence, the data of Borisov *et al.* [66BOR/ELE] and Moskvin [71MOS2] can not be selected in this review, *cf.* Appendix A.

Lebedev *et al.* [79LEB/FRE2] studied the spectral changes in the americium ab-

Table V.15: Literature equilibrium constants for the americium-phosphate system.

Method	Ionic Media	pH	t (°C)	$\log_{10}\beta$	References
$Am^{3+} + HPO_4^{2-} \rightleftharpoons AmHPO_4^+$					
dis	$I \longrightarrow 0$	7, 8	30	$4.14 \pm 0.08^{(a,b)}$	[86RAO/MAH]
dis	0.5 M NH_4ClO_4	7	10	3.63	[88RAO/MAH]
			20	3.76	
$Am^{3+} + H_2PO_4^- \rightleftharpoons AmH_2PO_4^{2+}$					
cix	0.2 M NH_4ClO_4	2, 3, 4	20	1.69 ± 0.05	[66BOR/ELE]
cix	$I \longrightarrow 0$	2, 3, 4	20	2.51	
cix	1.0 M NH_4Cl	0.3, 1.8	?	1.48	[69MOS, 71MOS2]
cix	$I \longrightarrow 0$		?	2.39	[69MOS]
sp	1 to 13 M $H(ClO_4, H_2PO_4)$	0 to 1	23	$2.73 \pm 0.06^{(c)}$	[79LEB/FRE2]
dis	0.5 M NH_4ClO_4	2, 3	30	1.97	[86RAO/MAH]
dis	$I \longrightarrow 0$	2, 3	30	$2.13 \pm 0.08^{(a)}$	
dis	0.5 M NH_4ClO_4	2	10	1.64	[88RAO/MAH]
			20	1.69	
			41	2.36	
$Am^{3+} + 2\,H_2PO_4^- \rightleftharpoons Am(H_2PO_4)_2^+$					
cix	1.0 M NH_4Cl	0.3, 1.8	?	2.10	[69MOS, 71MOS2]
cix	$I \longrightarrow 0$		?	3.63	[69MOS]
sp	1 to 13 M	0 to 1	23	$3.72 \pm 0.02^{(c)}$	[79LEB/FRE2]
$Am^{3+} + 3\,H_2PO_4^- \rightleftharpoons Am(H_2PO_4)_3(aq)$					
cix	1.0 M NH_4Cl	0.3, 1.8	?	2.85	[69MOS, 71MOS2]
cix	$I \longrightarrow 0$		?	5.62	[69MOS]
$Am^{3+} + 4\,H_2PO_4^- \rightleftharpoons Am(H_2PO_4)_4^-$					
cix	1.0 M NH_4Cl	0.3, 1.8	?	3.40	[69MOS, 71MOS2]
cix	$I \longrightarrow 0$		?	6.3	[69MOS]

Table V.15 (continued)

Method	Ionic Media	pH	t (°C)	$\log_{10}\beta$	References
$Am^{4+} + 3\,H_2PO_4^- \rightleftharpoons Am(H_2PO_4)_3^+$					
pot	10 to 15 M $H(ClO_4, H_2PO_4)$	0 to 1	23	$14.2 \pm 1^{(c)}$	[79LEB/FRE2]
$AmO_2^{2+} + 2\,H_2PO_4^- \rightleftharpoons AmO_2(H_2PO_4)_2(aq)$					
sp	0.1 to 2 M $H(ClO_4, H_2PO_4)$	0.4 to 1.4	23	$3.3 \pm 0.1^{(c)}$	[79LEB/FRE]
pot	0.2 to 5 M $H(ClO_4, H_2PO_4)$	0 to 1		$4.61 \pm 0.05^{(c)}$	

(a) Value corrected from $I = 0.5$ M NH_4ClO_4 to $I = 0$ by the authors of the original publication [86RAO/MAH] using the Davies equation.

(b) Rao *et al.* [86RAO/MAH] report the following values at 0.5 M NH_4ClO_4 for the formation of $AmHPO_4^+$: $\log_{10}\beta_1(pH = 7) = 3.60$ and 3.92, and $\log_{10}\beta_1(pH = 8) = 2.41$ and 4.14.

(c) Value corrected to $I = 0$ by the authors [79LEB/FRE, 79LEB/FRE2] and it corresponds therefore to β°. Because of the extreme concentration conditions, the reaction involves the exchange between ligands and solvation water molecules, and the corresponding equilibrium constant was also corrected for the variation in water activity.

sorption band at 506 nm produced by $H_2PO_4^-$ complexation, at high concentrations of phosphoric acid: $0.1 \leq [H_3PO_4] \leq 13$ M. The ionic strength in these solutions is estimated to be (0.35 ± 0.10) M from the calculated dissociation of $H_3PO_4(aq)$ into $H_2PO_4^-$. As discussed in Appendix A, this data are not considered due to the extreme concentration conditions.

Rao, Mahajan and Natarajan [86RAO/MAH] conducted a solvent extraction experiment using a liquid cation exchanger. They measured the distribution coefficient at different total phosphate concentrations (at 30°C and 0.5 M NH_4ClO_4). They interpreted their results assuming the presence of $AmH_2PO_4^{2+}$ (at pH = 2 and 3) and $AmHPO_4^+$ (at pH = 7 and 8). The reanalysis of the experimental data agrees with the formation of the first dihydrogen phosphate complex, but this review considers that the experimental data obtained in neutral and weakly basic solutions might suffer from systematic errors, and furthermore the stoichiometry of the predominant complex ($AmHPO_4^+$ or $AmPO_4(aq)$) can not be determined unambiguously from the available data (*cf.* Appendix A), hence the equilibrium constant for the formation

of $AmHPO_4^+$ listed in Table V.15, is disregarded by this review. Similar conditions (pH = 2 and 7, and $I = 0.5$ M NH_4ClO_4) were used by Rao, Mahajan and Natarajan in another study [88RAO/MAH] to investigate the effect of temperature variation (at 10, 20 and 41°C). The authors based their conclusions on the chemical model presented previously [86RAO/MAH]. For the same reasons this review selects only the data obtained at pH = 2, and concludes that the existence of $AmHPO_4^+$ is not clearly proven in the studies of Rao *et al.* [86RAO/MAH, 88RAO/MAH].

For the equilibrium:

$$Am^{3+} + H_2PO_4^- \rightleftharpoons AmH_2PO_4^{2+} \qquad \text{(V.25)}$$

the stability constant from [86RAO/MAH] at 30°C and $I = 0.5$ M is converted to molal units and extrapolated to zero ionic strength using the specific ion interaction equations, *cf.* Appendix B, yielding the following selected value:

$$\log_{10} \beta_1^\circ(\text{V.25}, 298.15\,\text{K}) \;=\; 3.0 \pm 0.5.$$

where the uncertainty has been increased to take into account the temperature difference. The Gibbs energy of formation is calculated to be

$$\Delta_f G_m^\circ(AmH_2PO_4^{2+}, \text{aq}, 298.15\,\text{K}) \;=\; -(1753.0 \pm 5.8)\ \text{kJ} \cdot \text{mol}^{-1}.$$

The data of Rao, Mahajan and Natarajan's obtained at different temperatures [86RAO/MAH, 88RAO/MAH] yield for reaction (V.25): $\Delta_r H_{m,1} = (14 \pm 6)$ kJ·mol^{-1} and $\Delta_r S_{m,1} = (82 \pm 19)$ J·K^{-1}·mol^{-1} at 25° and $I = 0.5$ M. Because of the uncertainty in the influence of temperature on activity coefficients, the equilibrium constants are not extrapolated to $I = 0$ to obtain standard values for the enthalpy and entropy of complex formation. Furthermore, the temperature variation of $\log_{10} \beta_1$ is small and of the same order of magnitude as the uncertainty in the individual values of the equilibrium constants.

V.6.2.1.2. Higher valences of americium

Yanir *et al.* [69YAN/GIV] studied the stability of higher oxidation states of americium in 4 to 16 M H_3PO_4 solutions, using spectrophotometry. The authors reported that anodic oxidation of the initial Am(III) solution lead to Am(VI) in $[H_3PO_4] \leq 5$ M, while Am(IV) was formed at higher phosphoric acid concentrations, with a maximum oxidation yield at $[H_3PO_4] \approx 12$ M. This qualitative information indicates that the experimental determination of the Am(IV)/Am(III) and Am(VI)/Am(V) redox potentials is possible in phosphate media. Erin *et al.* [75ERI/SHA] demonstrated that Am(IV) could also be produced in solutions with $[H_3PO_4] \leq 5$ by oxidation of Am(III) followed by chromatographic separation using columns filled with zirconium phosphate.

The formal potential of the Am(IV)/Am(III) couple was measured by Yanir *et al.* [70YAN/GIV] in 11.5 to 14.5 M H_3PO_4 solutions, obtaining E°(IV/III) = (1.75 ± 0.01) V *versus* SHE at 25°C. Nugent *et al.* [71NUG/BAY] reported a value of 1.78 V,

measured in 10 M H_3PO_4 solutions at 25°C, referring to unpublished work by J.R. Stokely and R.D. Baybarz. Myasoedov *et al.* [77MYA/LEB] measured $E°(IV/III) = (1.800 \pm 0.005)$ and (1.770 ± 0.005) V in 12 and 15 M H_3PO_4 solutions, respectively. All these experimental results indicate that the conditional redox potential in high phosphoric acid concentrations ($[H_3PO_4] > 11$ M) is $E°(IV/III) = (1.77 \pm 0.02)$ V *versus* SHE.

The complex formation of Am(IV) with $H_2PO_4^-$ has been studied by Lebedev *et al.* [79LEB/FRE2] who measured the oxidation potentials of the Am(IV)/Am(III) couple in 10 to 15 M H_3PO_4 solutions. Using the stability constants for the Am(III) complexes, $AmH_2PO_4^{2+}$ and $Am(H_2PO_4)_2^+$, measured spectrophotometrically in the same study, *cf.* Table V.15, Lebedev *et al.* obtained $\log_{10} \beta_3^\circ = (14.2 \pm 1)$ for the following reaction:

$$Am^{4+} + 3\,H_2PO_4^- \rightleftharpoons Am(H_2PO_4)_3^+ .$$

However, as discussed in Appendix A, it is not possible to separate media effects from complex formations in these highly concentrated solutions, and an equilibrium constant for this reaction can not be recommended by this review.

While in aqueous solutions electrochemical oxidation of Am(III) to Am(IV) is found to take place at high H_3PO_4 concentration (> 10 M), *cf.* Ref. [79LEB/FRE2], in acetonitrile media this oxidation occurs at $[H_3PO_4] = 0.3$ to 2 M [87PER/LEB]. The stabilisation of tetravalent americium is certainly important, but the reported values are not considered because of the non-aqueous media.

The formal potential of the Am(VI)/Am(V) couple was measured by Yanir *et al.* [70YAN/GIV], obtaining $E°(VI/V) = (1.34 \pm 0.07)$ V *versus* SHE, in 0.5 to 4.3 M H_3PO_4 solutions at 22°C. Lebedev *et al.* [79LEB/FRE] studied the americyl-phosphate system using spectrophotometry and potentiometry at $0 \leq [H_3PO_4] \leq 12$ M. They interpreted their measurements by the presence of $AmO_2(H_2PO_4)_2(aq)$ at $[H_3PO_4] \geq 0.1$ M. The values of $\log_{10} \beta_2^\circ$ for:

$$AmO_2^{2+} + 2\,H_2PO_4^- \rightleftharpoons AmO_2(H_2PO_4)_2(aq)$$

were found to be (3.3 ± 0.1) and (4.61 ± 0.05) by spectrophotometric and potentiometric techniques respectively. The experimental data are not adequate to prove the proposed chemical model, and this equilibrium constant is not recommended by this review.

Marcus *et al.* [72MAR/YAN] evaluated the effect of phosphoric acid media on their previous measurements of the formal potential for Am(IV)/Am(III) [70YAN/GIV] to obtain a value of the standard redox potential, $E°(IV/III)$, using stability constant estimates (from analogous lanthanides and actinides) on assumed stoichiometries for the complexes. However, these types of correlations are unreliable owing to the lack of any direct evidence on the Am(IV; V; VI) speciation in phosphoric acid solutions. Reliable evaluations of the standard potentials $E°(IV/III)$ and $E°(VI/V)$ are thus not possible from the available measurements in phosphate media.

V.6.2.1.3. Other aqueous americium-phosphate systems

Elesin *et al.* [67ELE/LEB] studied the complex formation of americium and other trivalent actinides with trimetaphosphoric acid, $H_3P_3O_9$, using an ion exchange technique (0.2 M NH_4ClO_4, 25°C). At, pH = 2 and 4, two complexes were suggested to describe the experimental results: AmP_3O_9(aq) and $AmHP_3O_9^+$. The formation constants at $I = 0.2$ M for these complexes were reported to be $\log_{10}\beta_1 = (3.48 \pm 0.04)$ and (3.3 ± 0.2) respectively. No reliable auxiliary data (protonation constants for $P_3O_9^{3-}$) are available and therefore these complexes are not included in the selected data set.

Different Soviet investigations have reported the production and stabilisation of tetra-, penta- and hexavalent americium in aqueous potassium phosphotungstate solutions, $K_{10}P_2W_{17}O_{61}$ [76SAP/SHI, 76SAP/SPI, 77KOS/TIM, 80MIL/LIT, 82ERI/KOP, 82KUL/LEB, 83ERI/KOP, 86ERI/KOP], based on the following redox reaction schemes:

$$\begin{aligned} 2\mathrm{Am(V)} &\rightleftharpoons \mathrm{Am(IV)} + \mathrm{Am(VI)} \\ \mathrm{Am(VI)} + \mathrm{Am(III)} &\rightleftharpoons \mathrm{Am(V)} + \mathrm{Am(IV)} \\ \mathrm{Am(V)} + \mathrm{Am(III)} &\rightleftharpoons 2\mathrm{Am(IV)} \end{aligned}$$

Milyukova, Litvina and Myasoedov [80MIL/LIT] reported $\log_{10}\beta_2 = 5.4$ and 9 for the Am(III) and Am(IV) complexes $Am(P_2W_{17}O_{61})_2^{17-}$ and $Am(P_2W_{17}O_{61})_2^{16-}$ respectively. These equilibrium constants, apparently obtained at room temperature, were calculated from spectrophotometric data on solutions of varying ionic medium. This review does not recommend values for any of these interactions.

V.6.2.2. Solid americium phosphorus compounds

V.6.2.2.1. Solid americium phosphides

Only the monophosphide has been identified, even in the presence of excess phosphorus.

Charvillat *et al.* [75CHA/BEN, 76CHA/BEN] heated americium hydride with excess red phosphorus at 580°C for 3 days, finding a single-phase product with the NaCl(cr) structure, space group Fm3m, with a lattice parameter of $(5.7114 \pm 0.0003) \times 10^{-10}$ m. Again, oxygen contamination is possible, but is probably less serious than with the nitride.

V.6.2.2.2. Solid americium phosphates

Keller and Walter [65KEL/WAL] have precipitated Am(III) phosphates by addition of dilute solutions of Na_2HPO_4 or $(NH_4)_2HPO_4$ to weakly acid Am(III) solutions. The hydrate contains up to 0.5 H_2O per mole of $AmPO_4$ and crystallises with a hexagonal unit cell $a = (6.99 \pm 0.01) \times 10^{-10}$ m, $c = (6.39 \pm 0.01) \times 10^{-10}$ m. The light pink completely anhydrous $AmPO_4$(cr) is formed by calcination above 200°C, and has the

monoclinic $ThSiO_4$-type lattice, space group $P2_1/h$ with $a = (6.73 \pm 0.02) \times 10^{-10}$ m, $b = (6.93 \pm 0.02) \times 10^{-10}$ m, $c = (6.41 \pm 0.02) \times 10^{-10}$ m, $\beta = 103.83°$. This has an appreciably higher density than the hydrate.

Rai *et al.* [92RAI/FEL] performed a solubility study of ^{243}Am(III) in phosphate media. The experimental data at pH< 3 were interpreted according to the following reaction

$$AmPO_4 \cdot xH_2O(am) \rightleftharpoons Am^{3+} + PO_4^{3-} + x\,H_2O(l) \qquad (V.26)$$

This review selects the solubility constant obtained by Rai *et al.* [92RAI/FEL] with the uncertainty increased to ± 0.6 $\log_{10}$-units (*cf.* Appendix A):

$$\log_{10} K^{\circ}_{s,0}(V.26, 298.15\,K) = -24.79 \pm 0.60.$$

The temperature at which the experiments were performed was not specified by Rai *et al.*, but the increased uncertainty will compensate for possible temperature effects. The corresponding value of $\Delta_f G^{\circ}_m$ for $AmPO_4$(am, hydr) can not be selected by this review due to the unknown stoichiometry of the solid phase.

Ternary phosphates of Am(VI) with the general formula $M AmO_2PO_4 \cdot xH_2O$(cr), $(0 < x < 3)$ and (M = NH_4, K, Rb and Cs) were prepared by Lawaldt *et al.* [82LAW/MAR] from Am(VI) in 2 M nitric acid solutions by addition of 0.1 M H_3PO_4 and M_2CO_3(s) to obtain a pH of 3.5. The lemon-yellow compounds have a tetragonal structure, space group P4/nmm or I4/mmm with a = (6.91 to 6.99) $\times 10^{-10}$ m, c = (8.82 to 9.06) $\times 10^{-10}$ m. The Rb and Cs compounds may have some M replaced by H.

V.6.3. Arsenic compounds

V.6.3.1. Arsenides

Only the monoarsenide has been identified, even in the presence of excess arsenic.

Charvillat and Damien [73CHA/DAM] heated some americium hydride (^{241}Am) with excess arsenic in a Pyrex tube at 600 K for one week. The X-ray diffraction patterns of the product ($\sim$ 50 mg) indicated the presence of arsenic and an fcc phase. After vaporisation of the excess arsenic, the lattice parameter of the fcc phase, NaCl-type, space group Fm3m, was $a = 5.873 \times 10^{-10}$ m after annealing at 1000°C for 10 h. By analogy with the corresponding neptunium and plutonium phases, this was assumed to be the monoarsenide.

Roddy [74ROD] repeated this preparation using the longer-lived ^{243}Am isotope, and various heat treatments. He found the following lattice parameters: (5.880 $\pm$ 0.001) 10^{-10} m after heating of 675°C for 1 h and at 400°C for 7 d, and (5.880 $\pm$ 0.002) 10^{-10} m after annealing at 1000°C for 10 h. The lower lattice parameter after annealing at 1000°C may of course result from some oxygen contamination, as noted by Roddy.

V.6.3.2. Arsenates

Keller and Walter [65KEL/WAL] have obtained the $AmAsO_4$(cr) by calcination at 1000°C of the precipitate from mixing $Am(NO_3)_3$ and $(NH_4)_2HAsO_4$ solutions. It has the monoclinic $ThSiO_4$-type lattice, space group $P2_1/h$ with $a = (6.89 \pm 0.02) \times 10^{-10}$ m, $b = (7.06 \pm 0.02) \times 10^{-10}$ m, $c = (6.62 \pm 0.02) \times 10^{-10}$ m, $\beta = 105.5°$.

Ternary arsenates of Am(VI) with the general formula $M AmO_2AsO_4 \cdot xH_2O$(cr), $(0 < x < 3)$ and (M = NH_4, K, Rb and Cs) were prepared by Lawaldt *et al.* [82LAW/MAR] from Am(VI) in 2 M nitric acid solutions by addition of 0.1 M H_3AsO_4 and M_2CO_3(s) to obtain a pH of 3.5. The lemon-yellow compounds have a tetragonal structure, space group P4/nmm or I4/mmm with a = (7.09 to 7.15) $\times 10^{-10}$ m, c = (8.93 to 17.73) $\times 10^{-10}$ m. The Rb and Cs compounds may have some M replaced by H.

No thermodynamic data are available for the arsenates of americium.

V.6.4. Antimony compounds

V.6.4.1. Antimonides

Three antimonides have been identified: Am_4Sb_3(cr), and AmSb(cr) and $AmSb_2$(cr); the detailed phase relationships are not known.

The mixed compound AmSbTe(cr) is also discussed in Section V.6.4.1.4.

V.6.4.1.1. Am_4Sb_3(cr)

Charvillat *et al.* [75CHA/BEN] obtained this phase by heating americium hydride with antimony in a molar ratio of 4:3 in a sealed evacuated tube at 550°C for 7 days. The X-ray diffraction patterns of the product indicated the presence of two phases, an fcc phase, NaCl(cr) type, with $a = 6.240 \times 10^{-10}$ m, and a bcc phase of type (anti) Th_3P_4(cr), space group $I\bar{4}d$ with $a = 9.2392 \times 10^{-10}$ m. Phases of this type are well-known in the lanthanide-antimony systems.

V.6.4.1.2. AmSb(cr)

Mitchell and Lam [70MIT/LAM] first prepared the monoantimonide, both by arc-melting the elements, and by heating equimolar amounts of the elements at 630°C for 1 h in an evacuated quartz capsule.

This phase has also been identified by Roddy [74ROD], using ^{243}Am, and Charvillat *et al.* [76CHA/BEN], by reacting the elements with or without hydrogen in sealed containers.

AmSb has the usual NaCl(cr) fcc structure, space group Fm3m, with a parameter between 6.2380×10^{-10} and 6.241×10^{-10} m, depending on the heat treatment or possibly purity. The as-cast material had a slightly larger parameter of 6.2426×10^{-10} m [70MIT/LAM].

V.6.4.1.3. $AmSb_2$(cr)

$AmSb_2$(cr) was prepared by Charvillat *et al.* [77CHA/DAM] by reaction of excess antimony and americium hydride in a sealed quartz tube at 700°C. Annealing for 7 d was required to obtain well-crystallised products. The structure was found to be orthorhombic with $a = 6.18 \times 10^{-10}$, $b = 6.05 \times 10^{-10}$ and $c = 17.59 \times 10^{-10}$ m. Based on the analogous compound of plutonium, for which single crystal X-ray pictures were taken, the structure is taken to that to $LaSb_2$(cr), space group Cmca.

The precise composition (and oxygen content) of this phase is not known.

V.6.4.1.4. AmSbTe(cr)

Charvillat *et al.* [77CHA/DAM] also prepared the mixed antimonide-telluride, by reaction of stoichiometric amounts of AmSb(cr) and Te(cr) in quartz tubes at 750°C for 7 d. It has the tetragonal (anti) Cu_2Sb(cr) structure, space group P4/nmm, with $a = 4.326 \times 10^{-10}$, $c = 9.17 \times 10^{-10}$ m. Again, the precise composition is not known.

V.6.5. Bismuth compounds

Only the monobismuthide has been identified.

This phase was obtained by Roddy [74ROD], using ^{243}Am, by reacting the elements with or without hydrogen in quartz tubes. The final mixture contained americium metal and an fcc phase, NaCl(cr) structure, space group Fm3m, with $a = 6.338 \times 10^{-10}$ m (975°C for 2 d) or 6.335×10^{-10} m (as above 800°C for 14 d). No higher compounds were found.

V.7. Group 14 compounds and complexes

V.7.1. Carbon compounds and complexes

V.7.1.1. Americium carbides

The phase diagram of the Am-C system has not been established in any detail, but the "monocarbide" and sesquicarbide have been identified. Workers at Euratom [73EUR] prepared samples of americium carbides by carbothermic reduction and by arc melting. Samples of overall composition $AmC_{1.04}$ and $AmC_{1.25}$ annealed at 1000°C for 24 h, contained an fcc NaCl-type phase with $a = 5.02 \times 10^{-10}$ m, mixed with a sesquicarbide phase having a slightly smaller lattice parameter than that noted below. Although the precise composition and oxygen and nitrogen contents of the fcc phase were not established, it is presumably the monocarbide AmC(cr).

Americium sesquicarbide has been prepared by Mitchell and Lam [70MIT/LAM2]. It is isostructural with Pu_2C_3(cr), space group $I\bar{4}3d$, $a = (8.2757 \pm 0.0002) \times 10^{-10}$ m for a sample annealed at 1000°C for 1 h. The precise composition was not established.

From the systematics of the actinide carbides, Holley *et al.* [84HOL/RAN] have estimated thermodynamic properties of Am_2C_3(cr) which correspond to:

$$S^\circ_m(Am_2C_3, cr, 298.15\,K) = (145\pm20)\ J\cdot K^{-1}\cdot mol^{-1}\ ,$$
$$\Delta_f H^\circ_m(Am_2C_3, cr, 298.15\,K) = -(151\pm42)\ kJ\cdot mol^{-1}\ ,$$

which are accepted by this review. The standard Gibbs energy of formation is calculated from these selected enthalpy of formation and entropy:

$$\Delta_f G^\circ_m(Am_2C_3, cr, 298.15\,K) = -(156\pm42)\ kJ\cdot mol^{-1}.$$

Americium carbides with C/Am > 2, annealed at 1000°C for 24 h, showed no evidence of a dicarbide structure [73EUR], so this phase is presumably stable only at high temperatures, if at all (*cf.* PuC_2(cr) [84HOL/RAN]).

V.7.1.2. Americium carbonate compounds and complexes

Several compilations have been published on available and estimated thermodynamic data for americium carbonate systems [85PHI/PHI, 86WAN, 88PHI/HAL], but only a few have attempted a critical review [84KER, 86KER/SIL, 85NEW/SUL, 88MOU/ROB, 89NIT/STA]. Several articles have appeared with estimates of formation constants [82ALL, 83ALL, 87BRO/WAN, 88CAN], however, the number of experimentally derived thermodynamic values for solubility products of solids and formation constants of solution species are rather limited. This review concentrates on thermodynamic constants determined from experiments (*cf.* Table V.16) and considers estimates only when they have good chemical justification and when credible measured data are missing.

V.7.1.2.1. Aqueous americium hydroxide-carbonate systems

Many different soluble species have been proposed for the americium-water-carbonate system: pure carbonate and/or bicarbonate and/or mixed hydroxy-carbonate complexes. After reinterpretation of literature data, this review finds no evidence for the formation of Am(III)-bicarbonate or hydroxo-carbonate complexes (*cf.* Sections V.7.1.2.1.b and V.7.1.2.1.c). Only the complexes $AmCO_3^+$, $Am(CO_3)_2^-$ and $Am(CO_3)_3^{3-}$ have been well established. All the reported stability constants are presented in Table V.16. Only the data from a few selected references are used in the selection procedures described below.

a) Am(III) carbonate complexes

Americium complexation by carbonate has been investigated by solvent extraction, spectrophotometry, electromigration [82BID, 82LUN, 89NIT/STA] and solubility [84BER/KIM, 89ROB, 90FEL/RAI, 91MEI/KIM]. These studies have demonstrated the existence of $Am(CO_3)_n^{(3-2n)}$, with $n = 1$, 2 and 3. There is no experimental evidence on the existence of $Am(CO_3)_4^{5-}$, even at the highest carbonate concentrations (*cf.* discussion of Refs. [69SHI/GIV, 83BOU/GUI, 89ROB] in Appendix A).

Bidoglio [82BID] used a solvent extraction technique to study the americium speciation at $I = 0.2$ M ($NaClO_4$). He interpreted his experimental data assuming the

Table V.16: Literature equilibrium constants for the americium(III)-carbonate-water system.

Method	Ionic Medium	t (°C)	$\log_{10} K$	Reference
$AmCO_3OH(s) + 2\,H^+ \rightleftharpoons Am^{3+} + HCO_3^- + H_2O(l)$				
sol	0.1 M $NaClO_4$	25	2.74 ± 0.17	[84SIL/NIT]
sol	0.1 M $NaClO_4$	25	2.77 ± 0.15	[85SIL]
sol	$I \to 0$	25	2.53 ± 0.16	[85SIL]
$AmCO_3OH(s) \rightleftharpoons Am^{3+} + CO_3^{2-} + OH^-$				
sol	0.1 to 0.3 M $NaClO_4$	25?	-21.03 ± 0.11	[84BER/KIM]
sol	$I \to 0$	?	$-22.5^{(a)}$	[90FEL/RAI]
sol	0.1 M $NaClO_4$	25	-18.70 ± 0.12	[92RUN/MEI]
$0.5\,Am_2(CO_3)_3(s) \rightleftharpoons Am^{3+} + 1.5\,CO_3^{2-}$				
sol	3.0 M $NaClO_4$	20	-15.08 ± 0.15	[89ROB]
sol	0.1 M $NaClO_4$	25	-14.945 ± 0.09	[91MEI/KIM]
sp	0.1 – 0.3 M $NaClO_4$	25	-14.85 ± 0.05	[91MEI/KIM]
sol	0.1 M $NaClO_4$	22	-14.785 ± 0.05	[91MEI/KIM2]
sol	0.1 M $NaClO_4$	25	-14.725 ± 0.09	[92RUN/MEI]
sol	0.1 M NaCl	21	-17.1 ± 0.15	[93GIF/VIT]
sol	4 M NaCl	21	-15.2 ± 0.2	[93GIF/VIT]
$NaAm(CO_3)_2(s) \rightleftharpoons Na^+ + Am^{3+} + 2\,CO_3^{2-}$				
sol	0.1 M	?	$-18.32^{(b)}$	[85KIM, 85KIM2]
	$I \to 0$	?	$-17.56^{(b)}$	[85KIM2]
sol	$I \to 0$	?	$-17.38^{(b)}$	[86AVO/BIL]
$Am^{3+} + CO_3^{2-} \rightleftharpoons AmCO_3^+$				
dis	1.0 M $NaClO_4$	25	5.81 ± 0.04	[82LUN]
em	1.0 M $NaClO_4$	25	5.3 ± 0.4	[82LUN]
sol	0.1 to 0.3 M $NaClO_4$	25?	5.08 ± 0.92	[84BER/KIM]
sp	0.1 M $NaClO_4$	22.5	6.69 ± 0.15	[89NIT/STA]
sp	$I \to 0$	25	8.16 ± 0.10	[89NIT/STA]
sol	3.0 M $NaClO_4$	20	5.45 ± 0.12	[89ROB]

Table V.16 (continued)

Method	Ionic Medium	t (°C)	$\log_{10}K$	Reference
$Am^{3+} + CO_3^{2-} \rightleftharpoons AmCO_3^+$ *(continued)*				
sol	$I \to 0$	?	7.6	[90FEL/RAI]
sol	0.1 – 0.3 M $NaClO_4$	25	5.97 ± 0.15	[91MEI/KIM]
sp	0.1 – 0.3 M $NaClO_4$	25	6.48 ± 0.03	[91MEI/KIM]
sol	0.1 M NaCl	21	7.7 ± 0.18	[93GIF/VIT]
sol	4 M NaCl	21	5.3 ± 0.25	[93GIF/VIT]
$Am^{3+} + 2\,CO_3^{2-} \rightleftharpoons Am(CO_3)_2^-$				
dis	0.2 M $NaClO_4$	25	11.45 ± 0.08	[82BID]
dis	1.0 M $NaClO_4$	25	9.72 ± 0.10	[82LUN]
em	1.0 M $NaClO_4$	25	8.5 ± 0.5	[82LUN]
sol	0.1 to 0.3 M $NaClO_4$	25?	9.27 ± 2.2	[84BER/KIM]
sol	3.0 M $NaClO_4$	20	8.92 ± 0.15	[89ROB]
sol	$I \to 0$	?	12.3	[90FEL/RAI]
sol	0.1 – 0.3 M $NaClO_4$	25	9.58 ± 0.24	[91MEI/KIM]
sp	0.1 – 0.3 M $NaClO_4$	25	9.94 ± 0.24	[91MEI/KIM]
sol	0.1 M NaCl	21	11.21 ± 0.21	[93GIF/VIT]
sol	4 M NaCl	21	9.2 ± 0.36	[93GIF/VIT]
$Am^{3+} + 3\,CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-}$				
sol	0.1 to 0.3 M $NaClO_4$	25?	12.12 ± 0.85	[84BER/KIM]
sol	3.0 M $NaClO_4$	20	11.44 ± 0.12	[89ROB]
sol	$I \to 0$	?	15.2	[90FEL/RAI]
sol	0.1 M NaCl	21	12.8 ± 0.25	[93GIF/VIT]
sol	4 M NaCl	21	11.4 ± 0.25	[93GIF/VIT]
$Am^{3+} + HCO_3^- \rightleftharpoons AmHCO_3^{2+}$				
dis	0.2 M $NaClO_4$	25	4.79 ± 0.08	[82BID]
dis	0.5 M $NaClO_4$	15	1.91	[88RAO/MAH]
		25	2.00	
		25	2.13	
$Am^{3+} + 2\,HCO_3^- \rightleftharpoons Am(HCO_3)_2^+$				
dis	0.2 M $NaClO_4$	25	8.15 ± 0.09	[82BID]
dis	0.5 M $NaClO_4$	35	3.83	[88RAO/MAH]

Table V.16 (continued)

Method	Ionic Medium	t (°C)	$\log_{10}K$	Reference
$Am^{3+} + CO_3^{2-} + OH^- \rightleftharpoons AmCO_3OH(aq)$				
sol	0.1 to 0.3 M $NaClO_4$	25?	12.15 ± 0.15	[84BER/KIM]
$Am^{3+} + CO_3^{2-} + 2\,OH^- \rightleftharpoons AmCO_3(OH)_2^-$				
sol	0.1 to 0.3 M $NaClO_4$	25?	18.29 ± 0.17	[84BER/KIM]
$Am^{3+} + 2CO_3^{2-} + OH^- \rightleftharpoons Am(CO_3)_2OH^{2-}$				
dis	0.2 M $NaClO_4$	25	15.57 ± 0.08	[82BID]
sol	0.1 to 0.3 M $NaClO_4$	25?	16.16 ± 0.14	[84BER/KIM]

(a) Felmy, Rai and Fulton [90FEL/RAI] combined their solubilities at pH> 6.5 with those of Silva [85SIL] to obtain this solubility constant.

(b) These values refer to solubility experiments performed by Vitorge [84VIT] within the MIRAGE project. However, Vitorge did not publish himself the results from the treatment of the data.

formation of the first and second bicarbonate, the second carbonate and the mixed hydroxy-carbonate $Am(CO_3)_2OH^{2-}$ complexes. Lundqvist [82LUN] and Nitsche, Standifer and Silva [89NIT/STA] showed using two different CO_2 partial pressures that the bicarbonate complexes must be much weaker than reported by Bidoglio; hence, the interpretation of the extraction data seems to be in error and the stability constants initially reported [82BID] are not considered in this review. The only qualitative information available from the data of Bidoglio [82BID] is the predominance of $Am(CO_3)_2^-$ at $8 \leq pH \leq 9$ and $-4.4 \leq \log_{10}[CO_3^{2-}] \leq -3$ (*cf.* Appendix A), which is in agreement with the observations of Lundqvist, Robouch, and Meinrath and Kim [82LUN, 89ROB, 91MEI/KIM].

Lundqvist [82LUN] studied americium complexation in carbonate media using a solvent extraction technique at $I = 1.0$ M ($NaClO_4$) and reported the formation of $AmCO_3^+$ and $Am(CO_3)_2^-$. Although HCO_3^- was the predominating ion of the carbonate system under the experimental conditions ($p_{CO_2} = 0.1$ and 1.0 atm), there was no evidence for $Am(HCO_3)_n^{(3-n)}$ complexes.

Bernkopf and Kim [84BER/KIM] reported solubility measurements of a solid with starting composition $Am(OH)_3(s)$ at $I = 0.1$ and 0.3 M $NaClO_4$, $p_{CO_2} = 10^{-3.5}$ atm (*cf.* Section V.7.1.2.2.a). Bernkopf and Kim interpreted their solubility data assuming the presence of hydroxide ($Am(OH)_i^{(3-i)}$; $i = 1, 2, 3$), carbonate ($Am(CO_3)_n^{(3-2n)}$; $n = 1, 2, 3$) and mixed hydroxy-carbonate ($Am(OH)_i(CO_3)_n^{(3-i-2n)}$; $i = 1, 2$ and

$n = 1, 2$) complexes. The solid phase was assumed to be $AmCO_3OH(s)$. This review considers that the transformation of the initial solid, $Am(OH)_3(s) \rightarrow$ "$AmCO_3OH(s)$", may be slow and it may have occurred during the experiments (*cf.* Appendix A), and therefore the reported equilibrium constants from this study are not considered in the selection procedure.

Rao, Mahajan and Natarajan [88RAO/MAH] reported americium(III) solvent extraction experiments at pH = 6 and 7 and at $I = 0.5$ M. This review reinterprets the data showing that these experiments reveal the existence of carbonate complexes (*cf.* Appendix A), which is in agreement with other experimental observations presented in the literature. Therefore, the stability constants for the bicarbonate complexes reported in [88RAO/MAH] are rejected by this review, *cf.* Section V.7.1.2.1.b.

Nitsche, Standifer and Silva [89NIT/STA] determined the formation constant of $AmCO_3^+$ in 0.1 M $NaClO_4$ solutions by absorption spectrophotometry. No evidence was found for the existence of americium bicarbonate complexes.

Robouch [89ROB] measured the solubility of $Am_2(CO_3)_3(cr)$ as a function of carbonate concentration at $I = 3$ M $NaClO_4$. The solubility data were analysed in terms of carbonate complexes ($Am(CO_3)_n^{(3-2n)}$; $n = 1, 2, 3$) and a solubility product for $Am_2(CO_3)_3(cr)$ (*cf.* Section V.7.1.2.2.b). No evidence of $Am(CO_3)_4^{5-}$ formation was found by spectrophotometry in the 0.1 to 3.0 M Na_2CO_3 range. The equilibrium constants reported by Robouch (*cf.* Table V.16) are re-evaluated by this review. As the data obtained by Robouch [89ROB] in batch experiments ($\log_{10}[CO_3^{2-}] \geq -3.5$) can equally well be described with the solubility of $Am_2(CO_3)_3(s)$ or $AmCO_3OH(s)$, only the equilibrium constants unequivocally resulting from the measurements at constant p_{CO_2}, *i.e.* $\log_{10} \beta_1^\circ$ and $\log_{10} K_{s,0}^\circ$(V.36), are used in the selection procedure.

Meinrath and Kim [91MEI/KIM] investigated the americium complexation in carbonate media, performing solubility and spectroscopic experiments. The data collected at ionic strengths of 0.1 and 0.3 M $NaClO_4$, at pH = 6 to 9, and under a controlled CO_2 partial pressure ($p_{CO_2} = 0.01$ atm) were interpreted by the formation of $AmCO_3^+$ and $Am(CO_3)_2^-$. The stability constants obtained from the solubility data reported by Meinrath and Kim agree with the re-evaluation performed by this review (*cf.* Appendix A). The values of β_1 and β_2 reported in [91MEI/KIM] are therefore included in the selection procedure. The value of β_2 determined spectrophotometrically is however disregarded (*cf.* Appendix A). The value for the solubility product of $Am_2(CO_3)_3(cr)$ is discussed in Section V.7.1.2.2.b.

The solubility of $^{243}AmCO_3OH(cr)$ in carbonate media was investigated by Felmy, Rai and Fulton [90FEL/RAI], over wide ranges of $[CO_3^{2-}]$, $[HCO_3^-]$ and pH values. As shown in Figure 3 of [90FEL/RAI], the authors included the solubility data reported by Silva and Nitsche [84SIL/NIT, 85SIL] during the fitting of their own solubility data. This review considers instead the equilibrium constants for reactions

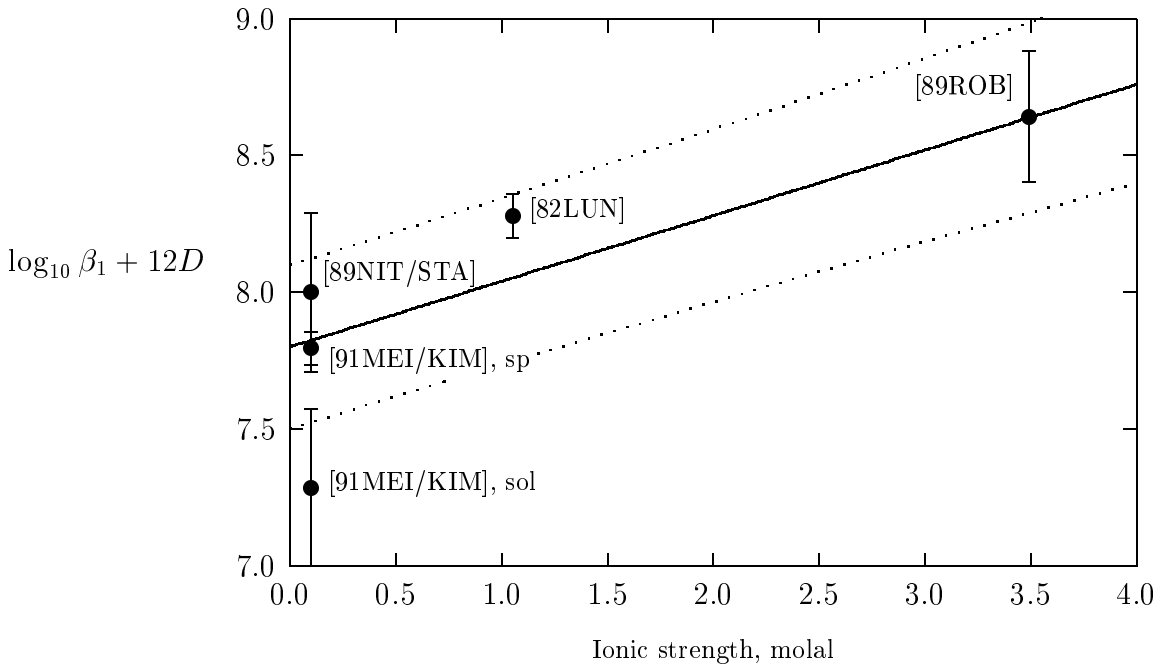
$$AmCO_3OH(cr) + H^+ + (n-1)\,CO_3^{2-} \rightleftharpoons Am(CO_3)_n^{(3-2n)} + H_2O(l) \quad (V.27)$$

obtained exclusively from solubility data of Felmy, Rai and Fulton (*cf.* discussion of Ref. [90FEL/RAI] in Appendix A). The stepwise equilibrium constants for carbonate complexation (K_2 and K_3, derived from values of $K_{s,n}$(V.27)) are included in the selection procedure.

Figure V.10: Extrapolation to $I = 0$ of literature equilibrium constants [82LUN, 89NIT/STA, 91MEI/KIM] and the reinterpreted value from [89ROB] for the formation of $AmCO_3^+$, according to

$$Am^{3+} + CO_3^{2-} \rightleftharpoons AmCO_3^+,$$

using the specific ion interaction equations (*cf.* Appendix B). The dashed lines represent the uncertainty limits estimated by this review, *cf.* Eq. (V.28).



Giffaut and Vitorge [93GIF/VIT] reported equilibrium constants for the formation of $Am(CO_3)_n^{(3-2n)}$ ($n = 1$ to 3) from an interpretation of their solubility data at 0.1 and 4 M NaCl, *cf.* Table V.16. However, due to the lack of details in this publication, the reported equilibrium constants can not be credited in this review, *cf.* Appendix A.

The values of $\log_{10}\beta_1$ from Refs. [82LUN, 89NIT/STA, 91MEI/KIM] and the reinterpreted value from [89ROB] are extrapolated to $I = 0$ using the specific ion interaction equations and the weighted linear regression procedure as described in Appendices B and C (*cf.* Figure V.10). The extrapolation is performed with a value of $\Delta\varepsilon_1 = -(0.24 \pm 0.05)\,\mathrm{kg \cdot mol^{-1}}$ obtained from the ion interaction coefficients given in Section B.1.4. The result of the extrapolation to $I = 0$ for $AmCO_3^+$ yields:

$$\log_{10}\beta_1^\circ(298.15\,\mathrm{K}) \quad = \quad 7.8 \pm 0.3 \qquad \text{(V.28)}$$

This value agrees within the uncertainties with the constants given by Moulin *et al.* [88MOU/ROB] ($\log_{10}\beta_1^\circ = 7.6$), Nitsche, Standifer and Silva [89NIT/STA] ($\log_{10}\beta_1^\circ = (8.16 \pm 0.10)$), and the value estimated by Cantrell [88CAN] ($\log_{10}\beta_1^\circ = 7.7$).

The values of the second stepwise equilibrium constant, K_2, from Refs. [82LUN, 91MEI/KIM, 90FEL/RAI] are converted to molal units and extrapolated to zero ionic

strength with the specific ion interaction equations of Appendix B. The $\Delta\varepsilon$ value for this reaction is obtained from the estimated ion interaction coefficients given in Section B.1.4 ($\Delta\varepsilon_2 = -(0.14 \pm 0.07)\,\mathrm{kg \cdot mol^{-1}}$). The weighted average of the three values of $\log_{10} K_2^\circ$ yields:

$$\log_{10} K_2^\circ(298.15\,\mathrm{K}) = 4.5 \pm 0.2$$

The value of the third stepwise equilibrium constant, K_3, obtained by Felmy, Rai and Fulton [90FEL/RAI] is selected

$$\log_{10} K_3^\circ(298.15\,\mathrm{K}) = 2.9 \pm 0.5$$

where the uncertainty has been increased because of the unknown temperature of this study. These stepwise equilibrium constants lead to the following selected values for the overall formation constants:

$$\log_{10} \beta_2^\circ(298.15\,\mathrm{K}) = 12.3 \pm 0.4$$
$$\log_{10} \beta_3^\circ(298.15\,\mathrm{K}) = 15.2 \pm 0.6$$

The value of $\log_{10} \beta_2^\circ$ agrees with the values selected by Moulin *et al.* [88MOU/ROB], ($\log_{10} \beta_2^\circ = 11.8$), and with the value estimated by Cantrell [88CAN] ($\log_{10} \beta_2^\circ = 12.8$).

The Gibbs energies of formation for the carbonate complexes of americium(III) derived from the selected formation constants are:

$$\Delta_\mathrm{f} G_\mathrm{m}^\circ(\mathrm{AmCO_3^+}, \mathrm{aq}, 298.15\,\mathrm{K}) = -(1171.1 \pm 5.1)\ \mathrm{kJ \cdot mol^{-1}}$$
$$\Delta_\mathrm{f} G_\mathrm{m}^\circ(\mathrm{Am(CO_3)_2^-}, \mathrm{aq}, 298.15\,\mathrm{K}) = -(1724.7 \pm 5.3)\ \mathrm{kJ \cdot mol^{-1}}$$
$$\Delta_\mathrm{f} G_\mathrm{m}^\circ(\mathrm{Am(CO_3)_3^{3-}}, \mathrm{aq}, 298.15\,\mathrm{K}) = -(2269.2 \pm 6.0)\ \mathrm{kJ \cdot mol^{-1}}.$$

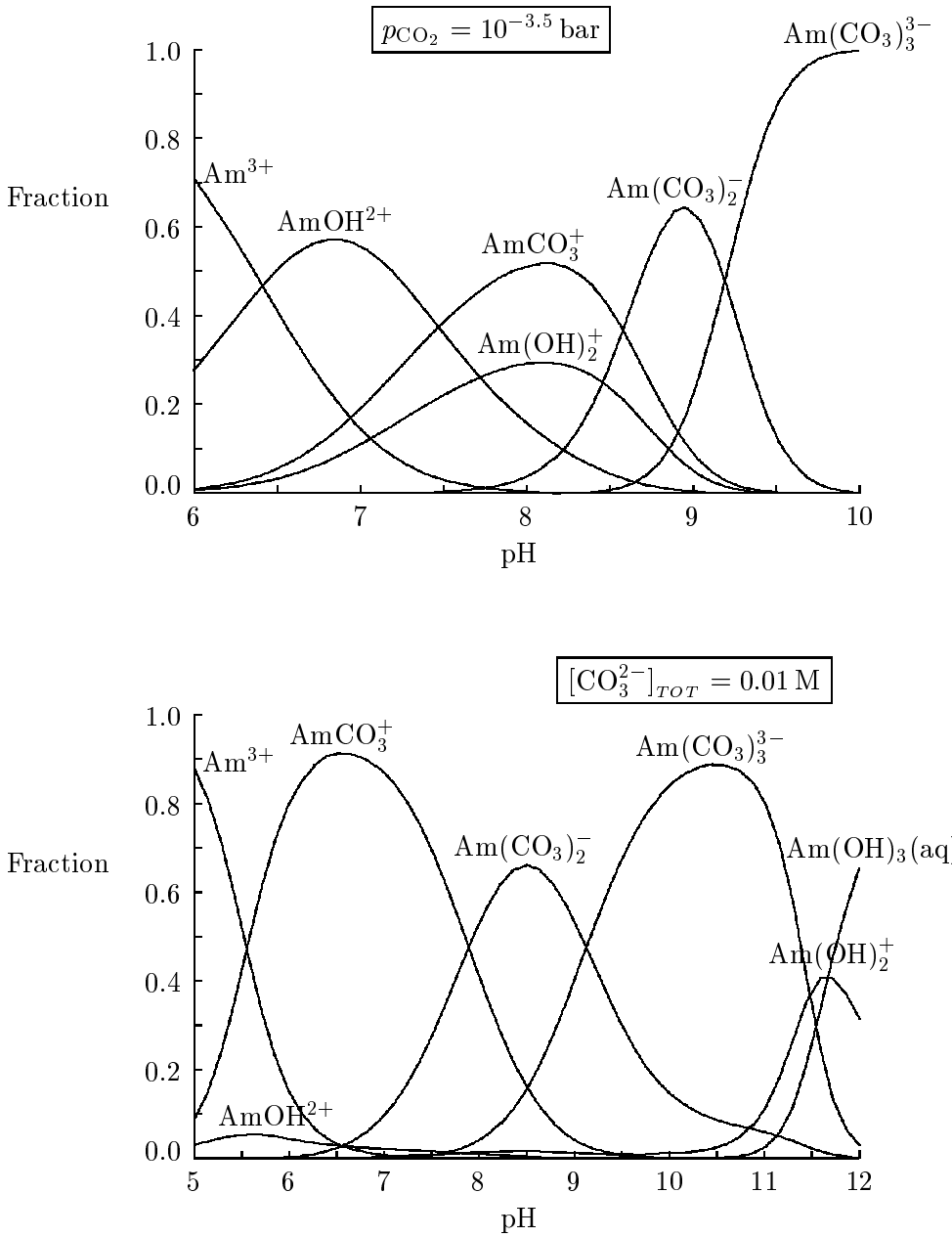
As an illustration, Figure V.11 shows the distribution of carbonate complexes of $\mathrm{Am^{3+}}$ in competition with the hydrolysis products.

b) Am(III) bicarbonate complexes

Formation constants for the first two bicarbonate complexes of americium were reported by Bidoglio [82BID], *cf.* Table V.16. However, the first stability constants appears too large compared with $\log_{10} \beta_1(M\mathrm{HCO_3^{2+}}) = 2$ to 3 for $M = \mathrm{Y}$ [85SPA, 92GRE/SPA], $M = \mathrm{La}$ [81CIA/FER] and for other rare earths [90WOO, 87CAN/BYR, 93LEE/BYR]. Lundqvist [82LUN] and Nitsche, Standifer and Silva [89NIT/STA] showed that, if the bicarbonate formation constants of Bidoglio were correct, these species would have been detected in their experiments. Furthermore, the re-evaluation of the distribution coefficients reported by Bidoglio [82BID] indicates that $\mathrm{Am(CO_3)_2^-}$ was the predominant americium complex in the aqueous phase (*cf.* Appendix A).

Although $\mathrm{HCO_3^-}$ was the predominating ion of the carbonate system in the solvent extraction experiments performed by Lundqvist [82LUN], there no evidence for $\mathrm{Am(HCO_3)_n^{(3-n)}}$ complexes (*cf.* previous Section).

Figure V.11: Calculated distribution diagrams for the aqueous americium(III) hydroxide-carbonate system at $I = 0$ and 25°C. The diagrams have been calculated using the selected equilibrium constants in Table III.2 for a fixed partial pressure of CO_2(g) (upper diagram) and for a constant level of total inorganic carbon (lower diagram). Solid phase precipitation has been suppressed in these calculations.



Rao, Mahajan and Natarajan [88RAO/MAH] interpreted their solvent extraction experiments at pH = 6 and 7 and at $I = 0.5$ M assuming the formation of $AmHCO_3^{2+}$ and $Am(HCO_3)_2^+$. This review re-evaluates the data showing that these experiments reveal instead the existence of carbonate complexes (*cf.* Appendix A). Therefore, even if the equilibrium constants reported in [88RAO/MAH] for the bicarbonate complexes appear to be of the right order of magnitude, they are nevertheless rejected by this review.

Ewart *et al.* [92EWA/SMI] used a chemical model including the equilibrium constants for $AmHCO_3^{2+}$ and $Am(HCO_3)_2^+$ selected by Phillips *et al.* [88PHI/HAL] (which originate from the values reported by Bidoglio [82BID]), to fit the americium concentrations measured in "concrete equilibrated waters". However, due to experimental shortcomings in these measurements, no quantitative information can be extracted from the data, *cf.* the discussion of Ref. [86EWA/HOW] in Appendix A.

This review concludes that there is no experimental evidence which can prove the existence of americium bicarbonate complexes. Further experimental work is necessary before the reality of these complexes in aqueous solutions is established.

c) Mixed Am(III) hydroxide-carbonate complexes

Several authors have suggested the formation of mixed carbonate/hydroxide complexes of americium:

- Bernkopf and Kim [84BER/KIM] proposed the formation of three mixed complexes ($AmCO_3OH(aq)$, $AmCO_3(OH)_2^-$ and $Am(CO_3)_2OH^{2-}$) to explain their solubility data.

- Bidoglio [82BID] assumed the presence of $Am(CO_3)_2OH^{2-}$ in the analysis of his solvent extraction data.

- Shiloh, Givon and Marcus [69SHI/GIV] proposed the complex $Am(CO_3)_3OH^{4-}$ to explain their solubility data.

- Ewart *et al.* [86EWA/HOW, 87CRO/EWA] used the chemical model proposed by Bernkopf and Kim [84BER/KIM], adjusting the equilibrium constants for $AmCO_3(OH)_2^-$ and $Am(CO_3)_2OH^{2-}$ to fit the americium concentrations measured in "concrete equilibrated waters".

However, the discussions in Sections V.7.1.2.1.a and V.7.1.2.2, and in Appendix A, show that all the available experimental data can be reinterpreted with the assumption that only americium carbonate complexes and/or hydrolysis products are formed in aqueous solutions.

Further experimental work is needed to confirm or deny the existence of mixed Am(III) hydroxy-carbonate complexes in aqueous solutions.

d) Higher valences of americium

Although Am(V) is very unstable with respect to reduction and disproportionation in non-complexing aqueous media, it becomes quite stable in carbonate solutions.

Moskvin and Poznyakov [79MOS/POZ] report a coprecipitation study (using Fe(III) hydroxide as the host solid phase) of several actinides(V) as a function of the concentration of some ligands in NH_4Cl solutions at pH $\approx$ 8.5. For Am(V), Moskvin and Poznyakov report $\log_{10}\beta_1 = (2.02 \pm 0.09)$ for:

$$AmO_2^+ + HCO_3^- \rightleftharpoons AmO_2HCO_3(aq)$$

at $I = 0.25$ M, and (20 ± 2)°C. Although this study reveals an interaction between Am(V) and either carbonate or bicarbonate, the experimental evidence is not conclusive as to the composition of the complexes formed. This equilibrium constant is therefore rejected by this review.

Giffaut and Vitorge [93GIF/VIT] studied the solubility of ^{241}Am in 0.1 and 4 M NaCl solutions at 21°C. The larger solubility in the concentrated chloride solutions was interpreted as the radiolytic oxidation of Am(III) to Am(V), and the solubility curve at 4 M NaCl was interpreted with the formation of two Am(V) carbonate complexes:

$$AmO_2^+ + CO_3^{2-} \rightleftharpoons AmO_2CO_3^-$$
$$AmO_2^+ + 2\,CO_3^{2-} \rightleftharpoons AmO_2(CO_3)_2^{3-}$$

for which they report $\log_{10}\beta_1 = (5.5 \pm 0.3)$, $\log_{10}\beta_2 = (8.9 \pm 0.4)$. Giffaut and Vitorge also claimed that these complexes were in equilibrium with $NaAmO_2CO_3(s)$. However, owing to the lack of details in Ref. [93GIF/VIT], the reported equilibrium constants can not be credited in this review, *cf.* Appendix A.

The apparent normal potential of the Am(VI)/Am(V) couple was measured by Simakin *et al.* [74SIM/VOL]: $E°(VI/V) = (0.90 \pm 0.01)$ V *vs.* SHE in 1 M K_2CO_3 solutions at 20°C. Later Simakin [77SIM] reported that this normal potential was independent of the concentration of Na_2CO_3 ($E°(VI/V) = 0.90$ V *vs.* SHE), but that it decreased with the concentration of K_2CO_3 [77SIM]. Bourges *et al.* [83BOU/GUI] performed careful spectrophotometric and potentiometric measurements of this redox couple in carbonate media at 25°C. The apparent normal potential was found to be independent of $[CO_3^{2-}]$ in 2 M $NaHCO_3$-$NaCO_3$ mixtures: $E°(VI/V) = (0.975 \pm 0.01)$ V *vs.* SHE. Myasoedov *et al.* [86MYA/LEB] reported $E°(VI/V) = (0.910 \pm 0.003)$ V *vs.* NHE for 3 M K_2CO_3 solutions.

The apparent normal potential of the Am(IV)/Am(III) couple has been measured in $[NaHCO_3 + Na_2CO_3] = 2$ M solutions: $E°(IV/III) = (0.92 \pm 0.01)$ V *vs.* SHE at pH = 9.7 [82HOB/SAM], and $E°(IV/III) = (0.924 \pm 0.01)$ V *vs.* SHE at 25°C, $[CO_3^{2-}] = 1$M [83BOU/GUI]. The potential of the Am(IV)/Am(III) couple was found by Bourges *et al.* [83BOU/GUI] to decrease with the concentration of the carbonate anion in these $[NaHCO_3 + Na_2CO_3] = 2$ M solutions. Myasoedov *et al.* [86MYA/LEB] measured $E°(IV/III) = (0.870 \pm 0.002)$ V *vs.* NHE in 3 M $KHCO_3/K_2CO_3$ solutions.

The measurements of Bourges *et al.* [83BOU/GUI] for both the Am(VI)/Am(V) and Am(IV)/Am(III) couples performed in 2 M $NaHCO_3/Na_2CO_3$ media, have been reinterpreted by Robouch [89ROB] assuming the following equilibria:

$$AmO_2(CO_3)_3^{4-} + e^- \rightleftharpoons AmO_2(CO_3)_3^{5-} \quad (V.29)$$
$$Am(CO_3)_5^{6-} + e^- \rightleftharpoons Am(CO_3)_3^{3-} + 2\,CO_3^{2-} \quad (V.30)$$

which presume that $Am(IV)(CO_3)_5^{6-}$, $Am(V)O_2(CO_3)_3^{5-}$ and $Am(VI)O_2(CO_3)_3^{4-}$ are the limiting complexes for the IV, V and VI oxidation states (as expected by analogy with U(IV); Np(V) and U(VI)-Pu(VI), respectively). Furthermore, the measurements of Bourges *et al.* show that $Am(CO_3)_3^{3-}$ is the Am(III) limiting complex, which confirms Shiloh, Givon and Marcus's [69SHI/GIV] observations, (*cf.* Appendix A).

Based on the redox reactions mentioned above, Ferri, Grenthe and Salvatore [83FER/GRE] used the data of Bourges *et al.* [83BOU/GUI] to calculate the formation constant for the equilibrium

$$AmO_2^+ + 3\,CO_3^{2-} \rightleftharpoons AmO_2(CO_3)_3^{5-}$$

which they report to be $\log_{10}\beta_3(Am(V)) = (16.4 \pm 0.4)$ at $I = 3$ M $NaClO_4$. This appears to be a mistake, and this review believes that the reported value corresponds instead to reaction (V.29).

Grenthe, Robouch and Vitorge [86GRE/ROB] also used the data of Bourges *et al.* [83BOU/GUI] to estimate $\log_{10}\beta_5 = 40$ at an unspecified ionic strength for reaction

$$Am^{4+} + 5\,CO_3^{2-} \rightleftharpoons Am(CO_3)_5^{6-}$$

Similarly, this review reinterprets the data of Bourges *et al.* [83BOU/GUI] (*cf.* Appendix A) according to reactions (V.29) and (V.30) and selects the following values at zero ionic strength:

$$\log_{10} K^\circ(V.29, 298.15\,K) = 13.1 \pm 0.6$$
$$E^\circ(V.29, 298.15\,K) = (0.775 \pm 0.038)\ V,$$

and

$$\log_{10} K^\circ(V.30, 298.15\,K) = 20.1 \pm 0.9$$
$$E^\circ(V.30, 298.15\,K) = (1.19 \pm 0.05)\ V.$$

It should be noted that the result for reaction (V.29) can be combined with the standard redox potential for the AmO_2^{2+}/AmO_2^+ couple, and the formation reactions for the carbonate complexes:

$$AmO_2^{2+} + e^- \rightleftharpoons AmO_2^+ \quad (V.31)$$
$$AmO_2^{2+} + 3\,CO_3^{2-} \rightleftharpoons AmO_2(CO_3)_3^{4-}$$
$$AmO_2^+ + 3\,CO_3^{2-} \rightleftharpoons AmO_2(CO_3)_3^{5-}$$

where $\log_{10} K^\circ(\text{V.29}) = \log_{10} K^\circ(\text{V.31}) + \log_{10} (\beta_3^\circ(\text{Am(V)})/\beta_3^\circ(\text{Am(VI)}))$. A value for $\log_{10} K^\circ(\text{V.31}) = (27.0 \pm 1.5)$ can be calculated from the selected Gibbs energies in Table III.1, yielding:

$$\log_{10} \frac{\beta_3^\circ(\text{Am(VI)})}{\beta_3^\circ(\text{Am(V)})} = 13.9 \pm 1.6$$

This can be compared with the value (14.2 ± 0.3) which is calculated from the data in the uranium NEA-review [92GRE/FUG]. Comparisons with values for neptunium and plutonium should be made when the corresponding NEA-reviews are available.

The result for reaction (V.30) is combined with the Gibbs energy of formation for $\text{Am(CO}_3)_3^{3-}$ and CO_3^{2-} to obtain

$$\Delta_\text{f} G_\text{m}^\circ(\text{Am(CO}_3)_5^{6-}, \text{aq}, 298.15\,\text{K}) = -(3210.2 \pm 7.9)\ \text{kJ} \cdot \text{mol}^{-1}.$$

which is combined with the selected value for $\Delta_\text{f} G_\text{m}^\circ(\text{Am}^{4+}, \text{aq}, 298.15\,\text{K})$ to give:

$$\text{Am}^{4+} + 5\,\text{CO}_3^{2-} \rightleftharpoons \text{Am(CO}_3)_5^{6-} \qquad \log_{10} \beta_5^\circ = 39.3 \pm 2.1$$

This value is comparable with the analogous equilibrium constant obtained for uranium ($\log_{10} \beta_5^\circ = (34.0 \pm 0.9)$ [92GRE/FUG]). The large uncertainty in the value of $\log_{10} \beta_5^\circ$ given above for the formation of $\text{Am(CO}_3)_5^{6-}$ arises from the uncertainty in the value of $\Delta_\text{f} G_\text{m}^\circ(\text{Am}^{4+}, \text{aq}, 298.15\,\text{K})$ obtained by the estimation procedures discussed in Section V.2.3.

V.7.1.2.2. Solid americium carbonates

Only thermodynamic data for four americium carbonate solids have been reported:

- $\text{AmCO}_3\text{OH(s)}$ [84BER/KIM, 84SIL/NIT, 85SIL, 88STA/NIT, 90FEL/RAI, 92RUN/MEI]
- $\text{Am}_2\text{(CO}_3)_3\text{(s)}$ [69SHI/GIV, 89ROB, 91MEI/KIM, 91MEI/KIM2, 92RUN/MEI, 93GIF/VIT]
- $\text{NaAm(CO}_3)_2\text{(s)}$ [84VIT, 85KIM, 85KIM2, 86AVO/BIL]
- $\text{NaAmO}_2\text{CO}_3\text{(s)}$ [93GIF/VIT]

The values of the solubility products reported in the literature are given in Table V.16, *p*.149.

As described in the following two sections, the expected partial pressure of $\text{CO}_2\text{(g)}$ below which $\text{Am}_2\text{(CO}_3)_3\text{(s)}$ will (perhaps slowly) be converted into $\text{AmCO}_3\text{OH(s)}$ is $p_{\text{CO}_2} \approx 0.1$ bar (*cf.* [91MEI/KIM2, 92RUN/MEI, 92VIT]).

a) $AmCO_3OH(s)$

Americium hydroxy-carbonate displays two structural forms, orthorhombic and hexagonal. The cell parameters of the orthorhombic structure are $a = 4.958 \times 10^{-10}$, $b = 8.487 \times 10^{-10}$ and $c = 7.215 \times 10^{-10}$ m [85SIL]. Standifer and Nitsche [88STA/NIT] reported a crystallographic study identifying $\text{AmCO}_3\text{OH(cr)}$, precipitated at 60°C

and pH = 5.9, exhibiting an hexagonal structure. The corresponding cell parameters are $a = 12.22 \times 10^{-10}$ and $c = 9.70 \times 10^{-10}$ m. Solubility studies (*cf.* Table V.16) have been performed only for the orthorhombic form.

Shiloh, Givon and Marcus [69SHI/GIV] studied the solubility of a chemically characterised $Am_2(CO_3)_3(s)$ in 0.1 to 0.6 M potassium carbonate media; the authors interpreted their results assuming the formation of $Am(CO_3)_3OH^{4-}$. This review reinterprets their results, taking into account the influence of the ionic strength, and proposes the following equilibrium:

$$AmCO_3OH(s) + 2\,CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-} + OH^-, \qquad (V.32)$$

showing that $Am(CO_3)_3^{3-}$ is the predominant complex up to $[CO_3^{2-}] = 2$ M. However, from these measurements is not possible to determine if the solid phase in equilibrium with the carbonate solutions is $AmCO_3OH(s)$ or $Am_2(CO3)_3(s)$, *cf.* Appendix A.

Bernkopf and Kim [84BER/KIM] reported a solubility product constant for the compound $AmCO_3OH(s)$. The value was obtained from solubility measurements conducted in dilute bicarbonate media (0.1 to 0.3 M $NaClO_4$), at constant CO_2 partial pressure ($p_{CO_2} = 10^{-3.5}$ atm), and starting with $Am(OH)_3(s)$. The solid phase was not characterised but was assumed to be $AmCO_3OH(s)$. This review considers that the transformation of the initial solid, $Am(OH)_3(s) \rightarrow$"$AmCO_3OH(s)$", may be slow and it may have occurred during the experiments (*cf.* Appendix A), and therefore does not consider the reported solubility constant in the selection procedure.

Silva and Nitsche [84SIL/NIT, 85SIL] studied the solubility of americium in dilute carbonate solutions. The experiments were performed at constant ionic strength ($I =$ 0.1 M $NaClO_4$), constant pH (pH = 6.12 ± 0.03), and under controlled CO_2 partial pressure ($p_{CO_2} = 0.00792$ atm). The solid phase, characterised by its X-ray diffraction pattern to be orthorhombic $AmCO_3OH(cr)$.

The solubility of americium in carbonate media was also investigated by Runde, Meinrath and Kim [92RUN/MEI] under controlled p_{CO_2} atmosphere, with pH varying from 4 to 6 at $I = 0.1$ M $NaClO_4$. $AmCO_3OH(s)$ was assumed to be stable at $p_{CO_2} = 3 \times 10^{-4}$ atm by analogy with the neodymium-carbonate system [92RUN/MEI].

The solubility product re-evaluated from Silva's study (*cf.* discussion of Ref. [85SIL] in Appendix A) for the reaction

$$AmCO_3OH(cr) \rightleftharpoons Am^{3+} + CO_3^{2-} + OH^-, \qquad (V.33)$$

as well as the value reported by Runde, Meinrath and Kim [92RUN/MEI] are extrapolated to zero ionic strength using $\Delta\varepsilon = (0.45 \pm 0.04)\,\mathrm{kg \cdot mol^{-1}}$ as calculated from the selected ion interaction coefficients (Appendix B). The solubility products at $I = 0$ are averaged to give

$$\log_{10} K^\circ_{s,0}(V.33, 298.15\,K) = -21.2 \pm 1.4.$$

where the uncertainty has been assigned to cover the maximum range of expectancy. The derived Gibbs energy of formation is

$$\Delta_f G^\circ_m(AmCO_3OH, cr, 298.15\,K) = -(1404.8 \pm 9.3)\ \mathrm{kJ \cdot mol^{-1}}.$$

The solubility constant, $\log_{10} K^\circ_{s,3}(\text{V.32}) = \log_{10}(K^\circ_{s,0}(\text{V.33}) \times \beta^\circ_3) = -(5.51 \pm 0.08)$, determined by this review from the data of Shiloh, Givon and Marcus [69SHI/GIV] (*cf.* Appendix A), agrees with the value obtained with the selected equilibrium constants: $\log_{10}(K^\circ_{s,0}(\text{V.33}) \times \beta^\circ_3) = -(6.0 \pm 1.5)$. However, as mentioned above, it is not possible from the data in [69SHI/GIV] to conclude with confidence which is the solid phase in equilibrium.

The equilibrium constant at 298.15 K for the reaction

$$\text{Am(OH)}_3\text{(cr)} + \text{CO}_2\text{(g)} \rightleftharpoons \text{AmCO}_3\text{OH(cr)} + \text{H}_2\text{O(l)} \qquad \text{(V.34)}$$

can be calculated from the auxiliary data in Chapter III and from the values of $\log_{10} K^\circ_{s,0}(\text{V.33})$ and $\log_{10}{}^{*}K^\circ_{s,0}(\text{V.12})$:

$$\log_{10} K^\circ_{p}(\text{V.34}, 298.15\,\text{K}) = 4.2 \pm 1.5$$

which results in a CO_2(g) equilibrium partial pressure for the equilibrium between the two solids in reaction (V.34) of $p_{CO_2} = (0.6 \pm 2) \times 10^{-4}$ bar. This value is consistent with the conclusions presented by Vitorge [92VIT].

b) $Am_2(CO_3)_3$(s)

Shiloh, Givon and Marcus [69SHI/GIV] studied the solubility of a chemically characterised $Am_2(CO_3)_3$(s) in 0.1 to 0.6 M potassium carbonate media; the authors interpreted their results assuming the formation of $Am(CO_3)_3OH^{4-}$. Newton and Sullivan [85NEW/SUL] reinterpreted their results, taking into account the influence of the ionic strength, and proposed the following equilibrium:

$$0.5\,\text{Am}_2(\text{CO}_3)_3\text{(s)} + 1.5\,\text{CO}_3^{2-} \rightleftharpoons \text{Am(CO}_3)_3^{3-}, \qquad \text{(V.35)}$$

showing that $Am(CO_3)_3^{3-}$ is the predominant complex up to $[CO_3^{2-}] = 2$ M. However, from these measurements is not possible to determine which is the solid phase in equilibrium with the carbonate solutions: $Am_2(CO_3)_3$(s) or $AmCO_3OH$(s), *cf.* Appendix A.

Robouch [89ROB] measured the solubility of $Am_2(CO_3)_3$(cr) as a function of carbonate concentration at $I = 3$ M $NaClO_4$. Two set of experiments were performed: one where the total carbonate concentrations were known, and another using controlled CO_2(g) partial pressure. The solubility data were analysed in terms of carbonate complexes ($Am(CO_3)_n^{(3-2n)}$, $n = 1, 2, 3$) and a solubility product for $Am_2(CO_3)_3$(cr). The solid phase was characterised by its X-ray diffraction pattern. The reported equilibrium constants (*cf.* Table V.16) are re-evaluated by this review (*cf.* Appendix A).

Meinrath and Kim [91MEI/KIM] studied the solubility of americium in carbonate media. The data were collected at 0.1 and 0.3 M $NaClO_4$ ionic strength, pH = 6 to 9, under $p_{CO_2} = 0.01$ atm, and was interpreted by the formation of $AmCO_3^+$ and $Am(CO_3)_2^-$ in the aqueous solutions. The solid phase was characterised as

$Am_2(CO_3)_3$(cr) by X-ray diffraction, thermogravimetry and differential thermal analysis. A reinterpretation of these experimental data, *cf.* Appendix A, results in values for equilibrium constants which agree with those originally reported in [91MEI/KIM].

Two additional investigation of the solubility of americium in carbonate media have been reported by Meinrath and Kim [91MEI/KIM2] and Runde, Meinrath and Kim [92RUN/MEI] under controlled p_{CO_2}, with pH varying from 4 to 6, at I = 0.1 M $NaClO_4$. $AmCO_3OH$(s) was assumed [92RUN/MEI] to be the stable phase at $p_{CO_2} = 3 \times 10^{-4}$ atm by analogy with the neodymium system (*cf.* Appendix A), while at $p_{CO_2} \geq 0.01$ atm the stable solid phase was assumed on the same grounds to be $Am_2(CO_3)_3$(s) [91MEI/KIM2, 92RUN/MEI], which is in agreement with previous experimental observations [84SIL/NIT, 85SIL, 89ROB].

Giffaut and Vitorge [93GIF/VIT] reported solubility constants for $Am_2(CO_3)_3$(s) from an interpretation of their solubility data at 0.1 and 4 M NaCl, *cf.* Table V.16. However, due to the lack of details in this publication, the reported values can not be credited in this review, *cf.* Appendix A.

Four values of the equilibrium constant for reaction,

$$0.5\,Am_2(CO_3)_3(cr) \rightleftharpoons Am^{3+} + 1.5\,CO_3^{2-}, \qquad \text{(V.36)}$$

are considered in this review: the re-evaluated constant from the data by Robouch [89ROB] (*cf.* Appendix A), the values obtained by Meinrath and Kim [91MEI/KIM, 91MEI/KIM2] from their solubility measurements, and the value reported by Runde, Meinrath and Kim [92RUN/MEI]. These constants are converted to molal units and extrapolated to zero ionic strength using the specific ion interaction equations of Appendix B. The value obtained from the data of Robouch [89ROB] is discrepant. The difference in temperatures seems not large enough to explain the disagreement in the values of $K^\circ_{s,0}$(V.36), and there is no apparent reason to prefer the values from Kim *et al.* over those of Robouch. Therefore an unweighted average of the four values is performed, giving:

$$\log_{10} K^\circ_{s,0}(\text{V.36}, 298.15\,\text{K}) = -16.7 \pm 1.1.$$

where the uncertainty has been assigned to cover the maximum range of expectancy. The Gibbs energy of formation, is derived to be

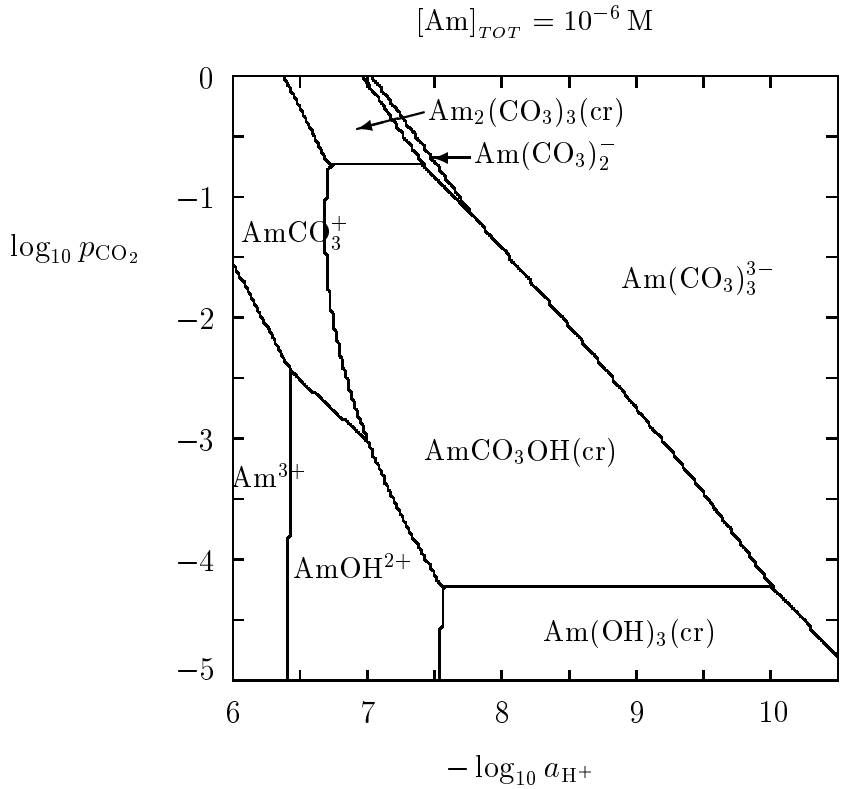
$$\Delta_f G^\circ_m(Am_2(CO_3)_3, cr, 298.15\,\text{K}) = -(2971.7 \pm 15.8)\ \text{kJ} \cdot \text{mol}^{-1}.$$

It should be mentioned that the solubility constant, $\log_{10} K^\circ_{s,3}$(V.35) = $\log_{10}(K^\circ_{s,0}(\text{V.36}) \times \beta^\circ_3) = -(3.68 \pm 0.08)$, determined by this review from the data of Shiloh, Givon and Marcus [69SHI/GIV] (*cf.* Appendix A), differs from the value obtained with the selected equilibrium constants: $\log_{10}(K^\circ_{s,0}(\text{V.36}) \times \beta^\circ_3) = -(1.5 \pm 1.3)$. However, as mentioned above, it is not possible from the data in [69SHI/GIV] to conclude with confidence which is the solid phase in equilibrium.

The equilibrium constant at 298.15 K for the reaction

$$AmCO_3OH(cr) + \frac{1}{2}CO_2(g) \rightleftharpoons \frac{1}{2}Am_2(CO_3)_3(cr) + \frac{1}{2}H_2O(l) \qquad \text{(V.37)}$$

Figure V.12: Calculated solubility and predominance area diagram for the americium(III) hydroxide-carbonate system in the range $6 \leq \text{pH} \leq 10.5$ as a function of the CO_2(g) partial pressure, at $I = 0$ and 25°C. Solubility limiting phases are indicated on the graph.



may be calculated from the auxiliary data in Chapter III, and the values of $\log_{10} K^\circ_{s,0}$(V.36) and $\log_{10}{}^* K_{s,0}$(V.33):

$$\log_{10} K^\circ_{p}(\text{V.37}, 298.15\,\text{K}) \quad = \quad 0.4 \pm 1.8$$

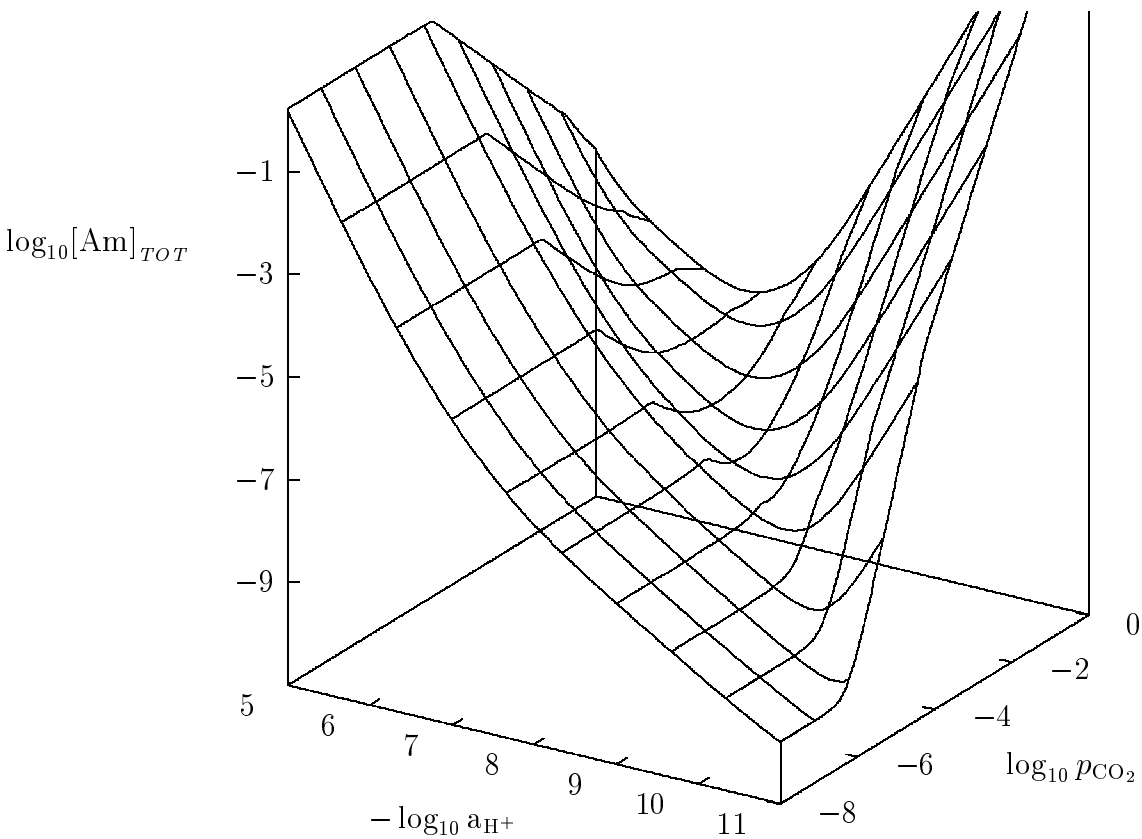
which results in a CO_2(g) equilibrium partial pressure for the equilibrium between the two solids in reaction (V.37) of $p_{CO_2} = (0.16 \pm 1.2)$ bar. This value is consistent with the experimental observations in Refs. [91MEI/KIM2, 92RUN/MEI] and with the conclusions of Vitorge [92VIT].

The limits established by the values of $\log_{10} K^\circ_{p}$(V.37) and $\log_{10} K^\circ_{p}$(V.34) are shown in the predominance area diagram in Figure V.12 for a total americium(III) concentration of 10^{-6} M in dilute solutions at 298.15 K. The solubility of americium under similar conditions is shown in Figure V.13.

c) Double sodium-americium carbonates

Keller and Fang [69KEL/FAN] investigated the thermal decomposition of synthetic $NaAm(CO_3)_2$(s) and $Na_3Am(CO_3)_3$(s). No thermodynamic data are available on the last solid.

Figure V.13: Calculated solubility diagram for the americium(III) hydroxide-carbonate system in the range $5 \leq \mathrm{pH} \leq 11$ and $-8 \leq \log_{10} p_{\mathrm{CO_2}} \leq 0$, at 25°C and standard conditions ($I = 0$).



Several publications have appeared with values for the solubility product of $NaAm(CO_3)_2(s)$ [85KIM, 85KIM2, 86AVO/BIL], *cf.* Table V.16. These values are based on solubility experiments performed by Vitorge [84VIT]. However, the experimental details have not appeared in the open literature. Robouch [89ROB] characterised this solid by X-ray diffraction in some of his experiments, but not enough details were given to allow a re-evaluation of his data (*cf.* Appendix A). Due to the lack of experimental details mentioned above, a value for the solubility product of $NaAm(CO_3)_2(s)$ can not be recommended by this review.

d) Other americium carbonate compounds

Schultz and Penneman [86SCH/PEN] listed the americium solids reported in the literature, and Weigel [85WEI] did a critical and exhaustive review of the Am(V) and Am(VI) carbonate solids, which can be summarised as follows:

- Pentavalent americium:
  1. Mono-carbonate solids of the type $M AmO_2CO_3(cr)$ (where M = K, Rb, Cs, NH_4) display a hexagonal symmetry, space group C6/mmc, $a = (5.10 \pm 0.02) \times 10^{-10}$ m, $c = (11.0 \pm 0.7) \times 10^{-10}$ m.
  2. $K_3AmO_2(CO_3)_2(s)$ is a tan precipitate formed in 3.5 M K_2CO_3 americium solutions oxidised with ozone.
  3. Tri-carbonates $M_5AmO_2(CO_3)_3(s)$ (where M = K, Cs, NH_4) have also been reported, no crystallographic parameters are available.
- Hexavalent americium: $Na_{2x-2}(AmO_2^{2+})(CO_3)_x$ of unknown stoichiometry is readily formed when adding methanol to an Am(VI) – 0.1 M $NaHCO_3$ solution. Similar precipitates were obtained with Ca and Ba cations, but no stoichiometric, or crystallographic data have been reported.

More recently Giffaut and Vitorge [93GIF/VIT] have studied the solubility of ^{241}Am in 0.1 and 4 M NaCl solutions at 21°C. The larger solubility in the concentrated chloride solutions was interpreted as the radiolytic oxidation of Am(III) to Am(V), and the solubility curve at 4 M NaCl was interpreted with the following solubility equilibria:

$$NaAmO_2CO_3(s) \rightleftharpoons Na^+ + AmO_2^+ + CO_3^{2-}$$

for which they report $\log_{10} K_{s,0} = -(10.5 \pm 0.3)$. Giffaut and Vitorge also claimed the formation of two Am(V) carbonate complexes ($AmO_2CO_3^-$ and $AmO_2(CO_3)_2^{3-}$). However, owing to the lack of details in Ref. [93GIF/VIT], the reported solubility constant can not be credited in this review, *cf.* Appendix A.

V.7.1.3. Americium cyanide complexes

Qualitative information on the interaction between americium(III) and cyanide ions was provided by Cuillerdier *et al.* [77CUI/MUS, 81CUI], who report $\log_{10} \beta_1 \approx 4$ at

$I = 5$ M and 25°C without giving any experimental details. More experimental work is needed to confirm the composition and stability of the complexes formed. No value can be recommended for this system.

V.7.1.4. Americium thiocyanate complexes

There are several separation procedures of lanthanoid and actinoid elements in aqueous thiocyanate media. However, very few direct experimental determinations of the thermodynamic values of the americium(III)-thiocyanate system have been reported; and no critical compilations of these data seem to exist.

Americium complexation by thiocyanate is quite weak, and its study requires large concentrations of the thiocyanate ligand. Therefore, large background electrolyte concentrations have been used in order to keep activity coefficients nearly constant. Most investigations have been performed by solvent extraction using 1.0 or 5.0 M $NaSCN/NaClO_4$ aqueous solutions. Mononuclear species, such as $AmSCN^{2+}$, $Am(SCN)_2^+$, $Am(SCN)_3(aq)$ and $Am(SCN)_4^-$, have been suggested to interpret the different experimental measurements, according to:

$$Am^{3+} + n\,SCN^- \rightleftharpoons Am(SCN)_n^{(3-n)}. \qquad (V.38)$$

Table V.17 presents all the stability constants ($\beta_1, \beta_2, \beta_3$ and β_4,) reported in the literature and the experimental details: temperature, pH, ionic media and the technique used for the investigations. We note that Ref. [70KIN/CHO] is only a preliminary report of the study in [74KIN/CHO]. It should be noted that some authors reported the presence of only $AmSCN^{2+}$ and $Am(SCN)_2^+$ (model "β_1, β_2") [65CHO/KET, 71HAR, 71KHO/NAR, 72HAR/PET2, 74KHO/MAT], while others reported that the complex $Am(SCN)_2^+$ is negligible and interpreted their data assuming the formation of $Am(SCN)_3(aq)$ (model "β_1, β_3") [64SEK, 65SEK3, 74KIN/CHO] † . Hence, the direct comparison of stability constants reported in the literature is hindered by the fact that either β_2 or β_3 was not calculated in several cases.

The solvent extraction experiments performed by Choppin and Ketels [65CHO/KET], display a temperature dependence opposite to that reported in later publications [72HAR/PET, 74KIN/CHO]. Therefore, this work was not considered by this review.

Khopkar and Narayanankutty [71KHO/NAR] and Khopkar and Mathur [74KHO/MAT] studied the Am(III)–SCN^- system, using dinonylnaphthalene sulphonate liquid ion exchangers. The variation of the distribution coefficient *vs.* $[SCN^-]$ was interpreted assuming the presence of $AmSCN^{2+}$ and $Am(SCN)_2^+$ complexes. Reanalysis of the data shows that a better fit is obtained assuming the formation of $Am(SCN)_3(aq)$, instead of $Am(SCN)_2^+$. The complexation of americium by thiocyanate ligands is rather weak and the determination of the stability constants is very sensitive to changes in the chemical model. This review considers that the work of Khopkar *et al.* evidences only the existence of $AmSCN^{2+}$.

† It should be noted however, that while Kinard and Choppin [74KIN/CHO] used the "β_1, β_3" model to interpret their data, they only reported values of β_1.

Table V.17: Experimental equilibrium constants for the americium(III)-thiocyanate system.

Method	Ionic Medium[a]	pH	t (°C)	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	Reference
cix	5.0 M NH_4ClO_4	4.0	?	0.24[b]		−0.04[b]	[62LEB/YAK]
	0.5 M NH_4ClO_4	4.0	?	0.66±0.02			
	$I \longrightarrow 0$	4.0	?	1.61±0.01[b]			
dis	5.0 M $NaClO_4$	3–4	25	0.85±0.05		0.55±0.15[c]	[64SEK, 65SEK3]
dis	1.0 M $NaClO_4$	2.0	25	0.50±0.01	0.85±0.02		[65CHO/KET]
			40	0.40±0.04			
			55	0.19±0.05			
dis	5.0 M $NaClO_4$	3.0	10	0.42±0.02			[70KIN/CHO]
			25	0.60±0.05			
			40	0.68±0.02			
			50	0.72±0.02			
sp	1.0 M $NaClO_4$	2.0	22	0.76±0.02	0.83 ±0.07		[71HAR]
dis	1.0 M $NaClO_4$	2.0	17.7	0.31±0.06	−0.8 ±2.5	0.35±0.14	
			25	0.36±0.02	0.05 ±0.14	−0.16±0.18	
			30	0.37±0.04	−0.8 ±2.0	0.21±0.17	
			35	0.33±0.03	−0.6 ±0.7	0.11±0.11	
			44.3	0.43±0.03	−0.15 ±0.3	−0.20±0.28	
dis	1.0 M $LiClO_4$	2.5	30	0.07±0.04	0.24 ±0.03		[71KHO/NAR]
	1.0 M $NaClO_4$	2.5	30	0.17±0.05	0.51 ±0.03		
	1.0 M NH_4ClO_4	2.5	30	0.12±0.06	0.54 ±0.03		
dis	1.0 M $NaClO_4$	2.0	25	0.36±0.03	0.04 ±0.20	−0.15±0.23	[72HAR/PET]
			18	0.30±0.08[d]		0.36±0.14[d]	
			25	0.36±0.03[d]		0.17±0.06[d]	
			30	0.38±0.03[d]		0.22±0.18[d]	
			35	0.35±0.03[d]		0.11±0.11[d]	
			45	0.47±0.03[d]		0.01±0.06[d]	
sp	1.0 M $NaClO_4$	2.0	22	0.76±0.03	0.83 ±0.07		[72HAR/PET2]
dis	2.0 M NH_4NO_3	2.0	25	−0.52±0.14	0.74 ±0.03	0.87±0.05	[73CHI/DAN]
dis	1.0 M NH_4ClO_4	2.8	30	0.17±0.07	0.62 ±0.03		[74KHO/MAT]
			15	0.14±0.08[e]	0.68 ±0.03[e]		
			37	0.12±0.07[e]	0.64 ±0.03[e]		
			45	0.21±0.04[e]	0.59 ±0.02[e]		

Table V.17 (continued)

Method	Ionic Medium[(a)]	pH	t (°C)	$\log_{10}\beta_1$	$\log_{10}\beta_2$	$\log_{10}\beta_3$	Reference
dis	5.0 M $NaClO_4$	3.0	10	0.42±0.02			[74KIN/CHO]
			25	0.60±0.05			
			40	0.68±0.02			
			55	0.72±0.02			

(a) A significant amount of the anion in the background electrolyte was substituted by SCN^- in these studies.
(b) Values corrected to $I = 0$ using Davies equation.
(c) Sekine [64SEK, 65SEK3] reports $\log_{10}\beta_4 = 0.00 \pm 0.15$
(d) Values digitised by this review from Figure 12 and Figure 7 in Refs. [71HAR, 72HAR/PET] respectively (β_1, β_3 model).
(e) Values digitised by this review from Figure 3 in Ref. [74KHO/MAT].

Harmon *et al.* [71HAR, 72HAR/PET] observed the spectral changes in the 503 nm americium absorption band produced by SCN^- complexation. The authors calculated the formation constant of $AmSCN^{2+}$ and $Am(SCN)_2^+$ from the spectral data. This review considers that, because of the scattering in the data, no reliable conclusion on the existence of $Am(SCN)_2^+$ and/or $Am(SCN)_3(aq)$ can be extracted. Hence, the stability constants obtained by Harmon *et al.* from their spectrophotometric measurements are not accepted here.

Chiarizia *et al.* [73CHI/DAN] studied the competitive complexation in NH_4SCN/-NH_4NO_3 media and interpreted the thiocyanate system assuming the formation of $AmSCN^{2+}$, $Am(SCN)_2^+$ and $Am(SCN)_3(aq)$ complexes. The resulting speciation diagram indicates that $AmSCN^{2+}$ and $Am(SCN)_3(aq)$ are the predominant species, while $AmSCN^{2+}$ never exceeds 5%. This contradicts all other experimental evidence, and therefore, the reported stability constants ($\log_{10}\beta_n$) are disregarded by this review.

Lebedev and Yakovlev's ion exchange study [62LEB/YAK], and Sekine's [64SEK, 65SEK3], Kinard and Choppin's [74KIN/CHO] solvent extraction experiments clearly evidenced the existence of the $AmSCN^{2+}$ and $Am(SCN)_3(aq)$ complexes, at high ionic strength ($I = 5$ M). As the specific ion interaction equations are valid up to $I \approx 3$ M, the corresponding stability constants are not extrapolated to zero ionic strength, and therefore these values are not selected in this review, even though they are considered reliable.

At lower ionic strength ($I \leq 1$ M) there is some experimental evidence showing the existence of some weak complexes $Am(SCN)_n^{(3-n)}$ with $n > 1$, but more experimental work is needed to confirm the stoichiometry of the species formed. Hence, the values of β_2 and β_3 reported in the literature at $I \leq 1$ M, *cf.* Table V.17, are disregarded by this review, and the corresponding stability constants are not selected.

Attempts to investigate the formation of higher order thiocyanate complexes, using tributylphosphate or quaternary amines as extracting agents, indicated the presence

Table V.18: Literature review of the thermodynamic functions for the Am(III)-thiocyanate system.

I (M)	t (°C)	$\log_{10}\beta_n^\circ$	$\Delta_r G_m$ ($kJ \cdot mol^{-1}$)	$\Delta_r H_m$ ($kJ \cdot mol^{-1}$)	$\Delta_r S_m$ ($J \cdot K^{-1} \cdot mol^{-1}$)	Reference
$Am^{3+} + SCN^- \rightleftharpoons AmSCN^{2+}$						
1.0	25	0.50 ± 0.01	-2.89 ± 0.08	-18.2 ± 1.3	-52 ± 4	[65CHO/KET]
5.0	25		-3.39 ± 0.29	10.6 ± 1.2	47	[70KIN/CHO]
1.0	25	0.36 ± 0.03	-1.97 ± 0.08	6.7 ± 2.9	29 ± 8	[71HAR, 72HAR/PET]
5.0	25	0.60 ± 0.05	-3.40 ± 0.31	11.8 ± 2.1	50 ± 7	[74KIN/CHO]
1.0	30	0.12 ± 0.07	-0.71 ± 0.42	2.5 ± 2.3	10 ± 8	[74KHO/MAT]
$Am^{3+} + 2\,SCN^- \rightleftharpoons Am(SCN)_2^+$						
1.0	30	0.65 ± 0.03	-3.68 ± 0.17	-4.8 ± 1.1	-4 ± 4	[74KHO/MAT]
$Am^{3+} + 3\,SCN^- \rightleftharpoons Am(SCN)_3(aq)$						
1.0	25	-0.15 ± 0.23	-0.79 ± 0.63	-25 ± 17	-84 ± 63	[71HAR, 72HAR/PET]

of anionic species $Am(SCN)_4^-$ [64SEK, 65SEK3, 74KIN/CHO], but no reliable stability constants have been reported.

The values for the equilibrium constant for $AmSCN^{2+}$ determined at $I = 0.5$ M by Lebedev and Yakovlev [62LEB/YAK] and at $I = 1$ M by Harmon *et al.* [71HAR, 72HAR/PET] and Khopkar *et al.* [71KHO/NAR, 74KHO/MAT] are extrapolated to zero ionic strength (*cf.* Appendix A) with the specific ion interaction equations of Appendix B using $\Delta\varepsilon_1 = -(0.15 \pm 0.05)\,kg \cdot mol^{-1}$. The unweighted average of the extrapolated values yields:

$$\log_{10}\beta_1^\circ(\text{V.38}, n = 1, 298.15\,\text{K}) \quad = \quad 1.3 \pm 0.3.$$

The Gibbs energy of formation is derived to be

$$\Delta_f G_m^\circ(AmSCN^{2+}, aq, 298.15\,\text{K}) \quad = \quad -(513.4 \pm 6.4)\ kJ \cdot mol^{-1}.$$

Table V.18 presents a literature review of thermodynamic functions for the formation of $AmSCN^{2+}$, $Am(SCN)_2^+$, and $Am(SCN)_3(aq)$ complexes. As mentioned earlier, the study of [65CHO/KET] is disregarded by this review because its opposite temperature dependence of β_1. The enthalpy changes obtained in Appendix A

Table V.19: Structural data for americium silicides

Phase	Symmetry	Space Group	Iso-type Compound	Cell Parameters / (10^{-10} m)
Am_5Si_3(cr)	tetragonal	I4/mcm	W_5Si_3(cr)	$a = 11.419 \pm 0.016$ $c = 5.538 \pm 0.008$
AmSi(cr)	orthorhombic	Pnma	FeB(cr)	$a = 8.400 \pm 0.015$ $b = 4.064 \pm 0.007$ $c = 6.036 \pm 0.011$
$AmSi_{1.6\pm x}$(cr)	hexagonal	P6/mmm	AlB_2(cr)	$a = 3.871 \pm 0.009$ $c = 4.120 \pm 0.009$
$AmSi_2$(cr)	tetragonal	$I4_1$/amd	α-$ThSi_2$	$a = 4.015 \pm 0.007$ $c = 13.733 \pm 0.022$

from the equilibrium constants determined at $I = 1$ M by Harmon *et al.* [71HAR, 72HAR/PET] and by Khopkar and Mathur [74KHO/MAT] yield the following values:

$$\begin{aligned} \Delta_r H^\circ_m(\text{V.38}, n = 1, I = 1\,\text{M}, 298.15\,\text{K}) &= (5.5 \pm 7)\ \text{kJ} \cdot \text{mol}^{-1} \\ \Delta_r S^\circ_m(\text{V.38}, n = 1, I = 1\,\text{M}, 298.15\,\text{K}) &= (23 \pm 27)\ \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}. \end{aligned}$$

Extrapolation of these equilibrium constants to $I = 0$ according to the equations of Appendix B, followed by a weighted linear regression "$\ln \beta_1$ *vs.* $1/T(\text{K}^{-1})$" constrained with the selected value of $\log_{10} \beta^\circ_1 = 1.3$, would lead to the following standard values at 298.15 K: $\Delta_r H^\circ_m(\text{V.38}, n = 1) = (10 \pm 12)$ kJ $\cdot$ mol^{-1} and $\Delta_r S^\circ_m(\text{V.38}, n = 1) = (60 \pm 40)$ J $\cdot$ K^{-1} $\cdot$ mol^{-1}. However, this review does not recommend these values because of the uncertainty in the influence of temperature on activity coefficients.

V.7.2. Silicon compounds and complexes

V.7.2.1. Americium silicides

Weigel *et al.* [84WEI/WIT] have prepared the four silicides of americium given in Table V.19. The samples were prepared by the reaction of $^{241}AmF_3$(cr) and silicon in alumina crucibles at 980 - 1200°C in vacuo, by the following general reaction:

$$4\,AmF_3(cr) + (7 + 4y)\,Si(cr) \longrightarrow 4\,AmSi_{1+y}(cr) + 3\,SiF_4(g)$$

Inhomogeneous samples were re-annealed in vacuo at 1000 - 1200°C. The silicides were characterised by high temperature X-ray diffraction up to 900°. Insufficient

information was obtained to draw a reliable phase diagram, but all four silicides were reported to melt between 1173 and 1273 K, and a possible phase transformation in AmSi(cr) was observed between 813 and 943 K. The phase relationships in the Am-Si system are thus very similar to those in the U-Si and Pu-Si systems. The $AmSi_{1.6\pm x}$(cr) is probably a single phase region extending from Am_2Si_3(cr) to Am_3Si_5(cr).

V.7.2.2. Aqueous americium silicates

No thermodynamic data have been reported in the literature on americium silicate complexes in aqueous solution nor have any species been demonstrated. Because of a lack of data, the trivalent lanthanoids can not be used for guidance. Complexes of the form $FeSiO(OH)_3^{2+}$ were prepared with trivalent iron [71POR/WEB].

V.7.2.3. Solid americium silicate compounds

Very little has been reported on silicate compounds of americium. $AmSiO_4$(cr) was reported by Keller [63KEL, 67KEL] as having a tetragonal structure with the unit cell parameters $a = 6.87 \times 10^{-10}$ and $c = 6.20 \times 10^{-10}$ m. However, tetravalent Am is unlikely to be of importance in natural aquatic systems. High-temperature solid state reactions in the Am^{III}-oxide-SiO_2 system can lead to compounds of the form $Am_{9.33}\square_{0.67}(SiO_4)_6O_2$(cr) (where $\square$ stands for vacancies in the crystal lattice) and $Am_8(SiO_6)_2$(cr) [79ALL], similar to the corresponding lanthanoid compounds. The former are stated to crystallise with the hexagonal apatite type of structure as do the polyoxides $M^{I}Am_9(SiO_4)_6O_2$(cr) and $M^{II}Am_8(SiO_4)_6O_2$(cr). Because of the similarity in chemical behaviour between the trivalent actinoids and lanthanoids, one would expect americium(III) to form a variety of compounds with silica as do the rare earths [86GSC/EYR]. Rare earth disilicates precipitate as a gel from solutions of rare earth chloride and silicic acid [77BOC/CHA]. No data are available on the solubility constant of any americium silicate compounds.

V.7.3. Germanium compounds

Crystallographic information for $AmGeO_4$(cr) is given in Table V.6.

V.8. Group 13 compounds

V.8.1. Aluminium compounds

Crystallographic information for $AmAlO_3$(cr) is given in Table V.6.

V.8.2. Thallium compounds

The existence of $TlAm(SO_4)_2 \cdot xH_2O$(s) and $Tl_8Am_2(SO_4)_7$(s) has been reported by Yakovlev and Kosyakov [58YAK/KOS] (*cf.* Section V.5.1.2.2). No thermodynamic data has been reported on these compounds.

V.9. Group 9 compounds

V.9.1. Cobalt compounds

Fedoseeva and Budantseva reported the synthesis of the americium(V) sulphate compound $Co(NH_3)_6AmO_2(SO_4)_2 \cdot 2H_2O(s)$ [89FED/BUD] (*cf.* Section V.5.1.2.2). No thermodynamic data has been reported on this compound.

V.10. Group 6 complexes

V.10.1. Molybdates and tungstates

Crystallographic information for the molybdates and tungstates of americium are given in Table V.6.

V.10.2. Polyphosphotungstate complexes

The stabilisation of Am(IV), Am(V) and Am(VI) by phosphotungstate ions in aqueous solutions is discussed in Section V.6.2.1.3, *p*.144. In addition, complexes of Am(III) and Am(IV) with the anions $W_{10}O_{36}^{12-}$, $PW_{11}O_{39}^{7-}$ and $SiW_{11}O_{39}^{8-}$ are mentioned in [89YUS, 89YUS/FED]. No thermodynamic data can be selected for any of these systems.

V.11. Group 5 complexes

Crystallographic information for the ternary and quaternary oxides of americium and vanadium, niobium or tantalum are given in Table V.6.

V.12. Group 4 complexes

Crystallographic information for the quaternary oxides of americium and titanium are given in Table V.6.

V.13. Actinide compounds and complexes

V.13.1. Actinide compounds

V.13.1.1. $U_{0.5}Am_{0.5}O_2$(cr)

Bartscher and Sari [83BAR/SAR] have measured the oxygen potentials in $U_{0.5}Am_{0.5}O_{2\pm X}$(cr) for both hypo- and hyper-stoichiometric oxides, $1.87 \leq O/(U + Am) < 2.09$, between 873 and 1573 K by equilibration with $CO(g)/CO_2(g)$ and $H_2(g)/H_2O(g)$ mixtures. These results have been used to derive partial molar enthalpies and entropies of dissolution of oxygen in the oxides (presented only in the form of plots). The results are compared to the similar U-Pu-O and U-Ce-O systems [83BAR/SAR].

V.13.1.2. Other ternary and quaternary oxides

Crystallographic information for the ternary and quaternary oxides of americium and protactinium are given in Table V.6.

V.13.2. Actinide complexes

V.13.2.1. Actinide-actinide interactions

The tendency of actinide(V) cations, MO_2^+, to interact with certain cations (mostly multicharged) has been described in many publications using an array of techniques, mainly absorption spectrophotometry, proton spin relaxation, potentiometric techniques and Raman spectroscopy. These interactions have been reviewed by Grenthe *et al.* in the uranium NEA-TDB review [92GRE/FUG], where it is noted that all relevant studies before 1977 were extensively reviewed in Ref. [79FRO/RYK].

Complexes of AmO_2^+ with UO_2^{2+} and NpO_2^{2+}

$$MO_2^+ + M'O_2^{2+} \rightleftharpoons MM'O_4^{3+}$$

were reported [81GUI/HOB, 82GUI/BEG] for $I = 10$ M (perchlorate) and in media of variable ionic strength for the species AmO_2^+-UO_2^{2+}. As discussed by Grenthe *et al.* [92GRE/FUG], no data can be recommended for these cation association reactions.

V.14. Group 2 (alkaline-earth) and group 3 compounds

Crystallographic information for $AmScO_3$(cr) and for the ternary and quaternary oxides of americium and the alkaline-earths are given in Table V.6.

V.15. Group 1 (alkali) compounds

V.15.1. Ternary and quaternary oxides

The only thermodynamic data for the ternary oxides are the enthalpies of formation of the perovskite-type compounds $BaAmO_3$(cr) and $SrAmO_3$(cr), as discussed in Section V.3.2.6. Crystallographic information for the other ternary and quaternary oxides are given in Table V.6.

V.15.2. Ternary fluorides

A discussion on the ternary fluorides $LiAmF_5$(cr), $Na_7Am_6F_{31}$(cr) and Rb_2AmF_6(cr) is presented in Section V.4.2.2.6.

V.15.3. Ternary and quaternary chlorides

A discussion on the ternary chlorides $CsAmCl_4$(cr), Cs_3AmCl_6(cr), M_2AmCl_5(cr) (M = K, NH_4, Rb) and the quaternary chloride $Cs_2NaAmCl_6$(cr) is presented in Section V.4.2.3.4.

V.15.4. Alkali sulphates

The existence of $M\mathrm{Am(SO_4)_2} \cdot x\mathrm{H_2O(s)}$ (with M = K, Rb and Cs) as well as $\mathrm{K_3Am(SO_4)_3} \cdot \mathrm{H_2O(s)}$ and $\mathrm{K_8Am_2(SO_4)_7(s)}$ has been reported by Yakovlev and Kosyakov [58YAK/KOS]. No thermodynamic data has been reported on these compounds (*cf.* Section V.5.1.2.2).

V.15.5. Alkali phosphates

Ternary phosphates of Am(VI), $M\mathrm{AmO_2PO_4} \cdot x\mathrm{H_2O(cr)}$ (with M = K, Rb and Cs) have been reported by Lawaldt *et al.* [82LAW/MAR], *cf.* Section V.6.2.2.2.

V.15.6. Alkali arsenates

Ternary arsenates of Am(VI), $M\mathrm{AmO_2AsO_4} \cdot x\mathrm{H_2O(cr)}$ (with M = K, Rb and Cs) have been reported by Lawaldt *et al.* [82LAW/MAR], *cf.* Section V.6.3.2.

V.15.7. Alkali carbonates

The Am(III) compounds $\mathrm{NaAm(CO_3)_2(cr)}$ and $\mathrm{Na_3Am(CO_3)_3(s)}$, are discussed in Section V.7.1.2.2.c. The americium(V) carbonates: $M\mathrm{AmO_2CO_3(cr)}$, with M = Na, K, Rb, Cr; $\mathrm{K_3AmO_2(CO_3)_2(s)}$ and $M_5\mathrm{AmO_2(CO_3)_3(s)}$, with M = K and Cs are discussed in Section V.7.1.2.2.d, where carbonates of americium(VI) of unknown stoichiometry are also mentioned.

Chapter VI

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Chapter VII

Authors list

This chapter contains an alphabetical list of the authors of the references cited in this book, *cf.* Chapter VI. The reference codes given with each name corresponds to the publications of which the person is the author or a co-author. Note that inconsistencies may occur due to different interpretations of foreign alphabets. These inconsistencies are not corrected in this review.

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Sekine, T.	[64SEK], [65SEK], [65SEK2], [65SEK3], [69SEK/SAK]
Seleznev, A.G.	[77SEL/KOS], [78SEL/SHU], [82RAD/RYA], [83SHU/SEL]
Sergeyeva, E.I.	[92FUG/KHO]
Serik, V.F.	[80DRO/PRU]
Serne, R.J.	[78RAI/SER]
Settle, J.L.	[93ACK/SET]
Shafiev, A.I.	[75ERI/SHA]
Shalinets, A.B.	[72SHA/STE]
Shalinoff, G.V.	[86SOD/EDE]
Shannon, R.D.	[76SHA]
Sharma, H.D.	[64BAN/PAT]
Shestakov, B.I.	[73MAK/STE]
Shiloh, M.	[64SHI/MAR], [69MAR/SHI], [69SHI/GIV]
Shilov, V.N.	[75NIK/SHI]
Shimbarev, E.V.	[82RAD/RYA], [86LYA/SUD], [90VAS/KAL]
Shirley, V.S.	[78LED/SHI]
Shock, E.L.	[88SHO/HEL], [89SHO/HEL], [89SHO/HEL2], [92SHO/OEL]
Shushakov, V.D.	[77SEL/KOS], [78SEL/SHU], [83SHU/SEL]

Author	References
Shushakova, T.V.	[83SHU/SEL]
Shvedov, V.P.	[65STE/SHV]
Siegel, M.D.	[88PHI/HAL]
Sillén, L.G.	[58BJE/SCH], [64SIL/MAR], [71SIL/MAR]
Silva, R.	[83EDE/BUC]
Silva, R.J.	[82SIL], [83SIL], [84SIL], [84SIL/NIT], [85SIL], [86KER/SIL], [89NIT/STA]
Silvester, L.F.	[76PIT/SIL], [78PIT/PET], [88PHI/HAL]
Simakin, G.A.	[74SIM/VOL], [77SIM]
Simpson, O.C.	[50ERW/SIM], [50PHI/SEA]
Sjoblom, R.	[77COO/WOO]
Sjoblom, R.K.	[78GOR/MUL]
Skeen, J.	[85PHI/PHI]
Šmirous, F.	[74CEL/HOL]
Smith, R.M.	[76SMI/MAR], [89SMI/MAR]
Smith-Briggs, J.L.	[92EWA/SMI]
Soderholm, L.	[86SOD/EDE]
Söhnel, O.	[85SOH/NOV]
Sokolov, V.B.	[80DRO/PRU]
Sonnenberger, D.C.	[85MOR/SON]
Spahiu, K.	[81CIA/FER], [83SPA], [85SPA], [92GRE/SPA]
Spirlet, J.C.	[72FUG/SPI], [74MAR/SPI], [76HAL/MOR], [80HAL/LEE]
Stadler, S.	[88KIM/BUC], [88STA/KIM], [88STA/KIM2]
Standifer, E.M.	[88STA/NIT], [89NIT/STA]
Starik, I.E.	[61STA/GIN]
Stebunov, O.B.	[66VDO/KOL], [69VDO/STE]
Steinfink, H.	[66NOR/STE]
Stepanov, A.V.	[65STE/SHV], [72SHA/STE], [73MAK/STE]
Stephens, D.R.	[68STE/STR]
Steward, M.A.A.	[68BAG/LAI]
Stokely, J.R.	[76FRI/STO]
Stokes, R.H.	[59ROB/STO]
Storms, E.K.	[84HOL/RAN]
Strazik, W.F.	[65CHO/STR]
Strickert, R.G.	[82RAI/STR], [83RAI/STR]
Stromberg, H.D.	[68STE/STR]
Strouse, C.E.	[72BAY/ASP]
Stumm, W.	[81STU/MOR]
Stupin, V.A.	[77SEL/KOS]
Sudakov, L.V.	[82RAD/RYA], [86LYA/SUD]
Sullivan, J.C.	[76SUL/GOR], [77COO/WOO], [78GOR/MUL], [85NEW/SUL]
Sundén, N.	[54SUN]
Suzuki, S.	[85SAT/MIT]
Sverjensky, D.A.	[89SHO/HEL2], [92SHO/OEL]

Author	References
Tanamas, R.	[74BER/TAN]
Tananaev, I.G.	[89TAN], [90TAN], [90TAN2]
Tanet, G.	[87BID/TAN]
Tanger IV, J.C.	[88TAN/HEL]
Tardy, Y.	[84VIE/TAR]
Tasker, P.W.	[87EWA/TAS]
Taylor, J.C.	[76TAY]
Taylor, J.R.	[82TAY]
Teague, L.S.	[80BEN/TEA]
Templeton, D.H.	[53TEM/DAU], [56GRA/CUN]
Tetenbaum, M.	[81FLO/TET]
Thayer, W.	[79AKE/JOH]
Thomason, H.P.	[86EWA/HOW], [92EWA/SMI], [92THO/WIL]
Thorn, R.J.	[66ACK/FAI]
Thorstenson, D.C.	[80PAR/THO]
Timofeev, G.A.	[86MYA/LEB]
Torstenfelt, B.	[84ALL/OLO]
Tran The, P.	[91VIT/TRA]
Trofimov, T.I.	[82KUL/LEB]
Tweed, C.J.	[87CRO/EWA]
Unrein, P.J.	[63CHO/UNR], [76CHO/UNR]
Vandevender, W.H.	[80HAS/VAN]
Vaninbroukx, R.	[86VAN]
Varga, L.P.	[73VAR/BAY]
Vasil'ev, V.I.	[90VAS/KAL]
Vasil'ev, V.P.	[62VAS]
Vasil'ev, V.Y.	[75VAS/AND], [83ERI/KOP], [86ERI/KOP]
Vasil'ev, V.Ya.	[82RAD/RYA], [90VAS/KAL]
Vdovenko, V.M.	[66VDO/KOL], [69VDO/STE]
Veits, I.V.	[82GLU/GUR]
Vieillard, P.	[84VIE/TAR]
Visyashcheva, G.I.	[74SIM/VOL]
Vitorge, P.	[84VIT], [86GRE/ROB], [88MOU/ROB], [89RIG/ROB], [91VIT/TRA], [92VIT], [93GIF/VIT], [93GIF/VIT2]
Volkov, Y.F.	[74SIM/VOL]
Von Keller, C.	[69KEL/FAN]
Wade, W.Z.	[67WAD/WOL]
Wagman, D.D.	[76PAR/WAG], [82WAG/EVA], [89COX/WAG]
Wallmann, J.C.	[56GRA/CUN], [62MCW/CUN], [64WAL2]
Walter, K.H.	[65KEL/WAL]
Walton, E.L.	[80HAS/VAN]
Wang, P.	[90ARC/WAN]
Wanner, H.	[86WAN], [87BRO/WAN], [88WAN], [90WAN], [91WAN2], [91WAN3], [92GRE/FUG], [92GRE/WAN], [92WAN], [93PUI/RAR], [94WAN]
Ward, E.H.	[67CHO/KEL]

Author	References
Ward, J.W.	[76WAR/MUE], [79WAR/KLE], [86WAR/KLE]
Ward, M.	[56WAR/WEL]
Weber, Jr.	[71POR/WEB]
Weigel, F.	[76WEI/WIS], [79WEI/WIS], [82LAW/MAR], [82WEI/WIS], [84WEI/WIT], [85WEI], [85WEI/KOH], [85WEI/SCH]
Welch, G.A.	[56WAR/WEL]
Werner, G.D.	[82LAW/MAR]
Westrum, E.F., Jr.	[51WES/EYR], [62WES/GRO], [84GRO/DRO], [89COR/KON]
Whiffen, D.H.	[79WHI2]
White, H.J., Jr.	[87GAR/PAR]
Whitfield, M.	[79WHI]
Williams, C.W.	[94MOR/WIL]
Williams, S.J.	[86EWA/HOW], [92EWA/SMI], [92THO/WIL]
Wishnevsky, V.	[76WEI/WIS], [79WEI/WIS], [82WEI/WIS]
Wittmann, F.D.	[84WEI/WIT]
Wojakowski, A.	[75DAM/WOJ], [76CHA/BEN], [77CHA/DAM]
Wolf, M.	[79WEI/WIS]
Wolf, T.	[67WAD/WOL]
Wood, S.A.	[90WOO]
Woods, M.	[77COO/WOO]
Yakovlev, G.N.	[56YAK/KOS], [58YAK/GOR], [58YAK/KOS], [60LEB/PIR], [62LEB/YAK], [66BOR/ELE], [67ELE/LEB], [74SIM/VOL], [75ERI/SHA]
Yamauchi, S.	[84FLO/HAS]
Yanir, E.	[69YAN/GIV], [70YAN/GIV], [72MAR/YAN]
Young, J.P.	[83HAI/YOU], [85HAI/BEN]
Yudina, K.S.	[75ROZ/NIK]
Yungman, V.S.	[82GLU/GUR], [85HIL/GUR]
Yusov, A.B.	[89YUS], [89YUS/FED]
Zachariasen, W.H.	[48ZAC], [49ZAC2]
Zamorani, E.	[70SAR/ZAM]
Zebroski, E.L.	[51ZEB/ALT]
Zenkova, R.A.	[58YAK/GOR]

Chapter VIII

Formula list

This chapter presents, in standard order of arrangement (*cf.* Section II.1.8) a list of formulae of americium containing species. The meaning of the phase designators, (aq), (cr), *etc.*, is explained in Section II.1.4.

The formulae that are not discussed in the present review are provided with information on references that may contain thermodynamic data on these compounds or complexes (for complete citations see Chapter VI). The formulae for which selected data are presented in Chapter III, as well as those which are discussed but for which no data are recommended by this review, are marked correspondingly.

The inclusion of these formulae in this chapter is to be understood as information on the existence of published material on these formulae. It in no way implies that the present review gives any credit to either the thermodynamic data or the chemical composition or existence of these species.

Some americium formulae are reported only in [87BRO/WAN]. Note however, that there is no experimental indication for the existence of these species, and that only estimates for their equilibrium constants of formation are given in the theoretical work of [87BRO/WAN].

Formula	References
β-Am	data selected in the present review
Am(cr)	data selected in the present review
Am(g)	data selected in the present review
γ-Am	data selected in the present review
Am(l)	data selected in the present review
Am^{2+}	data selected in the present review
Am^{3+}	data selected in the present review
Am^{4+}	data selected in the present review
Am^{5+}	[82FUG]
Am^{6+}	[82FUG]
Am_3^+	[72KRE]
Am_4^+	[72KRE]
AmO(cr)	[62WES/GRO], [86BRA/LAG]
$AmO_{1.5}$(cr)	[86BRA/LAG]
$AmO_{1.6}$(cr)	see *p.* 89
$AmO_{1.71}$(cr)	see *p.* 89
AmO_2(cr)	data selected in the present review
AmO_2^+	data selected in the present review
AmO_2^{2+}	data selected in the present review
AmO_3^+	[81LEB]
Am_2O_3(cr)	data selected in the present review
AmH_2(cr)	data selected in the present review
AmH_3(cr)	see *p.* 100
$AmOH^+$	[84KER]
$AmOH^{2+}$	data selected in the present review
$AmOH^{3+}$	[87BRO/WAN]
$Am(OH)_2^+$	data selected in the present review
$Am(OH)_2^{2+}$	[87BRO/WAN]
AmO_2OH(aq)	see *pp.* 87, 96
AmO_2OH(cr)	see *p.* 96
AmO_2OH^+	see *p.* 87
$Am(OH)_3$(am)	data selected in the present review
$Am(OH)_3$(aq)	data selected in the present review
$Am(OH)_3$(cr)	data selected in the present review
$Am(OH)_3$(s)	[88STA/KIM2]
$Am(OH)_3^+$	[87BRO/WAN]
$AmO_2(OH)_2$(aq)	see *p.* 87
$AmO_2(OH)_2$(cr)	[87BRO/WAN]
$AmO_2(OH)_2^-$	see *p.* 87
$Am(OH)_4$(aq)	[87BRO/WAN]
$Am(OH)_4$(cr)	[52LAT], [72KRE], [73MOS], [85PHI/PHI]
$Am(OH)_4^-$	see *pp.* 80
$AmO_2(OH)_3^-$	see *p.* 87
$AmO_2(OH)_3^{2-}$	see *p.* 87
$Am(OH)_5^-$	[87BRO/WAN]
$Am(OH)_5^{2-}$	[87BRO/WAN]
$AmO_2(OH)_4^{2-}$	see *p.* 87

Formula	References
$AmO_2(OH)_4^{3-}$	see *p.* 87
$Am(OH)_6^{2-}$	[87BRO/WAN]
$Am(OH)_6^{3-}$	[87BRO/WAN]
$AmO_2(OH)_5^{3-}$	[87BRO/WAN]
$AmO_2(OH)_5^{4-}$	[87BRO/WAN]
$Am_2(OH)_2^{4+}$	[78ALL/BEA], [82SIL], [83ALL], [86WAN], [87BRO/WAN]
$(AmO_2)_2(OH)_2^{2+}$	[87BRO/WAN]
$Am_3(OH)_5^{4+}$	[82SIL], [83ALL], [86WAN], [87BRO/WAN]
$(AmO_2)_3(OH)_4^{2+}$	[87BRO/WAN]
$(AmO_2)_3(OH)_5^{+}$	[87BRO/WAN]
$(AmO_2)_3(OH)_7^{-}$	[87BRO/WAN]
$Am_4(OH)_{12}^{4+}$	[87BRO/WAN]
$(AmO_2)_4(OH)_7^{+}$	[87BRO/WAN]
$Am_6(OH)_{15}^{9+}$	[87BRO/WAN]
AmF^{2+}	data selected in the present review
AmF^{3+}	[87BRO/WAN]
$AmF_2(cr)$	[86BRA/LAG]
AmF_2^{+}	data selected in the present review
AmF_2^{2+}	[87BRO/WAN]
$AmF_3(aq)$	see *p.* 101
$AmF_3(cr)$	data selected in the present review
$AmF_3(g)$	data selected in the present review
AmF_3^{+}	[87BRO/WAN]
$AmF_4(aq)$	see *p.* 106
$AmF_4(cr)$	data selected in the present review
$AmF_4(g)$	see *p.* 112
AmF_4^{-}	[78ALL/BEA], [87BRO/WAN]
$AmF_5(g)$	see *p.* 114
$AmF_5(s)$	see *p.* 114
AmF_5^{-}	[87BRO/WAN]
AmF_5^{2-}	[87BRO/WAN]
$AmF_6(cr)$	see *p.* 114
$AmF_6(g)$	see *p.* 114
$AmF_6(s)$	see *p.* 114
AmF_6^{2-}	[87BRO/WAN]
AmF_6^{3-}	[87BRO/WAN]
$AmO_2F(aq)$	[87BRO/WAN]
AmO_2F^{+}	[87BRO/WAN]
$AmO_2F_2(aq)$	[87BRO/WAN]
$AmO_2F_2(cr)$	see *p.* 115
$AmO_2F_2^{-}$	[87BRO/WAN]
$AmO_2F_3^{-}$	[87BRO/WAN]
$AmO_2F_3^{2-}$	[87BRO/WAN]
$AmO_2F_4^{2-}$	[87BRO/WAN]
$AmO_2F_4^{3-}$	[87BRO/WAN]
$AmO_2F_5^{3-}$	[87BRO/WAN]
$AmO_2F_5^{4-}$	[87BRO/WAN]

Formula	References
$AmCl^{2+}$	data selected in the present review
$AmCl^{3+}$	[82JEN], [87BRO/WAN]
$AmCl_2(cr)$	see *p.* 116
$AmCl_2^+$	see *p.* 104
$AmCl_2^{2+}$	[87BRO/WAN]
$AmCl_3(aq)$	[87BRO/WAN]
$AmCl_3(cr)$	data selected in the present review
$AmCl_3(s)$	[54KOC/CUN]
$AmCl_3^+$	[87BRO/WAN]
$AmCl_4(aq)$	[87BRO/WAN]
$AmCl_4(cr)$	[72KRE], [86BRA/LAG]
$AmCl_4^-$	[87BRO/WAN]
$AmCl_5^-$	[87BRO/WAN]
$AmCl_5^{2-}$	[87BRO/WAN]
$AmCl_6^{2-}$	[87BRO/WAN]
$AmCl_6^{3-}$	[87BRO/WAN]
$AmClO(cr)$	[72KRE]
$AmOCl(cr)$	data selected in the present review
$AmOCl(s)$	[76WEI/WIS]
$AmO_2Cl(aq)$	[87BRO/WAN]
AmO_2Cl^+	[87BRO/WAN]
$AmO_2Cl_2(aq)$	[87BRO/WAN]
$AmO_2Cl_2^-$	[87BRO/WAN]
$AmO_2Cl_3^-$	[87BRO/WAN]
$AmO_2Cl_3^{2-}$	[87BRO/WAN]
$AmO_2Cl_4^{2-}$	[87BRO/WAN]
$AmO_2Cl_4^{3-}$	[87BRO/WAN]
$AmO_2Cl_5^{3-}$	[87BRO/WAN]
$AmO_2Cl_5^{4-}$	[87BRO/WAN]
$AmClO_4^{2+}$	see *p.* 105
$AmClO_4^-$	[76SMI/MAR]
$Am(ClO_4)_2^+$	see *p.* 105
$AmBr^{2+}$	see *p.* 105
$AmBr^{3+}$	[87BRO/WAN]
$AmBr_2(cr)$	see *p.* 121
$AmBr_2^+$	see *p.* 105
$AmBr_2^{2+}$	[87BRO/WAN]
$AmBr_3(aq)$	[87BRO/WAN]
$AmBr_3(cr)$	data selected in the present review
$AmBr_3(s)$	[82WEI/WIS]
$AmBr_3^+$	[87BRO/WAN]
$AmBr_4(aq)$	[87BRO/WAN]
$AmBr_4(cr)$	[72KRE], [86BRA/LAG]
$AmBr_4^-$	[87BRO/WAN]
$AmBr_5^-$	[87BRO/WAN]
$AmBr_5^{2-}$	[87BRO/WAN]
$AmBr_6^{2-}$	[87BRO/WAN]

Formula	References
$AmBr_6^{3-}$	[87BRO/WAN]
AmOBr(cr)	data selected in the present review
AmO_2Br(aq)	[87BRO/WAN]
AmO_2Br^+	see *p.* 106
AmO_2Br_2(aq)	[87BRO/WAN]
$AmO_2Br_2^-$	[87BRO/WAN]
$AmO_2Br_3^-$	[87BRO/WAN]
$AmO_2Br_3^{2-}$	[87BRO/WAN]
$AmO_2Br_4^{2-}$	[87BRO/WAN]
$AmO_2Br_4^{3-}$	[87BRO/WAN]
$AmO_2Br_5^{3-}$	[87BRO/WAN]
$AmO_2Br_5^{4-}$	[87BRO/WAN]
$AmBr_3 \cdot 6H_2O$(cr)	[73MOS2], [73MOS]
AmI^{2+}	[87BRO/WAN]
AmI^{3+}	[87BRO/WAN]
AmI_2(cr)	see *p.* 123
AmI_2^+	[87BRO/WAN]
AmI_2^{2+}	[87BRO/WAN]
AmI_3(aq)	[87BRO/WAN]
AmI_3(cr)	data selected in the present review
AmI_3^+	[87BRO/WAN]
AmI_4(aq)	[87BRO/WAN]
AmI_4(cr)	[72FUG], [72KRE], [86BRA/LAG]
AmI_4^-	[87BRO/WAN]
AmI_5^-	[87BRO/WAN]
AmI_5^{2-}	[87BRO/WAN]
AmI_6^{2-}	[87BRO/WAN]
AmI_6^{3-}	[87BRO/WAN]
AmOI(cr)	see *p.* 124
AmO_2I(aq)	[87BRO/WAN]
AmO_2I^+	[87BRO/WAN]
AmO_2I_2(aq)	[87BRO/WAN]
$AmO_2I_2^-$	[87BRO/WAN]
$AmO_2I_3^-$	[87BRO/WAN]
$AmO_2I_3^{2-}$	[87BRO/WAN]
$AmO_2I_4^{2-}$	[87BRO/WAN]
$AmO_2I_4^{3-}$	[87BRO/WAN]
$AmO_2I_5^{3-}$	[87BRO/WAN]
$AmO_2I_5^{4-}$	[87BRO/WAN]
$AmIO_3^{2+}$	[87BRO/WAN]
$AmIO_3^{3+}$	[87BRO/WAN]
AmO_2IO_3(aq)	[87BRO/WAN]
$AmO_2IO_3^+$	[87BRO/WAN]
$Am(IO_3)_2^+$	[87BRO/WAN]
$Am(IO_3)_2^{2+}$	[87BRO/WAN]
$AmO_2(IO_3)_2$(aq)	[87BRO/WAN]
$AmO_2(IO_3)_2^-$	[87BRO/WAN]

Formula	References
$Am(IO_3)_3(aq)$	[87BRO/WAN]
$Am(IO_3)_3^+$	[87BRO/WAN]
$AmO_2(IO_3)_3^-$	[87BRO/WAN]
$AmO_2(IO_3)_3^{2-}$	[87BRO/WAN]
$Am(IO_3)_4(aq)$	[87BRO/WAN]
$Am(IO_3)_4^-$	[87BRO/WAN]
$AmO_2(IO_3)_4^{2-}$	[87BRO/WAN]
$AmO_2(IO_3)_4^{3-}$	[87BRO/WAN]
$Am(IO_3)_5^-$	[87BRO/WAN]
$Am(IO_3)_5^{2-}$	[87BRO/WAN]
$AmO_2(IO_3)_5^{3-}$	[87BRO/WAN]
$AmO_2(IO_3)_5^{4-}$	[87BRO/WAN]
$Am(IO_3)_6^{2-}$	[87BRO/WAN]
$Am(IO_3)_6^{3-}$	[87BRO/WAN]
AmS(cr)	data selected in the present review
$AmS_{1.5}(cr)$	[86BRA/LAG]
$AmS_2(cr)$	see *p.* 126
$Am_2S_3(cr)$	see *p.* 126
$Am_3S_4(cr)$	see *p.* 126
$AmSO_4^+$	data selected in the present review
$AmSO_4^{2+}$	[87BRO/WAN]
$AmO_2SO_4(aq)$	[87BRO/WAN]
$AmO_2SO_4^-$	[87BRO/WAN]
$Am(SO_4)_2(aq)$	[87BRO/WAN]
$Am(SO_4)_2^-$	data selected in the present review
$AmO_2(SO_4)_2^{2-}$	[87BRO/WAN]
$AmO_2(SO_4)_2^{3-}$	[87BRO/WAN]
$Am(SO_4)_3^{2-}$	[87BRO/WAN]
$Am(SO_4)_3^{3-}$	[87BRO/WAN]
$AmO_2(SO_4)_3^{4-}$	[87BRO/WAN]
$AmO_2(SO_4)_3^{5-}$	[87BRO/WAN]
$Am(SO_4)_4^{4-}$	[87BRO/WAN]
$Am(SO_4)_4^{5-}$	[87BRO/WAN]
$AmO_2(SO_4)_4^{6-}$	[87BRO/WAN]
$AmO_2(SO_4)_4^{7-}$	[87BRO/WAN]
$Am(SO_4)_5^{6-}$	[87BRO/WAN]
$Am(SO_4)_5^{7-}$	[87BRO/WAN]
$AmO_2(SO_4)_5^{8-}$	[87BRO/WAN]
$Am(SO_4)_6^{8-}$	[87BRO/WAN]
$Am_2O_2S(cr)$	see *p.* 127
$(AmO_2)_2SO_4(cr)$	see *p.* 131
$Am_{10}OS_{14}(cr)$	see *p.* 127
$Am(H_2SO_4)_2^+$	see *p.* 128
$Am_2(SO_4)_3{\cdot}8H_2O(cr)$	see *p.* 131
AmSe(cr)	data selected in the present review
$AmSe_2(cr)$	see *p.* 132
$Am_3Se_4(cr)$	see *p.* 132

Formula	References
AmTe(cr)	data selected in the present review
$AmTe_2$(cr)	see *p.* 134
$AmTe_3$(cr)	see *p.* 134
Am_3Te_4(cr)	see *p.* 133
Am_2O_2Te(cr)	see *p.* 134
AmN(cr)	see *p.* 134
AmN_3^{2+}	data selected in the present review
$Am(N_3)_2^+$	see *p.* 135
$Am(N_3)_3$(aq)	see *p.* 135
$AmNO_2^{2+}$	data selected in the present review
$AmNO_3^{2+}$	data selected in the present review
$AmNO_3^{3+}$	[87BRO/WAN]
AmO_2NO_3(aq)	[87BRO/WAN]
$AmO_2NO_3^+$	[87BRO/WAN]
$Am(NO_3)_2^+$	see *p.* 136
$Am(NO_3)_2^{2+}$	[87BRO/WAN]
$AmO_2(NO_3)_2$(aq)	see *p.* 138
$AmO_2(NO_3)_2^-$	[87BRO/WAN]
$Am(NO_3)_3$(aq)	see *p.* 137
$Am(NO_3)_3$(s)	see *p.* 138
$Am(NO_3)_3^+$	[87BRO/WAN]
$AmO_2(NO_3)_3^-$	see *p.* 138
$AmO_2(NO_3)_3^{2-}$	[87BRO/WAN]
$Am(NO_3)_4$(aq)	[87BRO/WAN]
$Am(NO_3)_4^-$	[87BRO/WAN]
$AmO_2(NO_3)_4^{2-}$	[87BRO/WAN]
$AmO_2(NO_3)_4^{3-}$	[87BRO/WAN]
$Am(NO_3)_5^-$	[87BRO/WAN]
$Am(NO_3)_5^{2-}$	[87BRO/WAN]
$AmO_2(NO_3)_5^{3-}$	[87BRO/WAN]
$Am(NO_3)_6^{2-}$	[87BRO/WAN]
$Am(NO_3)_6^{3-}$	[87BRO/WAN]
$AmNH_3^{3+}$	[87BRO/WAN]
$AmNH_3^{4+}$	[87BRO/WAN]
$Am(NH_3)_2^{3+}$	[87BRO/WAN]
$Am(NH_3)_2^{4+}$	[87BRO/WAN]
$Am(NH_3)_3^{3+}$	[87BRO/WAN]
$Am(NH_3)_3^{4+}$	[87BRO/WAN]
$Am(NH_3)_4^{3+}$	[87BRO/WAN]
$Am(NH_3)_4^{4+}$	[87BRO/WAN]
$Am(NH_3)_5^{3+}$	[87BRO/WAN]
$Am(NH_3)_5^{4+}$	[87BRO/WAN]
$Am(NH_3)_6^{3+}$	[87BRO/WAN]
$Am(NH_3)_6^{4+}$	[87BRO/WAN]
$AmO_2NH_3^+$	[87BRO/WAN]
$AmO_2NH_3^{2+}$	[87BRO/WAN]
$AmO_2(NH_3)_2^+$	[87BRO/WAN]

Formula	References
$AmO_2(NH_3)_2^{2+}$	[87BRO/WAN]
$AmO_2(NH_3)_3^{+}$	[87BRO/WAN]
$AmO_2(NH_3)_3^{2+}$	[87BRO/WAN]
$AmO_2(NH_3)_4^{+}$	[87BRO/WAN]
$AmO_2(NH_3)_4^{2+}$	[87BRO/WAN]
$AmO_2(NH_3)_5^{+}$	[87BRO/WAN]
$AmO_2(NH_3)_5^{2+}$	[87BRO/WAN]
$(NH_4)_2AmCl_5(cr)$	see *p.* 120
$AmS_2(NO_3)_3(aq)$	[75ROZ/NIK]
$AmP(cr)$	see *p.* 144
$AmPO_4(am, hydr)$	data selected in the present review
$AmPO_4(aq)$	[87BRO/WAN]
$AmPO_4(cr)$	see *p.* 144
$AmPO_4^{+}$	[87BRO/WAN]
$AmO_2PO_4^{-}$	[87BRO/WAN]
$AmO_2PO_4^{2-}$	[87BRO/WAN]
$Am(PO_4)_2^{2-}$	[87BRO/WAN]
$Am(PO_4)_2^{3-}$	[87BRO/WAN]
$AmP_3O_9(aq)$	see *p.* 144
$AmO_2(PO_4)_2^{4-}$	[87BRO/WAN]
$AmO_2(PO_4)_2^{5-}$	[87BRO/WAN]
$Am(PO_4)_3^{5-}$	[87BRO/WAN]
$Am(PO_4)_3^{6-}$	[87BRO/WAN]
$AmO_2(PO_4)_3^{7-}$	[87BRO/WAN]
$AmO_2(PO_4)_3^{8-}$	[87BRO/WAN]
$Am(PO_4)_4^{8-}$	[87BRO/WAN]
$Am(PO_4)_4^{9-}$	[87BRO/WAN]
$AmO_2(PO_4)_4^{10-}$	[87BRO/WAN]
$AmO_2(PO_4)_4^{11-}$	[87BRO/WAN]
$Am(PO_4)_5^{11-}$	[87BRO/WAN]
$Am(PO_4)_5^{12-}$	[87BRO/WAN]
$AmO_2(PO_4)_5^{13-}$	[87BRO/WAN]
$AmO_2(PO_4)_5^{14-}$	[87BRO/WAN]
$Am(PO_4)_6^{14-}$	[87BRO/WAN]
$Am(PO_4)_6^{15-}$	[87BRO/WAN]
$AmHPO_4^{+}$	see *p.* 140
$AmHPO_4^{2+}$	[87BRO/WAN]
$AmH_2PO_4^{+}$	[84VIE/TAR]
$AmH_2PO_4^{2+}$	data selected in the present review
$AmH_2PO_4^{3+}$	[87BRO/WAN]
$AmO_2HPO_4(aq)$	[87BRO/WAN]
$AmO_2HPO_4^{-}$	[87BRO/WAN]
$AmO_2H_2PO_4(aq)$	[87BRO/WAN]
$AmO_2H_2PO_4^{+}$	[87BRO/WAN]
$Am(HPO_4)_2(aq)$	[87BRO/WAN]
$Am(HPO_4)_2^{-}$	[87BRO/WAN]
$Am(H_2PO_4)_2^{+}$	see *p.* 140

Formula	References
$Am(H_2PO_4)_2^{2+}$	[87BRO/WAN]
$AmHP_3O_9^+$	see *p.* 144
$AmO_2(HPO_4)_2^{2-}$	[87BRO/WAN]
$AmO_2(HPO_4)_2^{3-}$	[87BRO/WAN]
$AmO_2(H_2PO_4)_2(aq)$	see *pp.* 141, 143
$AmO_2(H_2PO_4)_2^-$	[87BRO/WAN]
$Am(HPO_4)_3^{2-}$	[87BRO/WAN]
$Am(HPO_4)_3^{3-}$	[87BRO/WAN]
$Am(H_2PO_4)_3(aq)$	see *p.* 140
$Am(H_2PO_4)_3^+$	see *pp.* 141, 143
$AmO_2(HPO_4)_3^{4-}$	[87BRO/WAN]
$AmO_2(HPO_4)_3^{5-}$	[87BRO/WAN]
$AmO_2(H_2PO_4)_3^-$	[87BRO/WAN]
$AmO_2(H_2PO_4)_3^{2-}$	[87BRO/WAN]
$Am(HPO_4)_4^{4-}$	[87BRO/WAN]
$Am(HPO_4)_4^{5-}$	[87BRO/WAN]
$Am(H_2PO_4)_4(aq)$	[87BRO/WAN]
$Am(H_2PO_4)_4^-$	see *p.* 140
$AmO_2(HPO_4)_4^{6-}$	[87BRO/WAN]
$AmO_2(HPO_4)_4^{7-}$	[87BRO/WAN]
$AmO_2(H_2PO_4)_4^{2-}$	[87BRO/WAN]
$Am(HPO_4)_5^{6-}$	[87BRO/WAN]
$Am(HPO_4)_5^{7-}$	[87BRO/WAN]
$Am(H_2PO_4)_5^-$	[87BRO/WAN]
$Am(H_2PO_4)_5^{2-}$	[87BRO/WAN]
$AmO_2(HPO_4)_5^{8-}$	[87BRO/WAN]
$AmO_2(HPO_4)_5^{9-}$	[87BRO/WAN]
$Am(HPO_4)_6^{8-}$	[87BRO/WAN]
$Am(HPO_4)_6^{9-}$	[87BRO/WAN]
$Am(H_2PO_4)_6^{2-}$	[87BRO/WAN]
$NH_4AmO_2PO_4(s)$	see *p.* 144
AmAs(cr)	see *p.* 145
$AmAsO_4(cr)$	see *p.* 146
$NH_4AmO_2AsO_4(s)$	see *p.* 146
AmSb(cr)	see *p.* 146
$AmSb_2(cr)$	see *p.* 147
$Am_4Sb_3(cr)$	see *p.* 146
AmSbTe(cr)	see *p.* 147
AmBi(cr)	see *p.* 147
AmC(cr)	see *p.* 147
$Am_2C_3(cr)$	data selected in the present review
$AmCO_3^+$	data selected in the present review
$AmCO_3^{2+}$	[87BRO/WAN]
$Am(C_2O_4)^+$	[85PAZ/KRI]
$AmC_2O_4^+$	[69SEK/SAK], [87BRO/WAN]
$AmC_2O_4^{2+}$	[87BRO/WAN]
$AmO_2CO_3(aq)$	[87BRO/WAN]

Formula	References
$AmO_2CO_3^-$	see *p.* 157
$Am(CO_3)_2(aq)$	[87BRO/WAN]
$Am(CO_3)_2(cr)$	[87BRO/WAN]
$Am(CO_3)_2^-$	data selected in the present review
$AmO_2C_2O_4(aq)$	[87BRO/WAN]
$AmO_2C_2O_4^-$	[87BRO/WAN]
$AmO_2(CO_3)_2^{2-}$	[87BRO/WAN]
$AmO_2(CO_3)_2^{3-}$	see *p.* 157
$Am(C_2O_4)_2(aq)$	[87BRO/WAN]
$Am(C_2O_4)_2^-$	[69SEK/SAK], [87BRO/WAN]
$Am(CO_3)_3^{2-}$	[87BRO/WAN]
$Am(CO_3)_3^{3-}$	data selected in the present review
$AmO_2(C_2O_4)_2^{2-}$	[87BRO/WAN]
$AmO_2(C_2O_4)_2^{3-}$	[87BRO/WAN]
$AmO_2(CO_3)_3^{4-}$	data selected in the present review
$AmO_2(CO_3)_3^{5-}$	data selected in the present review
$Am(CO_3)_4^{4-}$	[87BRO/WAN]
$Am(CO_3)_4^{5-}$	[78ALL/BEA], [87BRO/WAN]
$Am(C_2O_4)_3^{2-}$	[87BRO/WAN]
$Am(C_2O_4)_3^{3-}$	[69SEK/SAK], [87BRO/WAN]
$AmO_2(CO_3)_4^{6-}$	[87BRO/WAN]
$AmO_2(CO_3)_4^{7-}$	[87BRO/WAN]
$Am(CO_3)_5^{6-}$	data selected in the present review
$Am(CO_3)_5^{7-}$	[87BRO/WAN]
$AmO_2(CO_3)_5^{8-}$	[87BRO/WAN]
$AmO_2(CO_3)_5^{9-}$	[87BRO/WAN]
$Am(CO_3)_6^{8-}$	[87BRO/WAN]
$Am(CO_3)_6^{9-}$	[87BRO/WAN]
$Am_2(CO_3)_3(cr)$	data selected in the present review
$AmHCO_2^{2+}$	[87BRO/WAN]
$AmHCO_2^{3+}$	[87BRO/WAN]
$AmHCO_3^{2+}$	see *pp.* 149, 154
$AmHCO_3^{3+}$	[87BRO/WAN]
$AmCO_3OH(aq)$	see *pp.* 150, 156
$AmCO_3OH(cr)$	data selected in the present review
$AmO_2HCO_2(aq)$	[87BRO/WAN]
$AmO_2HCO_2^+$	[87BRO/WAN]
$Am(HC_2O_4)^{2+}$	[85PAZ/KRI]
$Am(HCO_2)_2^+$	[87BRO/WAN]
$Am(HCO_2)_2^{2+}$	[87BRO/WAN]
$AmO_2CH_3CO_2(aq)$	[79MOS/POZ]
$AmO_2HCO_3(aq)$	see *p.* 157
$AmO_2HCO_3^+$	[87BRO/WAN]
$Am(OH)_2CO_3^-$	see *pp.* 150, 156
$AmO_2OHCO_3^-$	[87BRO/WAN]
$Am(HCO_3)_2^+$	see *pp.* 149, 154
$Am(HCO_3)_2^{2+}$	[87BRO/WAN]

Formula	References
$AmO_2(HCO_2)_2(aq)$	[87BRO/WAN]
$AmO_2(HCO_2)_2^-$	[87BRO/WAN]
$Am(OH)_3CO_3^-$	[87BRO/WAN]
$Am(HCO_2)_3(aq)$	[87BRO/WAN]
$Am(HCO_2)_3^+$	[87BRO/WAN]
$AmO_2(CH_3CO_2)_2(cr)$	[73MOS]
$AmOH(CO_3)_2^{2-}$	see *pp.* 150, 156
$AmO_2(OH)_2CO_3^{2-}$	[87BRO/WAN]
$AmO_2(HCO_3)_2(aq)$	[87BRO/WAN]
$AmO_2(HCO_3)_2^-$	[87BRO/WAN]
$AmO_2(HCO_2)_3^-$	[87BRO/WAN]
$AmO_2(HCO_2)_3^{2-}$	[87BRO/WAN]
$Am(HCO_2)_4(aq)$	[87BRO/WAN]
$Am(HCO_2)_4^-$	[87BRO/WAN]
$Am(CH_3CO_2)_4(cr)$	[73MOS]
$Am(HCO_3)_3(aq)$	[87BRO/WAN]
$Am(HCO_3)_3^+$	[87BRO/WAN]
$Am(CO_3)_3OH^{4-}$	see *p.* 156
$AmO_2(HCO_2)_4^{2-}$	[87BRO/WAN]
$Am(HCO_2)_5^-$	[87BRO/WAN]
$Am(HCO_2)_5^{2-}$	[87BRO/WAN]
$AmO_2(HCO_3)_3^-$	[87BRO/WAN]
$AmO_2(HCO_3)_3^{2-}$	[87BRO/WAN]
$Am(HCO_3)_4(aq)$	[87BRO/WAN]
$Am(HCO_3)_4^-$	[87BRO/WAN]
$AmO_2(HCO_2)_5^{3-}$	[87BRO/WAN]
$Am(HCO_2)_6^{2-}$	[87BRO/WAN]
$AmO_2(HCO_3)_4^{2-}$	[87BRO/WAN]
$AmO_2(HCO_3)_4^{3-}$	[87BRO/WAN]
$Am(HCO_3)_5^-$	[87BRO/WAN]
$Am(HCO_3)_5^{2-}$	[87BRO/WAN]
$Am(HC_2O_4)_4^-$	[60MOS/KHA]
$AmO_2(HCO_3)_5^{3-}$	[87BRO/WAN]
$Am(HCO_3)_6^{2-}$	[87BRO/WAN]
$Am(HCO_3)_6^{3-}$	[87BRO/WAN]
$(AmO_2)_2(OH)_3CO_3^-$	[87BRO/WAN]
$Am_2(CO_3)_3 \cdot 2H_2O(cr)$	[73MOS2], [73MOS]
$Am_2(C_2O_4)_3 \cdot 10H_2O(cr)$	[73MOS]
$(AmO_2)_3(OH)_3CO_3^+$	[87BRO/WAN]
$AmCN^{2+}$	see *p.* 165
$AmCN^{3+}$	[87BRO/WAN]
$Am(CN)_2^+$	[87BRO/WAN]
$Am(CN)_2^{2+}$	[87BRO/WAN]
$Am(CN)_3(aq)$	[87BRO/WAN]
$Am(CN)_3^+$	[87BRO/WAN]
$Am(CN)_4(aq)$	[87BRO/WAN]
$Am(CN)_4^-$	[87BRO/WAN]

Formula	References
$Am(CN)_5^-$	[87BRO/WAN]
$Am(CN)_5^{2-}$	[87BRO/WAN]
$Am(CN)_6^{2-}$	[87BRO/WAN]
$Am(CN)_6^{3-}$	[87BRO/WAN]
$AmO_2CN(aq)$	[87BRO/WAN]
AmO_2CN^+	[87BRO/WAN]
$AmO_2(CN)_2(aq)$	[87BRO/WAN]
$AmO_2(CN)_2^-$	[87BRO/WAN]
$AmO_2(CN)_3^-$	[87BRO/WAN]
$AmO_2(CN)_3^{2-}$	[87BRO/WAN]
$AmO_2(CN)_4^{2-}$	[87BRO/WAN]
$AmO_2(CN)_4^{3-}$	[87BRO/WAN]
$AmO_2(CN)_5^{3-}$	[87BRO/WAN]
$AmO_2(CN)_5^{4-}$	[87BRO/WAN]
$NH_4AmO_2CO_3(cr)$	see *p.* 165
$AmN(CH_2COO)_3(aq)$	[72EBE/SAB]
$(NH_4)_5AmO_2(CO_3)_3(s)$	see *p.* 165
$Am(N(CH_2COO)_3)_2^{3-}$	[72EBE/SAB]
$AmSCN^{2+}$	data selected in the present review
$AmSCN^{3+}$	[87BRO/WAN]
$Am(SCN)_2^+$	see *p.* 166
$Am(SCN)_2^{2+}$	[87BRO/WAN]
$Am(SCN)_3(aq)$	see *p.* 166
$Am(SCN)_3^+$	[87BRO/WAN]
$Am(SCN)_4(aq)$	[87BRO/WAN]
$Am(SCN)_4^-$	see *p.* 169
$Am(SCN)_5^-$	[87BRO/WAN]
$Am(SCN)_5^{2-}$	[87BRO/WAN]
$Am(SCN)_6^{2-}$	[87BRO/WAN]
$Am(SCN)_6^{3-}$	[87BRO/WAN]
$AmO_2SCN(aq)$	[87BRO/WAN]
AmO_2SCN^+	[87BRO/WAN]
$AmO_2(SCN)_2(aq)$	[87BRO/WAN]
$AmO_2(SCN)_2^-$	[87BRO/WAN]
$AmO_2(SCN)_3^-$	[87BRO/WAN]
$AmO_2(SCN)_3^{2-}$	[87BRO/WAN]
$AmO_2(SCN)_4^{2-}$	[87BRO/WAN]
$AmO_2(SCN)_4^{3-}$	[87BRO/WAN]
$AmO_2(SCN)_5^{3-}$	[87BRO/WAN]
$AmO_2(SCN)_5^{4-}$	[87BRO/WAN]
$AmSi(cr)$	see *p.* 170
$AmSi_{1.6}(cr)$	see *p.* 170
$AmSi_2(cr)$	see *p.* 170
$Am_5Si_3(cr)$	see *p.* 170
$AmSiO_4(cr)$	see *p.* 171
$Am_8(SiO_6)_2(cr)$	see *p.* 171
$AmGeO_4(cr)$	see *p.* 98

Formula	References
$AmAlO_3$(cr)	see *p.* 98
$TlAm(SO_4)_2$(s)	see *p.* 131
$Tl_8Am_2(SO_4)_7$(s)	see *p.* 131
α-$Am_2(MoO_4)_3$	see *p.* 98
β-$Am_2(MoO_4)_3$	see *p.* 98
$Am_2(WO_4)_3$(cr)	see *p.* 98
$Am(P_2W_{17}O_{61})_2^{16-}$	see *p.* 144
$Am(P_2W_{17}O_{61})_2^{17-}$	see *p.* 144
$AmVO_3$(cr)	see *p.* 98
$AmVO_4$(cr)	see *p.* 98
$Am_{0.33}NbO_3$(cr)	see *p.* 98
α-$AmNbO_4$	see *p.* 98
β-$AmNbO_4$	see *p.* 98
$Am_{0.33}TaO_3$(cr)	see *p.* 98
$AmTaO_4$(cr)	see *p.* 98
$AmNbTiO_6$(cr)	see *p.* 98
$AmTaTiO_6$(cr)	see *p.* 98
$AmScO_3$(cr)	see *p.* 98
$AmO_2NpO_2^{3+}$	see *p.* 173
$U_{0.5}Am_{0.5}O_2$(cr)	see *p.* 172
$AmO_2UO_2^{3+}$	[81GUI/HOB]
$AmPaO_4$(cr)	see *p.* 98
$SrAmO_3$(cr)	data selected in the present review
Sr_3AmO_6(cr)	see *p.* 98
$SrAm_2O_4$(s)	see *p.* 98
$BaAmO_3$(cr)	data selected in the present review
Ba_3AmO_6(cr)	see *p.* 98
$BaAm_2O_4$(s)	see *p.* 98
Ba_2AmNbO_6(cr)	see *p.* 98
Ba_2AmTaO_6(cr)	see *p.* 98
Ba_2AmPaO_6(cr)	see *p.* 98
$LiAmO_2$(s)	see *p.* 98
Li_2AmO_3(s)	see *p.* 98
Li_3AmO_4(cr)	see *p.* 98
Li_4AmO_5(cr)	see *p.* 98
Li_6AmO_6(cr)	see *p.* 98
Li_7AmO_6(cr)	see *p.* 98
Li_8AmO_6(cr)	see *p.* 98
$LiAmF_5$(cr)	see *p.* 115
$LiAm(MoO_4)_2$(cr)	see *p.* 98
Na_2AmO_3(cr)	see *p.* 98
Na_3AmO_4(cr)	see *p.* 98
Na_4AmO_5(cr)	see *p.* 98
Na_6AmO_6(cr)	see *p.* 98
$Na_7Am_6F_{31}$(cr)	see *p.* 115
$NaAmO_2CO_3$(s)	see *p.* 165
$NaAm(CO_3)_2$(cr)	see *p.* 163

Formula	References
$Na_3Am(CO_3)_3$(cr)	see *p.* 163
$NaAm(MoO_4)_2$(cr)	see *p.* 98
$Na_5Am(MoO_4)_4$(cr)	see *p.* 98
K_2AmO_4(cr)	see *p.* 98
K_2AmCl_5(cr)	see *p.* 120
$KAm(SO_4)_2$(s)	see *p.* 131
$K_8Am_2(SO_4)_7$(s)	see *p.* 131
$K_3Am(SO_4)_3{\cdot}H_2O$(s)	see *p.* 131
$KAmO_2PO_4$(s)	see *p.* 144
$KAmO_2AsO_4$(s)	see *p.* 146
$KAmO_2CO_3$(cr)	see *p.* 165
$K_3AmO_2(CO_3)_2$(s)	see *p.* 165
$K_5AmO_2(CO_3)_3$(s)	see *p.* 165
$K_2Am_2(MoO_4)_4$(s)	see *p.* 98
$K_{10}Am_2(MoO_4)_8$(s)	see *p.* 98
Rb_2AmF_6(cr)	see *p.* 115
Rb_2AmCl_5(cr)	see *p.* 120
$RbAm(SO_4)_2$(s)	see *p.* 131
$RbAmO_2PO_4$(s)	see *p.* 144
$RbAmO_2AsO_4$(s)	see *p.* 146
$RbAmO_2CO_3$(cr)	see *p.* 165
$CsAmCl_4$(s)	see *p.* 119
Cs_3AmCl_6(s)	see *p.* 119
$CsAm(SO_4)_2$(s)	see *p.* 131
$CsAmO_2PO_4$(s)	see *p.* 144
$CsAmO_2AsO_4$(s)	see *p.* 146
$CsAmO_2CO_3$(cr)	see *p.* 165
$Cs_5AmO_2(CO_3)_3$(s)	see *p.* 165
$Cs_2NaAmCl_6$(cr)	data selected in the present review

Appendix A

Discussion of selected references

[54FEA]
Feay, D.C., Some chemical properties of curium, Ph.D. thesis, Radiation Laboratory, University of California, report UCRL-2547, Berkeley, California, 1954, 50p.

Feay reports the solubility of curium and americium trifluoride in aqueous solutions containing excess fluoride as a function of temperature (0, 23 and 47°C). Analysis of these solubility data [54FEA] yielded

$$\mathrm{AmF_2^+ + F^-} \rightleftharpoons \mathrm{AmF_3(aq)} \qquad \begin{aligned} \log_{10} K_3^\circ &= 3.11 \pm 0.07 \\ \Delta_\mathrm{r} H_\mathrm{m}^\circ &= (21.9 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}} \\ \Delta_\mathrm{r} S_\mathrm{m}^\circ &= (133 \pm 17)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \end{aligned}$$

$$\mathrm{AmF_3(s)} \rightleftharpoons \mathrm{AmF_3(aq)} \qquad \begin{aligned} \log_{10} K_{\mathrm{s},3}^\circ &= -4.83 \pm 0.07 \\ \Delta_\mathrm{r} H_\mathrm{m}^\circ &= (14.6 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}} \\ \Delta_\mathrm{r} S_\mathrm{m}^\circ &= (44 \pm 17)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \end{aligned}$$

The experiments were performed from undersaturation. However, equilibrium might not have been reached because of inadequate stirring (Feay states that the samples were both self stirred due to gas evolution, and manually with a platinum wire). Only few experimental determinations were performed at each temperature, and this review considers it possible that the solid might have redissolved completely in the samples most diluted in fluoride ($[\mathrm{F^-}]_{TOT} \approx 0.001$ M). Furthermore, it is not possible to determine the nature of the predominant americium species in solution based only on these few solubility measurements, and Feay did not report any characterisation of the solid phase either. Because of all these considerations, the equilibrium constants and thermodynamic data reported by Feay are disregarded in this review.

[56WAR/WEL]
Ward, M., Welch, G.A., The chloride complexes of trivalent plutonium, americium and curium, J. Inorg. Nucl. Chem., **2** (1956) 395–402.

The authors investigated the complex formation of selected trivalent actinides (Am, Cm and Pu) in hydrochloric acid solutions by using an ion exchange method. The

measurements were presumably made at room temperature. Preliminary experiments of actinide distribution between the cation exchanger and the solution phase were made at fairly high ionic strength, using mixtures of perchlorate and chloride ions. The results suggested the formation of the first two chloro complexes. As indicated in Figure 1 of the original paper, the preliminary americium experiments were performed at $[H^+] = 0.5$ M, while the chloride ion concentration was varied between 0 and 3.5 M.

Ward and Welch derived the dissociation constant of $AmCl^{2+}$ from duplicate measurements of the americium distribution coefficients in 0.206 M and 0.5 M HCl solutions. The authors claimed that of all the americium species present in the solution, only the adsorption of Am^{3+} ions on the resin was significant. Carleson and Irving [54CAR/IRV], Grenthe [62GRE] and Irving and Khopkar [64IRV/KHO] have shown that the individual distribution ratios of the uncomplexed lanthanide and actinide(III) ions on strong cation exchangers are about 10 to 20 times higher than those calculated for divalent complex species. Therefore, this indicates that corrections for the presence of $AmCl^{2+}$ in the resin should be negligible at the relatively low chloride concentrations used by Ward and Welch.

According to the terminology adopted by this review, the formation constants at $I = 0.206$ M and 0.5 M are $\log_{10} \beta_1 = 0.35$ and 0.24, respectively, with no uncertainty values assigned by Ward and Welch. Assuming that the variation of anionic composition at constant ionic strength does not change the ion interaction coefficients, *i.e.*, $\varepsilon_{(Am^{3+},Cl^-)} = \varepsilon_{(Am^{3+},ClO_4^-)}$ and $\varepsilon_{(AmCl^{2+},Cl^-)} = \varepsilon_{(AmCl^{2+},ClO_4^-)}$, the measured difference in the distribution coefficients of americium between chloride-free and hydrochloric acid solutions may entirely be attributed to complex formation effects. However, because of the very limited number of experimental points, this review assigns an uncertainty of $\pm$ 0.2 in the value of $\log_{10} \beta_1$. The Davies equation used by the authors to calculate the standard equilibrium constant is of doubtful application at ionic strengths larger than 0.1 M. The correction made by this review with the specific ion interaction equations in Appendix B using $\Delta\varepsilon_1 = -(0.22 \pm 0.1)\,\mathrm{kg \cdot mol^{-1}}$, results in $\log_{10} \beta_1^\circ = (1.13 \pm 0.20)$ and (1.18 ± 0.20) from the values reported at $I = 0.206$ M and 0.5 M respectively.

Americium uptake by an anion exchanger in 8 M HCl solutions was taken as an evidence for the formation of negatively charged chloro complexes. However, no quantitative data were reported.

[56YAK/KOS]

Yakovlev, G.N., Kosyakov, V.N., Gorbenko-Germanov, D.S., Zenkova, R.A., Korovin, A.P., Sobolev, Y.P., Spectrophotometric studies of the behaviour of americium ions in solutions, Proc. International Conf. on the Peaceful Uses of Atomic Energy, held 1955, in Geneva, Switzerland, Vol. **VII**, New York: United Nations, 1956, *pp.*363–368.

Formation of americium(III) complexes in perchloric, hydrochloric, nitric and sulphuric acids was investigated by Yakovlev *et al.* [56YAK/KOS] using spectrophotometry. At high acid concentrations (pH < 0), spectral shifts and decreases of molar extinction coefficients of the characteristic peaks in the UV and IR regions are attributed to the formation of americium complexes. However, the composition of the predominant species in solution and the corresponding stability constants can not be

extracted from these qualitative results.

[60LEB/PIR]
Lebedev, I.A., Pirozhkov, S.V., Yakovlev, G.N., Determination of the composition and the instability constants of oxalate, nitrate and sulphate complexes of Am^{III} and Cm^{III} by the method of ion exchange, Radiokhimiya, **2(5)** (1960) 549–558, in Russian; English transl.: *pp.*39–47.

Lebedev, Pirozhkov and Yakovlev [60LEB/PIR] used an ion exchange technique to study the americium(III) nitrate and sulphate systems at pH = 3.5 to 4, and $I = 1$ M and $I = 0.75$ M for the nitrate and sulphate systems respectively. The linear variation of the distribution coefficients with increasing ligand concentration reveals the presence of the complexes $AmNO_3^{2+}$ and $AmSO_4^+$ (*cf.* Tables V.14 and V.12, respectively). An additional experiment performed at high sulphate concentration (at $I = 1.5$ M) was interpreted assuming the formation of both $AmSO_4^+$ and $Am(SO_4)_2^-$, but the scarceness of the experimental data and the narrow concentration range investigated do not allow a reliable determination of equilibrium constants, and therefore the values reported by Lebedev, Pirozhkov and Yakovlev for the sulphate system at $I = 1.5$ M are disregarded by this review.

[61PEN/COL]
Penneman, R.A., Coleman, J.S., Keenan, T.K., Alkaline oxidation of americium; preparation and reactions of Am(IV) hydroxide, J. Inorg. Nucl. Chem., **17** (1961) 138–145.

The authors reported qualitative observations on the stability of $Am(OH)_4(s)$ prepared by hypochlorite or ozone oxidation of $Am(OH)_3(s)$ suspensions in NaOH solutions. A soluble hydrolysis species of Am(VI) was claimed to be produced when using ozone as oxidising agent.

[61PEP/MAS]
Peppard, D.F., Mason, G.W., Hucher, I., Stability constants of certain lanthanide(III) and actinide(III) chloride and nitrate complexes, Report TID-14716, UAC-5777, 1961, 13p.

This report appears to be the same study as Ref. [62PEP/MAS].

[61STA/GIN]
Starik, I.E., Ginzburg, F.L., State of microamounts of radioelements in dilute solution, Sov. Radiochem., **3** (1961) 49–55.

This qualitative study on the sorption of americium on ion exchangers contains no data pertinent to this review.

[62GRE]
Grenthe, I., Chloride complexes of trivalent americium. Short communication, Acta Chem. Scand., **16** (1962) 2300.

The author used a cation exchange resin to study the Am(III) complexation with Cl^- ions in a 4 M $H(ClO_4,Cl)$ medium at 20°C. A combination of graphical and curve fitting methods was used in the data analysis, as described in Ref. [62GRE2]. The calculations suggest a contribution of the complex species $AmCl^{2+}$ to the total ameri-

cium adsorption on the resin. Grenthe found the stability constants for the formation of $AmCl^{2+}$ and $AmCl_2^+$ to be $\log_{10}\beta_1 = -(0.16 \pm 0.02)$ and $\log_{10}\beta_2 = -(0.74 \pm 0.1)$, respectively. The uncertainties assigned by the author appear to be equal to the standard deviation of the mean values. Taking also into account the temperature difference from the reference state, this review estimates the uncertainty in $\log_{10}\beta_1$ as ± 0.05 and in $\log_{10}\beta_2$ as ± 0.2.

[62LEB/YAK]

Lebedev, I.A., Yakovlev, G.N., Determination of the composition and stability constants of thiocyanate complexes of Am(III), Cm(III) and Ce(III) by ion exchange, Sov. Radiochem., **4** (1962) 273–275.

Americium complexation by the thiocyanate ligand was studied using a cation exchange technique at two ionic strengths (0.5 and 5.0 M $NaSCN/NaClO_4$), at pH = 4. The experimental data, obtained at $I = 0.5$ M, show that only $AmSCN^{2+}$ is formed at $[SCN^-] \leq 0.36$ M. The distribution coefficient at $[SCN^-] \geq 0.4$ M deviated from linearity, indicating that a higher complex may be present. At $I = 5.0$ M, there is evidence for two complexes: $AmSCN^{2+}$ and $Am(SCN)_3(aq)$. The authors did not report the corresponding stability constants at $I = 5.0$ M, only the values corrected to zero ionic strength by the Davies equation were given. Because this empirical relation is not valid at ionic strengths greater than 0.1 M (*cf.* Appendix B), the reported constants at $I = 0$ are not considered by this review. The stability constant determined at $I = 0.5$ M, $\log_{10}\beta_1 = (0.66 \pm 0.05)$ (*cf.* Table V.17), is converted to molal units and extrapolated to zero ionic strength using the specific interaction equations, *cf.* Appendix B, with $\Delta\varepsilon = -(0.15 \pm 0.05)\,\mathrm{kg \cdot mol^{-1}}$. This results in $\log_{10}\beta_1^\circ = (1.42 \pm 0.2)$, where the uncertainty has been increased to take into account the unknown temperature at which this study was performed.

[62PEP/MAS]

Peppard, D.F., Mason, G.W., Hucher, I., Stability constants of certain lanthanide(III) and actinide(III) chloride and nitrate complexes, J. Inorg. Nucl. Chem., **24** (1962) 881–888.

The authors determined the formation constants of the first chloro and nitrate complexes of Am(III) and various lanthanides in 1 M $H(ClO_4^-, Cl^-$ or $NO_3^-)$ media at (22 ± 1)°C. Solvent extraction with di[para-(1,1,3,3-tetramethylbutyl)phenyl] phosphonic acid in toluene was used as the experimental method. Although the chelating agent used belongs to a group of compounds known to extract appreciable concentrations of acids, the extracted species did not contain bulk anions. This was established on the basis of the third order dependence of the americium distribution coefficient on the hydrogen ion concentration. Modelling of the experimental data gave $\log_{10}\beta_1 = -(0.05 \pm 0.01)$ and $\log_{10}\beta_1 = (0.26 \pm 0.07)$ for the formation of $AmCl^{2+}$ and $AmNO_3^{2+}$, respectively. The corrections for the small difference in temperature from the reference value of 25°C are negligible. These stability constants, converted to molal units, are extrapolated to zero ionic strength, using the selected interaction coefficients (*cf.* Appendix B, Section B.1.4), to give: $\log_{10}\beta_1^\circ = (0.95 \pm 0.15)$ and $\log_{10}\beta_1^\circ = (1.29 \pm 0.1)$ for $AmCl^{2+}$ and $AmNO_3^{2+}$, respectively, where the uncertainty for the nitrate complex has been increased to ± 0.1 for the reasons discussed

in Section V.6.1.4.1, *p*.138. These values have been used to calculate the standard equilibrium constants in Sections V.4.1.2.1 and V.6.1.4.1.

[64BAN/PAT]

Bansal, B.M.L., Patil, S.K., Sharma, H.D., Chloride, nitrate and sulphate complexes of europium(III) and americium(III), J. Inorg. Nucl. Chem., **26** (1964) 993–1000.

This study reports ion exchange measurements of equilibrium constants for the formation of Am(III) and Eu(III) complexes with Cl^-, NO_3^- and SO_4^{2-} ions at (26 ± 1)°C. The experiments were performed in the following ionic media: $Na(ClO_4,X)$ at pH = 3, and $H(ClO_4,X)$, where X, the complexing anions (Cl^-, NO_3^- or SO_4^{2-}), were progressively replaced with perchlorate ions to keep a fixed ionic strength of 1.0 M. For all ligands, slightly higher values of equilibrium constants were measured in Na^+-containing solutions. This may be ascribed to medium dependent variations of the activity coefficients. Bansal, Patil and Sharma reported $\log_{10} \beta_1(AmCl^{2+}) = -(0.05 \pm 0.05)$ and (0.15 ± 0.03), at pH = 0 and pH = 3 respectively. The assumption made by Bansal, Patil and Sharma that ion exchange occurred only for Am^{3+} appears to be correct. As discussed under Ref. [56WAR/WEL], the distribution of the partly complexed species at the highest ligand concentration studied should have been less than one tenth of that of the free metal ions. As also recalculated by this review, no statistically significant evidence for the formation of higher order complexes is found. The reported equilibrium constants are corrected to zero ionic strength using the specific ion interaction equations of Appendix B yielding $\log_{10} \beta_1^\circ(AmCl^{2+}) = (0.96 \pm 0.15)$ and (1.25 ± 0.15), at pH = 0 and pH = 3 respectively.

A reanalysis of the experimental data obtained in nitrate media by this review yields $\log_{10} \beta_1(AmNO_3^{2+}) = (0.27 \pm 0.02)$ (in H^+) and (0.23 ± 0.03) (in Na^+). These results are in agreement with other literature values. The reported and/or re-evaluated equilibrium constants are corrected to zero ionic strength using the specific ion interaction equations of Appendix B. This results in $\log_{10} \beta_1^\circ(AmNO_3^{2+}) = (1.30 \pm 0.1)$ and (1.38 ± 0.10), in $HClO_4$ and $NaClO_4$ solutions respectively, where the uncertainties have been increased to ± 0.1 for the reasons discussed in Section V.6.1.4.1, *p*.138.

The experimental data for the Am(III)–SO_4^{2-} system were interpreted by Bansal, Patil and Sharma assuming the formation of $AmSO_4^+$ and $Am(SO_4)_2^-$. These results refer to an unpublished work by Nair and Welch, and hence, are not considered by this review.

[64SEK]

Sekine, T., Complex formation of La(III), Eu(III), Lu(III) and Am(III) with oxalate, sulphate, chloride and thiocyanate ions, J. Inorg. Nucl. Chem., **26** (1964) 1463–1465.

A solvent extraction study of the americium chloride, sulphate and thiocyanate systems is summarised in this paper. The experimental details are given in [65SEK, 65SEK2, 65SEK3], respectively.

[64SHI/MAR]
Shiloh, M., Marcus, Y. The chemistry of trivalent neptunium plutonium and americium in halide solutions, Report IA-924, Israel Atomic Energy Commission, Soreq Research Establ., 1964, 26p.

The americium study described in this report is also presented in references [69MAR/SHI] (chloride complexation) and [69SHI/GIV] (bromide complexation).

[65CHO/KET]
Choppin, G.R., Ketels, J., Thiocyanate complexes of some trivalent lanthanide and actinide elements, J. Inorg. Nucl. Chem., **27** (1965) 1335–1339.

The authors studied americium complexation in SCN^- media using a solvent extraction technique (bis-2-ethyl-hexyl orthophosphoric acid, *hdehp*, in toluene and 1.0 M $NaSCN/NaClO_4$ at pH = 2). At 25°C, the data were interpreted assuming the formation of $AmSCN^{2+}$ and $Am(SCN)_2^+$ complexes. The extraction behaviour of americium was also investigated at higher temperatures (40 and 55°C) in order to determine the thermodynamic functions for the formation of $AmSCN^{2+}$ (*cf.* Table V.18): $\Delta_r H_m(298.15\ K) = -(18.25 \pm 1.25)\ kJ \cdot mol^{-1}$ and $\Delta_r S_m(298.15\ K) = -(51.49 \pm 4.18)\ J \cdot K^{-1} \cdot mol^{-1}$. $\Delta_r H_m$ and $\Delta_r S_m$ seem to have a temperature dependence opposite to that reported in the later publications [70KIN/CHO, 72HAR/PET, 74KIN/CHO] and are therefore not considered in this review. Values of $\Delta_r H_m$ and $\Delta_r S_m$concerning the formation of the second complex were not reported, due to the uncertainties in the determination of the corresponding formation constant.

[65CHO/STR]
Choppin, G.R., Strazik, W.F., Complexes of trivalent lanthanide and actinide ions: I. Outer-sphere ion pairs, Inorg. Chem., **4** (1965) 1250–1254.

Choppin and Strazik performed a solvent extraction experiment using dinonylnaphthalene sulphonic acid, dissolved in *n*-heptane, as a liquid cation exchanger. The ionic strength was kept constant (I = 1.0 M $HClO_4/HNO_3$). The data were interpreted assuming the formation of $AmNO_3^{2+}$ with $\log \beta_1 = (0.26 \pm 0.02)$. The reported equilibrium constant is corrected to zero ionic strength using specific ion interaction equations (*cf.* Appendix B). An uncertainty of ±0.1 is assigned to all nitrate $\log_{10} \beta_1$ values in order to take into account the variation in the anionic composition of the media. This results in $\log_{10} \beta_1^\circ = (1.29 \pm 0.10)$.

[65SEK]
Sekine, T., Solvent extraction studies of trivalent actinide and lanthanide complexes in aqueous solutions: I. Chloride complexes of La(III), Eu(III), Lu(III), and Am(III) in 4 M $NaClO_4$, Acta Chem. Scand., **19** (1965) 1435–1444.

A synergic solvent extraction system composed of 2-thenoyltrifluoroacetone and tributylphosphate in CCl_4 was used to study complex formation of Am^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} with chloride ions at 25°C. The measurements were made at a constant acidity of $\log_{10}[H^+] = -2$. The chloride ion concentration was varied between 0.4 M and 3.6 M by using $NaClO_4$ as inert electrolyte to keep the ionic strength fixed at 4 M Na^+. The extraction mechanism was proved to be the same both in the presence

and in the absence of the ligand. The experimental method and the calculation procedure used by the author are satisfactory. The stability constants of $AmCl^{2+}$ and $AmCl_2^+$ were reported to be $\log_{10}\beta_1 = -(0.15 \pm 0.07)$ and $\log_{10}\beta_2 = -(0.69 \pm 0.10)$. The uncertainties provided by Sekine (three times the standard deviation) reflect the accuracy of the curve fitting procedure. They do not take into account the large changes in the ionic medium during the experiments. This review therefore assigns larger uncertainties as follows: ± 0.14 in $\log_{10}\beta_1$ and ± 0.2 in $\log_{10}\beta_2$.

[65SEK2]
Sekine, T., Solvent extraction study of trivalent actinide and lanthanide complexes in aqueous solutions. II. Sulphate complexes of La(III), Eu(III), Lu(III), and Am(III) in 1 M $Na(ClO_4)$, Acta Chem. Scand., **19** (1965) 1469–1475.

Sekine studied the sulphate complexation of americium(III) at 25°C by a solvent extraction method ($3 < pH < 4$; $I = 1$ M $Na_2SO_4/NaClO_4$ at 25°C). The variation of the distribution coefficient with increasing $[SO_4^{2-}]$ was interpreted assuming the presence of $AmSO_4^+$ and $Am(SO_4)_2^-$ complexes. The author used an unspecified value from [58BJE/SCH] for the second dissociation constant of H_2SO_4. The complexation constants given by the author are used in the selection procedure described in Section V.5.1.2.1. Extrapolation to zero ionic strength (*cf.* Appendix B) yields $\log_{10}\beta_1^\circ = (3.87 \pm 0.11)$ and $\log_{10}\beta_2^\circ = (5.72 \pm 0.10)$.

[65SEK3]
Sekine, T., Solvent extraction study of trivalent actinide and lanthanide complexes in aqueous solutions: IV. Thiocyanate complexes of La(III), Eu(III), Lu(III) and Am(III) in 5 M $NaClO_4$ solution at 25°C, Acta Chem. Scand., **19** (1965) 1519–1525.

Sekine measured the distribution coefficient of Am(III) between an aqueous phase at $I = 5.0$ M $NaSCN/NaClO_4$ and $3 \leq pH \leq 4$, and an organic phase containing 2-thenoyltrifluoroacetone in CCl_4, at 25°C. The variation of the distribution coefficient as a function of $[SCN^-]$ indicated the formation of the complexes $AmSCN^{2+}$, $Am(SCN)_3(aq)$ and $Am(SCN)_4^-$. All the attempts to include the second complex, $Am(SCN)_2^+$, in the statistical data analysis scheme produced a poorer fit to the data, indicating that this constant was not statistically needed to fit the distribution data, *i.e.*, $Am(SCN)_2^+$ never exceeded 5% in the investigated experimental conditions [65SEK]. Even though the stability constants were obtained from accurate experimental data [65SEK], no extrapolation to zero ionic strength is performed because of the high electrolyte concentration used ($I = 5$ M).

[66BOR/ELE]
Borisov, M.S., Elesin, A.A., Lebedev, I.A., Filimonov, V.T., Yakovlev, G.N., Investigation of the complexing of trivalent actinides and lanthanides in phosphoric acid solutions, Sov. Radiochem., **8** (1966) 40–44.

Borisov *et al.* studied the complexation of americium(III) in phosphoric acid solutions using a cation exchange technique at 0.2 M NH_4ClO_4, (20 ± 2)°C. The experimental results were interpreted assuming the formation of $AmH_2PO_4^{2+}$. A plot of $\log_{10}((K_{d,0}/K_d) - 1)$ *vs.* $\log_{10}[H_2PO_4^-]$ (where $K_{d,0}$ is the distribution coefficient in

the absence of ligand) shows that the complexing ligand is $H_2PO_4^-$ and that only the first complex is formed. A reinterpretation of the data shows that $K_{d,1}$ (the partition coefficient of the complex) has to be negative, but this assumption is not proven experimentally by Borisov *et al.* Hence, the reported equilibrium constants are not selected by this review.

[66GIV]
Givon, M. Nitrate complexing of americium, in: Proc. XXXVI Meeting Israel Chem. Soc., held in Tel Aviv, October 1966, Israel J. Chem., **4 (1a)** (1966) 3p.

This abstract reports the americium(III)-nitrate study presented in detail later by Shiloh, Givon and Marcus [69SHI/GIV].

[66MAR]
Marcus,Y., Anion exchange of metal complexes: XV. Anion exchange and amine extraction of lanthanides and trivalent actinides from chloride solutions, J. Inorg. Nucl. Chem., **28** (1966) 209–219.

The distribution data of Am(III) between an anion exchanger and LiCl solutions in the concentration range 8 to 13.5 M were interpreted by assuming the presence of $AmCl_2^+$ and $AmCl_4^-$. No equilibrium constants were calculated.

[66VDO/KOL]
Vdovenko, V.M., Kolokol'tsov, V.B., Stebunov, O.B., Relaxation processes in complex formation. I. Copper and americium chlorides in aqueous solutions, Sov. Radiochem., **8** (1966) 266–269.

The authors calculated the equilibrium constants of chloride complexes of Am(III) from measurements of proton nuclear magnetic relaxation time as a function of LiCl concentration within the range 0.5 M and 4.5 M. There is no indication about the temperature of the experiments. The stability constants reported for $AmCl^{2+}$ and $AmCl_2^+$ were $\log_{10}\beta_1 = 0.032$ and $\log_{10}\beta_2 = -0.97$, respectively, without any uncertainty estimation. The computation procedure closely resembles that generally used for the interpretation of spectrophotometric measurements. The experimental data were revised in Ref. [69VDO/STE] by using an alternative method of estimation. Although the same notation was used in the two papers, the equilibrium constants were reported as stepwise dissociation constants in Ref. [66VDO/KOL], and as stepwise formation constants in Ref. [69VDO/STE]. They are represented here as overall stability constants. The reanalysis by Vdovenko and Stebunov [69VDO/STE] of the experimental data gave $\log_{10}\beta_1 = (0.26 \pm 0.12)$ and $\log_{10}\beta_2 = -(0.046 \pm 0.29)$. In view of the large changes in the activity coefficients of the various americium species, it is not possible to use these data to calculate standard equilibrium constants.

[67CAR/CHO]
De Carvalho R.G., Choppin G.R., Lanthanide and actinide sulphate complexes: I. Determination of stability constants, J. Inorg. Nucl. Chem., **29** (1967) 725–735.

Americium(III) complexation in sulphuric acid solutions was studied by De Carvalho and Choppin [67CAR/CHO] using a solvent extraction method at 2.0 M Na_2SO_4/-

$NaClO_4$ ionic media, pH = 3, and (25 ± 0.1)°C. The formation of $AmSO_4^+$ and $Am(SO_4)_2^-$ complexes was suggested to fit the experimental results. The authors used a value of $K = 10$ for the $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$ equilibrium; this value was taken as an average of two literature data [51ZEB/ALT, 54SUN] and is in good agreement with the estimate made by this review. The stability constants for $AmSO_4^+$ and $Am(SO_4)_2^-$ are used in the selection procedure described in Section V.5.1.2.1. Extrapolation to $I = 0$ (*cf.* Appendix B) yields $\log_{10} \beta_1^\circ = (3.79 \pm 0.18)$ and $\log_{10} \beta_2^\circ = (4.92 \pm 0.20)$.

[67CAR/CHO2]

De Carvalho R.G., Choppin G.R., Lanthanide and actinide sulphate complexes: II. Determination of thermodynamic parameters, J. Inorg. Nucl. Chem., **29** (1967) 737–743.

The authors report a list of stability constants calculated from solvent extraction data (similar to [67CAR/CHO]) at 0, 25, 40 and 55°C and at $I = 2$ M (*cf.* Table V.12). A weighted linear regression of "$\ln \beta_n$ *vs.* $1/T(K^{-1})$" (for $n = 1$ or 2) by this review leads to the re-determination of the enthalpy and entropy changes ($\Delta_r H_m$ and $\Delta_r S_m$), *cf.* Section V.5.1.2.1.

[67MAR]

Marcus, Y., The solubility of americium(III) chloride in concentrated lithium chloride solutions, Radiochim. Acta, **8** (1967) 212–214.

Marcus studied the solubility of well-characterised $AmCl_3$(cr) in aqueous LiCl solutions by approaching equilibrium both from over- and undersaturation. The LiCl concentration was varied between 9 M and 13.2 M without addition of an inert electrolyte to keep a constant ionic strength. No significant differences were observed between solubility measurements at (25 ± 1)°C and (40 ± 1)°C. The solubility curve was modelled by assuming the formation of $AmCl_2^+$. The numerical value of the equilibrium constant for the reaction $AmCl_3(s) \rightleftharpoons AmCl_2^+ + Cl^-$ was reported to be $\log_{10} K^\circ_{s,2,1} = -(0.45 \pm 0.04)$. The empirical relationship used to describe the variation of the mean activity coefficient of $AmCl_2^+$ with chloride concentration does not take into account properly activity effects in the high ionic strength media. Since it is not possible to obtain standard equilibrium constants from data obtained in solutions of varying and very high ionic strength, the reported value is not considered by the present review.

[67NAI]

Nair G.M., Americium(III) sulphate complexes, Proc. Nucl. Radiat. Chem. Symp., held 6-9 March 1967, in Poona, Chemistry Committee, Department of Atomic Energy, Goverment of India, *pp.*405–410.

Preliminary presentation of the americium(III) sulphate chemistry. The experimental details and the exhaustive treatment of data are presented in a later publication [68NAI].

[67RYA]

Ryan, J.L., Octahedral hexahalide complexes of the trivalent actinides, in: Lanthanide/actinide chemistry, Advances in Chemistry Series No **71**, American Chemical Society Publications, 1967, *pp.*331–334.

The author reported spectrophotometrical indications on the presence of $AmCl_6^{3-}$ species in non-aqueous solutions.

[68AZI/LYL]

Aziz A., Lyle S.J., Naqvi S.J., Chemical equilibria in americium and curium sulphate and oxalate systems and an application of a liquid scintillation counting method, J. Inorg. Nucl. Chem., **30** (1968) 1013–1018.

The authors studied the americium(III) sulphate system combining a cation exchange and solvent extraction techniques at $I = 0.5$ M ($Na_2SO_4/NaClO_4$), pH = 3.6 and (25 ± 0.5)°C. Both experimental methods indicate the formation of $AmSO_4^+$ and $Am(SO_4)_2^-$ complexes. The reported stability constants are used in the selection procedure described in Section V.5.1.2.1. Extrapolation to $I = 0$ (*cf.* Appendix B) yields $\log_{10} \beta_1^\circ = (3.91 \pm 0.04)$ and $\log_{10} \beta_2^\circ = (5.57 \pm 0.06)$.

[68NAI]

Nair, G.M., Americium(III) sulphate complexes, Radiochim. Acta, **10** (1966) 116–119.

Nair studied the americium(III)-sulphate system using a cation exchange technique, at 27°C, $I = 1$ M (H^+, Na^+)(HSO_4^-, SO_4^{2-}, ClO_4^-) media [67NAI, 68NAI]. The experimental results were interpreted assuming the formation of $AmSO_4^+$, $Am(HSO_4)_2^+$ and $Am(SO_4)_2^-$. The SO_4^{2-} concentration was calculated using $K = 0.302$ for the second dissociation constant of H_2SO_4, reported in Ref. [55EIC/RAB].

This review reinterprets the experimental distribution coefficients, K_d, obtained at pH = 0. The second dissociation constant of H_2SO_4 was calculated for each of the experimental points reported by Nair, and $\log_{10} K_1$ was found to vary between 1.16 and 1.29. As expected, these values are different from the dissociation constants of HSO_4^- given in Ref. [89SMI/MAR] for $NaClO_4$ media, because the activity coefficients of sulphate and bisulphate ions change when $NaClO_4$ is replaced by mixtures of sulphuric and perchloric acids. The ionic strength is found to vary only slightly in the experiments of Nair (0.97 M $< I <$ 1.04 M), which should not affect considerably the resulting stability constants. The linear variation of $((K_d^\circ/K_d) - 1)$ *vs.* $[SO_4^{2-}]$ indicates the presence of $AmSO_4^+$ only, with $\log_{10} \beta_1 = (1.88 \pm 0.10)$. There is no need to include either $Am(HSO_4)_2^+$ or $Am(SO_4)_2^-$ to interpret the experimental data.

The results obtained at pH = 3 are not affected by the acid constant. The stability constants reported by Nair, $\log_{10} \beta_1 = (1.49 \pm 0.01)$ and $\log_{10} \beta_2 = (2.36 \pm 0.01)$, are in agreement with our recalculations and are used by this review. The uncertainty of $\log_{10} \beta_2$ is however increased to ± 0.05. As expected there is a difference between the value of β_1 in sodium and acid sulphato/perchlorate media.

These stability constants are used in the selection procedure described in Section V.5.1.2.1. The values obtained at pH = 3 are extrapolated to $I = 0$ (*cf.* Appendix B) to yield $\log_{10} \beta_1^\circ = (3.79 \pm 0.06)$ and $\log_{10} \beta_2^\circ = (5.42 \pm 0.10)$.

[69AZI/LYL]

Aziz, A., Lyle, S.J., Equilibrium constants for aqueous fluoro complexes of scandium, yttrium, americium(III) and curium(III) by extraction into di-2-ethylhexyl phosphoric acid, J. Inorg. Nucl. Chem., **31** (1969) 3471–3480.

The complexation of Sc^{3+}, Y^{3+}, Am^{3+} and Cm^{3+} with fluoride ions in 0.5 M $NaClO_4$ at pH = 3.6 was studied by solvent extraction with di-2-ethylhexyl phosphoric acid, *hdehp*, in toluene. The temperature was kept constant at 25°C. Aziz and Lyle proposed an equilibrium model involving the formation of AmF^{2+}, AmF_2^+ and AmF_3(aq). The stability constants at zero ionic strength are, respectively, $\log_{10}\beta_1^\circ = (4.37 \pm 0.05)$, $\log_{10}\beta_2^\circ = (7.66 \pm 0.06)$ and $\log_{10}\beta_3^\circ = (11.1)$, as recalculated by this review using the ion interaction coefficients given in Appendix B.

The distribution coefficient, D, between the organic and the aqueous phase was found to decrease regularly with increasing the fluoride ion concentration up to 1.5×10^{-3} M. This was associated with the depressing role of complex formation in the aqueous solution on the extraction of the aqua ion Am^{3+}. At higher F^- concentrations, the extraction of the neutral complex AmF_3(aq) was also claimed to occur. However, at pH = 3.6, *hdehp* is known to be a good extracting agent also for divalent ions. Although this was apparently excluded on the basis of the observed third order dependence of D on the *hdehp* concentration, the extraction mechanism proposed by Aziz and Lyle is not adequately proven. The formation constants of AmF^{2+} and AmF_2^+ are at least one order of magnitude higher than reported in other two-phase distribution studies where the partition mechanism could be identified more precisely [76CHO/UNR, 84NAS/CLE2].

[69BAR/MIK]

Barbanel, Yu. A., Mikhailova, N.K., Study of the complex formation of Am(III) with the Cl^- ion in aqueous solutions by the method of spectrophotometry, Sov. Radiochem., **11** (1969) 576–579.

The absorption spectra of Am(III) ions were studied in aqueous HCl and LiCl solutions at (25±1)°C. The ligand concentrations were varied between zero and 12.6 M for HCl, and 10.75 M for LiCl solutions. The authors determined the stability constant of $AmCl^{2+}$ from the change of the molar absorbances in the wavelength region 500 to 510 nm, obtaining $\log_{10}\beta_1 = -(2 \pm 0.05)$. This is a mixed constant obtained by using the concentration of the Am species and the activity of the chloride ions. The experimental approach and the calculation procedure used by the authors are not satisfactory. The results of this study are not used in the present review because of the considerable variation of ionic strength throughout the experiments.

[69DES]

Désiré, B., Détermination de la première constante d'hydrolyse d'éléments trivalents des séries "4f" et "5f", Thèse Doctorale 3ème cycle, Faculté des Sciences de Paris, 1969, 45p, in French.

The content of this thesis was published in two different papers. Information on lanthanides is given in Ref. [71GUI/DES], while hydrolysis data of interest to this review are reported in Ref. [69DES/HUS].

[69DES/HUS]
Désiré, B., Hussonnois, M., Guillaumont, R., Détermination de la première constante d'hydrolyse de l'américium, du curium, du berkélium et du californium, C.R. Hebd. Acad. Sci. Paris, Ser. C, **269** (1969) 448–451, in French.

The authors investigated the hydrolysis behaviour of the trivalent actinides Am^{3+}, Cm^{3+}, Bk^{3+} and Cf^{3+} using a solvent extraction technique (2-thenoyltrifluoroacetone, *tta*, in benzene). The ionic strength was buffered at 0.1 M with (H, Li)ClO_4. For americium, the pH range studied was 4.2 to 5.9. The slope of the $\log_{10} D$ *vs.* pH plot (where D is the distribution coefficient) is very close to the theoretical slope of 3 expected in the presence of Am^{3+}. However, despite the spread observed in the data, a second-power dependence on pH was claimed to result above pH = 5.2. This was taken as an indication of $AmOH^{2+}$ formation in the aqueous phase. The first hydrolysis constant proposed by the authors is $\log_{10}{}^*\beta_1 = -(5.92 \pm 0.11)$ at (23 ± 1)°C. Our re-evaluation used a weighted least-squares procedure with error estimates on experimental parameters derived from Désiré's thesis [69DES] and from a companion paper [69GUI/FER]. Within the accuracy of the measurements this review can find no evidence that $AmOH^{2+}$ was present in any noticeable amount, which is in accordance with calculations done using the value for $\log_{10}{}^*\beta_1^\circ$ selected in the present review and extrapolated to 0.1 M ionic strength.

[69MAR2]
Marin, B., Comportement des lanthanides et transuraniens trivalents en milieu chlorhydrique, Ph.D. Thesis, Université de Paris, Report CEA-R-3803, 1969.

The complex formation of trivalent lanthanides, Am^{3+} and Cm^{3+} with chloride ions was studied by paper electrophoresis at 15°C. The stability constants of $AmCl^{2+}$ and $AmCl_2^+$ were determined to be, respectively, $\log_{10} \beta_1 = 1.0$ and $\log_{10} \beta_2 = 0.34$. No constant ionic medium was used, with Cl^- concentrations varying from 10^{-2} M to 10 M. Since no appropriate methods are available for their correction to $I = 0$, these values are not credited by this review.

[69MAR/KIK]
Marin, B., Kikindai, T., Etude comparée de l'hydrolyse de l'europium et de l'américium en milieu chlorure par électrophorèse sur papier, C.R. Hebd. Acad. Sci. Paris, Ser. C, **268** (1969) 1–4, in French.

The americium and europium hydrolysis in HCl/KCl medium ($I = 5 \times 10^{-3}$ M) was investigated between pH = 2.5 and 5 using paper electrophoresis. The temperature was fixed at (15 ± 1)°C. Two plateaux were found in the electrophoretic mobility curve. The first was assigned to the aqua ion Am^{3+} (at pH < 2.5), and the second to the hydroxo complex $AmOH^{2+}$ (at pH > 3.5). The individual electrical mobility values were then used to calculate the stability constant (called hydrolysis constant in the original paper) for the $AmOH^{2+}$ species. The hydrolysis constant $\log_{10}{}^*\beta_1$ as defined in the present review, was determined to be $-(3.05 \pm 0.05)$ for $AmOH^{2+}$ and $-(3.15 \pm 0.05)$ for $EuOH^{2+}$. Insufficient experimental details can be extracted from the paper (electrode calibration procedure, pH control on the support for elec-

trophoresis, total Am concentration, existence of electro-osmotic flow). Calculations of electrical mobilities from the position of broad Am peaks along the paper strip are likely to be affected by large errors. The reported constant is not credited by the present review.

[69MAR/SHI]
Marcus, Y., Shiloh, M., A spectrophotometric study of trivalent actinide complexes in solution: IV. Americium with chloride ligands, Israel J. Chem., **7** (1969) 31–43.

Marcus and Shiloh measured the spectral changes of Am(III) in various aqueous and non-aqueous solutions at increasing concentrations of chloride ions. In order to obtain further information about the nature of soluble americium species, attempts were made to compare the solution spectra with those obtained for characterised solid americium chlorides.

Pronounced changes were observed for the absorption bands at 235 nm and 503 nm in aqueous LiCl media at 0.5 M acidity. Both wavelengths were used to calculate the formation constants of $AmCl^{2+}$ and $AmCl_2^+$ with good internal agreement, obtaining $\log_{10}\beta_1 = -(2.2 \pm 0.1)$ and $\log_{10}\beta_2 = -(4.7 \pm 0.06)$ at 22°C. The LiCl concentration was changed from 0 to 13.7 M, but no constant ionic strength was maintained. The procedure for estimating equilibrium constants used the activity of the chloride ions and the concentration of the americium species giving, therefore, mixed constants. Marcus and Shiloh concluded that the weak complexes seen by spectrophotometry were of the inner-sphere type, with, however, a mixed inner-outer sphere character for $AmCl^{2+}$.

The large variation of activity coefficients, and the questionable assumption of invariance of the extinction coefficients with changes in the LiCl concentration render the reported values of limited application for the estimation of equilibrium constants at $I = 0$.

[69MOS]
Moskvin, A.I., Complex formation of the actinides with anions of acids in aqueous solutions, Sov. Radiochem., **11** (1969) 447–449.

This publication is a compilation of stability constants of actinide complexes, presented at the Moscow Seminar on Analytical Chemistry (1964). No experimental details were reported. The tabulated values for the americium(III) phosphate system are given at $I = 1.0$ M. These data are presented in Table V.15, but are not accepted by this review.

[69SHI/GIV]
Shiloh, M., Givon, M., Marcus, Y., A spectrophotometric study of trivalent actinide complexes in solutions: III. Americium with bromide, iodide, nitrate and carbonate ligands, J. Inorg. Nucl. Chem., **31** (1969) 1807–1814.

Spectrophotometric studies were used to identify the Am(III) complexes present in aqueous solutions containing bromide, iodide, nitrate or carbonate ions. The measurements were made at 25°C. No constant ionic strength medium was used.

The formation of $AmBr^{2+}$ was claimed to occur only in concentrated LiBr solutions

above 8.7 M. The observed spectral changes in the visible region were associated with inner-sphere interactions. The reported stability constant, $\log_{10}\beta_1 = -(3.3 \pm 0.1)$, is a mixed constant incorporating both activity and concentration terms. However, as discussed in this Appendix under Ref. [69MAR/SHI], it is difficult to derive reliable quantitative information on this weak complex because it requires large variations in the activity coefficients throughout the experiments. Similar arguments apply to the reported equilibrium constant for $AmNO_3^{2+}$, $\log_{10}\beta_1 = (-1.30 \pm 0.09)$, obtained from spectra in solutions containing up to 15 M HNO_3 [69SHI/GIV, Fig. 3].

Spectral changes in the americium iodide system were observed only in concentrated MgI_2 solutions (4.1 M), but no quantitative data were reported.

Shiloh, Givon and Marcus also studied the solubility of a chemically characterised $Am_2(CO_3)_3(s)$ in 0.1 to 0.6 M potassium carbonate media [69SHI/GIV]. The authors did not consider the influence of the ionic strength, which varied from 0.4 to 2 M, but interpreted their results by assuming the formation of $Am(CO_3)_3OH^{4-}$. Newton and Sullivan [85NEW/SUL] later pointed out, in their review of actinide carbonate complexes, that these solubility data did not distinguish between $Am(CO_3)_3OH^{4-}$ and $Am_2(CO_3)_5^{4-}$. They also found that, if a reasonable ionic strength correction is included in the analysis, the solubility data may be described by the reaction

$$0.5\,Am_2(CO_3)_3(s) + 1.5\,CO_3^{2-} \quad \rightleftharpoons \quad Am(CO_3)_3^{3-} \qquad (V.35)$$

with $K_{s,3}(V.35) = (K_{s,0}(V.36) \times \beta_3)$ showing that $Am(CO_3)_3^{3-}$ is the predominant complex up to $[CO_3^{2-}] = 2$ M. Following the reinterpretation by Robouch [89ROB], the solubility data, digitised from Figure 4 in [69SHI/GIV], are used by this review to perform an extrapolation using the specific interaction equations (*cf.* Appendix B) making the assumption $[CO_3^{2-}] \approx [K_2CO_3]$. The following relation for the ionic strength correction (*cf.* Figure A.1) is obtained:

$$\begin{aligned} &\log_{10} K_{s,3}(V.35, I) \\ &\quad = -(3.68 \pm 0.08) + 3D + (0.28 \pm 0.12) \times [K_2CO_3], \end{aligned} \qquad (A.1)$$

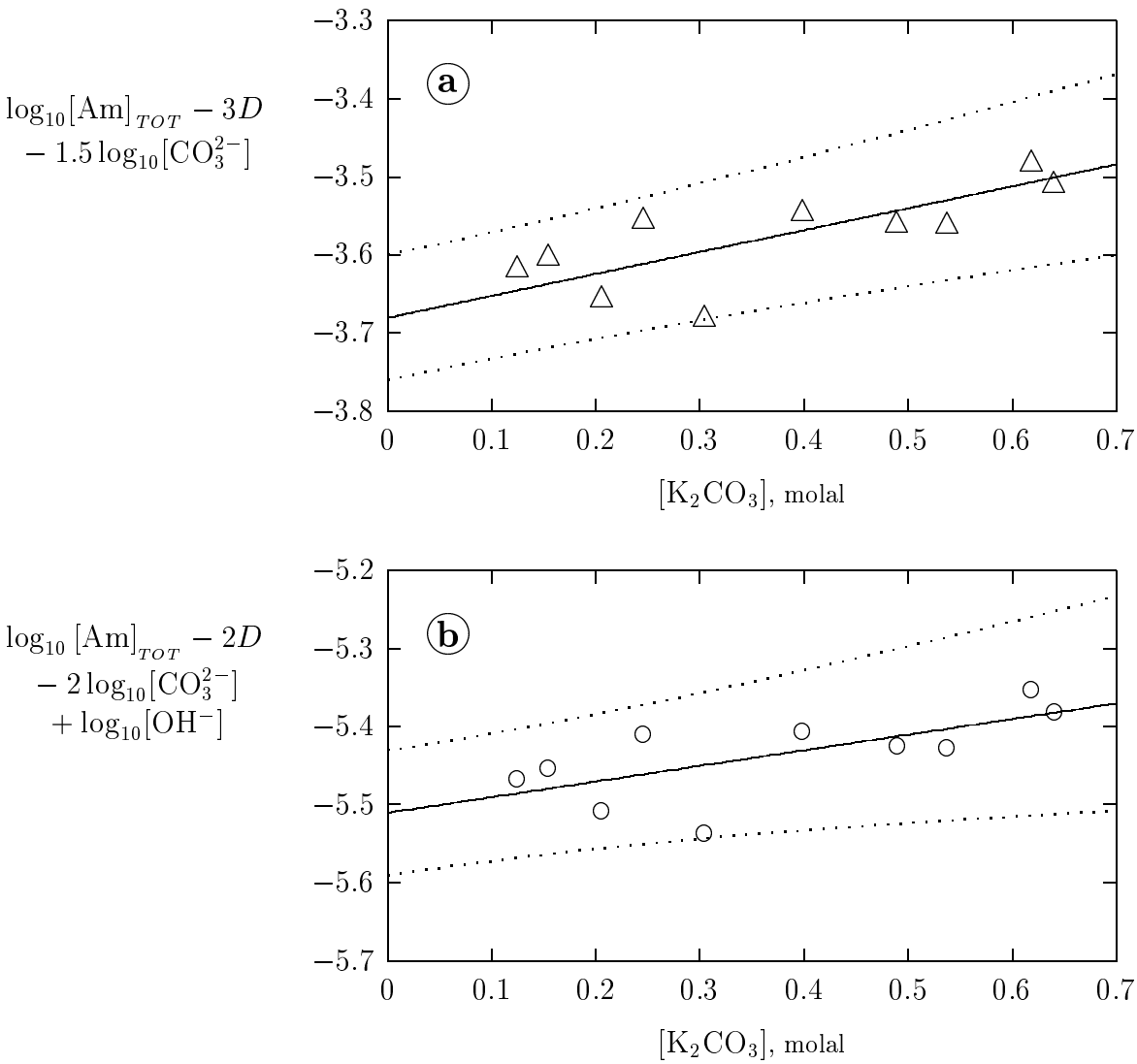
where $K_{s,3}(V.35)$ and $[K_2CO_3]$ are expressed in molal units, and the Debye-Hückel term, D, is defined in Eq. (B.2) of Appendix B.

However, the low equilibrium partial pressures of $CO_2(g)$ in experiments with high carbonate concentrations (specially in this work where the solutions were apparently equilibrated with atmospheric $CO_2(g)$) would favor the formation of $AmCO_3OH(s)$ at the expense of $Am_2(CO_3)_3(s)$, as outlined by Vitorge [92VIT] and according to Eq. (V.37) in *p*.162. In the presence of solid americium hydroxy-carbonate, the solubility data may be described by the reaction

$$AmCO_3OH(s) + 2\,CO_3^{2-} \quad \rightleftharpoons \quad Am(CO_3)_3^{3-} + OH^- \qquad (V.32)$$

with $K_{s,3}(V.32) = (K_{s,0}(V.33) \times \beta_3)$. Similar procedure and assumptions as those described above for reaction (V.35) are now applied to reaction (V.32). The following relation for the ionic strength correction (*cf.* Figure A.1) is then obtained:

Figure A.1: Experimental solubility data from [69SHI/GIV] extrapolated to $I = 0$ using the specific ion interaction equations (*cf.* Appendix B). Upper diagram (**a**) assuming reaction: $0.5\,Am_2(CO_3)_3(s) + 1.5\,CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-}$. Lower diagram (**b**) assuming reaction: $AmCO_3OH(s) + 2\,CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-} + OH^-$. The lines correspond to Eqs. (A.1) and (A.2) respectively, and the dotted curves represent the 95% confidence intervals.



$$\log_{10} K_{s,3}(\text{V.32}, I) = -(5.51 \pm 0.08) + 3D + (0.20 \pm 0.16) \times [K_2CO_3]. \quad (A.2)$$

Although the solubility data of Shiloh, Givon and Marcus show unequivocally that $Am(CO_3)_3^{3-}$ is the predominant complex up to $[CO_3^{2-}] = 2$ M, it is not possible to conclude with confidence which is the equilibrium reaction taking place, and the data can not be used in the selection procedures described in Section V.7.1.2.2.

[69VDO/STE]
Vdovenko, V.M., Stebunov, O.B., Relaxation processes during complex formation: IV. Determination of the stability constants of the complexes from the data of the proton relaxation method, Sov. Radiochem., **11** (1969) 625–629.

In this paper Vdovenko and Stebunov recalculated equilibrium constants for Am(III) complexation with chloride ions from experimental data in Ref. [66VDO/KOL].

[70KIN/CHO]
Kinard, W.F., Choppin, G.R., The thermodynamic of complexing of trivalent actinide ions by thiocyanate, Report TID-25671, Florida state University, Thallahasse, Florida, 1970, 13p.

This appears to be the same study reported as Ref. [74KIN/CHO] where more experimental details are given. The stability constants obtained at various temperatures are reported identically in the two publications, which indicates that a misprint may be present in Table I of Ref. [70KIN/CHO] (50 instead of 55°C).

[70LAH/KNO]
Lahr, H., Knoch, W., Bestimmung von Stabilitätskonstanten einiger Aktinidenkomplexe: II. Nitrat- und Chloridkomplexe von Uran, Neptunium, Plutonium und Americium, Radiochim. Acta **13** (1970) 1-5, in German.

Lahr and Knoch studied the formation of americium(III) nitrate complexes in 8 M H^+ at 20°C. They used an extraction method based on tri-*n*-octylamin dissolved in xylene. They found for the reaction $Am^{3+} + n\,NO_3^- \rightleftharpoons Am(NO_3)_n^{(3-n)}$: $\beta_n(NO_3^-) = 0.47; 0.17$ and 0.04 for $n = 1$, 2 and 3, respectively. The nitrate concentration varied from 0 to 8 M. This should result in large changes in the activity factors of the various species. The "equilibrium constants" given by the authors are better regarded as empirical parameters than as true stability constants. It is not possible to extrapolate data from this high ionic strength to $I = 0$. This review therefore disregards these data.

In spite of the title, no measurements of americium complexation in the chloride system are reported.

[70MAR/BOM]
Marcus, Y., Bomse, M., Octahedral chloride complexes of trivalent actinides and lanthanides in solution, Israel J. Chem., **8** (1970) 901–911.

The objective of this paper was to investigate the formation of hexacoordinated species of Am^{3+}, Cm^{3+} and various lanthanides in chloride-containing solutions. For this purpose, Marcus and Bomse used solvents of low dielectric constants. All measurements were made at 25°C by using spectrophotometry. The stepwise equilibrium constant for the formation of $AmCl_6^{3-}$ from $AmCl_5^{2-}$ was calculated to be $K_6 = (150 \pm 20)$ in a mixed solvent acetonitrile/succinonitrile, and $K_6 = (60 \pm 20)$ in propane-1,2-diol carbonate. These are conditional constants which due to the non-aqueous media are not considered in this review.

[71HAR]
Harmon, H.D., The thiocyanate and chloride complexes of some trivalent actinides, Ph.D. thesis in inorganic chemistry, University of Tennessee, Knoxville, Tennessee, 1971, 143p.

Attempts were made to select appropriate synergic mixtures for solvent extraction studies of Am^{3+}, Bk^{3+} and Es^{3+} complexation with chloride ions. However, only preliminary data were reported. See the discussion in this Appendix of [72HAR/PET] and [72HAR/PET2] for the experimental details on the americium(III)-thiocyanate system studied by spectrophotometry and solvent extraction.

[71KHO/NAR]
Khopkar, P.K., Narayanankutty, P., Effect of ionic media on the stability constants of chloride, nitrate and thiocyanate complexes of americium(III) and europium(III), J. Inorg. Nucl. Chem., **33** (1971) 495–502.

A solvent extraction technique with dinonylnaphthalene sulphonic acid (*hdnns*) in *n*-hexane was used to investigate the complexation of Am^{3+} and Eu^{3+} with chloride, nitrate and thiocyanate ions. The authors used constant ionic strength media (1 M) at (30 ± 0.1)°C, in which the ratio of perchlorate to ligand ions was varied. The effect of varying the cation of the background electrolyte (Li^+, H^+, Na^+ or NH_4^+) on the equilibrium constants was also studied.

Khopkar and Narayanankutty assumed that only Am^{3+} was extracted into the aqueous phase. To clarify this, the dependence of the americium distribution ratio with the *hdnns* concentration in the organic phase at constant concentrations of inorganic ligands in the aqueous solution should have been investigated. As *hdnns* behaves as a liquid cation exchanger, divalent or monovalent americium complexes may also have been extracted. However, the order of extractability of the complex ions is expected to decrease with decreasing the charge/size ratio. According to the considerations made in this Appendix under Ref. [56WAR/WEL], the assumption made by Khopkar and Narayanankutty appears to be reasonable, because the concentration of the complexing anions never exceeded 1 M.

The species $AmCl^{2+}$ and $AmCl_2^+$ were claimed to be present in the americium chloride system. The values of $\log_{10} \beta_1$ ranged from $-(0.25 \pm 0.02)$ to $+(0.12 \pm 0.02)$, depending upon whether lithium or ammonium was used, *cf.* Table V.8. Although less regularly, the value of $\log_{10} \beta_2$ was also found to increase with decreasing degree

of solvation of the bulk cation. Similar observations were made by Bansal, Patil and Sharma [64BAN/PAT]. The observed variations are likely to be due to changes in the activity coefficients which are independent of the nature of the medium only at very low ionic strengths. The stability constants of $AmCl^{2+}$ are slightly smaller than those measured by other authors at lower temperatures, as expected for the formation of outer-sphere complexes. However, according to the enthalpy value for $EuCl^{2+}$ reported by Choppin and Unrein [63CHO/UNR], the variation of the equilibrium constant with temperature between 30 and 25°C should be negligible. The difference between the various sets of values may also be ascribed to the calculation procedure.

With respect to the single variable β_1 model, the addition of β_2 is expected to give a smaller value for β_1. It is, however, difficult to estimate the statistical significance of the model with two predictor variables, because no experimental raw data were given in the paper. For this reason, only β_1 is considered for calculation of the thermodynamic value, but the associated uncertainty is increased to ± 0.1 logarithmic units. The stability constants at zero ionic strength are $\log_{10} \beta_1^\circ(AmCl^{2+}) = (0.87 \pm 0.15)$ and (1.12 ± 0.15) in acid and sodium ionic media respectively, as recalculated by this review using the ion interaction coefficients given in Appendix B. Apparently, the addition of $AmCl_2^+$ in the data analysis was found to be significant only for solutions at 30°C, while no improvement of the error sum was obtained for preliminary experimental data at room temperature.

$AmNO_3^{2+}$ and $Am(NO_3)_2^+$ were claimed to be present in the americium nitrate system. The values of $\log_{10} \beta_1(AmNO_3^{2+})$ ranged between (0.23 ± 0.02) and (0.30 ± 0.02), depending upon whether Li^+ or NH_4^+ was used, *cf.* Table V.14. These values are in fair agreement with other published results [62PEP/MAS, 64BAN/PAT, 65CHO/STR]. The stability constants are converted to molal units and extrapolated to zero ionic strength using the specific ion interaction equations of Appendix B, resulting in $\log_{10} \beta_1^\circ(AmNO_3^{2+}) = (1.32 \pm 0.1)$, (1.32 ± 0.1) and (1.41 ± 0.1) in acid, lithium and sodium ionic media respectively, where the uncertainties have been increased to ± 0.1 for the reasons discussed in Section V.6.1.4.1, *p*.138.

From the distribution data, $AmSCN^{2+}$ and $Am(SCN)_2^+$ seem to be evidenced in the americium thiocyanate system. The corresponding values of the stability constants, obtained in Na^+ and NH_4^+ media, are reported to be indistinguishable within the experimental errors. The experimental data were not reported, but the measured distribution coefficients (at 30°C and $I = 1.0$ M NH_4^+) were obtained by digitising the available figure. Two different models were then tested by this review. First, it was assumed the presence of the first two complexes obtaining values of $\log_{10} \beta_1$ and $\log_{10} \beta_2$ similar to those proposed by Khopkar and Narayanankutty. Then we fitted the data by assuming the formation of $AmSCN^{2+}$ and $Am(SCN)_3(aq)$, as suggested by Sekine [65SEK3] and Harmon [72HAR/PET], obtaining a somewhat better least squares fit to the data. This indicates that complexation by the thiocyanate ligand is rather weak and that the determination of the corresponding stability constants may be very sensitive to changes in the chemical model. The presence of $AmSCN^{2+}$ is certainly evidenced in the experiments of Khopkar *et al.*, but no conclusion on the formation of the second and/or third complex can be deduced. Hence, the reported formation constant of $Am(SCN)_2^+$ in [71KHO/NAR] is not selected by this review.

The value of $\log_{10}\beta_1$ at 30°C reported in [71KHO/NAR] is converted to molal units and extrapolated to zero ionic strength using the specific interaction equations, *cf.* Appendix B, with $\Delta\varepsilon = -(0.15\pm0.05)\,\mathrm{kg\cdot mol^{-1}}$. This results in $\log_{10}\beta_1^\circ = (1.23\pm0.11)$.

[71MOS2]
Moskvin, A.I., Investigation of the complex formation of trivalent plutonium, americium and curium in phosphate solutions, Sov. Radiochem., **13** (1971) 688–693.

Moskvin studied the americium(III) phosphate system by an cation exchange technique in 1.0 M, NH_4Cl solutions at an unknown temperature using a wide range of total phosphate concentration: $0.05 \leq [H_3PO_4]_{TOT} \leq 6.8$ M. The experiments were performed both at pH = 1.8 and at $[H^+] = 0.5$ M. The variation of the distribution coefficient, K_d, with increasing $[H_2PO_4^-]$ was interpreted assuming the formation of four complexes of the general composition $Am(H_2PO_4)_n^{(3-n)}$ with $n = 1$ to 4. However, using the speciation proposed by Moskvin, non-realistic negative values are calculated for the partition coefficients of the cationic americium species (Am^{3+}, $AmH_2PO_4^{2+}$ and $Am(H_2PO_4)_2^+$). The cation exchange technique appears inadequate to study this system where there are several potential ligands which may form many cationic complexes. Therefore the equilibrium constants proposed by Moskvin are rejected by this review.

[72BAI/CHO]
Baisden, P.A., Choppin, G.R., Kinard, W.F., Ion pairing of Am(III) with perchlorate, J. Inorg. Nucl. Chem., **34** (1972) 2029–2032.

The authors studied the ion pair formation between Am(III) and ClO_4^- ions by solvent extraction with dinonylnaphthalene sulphonic acid in *n*-heptane at 25°C. The ionic strength of the aqueous phase was fixed at 2 M by using HBF_4 as background electrolyte. Therefore, activity coefficients varied when the medium was changed from "inert" anions to ligand anions. The equilibrium constant derived by the authors, however, refers to a "pure" perchlorate medium. As described in an earlier report [67CHO/KEL], activity effects in the mixed electrolyte solutions were accounted for by introducing, as constant parameters, the activity coefficients of the pure background electrolyte and of the pure ligand solution, instead of correcting each data point of mixed composition. Moreover, as also stated by the authors, no activity coefficients were available for HBF_4. Apparently, these values were derived indirectly from the experimental measurements of stability constants for the Am(III) complex with *p*-toluene sulphonic acid (*hpts*) in the systems $HClO_4$-*hpts* and HBF_4-*hpts*.

It is difficult to evaluate the uncertainty associated with the approximations made by the authors. Hence, it is not clear if the very low value reported, $\beta_1 = (0.86\pm0.06)$, represents an effective formation constant or rather reflects changes of the ionic medium. Moreover, possible interactions of Am(III) with HBF_4 were not considered quantitatively. In view of these considerations, the present review does not include the reported constant in the selected data set.

[72COH]
Cohen, D., Americium(VI) in basic solution, Inorg. Nucl. Chem. Letters, **8** (1972) 533–535.

This is a spectrophotometric study of Am(VI) in 1 M CsOH. Reduction of Am(VI) and formation of an Am(V) precipitate was reported to occur in one or two days. No equilibrium constants were reported.

[72HAR/PET]
Harmon, H.D., Peterson, J.R., McDowell, W.J., Coleman, C.F., The tetrad effect: the thiocyanate complex stability constants of some trivalent actinides, J. Inorg. Nucl. Chem., **34** (1972) 1381–1397.

The authors studied the formation of americium(III) thiocyanate complexes in 1.0 M $NaSCN/NaClO_4$ media at pH = 2. Solvent extraction experiments were conducted at 18, 25, 30 and 35°C to investigate the temperature effects. The treatment of the data showed that mono-, di- and tri-thiocyanate complexes were formed at $0 < [SCN^-] \leq 1.0$ M, according to:

$$Am^{3+} + n\,SCN^- \rightleftharpoons Am(SCN)_n^{(3-n)}. \tag{A.3}$$

The authors used two models in which the presence of $Am(SCN)_2^+$ was considered ($\beta_1, \beta_2, \beta_3$) or omitted ($\beta_1, \beta_3$). The results indicate that neither of the above models was consistently superior, even if the (β_1, β_3) model was considerably more effective for Bk(III), Cf(III) and Es(III). As discussed in [71KHO/NAR] the complexation by the thiocyanate ligand is rather weak and the determination of the corresponding stability constants may be very sensitive to changes in the chemical model. The presence of $AmSCN^{2+}$ is certainly evidenced in this work, while no unambiguous evidence of the formation of the second and/or the third complex can be obtained from this solvent extraction data set. Therefore the values of β_2 and β_3 reported by Harmon *et al.* are not selected by this review. The first formation constant $\log_{10}\beta_1(I = 1\text{ M}) = (0.36 \pm 0.05)$, *cf.* Table V.17, is converted to molal units and extrapolated to zero ionic strength with the specific ion interaction equations of Appendix B using $\Delta\varepsilon_1 = -(0.15 \pm 0.05)\,\text{kg}\cdot\text{mol}^{-1}$. This results in $\log_{10}\beta_1^\circ = (1.41 \pm 0.08)$.

Due to the uncertainty in the speciation mentioned above, the values of β_3 obtained at different temperatures (18 to 45°C) are not used by this review to calculate enthalpy and entropy changes. However, the values of β_1 are used to determine the reaction enthalpy and entropy at $I = 1$ M by a weighted linear regression "$\ln\beta_1$ *vs.* $1/T$ (K^{-1})" obtaining: $\Delta_r H_m$(A.3, $n = 1$, $I = 1$ M) = (8.2 ± 4.8) kJ · mol^{-1} and $\Delta_r S_m$(A.3, $n = 1$, $I = 1$ M) = (34 ± 16) J·K^{-1}·mol^{-1}. These values are in agreement with the results reported by the authors (*cf.* Table V.18).

[72HAR/PET2]

Harmon, H.D., Peterson, J.R., Bell, J.T., McDowell, W.J., A spectrophotometric study of the formation of americium thiocyanate complexes, J. Inorg. Nucl. Chem., **34** (1974) 1711–1719.

The authors performed spectrophotometric measurements, in 1.0 M NaSCN/$NaClO_4$ media to observe the spectral changes of the 503 nm americium absorption peak, produced by SCN^- complexation. They determined the formation constants of $AmSCN^{2+}$ and $Am(SCN)_2^+$ and suggested the presence of $Am(SCN)_3(aq)$ at $[SCN^-] \geq 1.0$ M. In order to reproduce the tabulated equilibrium constants, this review digitised the molar absorptivities at 503 nm as a function of $[SCN^-]$ in Figure 2 of the original paper. The software SQUAD [85LEG] is used to extract the stability constants. The large scatter in the spectroscopic data makes it impossible to derive all three equilibrium constants. A value of $\log_{10}\beta_1 = (0.88 \pm 0.06)$ can only be obtained from the data at $[SCN^-] \leq 0.1$ M, but not from data at higher thiocyanate concentration. We attempted (fixing $\log_{10}\beta_1$) to determine $\log_{10}\beta_2$ or $\log_{10}\beta_3$. No reliable conclusion on the existence of $Am(SCN)_2^+$ and/or $Am(SCN)_3(aq)$ can be extracted from the data because of the considerable scatter in the values. This review therefore disregards all these spectrophotometric results.

[72MCD/COL]

McDowell, W.J., Coleman, C.F., The sulphate complexes of some trivalent transplutonium actinides and europium, J. Inorg. Nucl. Chem., **34** (1972) 2837–2850.

McDowell and Coleman performed a solvent extraction experiment to investigate sulphate complexes of americium(III), using a benzene solution of 1-nonyldecylamine and an aqueous sulphuric acid – sodium sulphate solution. The experimental data were interpreted assuming the formation of $Am(SO_4)_n^{(3-2n)}$ $(n = 1, 2, 3)$.

As low concentrations of H_2SO_4–Na_2SO_4 were used, the Debye-Hückel relation was appropriately applied. The stability constants $\log_{10}\beta_1^\circ$ and $\log_{10}\beta_2^\circ$ presented in Table V.12, are in good agreement with the values extrapolated by this review, *cf.* Section V.5.1.2.1, using the specific ion interaction equations of Appendix B. Further experimental work is necessary to confirm the presence of $Am(SO_4)_3^{3-}$. The value of $\log_{10}\beta_3^\circ$ is therefore not selected by this review.

[72SHA/STE]

Shalinets, A.B., Stepanov, A.V., Investigation of complex formation of the trivalent actinide and lanthanide elements by the method of electromigration. XVII. Hydrolysis, Sov. Radiochem., **14** (1972) 290–293.

The authors studied the hydrolysis of Am(III) and Cm(III) in 5×10^{-3} M NH_4ClO_4 at 25°C. An electromigration technique without solid support was used. 10^{-5} M Ce(III) was added to the solutions as a carrier, probably to reduce Am and Cm adsorption on the wall of the electromigration cell. The decrease of electrical mobilities with increasing pH from 2 to 5 was modelled assuming the formation of the mononuclear species $AmOH^{2+}$ and $Am(OH)_2^+$. The hydrolysis constants recalculated from the reported formation constants (using $\log_{10}K_w = -13.83$ which had been determined previously [65STE/SHV]) are $\log_{10}{}^*\beta_1 = -(3.13 \pm 0.1)$ and $\log_{10}{}^*\beta_2 = -6.76$.

These values are orders of magnitude higher than those obtained in a number of other, more careful studies. The experimental technique used by Shalinets and Stepanov can easily give inconsistent results because of convective fluxes and the difficult determination of the front of the migrating species which move as a plume rather than as a sharp peak. The reported hydrolysis constants are not used in the evaluation in this review.

[73CHI/DAN]

Chiarizia, R., Danesi, P.R., Scibona, G., Liquid anion exchange of thiocyanate-nitrate actinide and lanthanide complexes, J. Inorg. Nucl. Chem., **35** (1973) 3595–3604.

The authors studied the Am(III)-SCN^--NO_3^- system using a solvent extraction technique at 25°C. Tricaprylmethylammonium chloride in *o*-xylene was equilibrated with a 2.0 M NH_4SCN^-/NH_4NO_3 aqueous phase at pH = 2. The author claims to have determined the stability constants of the americium nitrate and thiocyanate complexes, from the distribution coefficients. There was however a considerable scatter in the data. The reported formation constant of the $AmNO_3^{2+}$ complex $\log_{10}\beta_1(NO_3^-) = (0.20 \pm 0.03)$ seems to be in agreement with previous literature values [62PEP/MAS, 64BAN/PAT, 65CHO/STR, 71KHO/NAR]. The formation of the thiocyanate complexes $AmSCN^{2+}$, $Am(SCN)_2^+$ and $Am(SCN)_3(aq)$ were suggested. However, the speciation diagram obtained by this review with the proposed equilibrium data shows that $AmSCN^{2+}$ never exceeds 5%, while $Am(SCN)_2^+$ is the predominant species at $-0.6 \leq \log_{10}[SCN^-] \leq -0.2$. This is in complete disagreement with all previous observations. This review considers that before conducting a study on competitive complexation (nitrate-thiocyanate), a better knowledge of the simple systems, Am-SCN^- and Am-NO_3^-, is necessary. Therefore, the stability constants reported by Chiarizia, Danesi and Scibona are disregarded by this review.

[73HUS/HUB]

Hussonnois, M., Hubert, S., Brillard, L., Guillaumont, R., Détermination de la première constante d'hydrolyse de l'einsteinium, Radiochem. Radioanal. Letters, **15** (1973) 47–56, in French.

The authors studied the hydrolysis behaviour of Es^{3+} [73HUS/HUB] using a liquid-liquid partition technique (2-thenoyltrifluoroacetone, *tta*, in benzene) in the presence of americium. The pH dependence of the americium extraction reported in Ref. [69DES/HUS] was used to calculate the equilibrium pH of the aqueous phases. For the same reasons as discussed in this Appendix under Ref. [69DES/HUS], the first hydrolysis constant obtained for this element ($\log_{10}{}^*\beta_1 = -(5.3 \pm 0.1)$ at 0.1 M (H,Li)ClO_4) is not accepted by this review. See also the comments under [76HUB/HUS].

[73KOR]

Korotkin, Y.S., Hydrolysis of transuranium elements: II. Hydrolysis of americium(III) and curium(III) in pure nitric acid solutions, Sov. Radiochem., **15** (1973) 682–685.

This is an experimental study involving distribution chromatography, electromigration and paper chromatography, similar to [74KOR2]. As discussed in this Appendix under references [73KOR2, 74KOR2], the experimental methods are not very reliable,

and the reported observations are not credited by this review.

[73KOR2]
Korotkin, Yu.S., Hydrolysis of transuranium elements: III. Hydrolysis of americium(III) in the presence of ions with positive and negative hydration energies, Sov. Radiochem., **15** (1973) 776–781.

The author investigated the Am(III)-H_2O system in lithium, sodium and potassium nitrates and perchlorates (0.1 M and 1 M ionic strength) at 18 to 20°C. The charge of the predominating species was determined as a function of pH using paper electromigration and reversed phase chromatography.

The proposed hydrolysis scheme between pH = 1 and 11 includes the formation of mixed hydroxo-nitrates, mono- and polynuclear hydroxo species, and negatively charged colloids. The experiments were carried out at a total americium concentration in the order of 2×10^{-6} M. Hence, the measurements in the neutral to alkaline pH range were likely influenced by the precipitation of $Am(OH)_3(s)$. Korotkin reported the following values for the first and the second hydrolysis constants in 0.1 M $LiNO_3$ (pH between 3 and 4) with no error estimate given: $\log_{10}{}^*\beta_1 = -2.5$ and $\log_{10}{}^*\beta_2 = -6.6$. This would imply that Am hydrolysis starts already in acidic media, an observation in contrast with those made by other investigations. There is no information available on the procedure used to calculate equilibrium constants and on the way pH measurements were made. Moreover, it is not clear how equilibrium data derived using a dynamic elution method were influenced by sorption-desorption kinetics of individual americium species on the stationary phase. In view of the shortcomings of this study, the reported hydrolysis constants are not used by the present review.

[73MAK/STE]
Makarova, T.P., Stepanov, A.V., Shestakov, B.I., Electromigration investigation of the comparative stability of fluoro-complexes of the MF^{2+} type of certain rare-earth and actinide elements, Russ. J. Inorg. Chem., **18** (1973), 783–785.

The authors investigated the formation of Am(III) complexes with fluoride ions in 0.1 M $NaClO_4$ at (25 ± 0.5)°C by using an electromigration technique. The experiments were carried out by using a porous bed of carborundum powder as stationary phase.

In the investigated concentration range (from 10^{-3} to 10^{-2} M total fluorides at pH = 1.8), the authors found the presence of AmF^{2+} only. Even after ion strength corrections, the value $\log_{10} \beta_1^\circ = (3.96 \pm 0.06)$ is higher than determined in more precise studies. It is often difficult to obtain reliable quantitative values of electrical mobility with the electromigration method used by the authors. The shape of the moving spot depends on the rate of equilibration between the species present in the system, their interactions with the stationary phase, and on the possible existence of electro-osmotic flows and associated phenomena of hydrodynamic dispersion. If not properly accounted for, all this is likely to introduce systematic errors into the measurements. For this reason, the reported equilibrium constant is not included in the selected set of data.

[74CEL/HOL]
Celeda, J., Holub, J., Smirous, F., A ionophoretic study of the association of Pm^{3+} and Am^{3+} ions in concentrated solutions of calcium perchlorate and nitrate, Collection Czechoslov. Chem. Commun., **39** (1974) 3599–3602.

This is a qualitative study on complex formation of Am(III) in $Ca(ClO_4)_2$ and $Ca(NO_3)_2$ media by using paper electrophoresis. The authors claimed that the monovalent complex $Am(NO_3)_2^+$ was present in the nitrate concentration range from 1 to 8 M.

[74KHO/MAT]
Khopkar, P.K., Mathur, J.N., Thiocyanate complexing of some trivalent actinides and lanthanides, J. Inorg. Nucl. Chem., **36** (1974) 3819–3825.

A solvent extraction technique (as in Ref. [71KHO/NAR]) was used at $I = 1.0$ M (NH_4SCN/NH_4ClO_4), to determine the thermodynamic parameters ($\Delta_r G_m$, $\Delta_r H_m$, $\Delta_r S_m$) corresponding to the complex formation between Am^{3+} and thiocyanate, *cf.* Table V.18. The formation of $AmSCN^{2+}$ and $Am(SCN)_2^+$ was suggested at 15, 30, 37 and 45°C. The presence of $AmSCN^{2+}$ is certainly evidenced in this experimental study, but no conclusions on the formation of the second complex can be obtained. Because the interpretation of the experimental data is dependent on the chemical model chosen, the reported formation constants for $Am(SCN)_2^+$ are not credited by this review. See also the comments in this Appendix for Ref. [71KHO/NAR]. The value of $\log_{10}\beta_1$ interpolated at 25°C is converted to molal units and extrapolated to zero ionic strength using the specific interaction equations, *cf.* Appendix B, with $\Delta\varepsilon = -(0.15 \pm 0.05)\,\mathrm{kg \cdot mol^{-1}}$. This results in $\log_{10}\beta_1^\circ = (1.20 \pm 0.15)$.

The values of β_1 are used to determine the reaction entropy and enthalpy at $I = 1$ M by a weighted linear regression "$\ln\beta_1$ *vs.* $1/T$ (K^{-1})" obtaining: $\Delta_r H_{m,1}$ ($I = 1$ M) $= (2.7 \pm 4.6)$ $\mathrm{kJ \cdot mol^{-1}}$ and $\Delta_r S_{m,1}$ ($I = 1$ M) $= (12 \pm 15)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. These values are in agreement with the results reported by the authors (*cf.* Table V.18).

[74KIN/CHO]
Kinard, W.F., Choppin, G.R., Complexing of trivalent actinide ions by thiocyanate, J. Inorg. Nucl. Chem. **36** (1974) 1131–1134.

The authors performed a solvent extraction study using dinonylnaphthalene sulphonic acid, dissolved in *n*-heptane, as a liquid cation exchanger. The ionic strength was kept constant ($I = 5.0$ M $NaSCN/NaClO_4$) at pH = 3. Only $AmSCN^{2+}$ was formed up to $[SCN^-] = 0.5$ M, while $Am(SCN)_3(aq)$ was evidenced at $1.5 \leq [SCN^-] \leq 2.5$ M. From the $\log_{10}\beta_1$ values, determined at different temperatures (10, 25, 40, 55°C), Kinard and Choppin calculated the entropy and enthalpy changes at 25°C: $\Delta_r H_m = (11.76 \pm 2.05)$ $\mathrm{kJ \cdot mol^{-1}}$ and $\Delta_r S_m = (50.2 \pm 6.6)$ $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. These values are in satisfactory agreement with the values reported by Harmon [72HAR/PET], but differ considerably from those reported earlier by Choppin and Ketels [65CHO/KET].

We used the equilibrium constants reported by Kinard and Choppin [74KIN/CHO] (*cf.* Table V.17) to verify the reported thermodynamic values by performing a weighted linear regression "$\ln\beta_1$ *vs.* $1/T$ (K^{-1}))", obtaining at $I = 5$ M: $\Delta_r H_m = (12.36 \pm$

3.21) $kJ \cdot mol^{-1}$, and $\Delta_r S_m = (51.95 \pm 10.49)$ $J \cdot K^{-1} \cdot mol^{-1}$. These values are in agreement with the results reported by Kinard and Choppin, *cf.* Table V.18. Even though the stability constants are obtained from accurate experimental data [74KIN/CHO], no extrapolation to zero ionic strength will be performed, because of the high electrolyte concentration used ($I = 5$ M).

[74KOR]
Korotkin, Y.S., Hydrolysis of transuranium elements. IV. Sorption homogeneity of microamounts of americium(III), Sov. Radiochem., **16** (1974) 218–222.

Qualitative information is given on the effect of various alkali metal cations on Am(III) hydrolysis between pH = 0 and 6 studied by cation exchange. Hydrolysis was reported to begin at pH = 0.4 both in $HClO_4$ and in aqueous solutions containing K^+ ions. According to Korotkin, small concentrations of Li^+ ions should shift hydrolysis towards pH = 4. This is in contradiction with an earlier statement by the same author [73KOR], claiming that 50% hydrolysis in 0.1 M $LiNO_3$ occurs already at pH = 2.5. Since the reliability of the experimental technique used by Korotkin is questionable, the reported observations are not credited by this review.

[74KOR2]
Korotkin, Y.S., Hydrolysis of transuranium elements: V. Hydrolysis of americium and curium in perchloric acid solutions, Sov. Radiochem., **16** (1974) 223–226.

This is a qualitative study of Am(III) and Cm(III) hydrolysis in the pH range from 1 to 9 using electromigration and reverse-phase chromatography. Hydrolysis was reported to begin at pH = 0.5 to 1. The same conclusion was drawn in Ref. [73KOR] dealing with Am^{3+} and Cm^{3+} hydrolysis in nitric acid solutions. This pH value is considerably different from that obtained by other determinations. As discussed in this Appendix under Refs. [73KOR2] and [74KOR], these experimental methods are not very reliable, and the reported observations are not credited by this review.

[75KOR]
Korotkin, Y.S., Study of the hydrolysis of americium and curium, Sov. Radiochem., **17** (1975) 528–533.

This paper gives results and conclusions very similar to those reported in Ref. [73KOR2].

[75VAS/AND]
Vasil'ev, V.Y., Andreichuk, N.N., Ryabinin, M.A., Rykov, A.G., Spectrophotometric study of complex formation and solvation of actinide ions: XII. Forms of existence of americium(VI) in nitric acid solutions, Sov. Radiochim. **17** (1975) 28–30.

The authors used a spectrophotometric technique to investigate the americium(VI)-nitrate system, in $0 \leq [HNO_3] \leq 18$ M media. They interpreted their experimental results assuming the presence of $AmO_2(NO_3)_2(aq)$ at $6 \leq [HNO_3] \leq 11$ M, and suggested the formation of $AmO_2(NO_3)_3^-$ at higher nitric acid concentrations. Because of the large change in the ionic media ($0 \leq I \leq 18$ M), this review considers that no reliable values of equilibrium constants can be obtained from these measurements.

[76CHO/UNR]
Choppin, G.R., Unrein, P.J., Thermodynamic study of actinide fluoride complexation, in: Transplutonium 1975 (Müller, W., Lindner, R., *eds.*), Amsterdam: North-Holland, 1976, *pp.*97–107.

Potentiometric and solvent extraction techniques were used to investigate the complex formation of various tri- and tetravalent actinides with fluoride ions in 1 M $NaClO_4$ at pH = 2.7. For Am(III), solvent extraction experiments with dinonylnaphthalene sulphonic acid in *n*-heptane were made at 10, 25, 40 and 55°C. Preliminary results from this work have been reported by Choppin [69JON/CHO, 75DEG/CHO].

In the investigated range of ligand concentration, Choppin and Unrein only found the existence of AmF^{2+}, and calculated a value for the stability constant of $\log_{10}\beta_1 = (2.49 \pm 0.02)$ at 25°C. The extrapolation to standard conditions by using the ion interaction coefficients reported in Appendix B gives $\log_{10}\beta_1^\circ = (3.58 \pm 0.21)$ where the uncertainty is increased to represent the 95% confidence level.

The enthalpy change of the reaction in the 1 M perchlorate medium was determined by Choppin and Unrein to be $\Delta_r H_m = (27.6 \pm 2.1)\ \mathrm{kJ \cdot mol^{-1}}$. This review applies the Van't Hoff relation to the equilibrium constants obtained by Choppin and Unrein at different temperatures after correction to infinite dilution. These calculations yield $\Delta_r H_m^\circ = (16.2 \pm 0.5)\ \mathrm{kJ \cdot mol^{-1}}$. However, this review does not feel confident to recommend this value because of the uncertainties affecting the specific ion interaction coefficients in the investigated temperature range.

[76HUB/HUS]
Hubert, S., Hussonnois, M., Brillard, L., Guillaumont, R., Thermodynamic functions for complexing of M^{3+} ions ($M^{3+} = Pu^{3+}_{aq}$ to Fm^{3+}_{aq}), in: Transplutonium 1975 (Müller, W., Lindner, R., *eds.*), Amsterdam: North-Holland, 1976, *pp.*109–118.

The authors reported enthalpy and entropy changes for the first hydrolysis reactions of trivalent transuranium elements from Pu to Fm in 0.1 M $(H,Li)ClO_4$ medium within the temperature range 10 to 50°C. They calculated the values of $\log_{10}{}^*\beta_1$ for Am(III) at each temperature from the difference in distribution coefficient measured between pH = 3.2 and pH = 5.4 using 2-thenoyltrifluoroacetone, *tta*, in benzene. This difference was attributed entirely to the formation of $AmOH^{2+}$ at pH = 5.4. However, as mentioned in the discussion of Ref. [69DES/HUS] in this Appendix, there is no statistical support for the selection of such a model from the data obtained at 25°C. The sign of the reported values for enthalpy and entropy changes is that expected for the formation of inner-sphere complexes. However, the authors' claim that enhancement of hydrolysis occurs with increasing temperature is based only on two data points. Because of the scarce experimental details, it is not possible to make a proper uncertainty estimate. It is thus difficult to obtain from these data unambiguous evidence for the proposed hydrolysis scheme. See also the comments under [73HUS/HUB].

[78RAO/BAG]

Rao, P.R.V., Bagawde, S.V., Ramakrishna, V.V., Patil, S.K., Sulphate complexing of some trivalent actinides, J. Inorg. Nucl. Chem., **40** (1978) 123–127.

The authors studied the americium(III) complexation in sulphate media by the dinonylnaphthalene sulphonic acid extraction method, at $I = 1$ and 2 M $H_2SO_4/HClO_4$, and 25°C. The variation of the distribution coefficient with increasing $[SO_4^{2-}]$ was interpreted by the formation of $Am(SO_4)_n^{(3-2n)}$ ($n = 1, 2$) complexes, *cf.* Table V.12. The authors used 0.066 and 0.084 (at $I = 1$ and 2 M, respectively) as the dissociation constants of HSO_4^-, taken from [51ZEB/ALT, 76FAR/BUC].

This review reinterprets the experimental results of Rao *et al.* to study the influence of the ionic media on the data treatment. In order to calculate the stability constants of the americium complexes, values of $[SO_4^{2-}]$ have to be computed from the reported total sulphuric and perchloric acid concentrations. Using the specific ion interaction equations (*cf.* Appendix B) we compute the equilibrium constant for the reaction $H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$ ($\log_{10} K^\circ = (1.98 \pm 0.05)$, *cf.* Table IV.2) as a function of ionic strength: $\log_{10} K(I) = (1.98 - 4D - \Delta\varepsilon I_m)$, where in $H_2SO_4/HClO_4$ media,

$$\begin{aligned}\Delta\varepsilon I_m &= m_{H^+}(\varepsilon_{(HSO_4^-,H^+)} - \varepsilon_{(SO_4^{2-},H^+)}) \\ &\quad - \varepsilon_{(H^+,ClO_4^-)}\, m_{ClO_4^-} - \varepsilon_{(H^+,HSO_4^-)}\, m_{HSO_4^-}\end{aligned}$$

Assuming that $\varepsilon_{(H^+,SO_4^{2-})} \approx \varepsilon_{(Li^+,SO_4^{2-})} = -(0.03 \pm 0.04)\,\mathrm{kg \cdot mol^{-1}}$, and $\varepsilon_{(H^+,HSO_4^-)} \approx \varepsilon_{(Na^+,HSO_4^-)} = -(0.01 \pm 0.02)\,\mathrm{kg \cdot mol^{-1}}$, we calculate the protonation constant of sulphate for each of the experimental points given by Rao *et al.* [78RAO/BAG, Table 3] (this gives $\log_{10} K_1$ values in the range 1.17 to 1.30 at $I = 1$ M, and between 1.20 to 1.32 at $I = 2$ M). As expected, these values are different from the dissociation constants of HSO_4^- given in Ref. [89SMI/MAR] for $NaClO_4$ media, because the activity coefficients of sulphate and bisulphate ions change when $NaClO_4$ is replaced by mixtures of sulphuric and perchloric acids.

Our calculations lead to: $\log_{10} \beta_1 = (1.97 \pm 0.02)$, $\log_{10} \beta_2 = (2.89 \pm 0.04)$ at $[H^+] \approx 1$ M, and $\log_{10} \beta_1 = (1.97 \pm 0.02)$, $\log_{10} \beta_2 = (2.96 \pm 0.04)$ at $[H^+] \approx 2$ M. However, as the assumption $\varepsilon_{(H^+,HSO_4^-)} \approx \varepsilon_{(Na^+,HSO_4^-)} = -(0.01 \pm 0.02)\,\mathrm{kg \cdot mol^{-1}}$ is quite doubtful, we increase the uncertainties of the calculated equilibrium constants for the americium complexes to ± 0.3 logarithmic units.

[79LEB/FRE]

Lebedev, I.A., Frenkel, V.Y., Kulyako, Y.M., Myasoedov, B.F., Complex formation by americium(VI) in phosphoric acid solutions, Sov. Radiochem., **21** (1979) 699–705.

Spectrophotometry and potentiometry were used to investigate the Am(VI)-phosphate system in $0 \le [H_3PO_4] \le 12$ M media. The ionic strength was not kept constant. The experimental data indicate the presence of the $AmO_2(H_2PO_4)_2(aq)$ complex. The difference in the stability constants determined by the two experimental techniques ($\log_{10} \beta_2(sp) = 3.3$; $\log_{10} \beta_2(pot) = 4.6$) are explained by the author as being due to the formation of "first- or second-sphere" complexes. This review believes that more experimental work is needed to obtain a reliable value for this

stability constant.

[79LEB/FRE2]
Lebedev, I.A., Frenkel, V.Y., Kulyako, Y.M., Myasoedov, B.F., Investigation of complex formation of americium(III) and americium(IV) in phosphoric acid solutions., Sov. Radiochem., **21** (1979) 692–698.

Lebedev *et al.* studied the americium-phosphate system in 0.01 to 13 M H_3PO_4 media using spectrophotometry. The ionic strength was not kept constant. The decrease in absorptivity of the 506 nm peak at $0.1 \leq [H_3PO_4] \leq 5$ M was attributed to the formation of $AmH_2PO_4^{2+}$, while the further decrease at $[H_3PO_4] \geq 5$ M was credited to the presence of $Am(H_2PO_4)_2^+$. This review considers that the decrease of molar extinction data (or scattering) at the high phosphoric acid concentrations may be an ionic strength artifact in quasi "non-aqueous" media ($I \approx (0.35 \pm 0.10)$ M for 4 M $\leq [H_3PO_4] \leq$ 13 M, from calculated $[H_2PO_4^-]$), and not to the formation of the second complex as suggested by the authors. Hence, the formation equilibrium constant for $Am(H_2PO_4)_2^+$ reported by Lebedev *et al.* [79LEB/FRE2] is disregarded.

The authors also measured the oxidation potentials of the couple Am(III)/Am(IV) in 10 to 15 M H_3PO_4 media. The ionic strength was not kept constant, and it is estimated to be $I \approx$ (0.3 to 1.6) M, from calculated $[H_2PO_4^-]$ values. The decrease of $E_{1/2}$ was assigned to the presence of $Am(H_2PO_4)_3^+$. As previously stated, this review does not rely on data obtained at such high concentrations, and therefore, the corresponding stability constant will not be considered.

[80KHO/MAT]
Khopkar, P.K., Mathur, J.N., Complexing of californium(III) and other trivalent actinides by inorganic ligands, J. Inorg. Nucl. Chem., **42** (1980) 109–113.

Khopkar and Mathur studied the americium(III)-sulphate complexes using a solvent extraction technique at 30°C, pH = 3 and $I = 1$ M $(NH_4)_2SO_4/NH_4ClO_4$. The linear variation of K_d^{-1} *vs.* $[SO_4^{2-}]$ indicates the formation of the $AmSO_4^+$ complex. The corresponding stability constant is used in the selection procedure described in Section V.5.1.2.1. Extrapolation to $I = 0$ (*cf.* Appendix B) yields $\log_{10} \beta_1^\circ = (4.04 \pm 0.07)$.

[81LEB/MAZ]
Lebedev, I.A., Mazur, Y.F., Investigation of the complex formation of americium(III), curium(III), and californium(III) with perchlorate ions in aqueous solution, Sov. Radiochem., **23** (1981) 291–299.

The authors measured the distribution coefficients of Am(III), Cm(III) and Cf(III) between di-2-ethylhexyl phosphoric acid in decane and aqueous $(Na,H)ClO_4$ solutions with perchlorate concentrations varied between 0.1 and 8 M at pH = 1. Interpretation of the data below 2 M considered the presence of $Am(ClO_4)^{2+}$ with $\beta_1^\circ = (4 \pm 0.9)$, while the outer-sphere complex $Am(ClO_4)_2^+$ was claimed to be present at higher concentrations. The formation constant for $Am(ClO_4)_2^+$ was measured at 25, 35, 45 and 55°C obtaining, respectively, $\beta_2^\circ = (2.0 \pm 0.1); (2.3 \pm 0.2); (2.6 \pm 0.3)$; and (2.9 ± 0.4). The positive values of $\Delta_r H_m^\circ = (9.8 \pm 1.8)$ kJ · mol^{-1} and $\Delta_r S_m^\circ =$

(38.8 ± 6.7) J $\cdot$ K^{-1} $\cdot$ mol^{-1} derived from these measurements appear to indicate, however, an inner-sphere character of the complex.

The model equation used by Lebedev and Mazur included two different terms accounting for the formation of outer-sphere and inner-sphere complex species. Both the latter reaction and the extraction process were formally written as a displacement of water molecules into the first hydration sphere of actinide ions. Thus, the water activity appeared as a variable raised to a power index, x, representing the hydration number of the trivalent actinides. Although postulated to be always equal to 8 in the concentration range from 2 M to 8 M, possible undetected variations of the hydration number with ionic strength could have influenced the data analysis. The 10-fold lower value of β_2° calculated in the case of Cf(III) resulted from the assignment of a lower hydration number to californium ions.

Moreover, activity corrections on behalf of the mean activity coefficients of $(Na,H)ClO_4$ only, appear to be too crude taking into account the large changes in the ionic strength. In view of the uncertainties of the ionic strength corrections, the reported equilibrium constants are not used in the present review.

[82BID]
Bidoglio, G., Characterisation of Am(III) complexes with bicarbonate and carbonate ions at groundwater concentration levels, Radiochem. Radioanal. Letters, **53** (1982) 45–60.

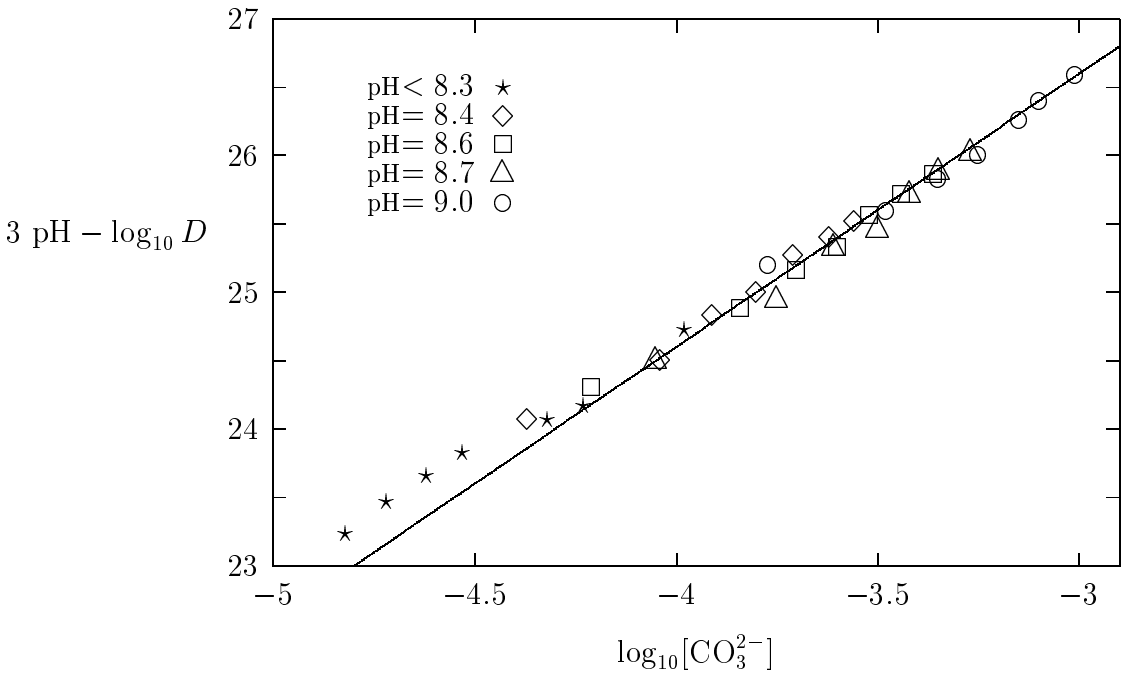
Bidoglio studied the extraction of americium from aqueous carbonate-bicarbonate solutions to an organic phase (a solution of 1,3-diphenyl 1,3-propanedione, *hdbm*, in benzene) at $I = 0.2$ M ($NaClO_4$) and 25°C. The experimental data were interpreted assuming the formation of the complexes $AmHCO_3^{2+}$, $Am(HCO_3)_2^+$, $Am(CO_3)_2^-$ and $Am(CO_3)_2OH^{2-}$. Lundqvist [82LUN] and Nitsche, Stanclife and Silva [89NIT/STA] showed using two different partial pressures of CO_2(g) that the bicarbonate complexes must be much weaker, Bidoglio, and therefore Bidoglio's interpretation of his extraction data seems to be in error. The author did not measure the distribution coefficient in the absence of carbonate ligand, and therefore no reliable stability constants can be determined from the experimental data.

Following the reinterpretation made by Robouch [89ROB], the distribution coefficients are plotted in Figure A.2 as a function of $[CO_3^{2-}]$. The fact that the points at different pH values fall on the same curve indicates the formation of only carbonate complexes in the aqueous solutions, and from the slope of the curve, it can be deduced that if the extracted species is $Am(OH)_3(hdbm)_3$, then the predominant species in the aqueous phase is $Am(CO_3)_2^-$ at $8.3 \leq pH \leq 9$ and $-4.4 \leq \log_{10}[CO_3^{2-}] \leq -3$, which is in agreement with the results of Lundqvist [82LUN], Robouch [89ROB] and Meinrath and Kim [91MEI/KIM].

No experimental evidence for the formation of hydroxy-carbonate complexes is present, and therefore the stability constants initially reported by Bidoglio [82BID] are not credited by this review.

The second hydrolysis constant ($\log_{10}{}^*\beta_2 = -14.7$) was calculated from the pH dependence of the distribution coefficients, D, in the absence of carbonate ligands. These D values could only be obtained by extrapolation from experimental curves at variable carbonate concentrations to $[CO_3^{2-}] = 0$. Because of the predominant

Figure A.2: Distribution coefficients of Am(III), D, combined with pH-values in 0.2 M $NaClO_4$ at 25°C [82BID]. The continuous line is drawn assuming the formation of only $Am(CO_3)_2^-$ in the aqueous phase.



complexation with carbonates, identification of the minor $Am(OH)_2^+$ species appears to be difficult, and therefore this constant is not considered in this review.

[82FUK/KAW]

Fukasawa, T., Kawasuji, I., Mitsugashira, T., Investigation on the complex formation of some lanthanoids(III) and actinoids(III) with chloride and bromide, Bull. Chem. Soc. Japan, **55** (1982) 726–729.

The authors investigated the complexation of various trivalent lanthanides and actinides (Sm, Eu, Gd, Tb, Ac, Am, Cm, Bk and Cf) with chloride and bromide ions by using a solvent extraction technique (bis(2-ethylhexyl)phosphoric acid, *hdehp*, in octane) at 20°C. The ionic strength was kept at 3.0 M using appropriate mixtures of $LiClO_4$, LiCl and LiBr. The experiments were carried out at constant acidity of 0.15 M perchloric acid. Investigation of the extraction mechanism showed that the same species was extracted into the organic phase both in the presence and in the absence in the aqueous phase of chloride and bromide ions. This allowed a simplified treatment of the experimental data for the determination of equilibrium constants. Fukasawa *et al.* reported $\log_{10}\beta_1 = -(0.26 \pm 0.02)$ and $\log_{10}\beta_2 = -(0.66 \pm 0.04)$ for the chloro complexes of americium and $\log_{10}\beta_1 = -(0.52 \pm 0.04)$ and $\log_{10}\beta_2 = -(0.55 \pm 0.03)$ for the bromo complexes of americium.

A reanalysis of the data made by this review confirms the proposed model. Although slightly different values for β_1 and β_2 are obtained, the values reported by

Fukasawa *et al.* are preferred because of the difficult digitalisation of the experimental data from the original paper. Extrapolation to zero ionic strength using the specific ion interaction coefficients of Appendix B and neglecting temperature effects on $\Delta\varepsilon$ values would give $\log_{10}\beta_1^\circ = (0.46 \pm 0.18)$ and $\log_{10}\beta_1^\circ = (0.09 \pm 0.19)$ for the first chloride and bromide complexes of Am^{3+}, respectively. Even considering a very large uncertainty, the $\log_{10}\beta_1^\circ$ value of $AmCl^{2+}$ would be outside the range of values selected by this review [56WAR/WEL, 62PEP/MAS, 64BAN/PAT, 71KHO/NAR]. This may be due to the effect of changes in the anionic composition at constant ionic strength on the values of $\Delta\varepsilon$. For this reasons the values proposed by Fukasawa *et al.* have not been retained for the calculation of recommended equilibrium constants.

[82LUN]
Lundqvist, R., Hydrophilic complexes of the actinides: I. Carbonates of trivalent americium and europium, Acta Chem. Scand., **A36** (1982) 741–750.

Lundqvist investigated Am(III) and Eu(III) complexation with carbonate and hydroxide in 1 M $NaClO_4$ solutions at 25°C by studying the distribution of Am(III) between the aqueous phase and tributyl phosphate.

Hydrolysis studies of ^{241}Am(III) were conducted both at tracer concentration levels and in the presence of non-radioactive Eu carrier (5×10^{-5} to 2×10^{-4} M) in order to reduce americium sorption on glass surfaces. The extraction curves differed in the two cases. Assuming a solubility constant $^*K_{s,0}$ for $Eu(OH)_3$(am) identical to that selected by this review for $Am(OH)_3$(am), precipitation might have occurred for the test solutions above pH = 8 to 8.5. However, this should not have influenced the relative distribution of americium between the organic and the aqueous phases, as long as equilibrium was achieved in the two phases. Lundqvist obtained more reproducible results with the carrier-containing solutions. Nevertheless, the author calculated $\log_{10}{}^*\beta_1 = -(7.5 \pm 0.3)$ from the pH value of 50% decrease of Am extraction in the absence of Eu carrier.

This review tries to re-estimate hydrolysis constants from the two sets of data. The experimental points at tracer concentrations of americium can only be fitted with a single variable model $^*\beta_1$ up to pH = 9.7, a result which is in disagreement with a number of other studies. A satisfactory regression equation of the second set of experimental data was obtained by using a ($^*\beta_1$, $^*\beta_2$) model. In this case, the addition of $^*\beta_2$ meets the 1% but not the 5% significance level of the F-test to enter. It is not possible, however, to select alternative hydrolysis schemes including polynuclear species, as suggested by the relatively high concentration of Eu carrier. The calculated equilibrium constants $\log_{10}{}^*\beta_1 = -7.3$ and $\log_{10}{}^*\beta_2 = -15.0$, are close to those selected by this review when corrected to the common reference state I=0 with $\Delta\varepsilon_1 = (0.04 \pm 0.05)$ and $\Delta\varepsilon_2 = -(0.04 \pm 0.07)\,\mathrm{kg \cdot mol^{-1}}$ (*cf.* Appendix B). This results in $\log_{10}{}^*\beta_1^\circ = -(6.4 \pm 0.4)$ and $\log_{10}{}^*\beta_2^\circ = -(13.8 \pm 0.2)$. The reported uncertainties reflect the difficulties in selecting a model.

The formation constants of $AmCO_3^+$ and $Am(CO_3)_2^-$ were obtained from studies of the solvent extraction of Am(III) as a function of $[CO_3^{2-}]$. It was assumed for the analysis of the distribution data that the americium carbonate complexes did not extract into the organic phase. This was confirmed by electromigration exper-

iments. Although HCO_3^- was the predominant ion of the carbonate system under the experimental conditions (p_{CO_2} = 0.1 and 1.0 atm), there was no evidence for $Am(HCO_3)_n^{(3-n)}$ complexes. The determined stability constants, converted to molal units, are extrapolated to zero ionic strength using the selected ion interaction coefficients (*cf.* Appendix B, Section B.1.4), to give $\log_{10}\beta_1^\circ = (8.00 \pm 0.10)$ and $\log_{10}\beta_2^\circ = (12.57 \pm 0.21)$. These values are used in the selection procedure described in Section V.7.1.2.1.

[82NAI/CHA]

Nair, G.M., Chander K., Joshi, J.K., Hydrolysis constants of plutonium(III) and americium(III), Radiochim. Acta, **30** (1982) 37–40.

The authors used a potentiometric method to measure the hydrolysis constants of Am(III), Pu(III), Sm(III) and Eu(III) in 1 M $NaClO_4$ at 25°C. The americium titration was carried out in the pH range from 4 to 7.2 until the precipitation of the hydroxide was observed. The authors estimated the value of the first hydrolysis constant, $\log_{10}{}^*\beta_1 = -(7.03 \pm 0.04)$, using a weighted least-square treatment of the experimental formation curve ($\bar{n}$ *vs.* pH). The weight of each point was iteratively calculated during the regression procedure rather than externally supplied as the inverse of the variance of individual measurements. This led to an underestimation of the uncertainty assigned to the ${}^*\beta_1$ value. For different $[Am]_{TOT}$ concentrations, the experimental points did not coincide into a single curve below pH = 6.5. Titrated concentrations were so low that scattering in the data may be ascribed to systematic errors in the measurement of small changes of ligand number ($\bar{n}$). A recalculation of the best fitting curve using a model including $Am(OH)_2^+$ as additional species provides a statistically significant decrease of the residual sum of squares. Although the hydrolysis constants derived from these calculations are of the correct order of magnitude, the choice of such a model is questionable, because the highest average ligand number achieved is only 0.6, and the addition of ${}^*\beta_2$ appears to be sensitive to only a few points of the formation curve. However, this does not seem to be a sufficient reason to discard the two-variable model. This review calculates $\log_{10}{}^*\beta_1 = -(7.2 \pm 0.2)$ and $\log_{10}{}^*\beta_2 = -(15.0 \pm 0.3)$. The associated uncertainties reflect the difficulties in selecting a model. Conversion to $I = 0$ using the specific ion interaction coefficients reported in Sections V.3.2.4 and B.1.4 yields $\log_{10}{}^*\beta_1^\circ = -(6.3 \pm 0.2)$ and $\log_{10}{}^*\beta_2^\circ = -(13.8 \pm 0.3)$.

[82RAI/STR]

Rai, D., Strickert, R.G., Solubilities of actinide solids under oxic conditions, Report PNL-SA-10368, Pacific Northwest Laboratory, Richland, Washington, 1982, 18p.

This reference includes the same solubility results for $Am(OH)_3(cr)$ as reference [83RAI/STR] but without giving any details.

[82SIL]
Silva, R.J., Thermodynamic properties of chemical species in nuclear waste. Topical report: The solubilities of crystalline neodymium and americium trihydroxides, LBL-15055, Lawrence Berkeley Laboratory, Berkeley, California, 1982, 57p.

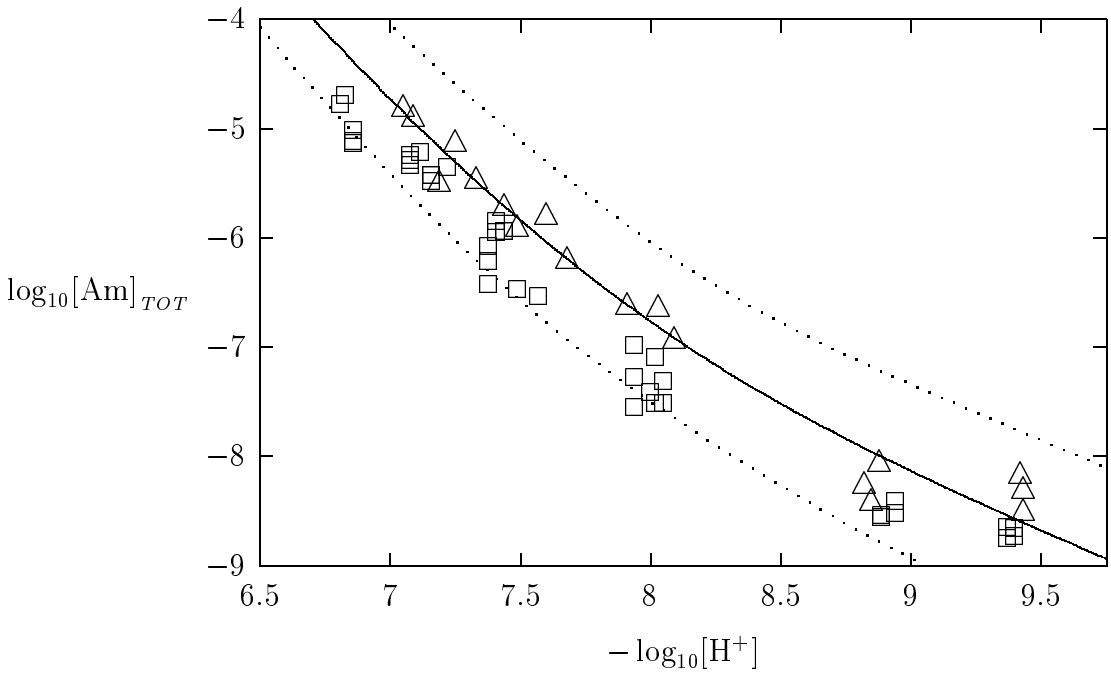
Solubility measurements of $^{243}Am(OH)_3(cr)$ and $Nd(OH)_3(cr)$ were made in 0.1 M $NaClO_4$ solutions at $(25 \pm 1)°C$ within the pH range 6 to 10.

This is the only solubility study with americium hydroxide using an X-ray characterised crystalline solid. The solid phase was prepared by rigorously controlled high-temperature transformation of $Am(OH)_3(am)$. Optical viewing by Scanning Electron Microscopy of $Nd(OH)_3(cr)$ samples at the end of the solubility experiments showed no changes in the crystals. By analogy, this was taken as a proof that no secondary solid phases were formed during the equilibration period of $^{243}Am(OH)_3(cr)$ (contact times of 17, 28 and 48 days). The α-radiation damage of the crystal structure observed by Haire *et al.* [77HAI/LLO] for $^{241}Am(OH)_3(cr)$ can reasonably be considered negligible in Silva's experiments, because of the much lower specific activity of ^{243}Am (6.8 MBq/mg) compared with ^{241}Am (120 MBq/mg).

Different techniques of solid/liquid separation were tested on the samples equilibrated for 48 days. Each measured americium concentration was then given equal weight and considered as an individual data point, instead of using average values. This improperly increased the degrees of freedom from $(18 - p)$ to $(30 - p)$, where the integer refers to the number of observations and p is the number of unknown regression coefficients in the model. Silva used a least-squares procedure keeping $\log_{10}{}^*\beta_1 = -(7.7 \pm 0.3)$ constant and solving simultaneously for ${}^*K_{s,0}$, ${}^*\beta_2$, ${}^*\beta_3$ and ${}^*\beta_4$. The $\log_{10}{}^*\beta_1$ value was taken from a previous work where the first hydrolysis constant of Cm(III) was measured by potentiometry [83EDE/BUC]. There is, however, a typing error in Table 9 of Ref. [82SIL]. The listed value of $\log_{10}{}^*\beta_1$ refers to an ionic strength of 0.1 M KCl. Silva reported thermodynamic constants after ionic strength corrections with the Davies equation. The same equation was used in this review to recalculate equilibrium constants at 0.1 M $NaClO_4$, obtaining $\log_{10}{}^*K_{s,0} = (16.6 \pm 0.4)$, $\log_{10}{}^*\beta_2 = -(16.7 \pm 0.7)$, $\log_{10}{}^*\beta_3 = -(25.0 \pm 0.3)$, and $\log_{10}{}^*\beta_4$ -34.9. Very similar values of hydrolysis constants for Nd(III) were derived from the $Nd(OH)_3(cr)$ solubility measurements.

This review performs a reinterpretation of the americium solubility data of Silva using only 18 experimental points. The lack of measurements in the pH range from 8 to 8.8, and the scarce data points in the plateau region make these data unsuitable for an interpretation using the full model. The results of the least-squares refinements indicate that the two-variable model including ${}^*K_{s,0}$ and ${}^*\beta_2$ yields the greatest initial decrease of the residual mean square (RMS). The stepwise additions of ${}^*\beta_1$ and ${}^*\beta_3$ further decrease the RMS, but the achieved reduction is not sufficient to justify the inclusion of ${}^*\beta_3$ in the regression equation. Figure A.3 shows that Silva's data compare well with those obtained by Stadler and Kim [88STA/KIM] who observed the solubility curve to level down at higher pH values, *cf.* Figure A.9. The statistical F-ratio tests indicate that adding ${}^*\beta_1$ to the model is significant at 5% but not at 1%. Examination of the residuals shows that the model does not perform satisfactorily below pH = 8 if ${}^*\beta_1$ is used, instead, as a fixed parameter. A statistically significant

Figure A.3: Solubility measurements of Am(III) hydroxide in 0.1 M $NaClO_4$ from Silva [82SIL] (△) and from Ref. [88STA/KIM] (□). The continuous curve represents the values calculated with the set of equilibrium constants re-estimated by this review from experimental data in Ref. [82SIL], and the dotted curves show the associated uncertainties.



description of the experimental data is then provided by

$$\begin{aligned}
\log_{10}{}^*K_{\mathrm{s},0} &= 15.9 \pm 0.6 \\
\log_{10}{}^*\beta_1 &= -6.9 \pm 0.6 \\
\log_{10}{}^*\beta_2 &= -15.1 \pm 0.6
\end{aligned}$$

Conversion to the molality scale and extrapolation to $I = 0$ with the selected specific ion interaction coefficients (*cf.* Section B.1.4) gives

$$\begin{aligned}
\log_{10}{}^*K^\circ_{\mathrm{s},0} &= 15.2 \pm 0.6 \\
\log_{10}{}^*\beta^\circ_1 &= -6.5 \pm 0.6 \\
\log_{10}{}^*\beta^\circ_2 &= -14.4 \pm 0.6
\end{aligned}$$

[83BOU/GUI]

Bourges, J.Y., Guillaume, B., Koehly, G., Hobart, D.E., Peterson, J.R., Coexistence of americium in four oxidation states in sodium carbonate - sodium bicarbonate medium, Inorg. Chem., **22** (1983) 1179–1184.

Bourges *et al.* combined spectrophotometry and cyclic voltammetry to study the speciation of americium in carbonate/bicarbonate media at 25°C. These results clearly demonstrate the coexistence of the four oxidation states of americium (III, IV,V,VI) in concentrated carbonate media. The authors measured the apparent normal potential of the Am(VI)/Am(V) and Am(IV)/Am(III) couples in $[HCO_3^-] = 1.15$ M,

$[CO_3^{2-}] = 0.85$ M solutions, obtaining: $E^\circ(\mathrm{VI/V}) = 0.971$ V *vs.* SHE and $E^\circ(\mathrm{IV/III}) = 0.925$ V *vs.* SHE respectively. Bourges *et al.* also investigated the influence of the carbonate concentration on these formal potentials in aqueous solutions containing mixtures of $NaHCO_3$ and Na_2CO_3 ($[HCO_3^-] + [CO_3^{2-}] = 2$ M). The apparent normal potential of the Am(VI)/Am(V) couple was found to be practically independent of $[CO_3^{2-}]$: $E^\circ(\mathrm{VI/V}) = (0.975 \pm 0.01)$ V *vs.* SHE. The value of $E^\circ(\mathrm{IV/III})$, instead decreased monotonically with increasing $[CO_3^{2-}]$. Corrections for the liquid junction potential were apparently not performed by Bourges *et al.*, and estimations with the Henderson's equation [73BAT, *pp.*36–44] show that an additional uncertainty of ± 0.015 V should be added to their measurements.

Several authors [83FER/GRE, 86GRE/ROB, 89ROB] have reinterpreted these experimental measurements, assuming the following equilibria:

$$AmO_2(CO_3)_3^{4-} + e^- \rightleftharpoons AmO_2(CO_3)_3^{5-} \tag{A.4}$$

$$Am(CO_3)_5^{6-} + e^- \rightleftharpoons Am(CO_3)_3^{3-} + 2\,CO_3^{2-}. \tag{A.5}$$

These reinterpretations indicate that $Am(CO_3)_5^{6-}$, $AmO_2(CO_3)_3^{5-}$ and $AmO_2(CO_3)_3^{4-}$ are the limiting complexes for the IV,V and VI oxidation states (as expected by analogy with U(IV); Np(V) and U(VI)-Pu(VI), respectively). Furthermore, the measurements of Bourges *et al.* show that $Am(CO_3)_3^{3-}$ is the Am(III) limiting complex, which is in agreement with the reinterpreted observations of Shiloh, Givon and Marcus (*cf.* the discussion of Ref. [69SHI/GIV] in this Appendix).

Following the reinterpretations in Refs. [83FER/GRE, 89ROB, 86GRE/ROB], this review assumes that the apparent normal potentials measured by Bourges *et al.* [83BOU/GUI], refer to reactions (A.4) and (A.5). From the formal redox potential of the Am(VI)/Am(V) couple it is possible to obtain $\log_{10} K(\mathrm{A.4}, [CO_3^{2-}]_{TOT} = 2\ \mathrm{M}) = (16.48 \pm 0.42)$. The extrapolation of this equilibrium constant from $[NaHCO_3] = 2$ M to standard conditions with the specific ion interaction equations of Appendix B is quite uncertain due to the uncertainty in the values of the ion interaction coefficients for the americium complexes. Nevertheless, assuming that $\Delta\varepsilon$ is similar to that of the same reaction involving uranium complexes in $NaClO_4$ medium but with increased uncertainty, $\Delta\varepsilon = (-0.61 \pm 0.3)\ \mathrm{kg \cdot mol^{-1}}$ [92GRE/FUG, *p.*322], and using $\Delta z^2 = 9$, we obtain $E^\circ(\mathrm{A.4}) = (0.775 \pm 0.038)$ V *vs.* SHE, *i.e.*, $\log_{10} K^\circ(\mathrm{A.4}) = (13.1 \pm 0.6)$.

The formal redox potential of the Am(IV)/Am(III) couple, which decreases with the ratio $[Na_2CO_3]/[NaHCO_3]$, *cf.* [83BOU/GUI, Figure 9], can be interpreted according to reaction (A.5):

$$E^{\circ\prime} = E^\circ(\mathrm{A.5}) + \frac{RT\ln(10)}{F}\log_{10}\left(\frac{\gamma_{Am(CO_3)_5^{6-}}}{\gamma_{Am(CO_3)_3^{3-}}[CO_3^{2-}]^2\gamma^2_{CO_3^{2-}}}\right)$$

where $E^{\circ\prime}$ stands for the formal redox potential of the Am(IV)/Am(III) couple. The specific ion interaction equations in Appendix B are used to calculate the activity coefficients with $\varepsilon_{(Am(CO_3)_5^{6-},Na^+))} \approx \varepsilon_{(U(CO_3)_5^{6-},Na^+))} = -(0.27 \pm 0.15)\ \mathrm{kg \cdot mol^{-1}}$, *cf.* Table B.4, obtaining $E^\circ(\mathrm{A.5}) = (1.19 \pm 0.05)$ V *vs.* SHE, *i.e.*, $\log_{10} K^\circ(\mathrm{A.5}) = (20.1 \pm 0.9)$.

[83CAC/CHO]

Caceci, M.S., Choppin, G.R., The determination of the first hydrolysis constant of Eu(III) and Am(III), Radiochim. Acta, **33** (1983) 101–104.

This is a solvent extraction study of Am(III) and Eu(III) hydrolysis in 0.7 M NaCl at 21°C using a competitive method of complex formation with oxalate ions. Experiments were performed only at pH $\approx$ 6 and pH $\approx$ 8. Stability constants of $Am(C_2O_4)_n^{(3-2n)}$ ($n = 1$ and 2) were first determined at pH = 5.9 where hydrolysis is negligible. The set of data at pH = 8.05 was then modelled assuming the existence of $Am(OH)^{2+}$ only. A calculation of the relative amounts of hydrolysis species shows, however, that the formation of $Am(OH)_2^+$ cannot be neglected in the data analysis. This calculation was made using the value for $\log_{10}{}^*\beta_2^\circ$ selected in the present review and the specific ion interaction equations in Appendix B assuming that $\Delta\varepsilon$ for the hydrolysis reaction would be the same in chloride as in perchlorate media ($\Delta\varepsilon_2 = -0.04\,\mathrm{kg}\cdot\mathrm{mol}^{-1}$). It is not possible from these data to obtain a hydrolysis constant for $Am(OH)_2^+$. This would have required additional experiments at various pH values. The ${}^*\beta_1$ value has to be derived from the best fit parameters of the experimental curve at pH = 8.05. These are obtained as a combination of equilibrium constants for all competitive reactions in the system (second hydrolysis, complex formation with chloride and oxalate). Taking into account the limited number of measurements, the single pH value studied, and the various corrections that have to be made, the reported value for $\log_{10}{}^*\beta_1$ is not accepted by this review.

[83EDE/BUC]

Edelstein, N., Bucher, J., Silva, R., Nitsche, H., Thermodynamic properties of chemical species in nuclear waste, Report ONWI-399, LBL-14325, Lawrence Berkley Laboratory, Berkley, California, 1983, 115p.

A number of techniques were used by the authors to investigate actinide complex formation in neutral and basic solutions.

The only quantitative information of interest to this review refers to the first hydrolysis constants of Cm(III) and Nd(III). These were determined by potentiometric measurements of $[H^+]$ in 0.1 M KCl solutions. Data analysis was limited to the portion of the titration curve before precipitation of metal hydroxides occurred. The formation of polymeric hydrolysis species was examined and discarded during the regression analysis. Although this would have required more systematic pH titrations over a range of metal concentrations, the single variable model proposed by the authors provides a $\log_{10}{}^*\beta_1$ value for Cm and Nd of the correct order of magnitude $-(7.7 \pm 0.3)$.

The authors measured also the solubility in 0.1 M $NaClO_4$ of ${}^{243}Am(OH)_3(s)$ at 25°C. The hydroxide was claimed to be amorphous, but no characterisation of the solid phase was made. It is difficult to make an interpretation of the few experimental data reported [83EDE/BUC, Appendix D]. However, the value proposed for $\log_{10}{}^*K_{s,0} = (17.5\pm0.3)$ at 0.1 M ionic strength is in agreement with that found by Rai *et al.* [83RAI/STR], for the solubility product of well-characterised $Am(OH)_3(am)$.

[83RAI/STR]

Rai, D., Strickert, R.G., Moore, D.A., Ryan, J.L., Am(III) hydrolysis constants and solubility of Am(III) hydroxide, Radiochim. Acta, **33** (1983) 201–206.

The authors measured Am(III) concentrations in the presence of americium(III) hydroxide at (22 ± 2)°C. The experiments were conducted using both ^{241}Am in 1.5×10^{-3} M $CaCl_2$ solutions, and ^{243}Am in pH-adjusted deionized water. Because of radiolysis effects in ^{241}Am solutions, the thermodynamic hydrolysis constants were estimated from the best fitting curve of the ^{243}Am solubility data. The following values were obtained by Rai *et al.*: $\log_{10}{}^{*}K^{\circ}_{s,0} = (17.5 \pm 0.3)$; $\log_{10}{}^{*}\beta^{\circ}_{2} = -(17.1 \pm 0.5)$; $\log_{10}{}^{*}\beta^{\circ}_{3} \leq -27$. The authors proposed an upper limit of $\log_{10}{}^{*}\beta^{\circ}_{1} \leq -8.2$, although no statistical improvement was found by adding $AmOH^{2+}$ in the model.

No background salt was added to keep the activity coefficients constant. However, the study was made at such low ionic strength that uncertainties in the activity coefficient corrections to $I = 0$, iterated during the calculations by means of the Davies equation, should have only affected data at higher americium solubilities.

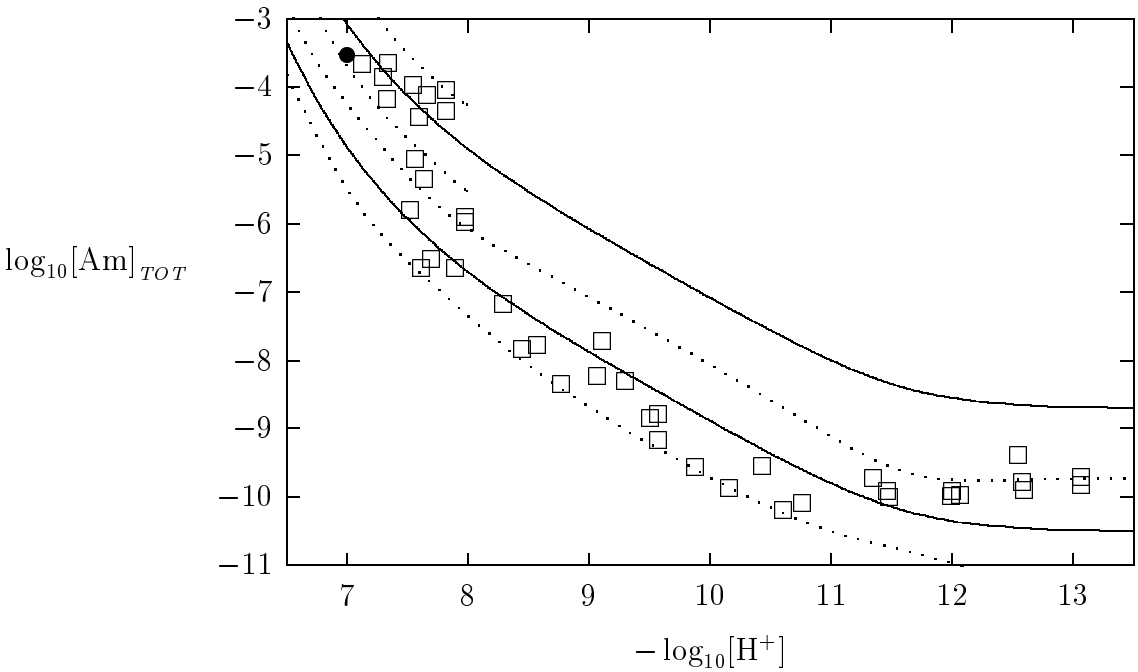
This is one of the few solubility studies of americium trihydroxide reporting the characterisation of the solid phase. X-ray diffraction analysis of the precipitate at pH = 7.5 and 9.6 indicate the presence of $Am(OH)_3$(am), while a mixed phase of a higher degree of crystallinity was detected above pH = 9.6. This fact was not addressed in the calculation of the equilibrium constants. The use of tetrapropyl ammonium hydroxide as basic titrant may have influenced the surface properties of the precipitate. Reanalysis of the experimental data below pH = 9.6 does not provide a statistical support for selecting a particular hydrolysis scheme. The solubility curve recalculated using the hydrolysis constants (*cf.* Table III.2) and the solubility product for the crystalline hydroxide, $\log_{10}{}^{*}K^{\circ}_{s,0} = (15.2 \pm 0.6)$ selected by this review, is in fair agreement (within ± 0.5 $\log_{10}$-units) with the experimental data between pH $\approx$ 7.5 and pH = 13. However, this is in contradiction with the X-ray diffraction measurements showing the presence of a crystalline phase only above pH = 9.6. Keeping the hydrolysis constants fixed to the values selected by this review and adjusting the solubility product to the experimental points below pH = 7.5, a value of $\log_{10}{}^{*}K^{\circ}_{s,0} = (17.0 \pm 0.6)$ has been obtained. This is very close to the value reported by Rai *et al.* Together with our statistical analysis, this might indicate that the points at pH $\leq$ 7.5 have the highest weight in the regression procedure. Figure A.4 shows the solubility data for characterised $Am(OH)_3$(am) obtained by Rai *et al.*, and by Nitsche and Edelstein [85NIT/EDE2] in 0.1 M $NaClO_4$. The Figure also shows calculated solubilities at the ionic strengths used by Rai *et al.*, determined on the basis of the dissolved americium concentrations, the amount of acid or base used to keep solutions electrically neutral, and the hydrolysis constants selected here (*cf.* Table III.2).

[83SIL]

Silva, R.J., The solubilities of crystalline neodymium and americium trihydroxide, in: Materials and Molecular Research Division, Annual Report 1982, LBL-15150, Lawrence Berkeley Laboratory, Berkeley, California, 1983, *pp.*251–253.

This is a summary of Ref. [82SIL].

Figure A.4: Solubility measurements of amorphous Am(III) hydroxide from [83RAI/STR] in pH-adjusted deionized water (□), and from [85NIT/EDE2] in 0.1 M $NaClO_4$ (●). The continuous curves represents the values calculated with the selected set of hydrolysis constants (*cf.* Table III.2) at low ionic strengths. The upper continuous curve corresponds to $\log_{10}{}^{*}K^{\circ}_{s,0} = (17.0 \pm 0.6)$, and the lower one to $\log_{10}{}^{*}K^{\circ}_{s,0} = (15.2 \pm 0.6)$. The dotted curves show the associated uncertainties.



[84BER/KIM]

Bernkopf, M.F., Kim, J.I., Hydrolysereaktionen und Karbonatkomplexierung von dreiwertigem Americium im natürlichen aquatischen System, Report RCM-02884, Inst. für Radiochemie, Technische Universität München, 1984, 200p., in German.

The authors measured the solubility of $^{241}Am(OH)_3(s)$, $^{241}AmO_2(s)$ and $Eu(OH)_3(s)$ in 0.1 M $NaClO_4$ solutions at room temperature (25°C ?). Results are also given on the solubility of $^{241}AmCO_3OH(s)$ and $EuCO_3OH(s)$ in $NaHCO_3$ and Na_2CO_3 solutions.

Similar experiments reported by the same authors in a companion publication [84KIM/BER] resulted in different solubility *vs.* pH curves (*cf.* Figure A.5). Apparently the same solid phases were used in the two studies. The experimental matrix in Table A.1 shows, however, that ageing conditions differed not only from one experiment to the other, but even within a single data set. Several investigators have shown that changes of solid phase in aqueous suspensions of Am(III) hydroxides due to ageing conditions become evident in hours and continue for weeks (*cf.* Section V.3). Figure A.5 indicates a fairly good agreement between solubility measurements of $Am(OH)_3(s)$ using the batch-type procedure. Major disagreement between the solu-

Table A.1: Experimental matrix describing the different procedures used to measure ^{241}Am(III) solubility in 0.1 M $NaClO_4$ by Kim *et al.* [84BER/KIM, 84KIM/BER].

Solid	Procedure	Activity (MBq·ml^{-1})	Contact time	Reference
$Am(OH)_3(s)$	batch, pH < 8	20	(a)	[84BER/KIM]
	titration, pH > 8	5.9	(b)	
$AmO_2(s)$	batch, pH ≤ 8	35	(c)	
	titration, pH > 8	1	(b)	
$Am(OH)_3(s)$	batch	23.7	(d)	[84KIM/BER]
$AmO_2(s)$	batch	63 (pH < 4)	(d)	
		12.6 (pH > 4)	(d)	

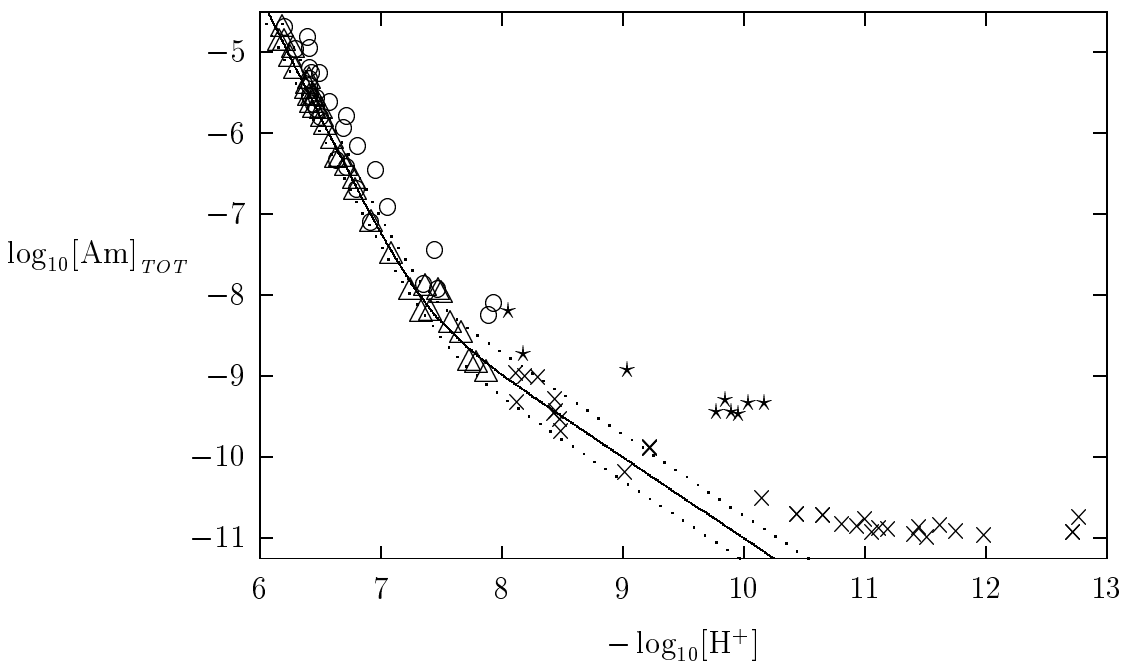
(a) several days
(b) one titration point per day
(c) two months
(d) from one week to several months.

bilities reported in [84BER/KIM] and in [84KIM/BER] exists above pH ≈ 8 where the experimental procedure changed from "batch" to "titration". This indicates that in some of the experiments either equilibrium is not reached or there is a conversion of the solid to a different phase.

This review re-estimates the hydrolysis constants from the solubility data below pH = 8 of the $Am(OH)_3(s)$ experiments in Ref. [84BER/KIM]. The reported values of $\log_{10}[OH^-]$ are corrected for liquid junction effects by experimental measurements using the same setup as Bernkopf and Kim [84BER/KIM]. The relationship between corrected and experimental values for the hydroxide ion concentration becomes: $\log_{10}[OH^-]_{corr.} = (\log_{10}[OH^-]_{exp.} - 0.07)$. Values of $\log_{10}[H^+]$ are calculated from the corrected hydroxide ion concentrations and the ionic product of water in 0.1 M $NaClO_4$, which is recalculated (using the specific ion interaction equations in Appendix B) to $\log_{10} K_w = -13.798$. The least squares adjustment of the hydrolysis constants from the solubility data is fully insensitive to the value of $^*\beta_1$ which cannot be derived from this set of experimental data. This review finds $\log_{10}{}^*K_{s,0} = (13.7 \pm 0.2)$ and $\log_{10}{}^*\beta_2 = -(14.7 \pm 0.2)$.

The recalculated solubility constant $^*K_{s,0}$ differs considerably from those found for well-characterised $Am(OH)_3(am)$ and $Am(OH)_3(cr)$ [83RAI/STR, 82SIL]. No characterisation of the solid was reported by Bernkopf and Kim. Hence, it is not clear if the difference is attributable to particle size effects or to a hydroxide phase of different solubility. For this reason, only $\log_{10}{}^*\beta_2$ is included in the set of selected equilibrium constants. The standard value is calculated with the specific ion interaction equations of Appendix B to be $\log_{10}{}^*\beta_2^\circ = -(14.0 \pm 0.2)$.

Figure A.5: Comparison of solubility data of Am(III) hydroxide in 0.1 M $NaClO_4$ reported by Bernkopf and Kim [84BER/KIM] (△ at pH < 8, and × at pH ≥ 8) and by Kim *et al.* [84KIM/BER] (○ at pH < 8, and ⋆ at pH ≥ 8). The data points in Ref. [84KIM/BER] above pH = 10 are not included because they cannot be distinguished unequivocally from those referring to the dissolution experiment of $AmO_2(s)$. Only the data points at pH < 8 (△ [84BER/KIM] and ○ [84KIM/BER]) have been considered in the least squares re-evaluations. The continuous curve represents the values calculated with the equilibrium constants $\log_{10}{}^{*}K_{s,0}$ and $\log_{10}{}^{*}\beta_2$ re-estimated by this review from data in Ref. [84BER/KIM], and the dotted curves show the associated uncertainties.



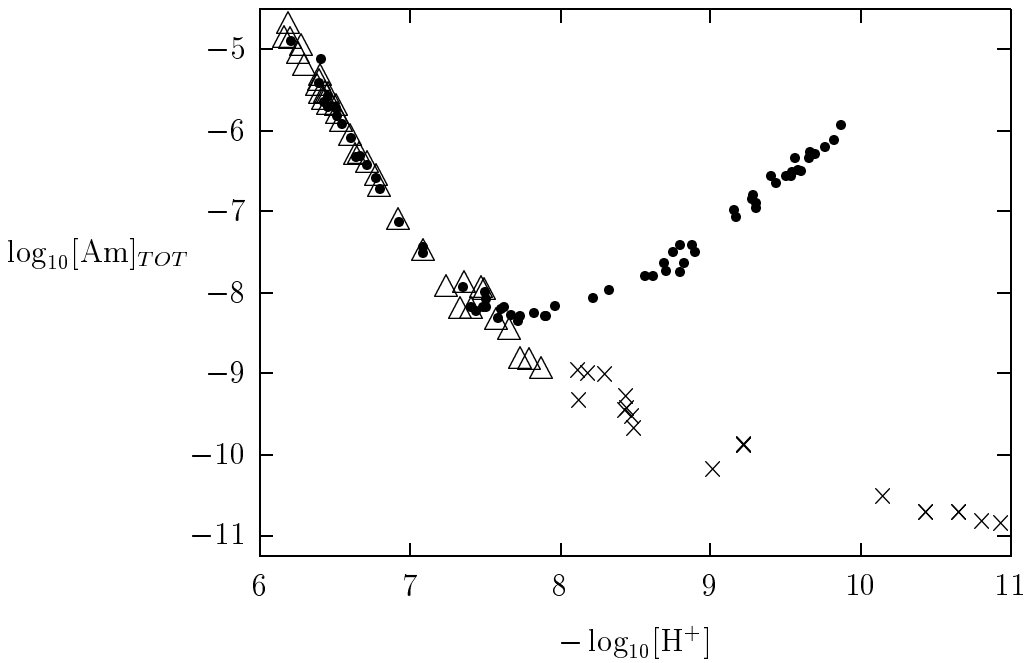
The reaction

$$AmO_2(s) + \frac{3}{2}H_2O(l) \rightleftharpoons Am^{3+} + 3\,OH^- + \frac{1}{4}O_2(g)$$

was proposed to control Am(III) solubility in the presence of $AmO_2(s)$. These solubility data are in complete disagreement with similar measurements reported by Kim *et al.* [84KIM/BER]. This review does not consider the postulated dissolution mechanism of $AmO_2(s)$ as proven. The equilibrium constants obtained from these sets of data are therefore not accepted in the present review.

Bernkopf and Kim also reported a solubility product constant for the mixed hydroxy-carbonate solid $AmCO_3OH(s)$ [84BER/KIM]. The value was obtained from the results of solubility measurements conducted under oversaturated conditions with respect to Am(III) in dilute bicarbonate media (at $I = 0.1$ to 0.3 M $NaClO_4$), starting with a solid $Am(OH)_3(s)$. The carbonate concentration was varied by changing the pH of the solution under constant $CO_2(g)$ partial pressure ($p_{CO_2} = 10^{-3.5}$

Figure A.6: Solubility data of americium(III) reported by Bernkopf and Kim [84BER/KIM] in the absence of CO_2(g) in 0.1 M $NaClO_4$ ($\triangle$ at pH < 8, and $\times$ at pH ≥ 8) and at $p_{CO_2} = 10^{-3.5}$ atm ($\bullet$) in 0.1 to 0.3 M $NaClO_4$.



atm). The solid phase was not characterised but was assumed to be $AmCO_3OH$(s). Bernkopf and Kim interpreted their solubility results assuming the presence of hydroxide ($Am(OH)_i^{(3-i)}$; $i = 1, 2, 3$), carbonate ($Am(CO_3)_n^{(3-2n)}$; $n = 1, 2, 3$) and mixed hydroxy-carbonate ($Am(OH)_i(CO_3)_n^{(3-i-2n)}$; $i = 1, 2$ and $n = 1, 2$) complexes. However, it is not possible to distinguish between $AmCO_3(OH)_2^-$ and $Am(CO_3)_2^-$ from solubility data obtained at a constant p_{CO_2}. The fact that $Am(OH)_3$(s) and $AmCO_3OH$(s) have exactly the same solubility in the pH range 6 to 8 (*cf.* Figure A.6 and Figure 6.23 in [84BER/KIM]), makes it difficult to distinguish between the two solids. It is possible that the transformation of the initial solid, $Am(OH)_3$(s) $\rightarrow$ "$AmCO_3OH$(s)", may have occurred slowly during the experiments. These solubility data, which may be based on a "varying" solid, are questionable; the proposed equilibrium constants are therefore not taken into account in the present review.

[84KIM/BER]

Kim, J.I., Bernkopf, M., Lierse, Ch., Koppold, F., Hydrolysis reactions of Am(III) and Pu(VI) ions in near neutral solutions, in: Geochemical Behaviour of Disposed Radioactive Waste (Barney, G.S., Navratil, J.D., Schulz, W.W., *eds.*), ACS Symp. Ser., No. **246**, Washington, D.C.: American Chemical Society, 1984, *pp.*115–134.

Kim *et al.* measured the solubility of Am(III) and Pu(VI) in 0.1 M $NaClO_4$ solutions as a function of pH, *cf.* Table A.1. Two sets of experiments were performed using different Am(III) solid phases: $^{241}Am(OH)_3{\cdot}xH_2O$(s) and $^{241}AmO_2$(s). The dis-

solution process of $AmO_2(s)$ could not be identified. It was postulated to involve a mechanism turning the solution phase into a more reducing medium with increasing pH. Since no meaningful solubility constant could be obtained, this set of experimental data is not considered in the present analysis. The formation constants of $Am(OH)_n^{(3-n)}$ species and the solubility product of $Am(OH)_3(s)$ reported by Kim *et al.* are $\log_{10}\beta_1 = (7.44 \pm 0.83)$; $\log_{10}\beta_2 = (13.92 \pm 0.63)$; $\log_{10}\beta_3 = (18.47 \pm 0.52)$; $\log_{10} K_{s,0} = -(27.16 \pm 0.47)$. There is probably a typing error in Table I of the original paper because the calculated value of $\log_{10}(K_{s,0} \times \beta_3) = -8.69$ does not correspond to the ordinate value of the plateau region of the solubility curve for the $Am(OH)_3(s)$ experiment ($\log_{10}[Am]_{TOT} = -9.4$, *cf.* Figure A.5). These formation constants are one or two orders of magnitude higher than those reported by Bernkopf and Kim [84BER/KIM] in a companion paper. This discrepancy might well be due to an erroneous procedure used to interpret the solubility measurements. Reanalysis of the data made by this review over the entire pH range indicated only $\log_{10}\beta_3$ as the main source of disagreement.

The equilibrium constants are re-estimated from experimental data in Figure 1 of [84KIM/BER]. The values of $\log_{10}[OH^-]$ are corrected for the liquid junction potential, and $\log_{10}[H^+]$ is derived as described in the discussion of Ref. [84BER/KIM] in this Appendix. The data are displayed in Figure A.5. Only experimental points below pH = 8 were included in the least-squares calculations. The reason for this selection is also given in the discussion of Ref. [84BER/KIM] in this Appendix. No improvement of statistics was obtained by using ${}^*\beta_1$ as additional predictor variable. The computation gives $\log_{10}{}^*K_{s,0} = (13.9 \pm 0.2)$ and $\log_{10}{}^*\beta_2 = -(14.3 \pm 0.3)$. Only the $\log_{10}{}^*\beta_2$ value has been selected by this review because the exact nature of the hydroxide is unclear. Extrapolation to $I = 0$ with the specific ion interaction equations of Appendix B yields $\log_{10}{}^*\beta_2^\circ = -(13.6 \pm 0.3)$.

[84NAS/CLE2]
Nash, K.L., Cleveland, J.M., Thermodynamics of the system: Americium(III)-fluoride. Stability constants, enthalpies, entropies and solubility product, Radiochim. Acta, **37** (1984) 19–24.

The authors investigated the formation of Am(III) fluoride complexes by using a cation exchange technique. The ionic strength of the aqueous phases was buffered at 0.1 M with $NaClO_4$ and the pH was fixed at 3.5. The concentration of free F^- ions in the test solutions was measured directly with ion selective electrodes carefully calibrated.

Nash and Cleveland reported the stepwise equilibrium constants for the formation of AmF^{2+} ($K_1 = 386 \pm 20$) and AmF_2^+ ($K_2 = 147 \pm 24$) at 25°C. Conversion to molality units and correction to $I = 0$ by using $\Delta\varepsilon_1 = -(0.12 \pm 0.1)$ and $\Delta\varepsilon_2 = -(0.36 \pm 0.1)\,\mathrm{kg \cdot mol^{-1}}$ (*cf.* Appendix B, Section B.1.4) result in $\log_{10}\beta_1^\circ = (3.23 \pm 0.05)$ and $\log_{10}\beta_2^\circ = (5.80 \pm 0.15)$, where β_n° refer to the overall formation reaction

$$Am^{3+} + n\,F^- \rightleftharpoons AmF_n^{(3-n)}. \tag{A.6}$$

and the uncertainties assigned by the authors are doubled to represent the 95% confidence level.

The experiments were also performed at 5° and 45°C. From the temperature variation of the equilibrium constants, the authors calculated the enthalpy change accompanying the reactions. No attempts can be made here to correct the reported value of $\Delta_r H_m$ to $I = 0$, because only equilibrium constants at 25°C were given by Nash and Cleveland. Making the approximation that ionic strength effects can be neglected, this would give $\Delta_r H^\circ_m(\text{A.6}, n = 1) = (23 \pm 4)$ kJ · mol^{-1} and $\Delta_r H^\circ_m(\text{A.6}, n = 2) = (24 \pm 10)$ kJ · mol^{-1} (uncertainties represent the 95% confidence level). The value for $n = 1$ is close to that obtained in Ref. [76CHO/UNR]. However, this approximation is not recommended by this review.

The ^{241}Am activity in the aqueous phase was found to decrease systematically with increasing F^- concentrations above 8×10^{-3} M. This was ascribed to the formation of the sparingly soluble AmF_3(s) with a solubility product $K_{s,0} = (5.1 \pm 1.6) \times 10^{-16}$. This equilibrium constant can be extrapolated to $I = 0$ with the specific ion interaction equations of Appendix B, yielding $\log_{10} K^\circ_{s,0} = -(16.5 \pm 0.3)$, a value which is considerably lower than that calculated by using the estimated Gibbs energy of formation of AmF_3(cr) selected by this review. Since freshly precipitated amorphous solids usually exhibit higher solubilities than crystalline forms, the observed loss of ^{241}Am activity from the aqueous phase may possibly refer to the formation of a different solid compound or, as also suggested by Nash and Cleveland, to sorption of colloidal particles on the walls of the reaction vessel.

[84SIL]
Silva, R.J., The behaviour of americium in aqueous carbonate systems, Sci. Basis Nucl. Waste Management **VII** (McVay, G.L., *ed.*), held November 1983 in Boston, New York: North Holland Elsevier, 1984, *pp.*875–881.

This reference summarizes the results from the solubility studies on $Am(OH)_3$(cr) and $AmCO_3OH$(cr) in Refs. [82SIL, 85SIL].

[84SIL/NIT]
Silva, R.J., Nitsche, H., Thermodynamic properties of chemical species of waste radionuclides, in: NRC Nuclear waste geochemistry '83 (Alexander, D.H., Birchard, G.F., *eds.*), Symp. held 30–31 August 1983, in Reston, Virginia, Report NUREG/CP-0052, U.S. Nuclear Regulatory Commission, Washington, D.C., 1984, *pp.*70–93.

This report contains the same experimental data as Ref. [85SIL].

[85MAG/CAR]
Magirius, S., Carnall, W.T., Kim, J.I., Radiolytic oxidation of Am(III) to Am(V) in NaCl solutions, Radiochim. Acta, **38** (1985) 29–32.

$Am(OH)_3$(s) was freshly precipitated by addition of NaOH to a 5 M NaCl solution containing 10^{-3} M Am(III). Radiolysis reactions occurred because of the relatively high dose rate of α-radiation (40 MBq/ml), leaving only Am(V) species in the aqueous phase. The solubility data were interpreted with a model considering AmO_2OH(s) as the solubility limiting solid phase, and AmO_2^+ and AmO_2OH(aq) as the predominating aqueous species. The reported values of the solubility product and the formation constant of AmO_2OH(aq) are respectively, $\log_{10} K_{s,0} = -(9.3 \pm 0.5)$

and $\log_{10} \beta_1 = (1.5 \pm 0.5)$. For the same reasons as discussed under Ref. [88STA/KIM] in this Appendix, these data are not included in the selected data set.

[85NIT/EDE]
Nitsche, H., Edelstein, N.M., Solubilities and speciation of actinides ions in near- neutral solution, Report LBL-18900, Lawrence Berkeley Laboratory, Berkeley, California, 1985, 75p.

This appears to be the same study as Ref. [85NIT/EDE2].

[85NIT/EDE2]
Nitsche, H., Edelstein, N.M., Solubilities and speciation of selected transuranium ions. A comparison of a non-complexing solution with a groundwater from the Nevada tuff site, Radiochim. Acta, **39** (1985) 23–33.

Actinide solubilities (Np^V, Np^{VI}, Pu^{IV}, Pu^V, Pu^{VI}, Am^{III}) in a natural groundwater and in 0.1 M $NaClO_4$ solutions were measured by monitoring with time the actinide precipitation from supersaturated solutions at pH = (7.0 ± 0.1) and at (25 ± 1)°C. No thermodynamic data were reported.

For ^{243}Am(III), equilibrium concentrations in 0.1 M $NaClO_4$ at pH = (7.0 ± 0.1) were found to be in agreement with those measured by Rai *et al.* [83RAI/STR], *cf.* Figure A.4. Accordingly, X-ray diffraction analysis of the precipitate, $Am(OH)_3(s)$, indicated that it mainly contained the amorphous hydroxide. The formation of hydrolysis species was claimed to decrease the molar absorptivity value of Am(III) at 503 nm in 0.1 M $NaClO_4$.

[85SAT/MIT]
Satoh, I., Mitsugashira, T., Hara, M., Kishimoto, M., Suzuki, S., A study of the production of transuranium elements and its application to the solution chemistry in Tohoku University, in: Americium and curium chemistry and technology (Edelstein, N.M., Navratil, J.D., Schulz, W.W., *eds.*), Dordrecht: D.Reidel Publ. Co., 1985, *pp.*261–273.

This is the same study as reported under Ref. [82FUK/KAW].

[85SIL]
Silva, R.J., Preparation, characterisation and solubility constant of $AmOHCO_3$, in: Americium and curium chemistry and technology (Edelstein, N.M., Navratil, J.D., Schulz, W.W. *eds.*), Dordrecht: D. Reidel Publ. Co., 1985, *pp.*225–238.

The solubility of $AmCO_3OH(cr)$ in dilute carbonate solutions was measured by Silva [85SIL]. The solid was identified from the similarity of its X-ray powder diffraction pattern with that reported for $NdCO_3OH(cr)$ type A [74DEX/CAR]. The solubility product was obtained from measurements made under both undersaturated and oversaturated solution conditions (*i.e.*, by dissolution of the characterised solid in a solution initially free of americium and by precipitation of the solid from a solution initially supersaturated with respect to americium). The experiments were performed at constant ionic strength (I = 0.1 M $NaClO_4$), constant pH (pH = (6.12 ± 0.03)) and under controlled CO_2 partial pressure (p_{CO_2} = 0.00792 atm) at (25 ± 1)°C. The stability of the precipitate was monitored *vs.* time (measured solubility: $\log_{10} S$ =

(5.60 ± 0.06)), but the variation of the solubility with pH and/or p_{CO_2} was not investigated. For reaction:

$$AmCO_3OH(s) + 2\,H+ \rightleftharpoons Am^{3+} + HCO_3^- + H_2O(l)$$

Silva obtained $\log_{10} {}^*K_{s,0} = (2.77 \pm 0.15)$ at $I = 0.1$ M, which he extrapolated to (2.53 ± 0.16) at $I = 0$. These values are equivalent to $\log_{10} K_{s,0} = -(20.94 \pm 0.16)$ at $I = 0.1$ M, and $\log_{10} K^\circ_{s,0} = -(21.80 \pm 0.16)$ at $I = 0$ for reaction:

$$AmCO_3OH(s) \rightleftharpoons Am^{3+} + OH^- + CO_3^{2-} \qquad \text{(V.33)}$$

The experimental data reported by Silva were reinterpreted as follows. Values of $[H^+]$ were obtained from the reported pH-values and single ion activity coefficients calculated with Eq.(B.4). Values of p_{CO_2} were converted from atm to bar units (*cf.* Section II.3.2), and were used together with the calculated $[H^+]$-values and the known equilibrium constant of the $CO_2(g)/CO_3^{2-}$ system (Table IV.2 and Appendix B) to determine the free carbonate concentrations: $\log_{10}[CO_3^{2-}] = (-17.53 + \log_{10} p_{CO_2} - 2\ \log_{10}[H^+])$, at $I = 0.1$ M $NaClO_4$. The selected value for the stability constant of $AmCO_3^+$ (*cf.* Table III.2) was extrapolated to 0.1 M $NaClO_4$ with the specific ion interaction equations of Appendix B, $\log_{10} \beta_1 = (6.51 \pm 0.20)$, and used to calculate the free americium concentrations that correspond to the $[Am]_{TOT}$ values measured by Silva [85SIL]. This procedure resulted in $\log_{10} K_{s,0}$(V.33) $= -(20.8 \pm 0.3)$ at $I = 0.1$ M. This solubility product is converted to molal units and extrapolated to zero ionic strength, using the selected interaction coefficients (*cf.* Appendix B, Section B.1.4), to give: $\log_{10} K^\circ_{s,0} = -(22.3 \pm 0.3)$. While the reinterpreted value at 0.1 M $NaClO_4$ agrees with the value obtained by Silva [85SIL], the difference in the values at $I = 0$ is due to the dissimilar methods used for ionic strength extrapolations.

[86EWA/HOW]

Ewart, F.T., Howse, R.M., Thomason, H.P., Williams, S.J., Cross, J.E., The solubility of actinides in the near-field, Sci. Basis Nucl. Waste Management IX (Werme, L.O., *ed.*), Mat. Res. Soc. Symp. Proc., **50** (1986) 701–708.

Ewart *et al.* determined the solubility of plutonium, americium and neptunium in "concrete equilibrated water" (demineralised water equilibrated for some weeks with aged concrete). The analysis of the water gave as main components $[Ca^{2+}] = 0.01$ M, $[Cl^-] = 0.002$ M and $[SO_4^{2-}] = 0.003$ M, with pH = 12 and $[CO_3^{2-}]_{TOT} = 3 \times 10^{-5}$ M. This water was filtered and the pH adjusted with NaOH or HCl before actinide chlorides were added to reach a total concentration of $\approx 10^{-5}$ M. The solutions were mixed, and after an equilibration time (30 minutes in the case of Am [86EWA/HOW]) they were filtered, acidified, and the actinide concentrations measured by liquid scintillation. In another report within the same project, Thomason and Williams [92THO/WIL, Figure 1] show that the Am(III) concentrations measured after 3 hours did not differ from the measurements after 30 mins. of equilibration time. The temperature of the experiments was not reported by Ewart *et al.* [86EWA/HOW]. The actinide solid phases controlling the measured solubilities were not determined experimentally, and therefore these concentrations are not adequate to determine equilibrium constants.

Figures comparing the experimental solubilities and those calculated with the PHREEQE code [80PAR/THO] were presented by Ewart *et al.* in this paper [86EWA/HOW], as well as in later publications [87CRO/EWA, 87EWA/TAS, 92EWA/SMI] where a few more experimental data were included in the graphs. Although the spread in the data is about one logarithmic unit, the americium(III) solubilities measured at pH = 10.5 suggest a discontinuity in the shape of the solubility curve. Figure A.7 displays the experimental data extracted from Figure 6 in [92EWA/SMI]. In the initial publication [86EWA/HOW], Ewart *et al.* described their americium concentrations assuming that the solubility limiting solid phase changed from $AmCO_3OH(s)$ to $Am(OH)_3(s)$ at pH $\approx$ 9.2 and that americium(III) mixed hydroxo-carbonate complexes were present in the aqueous solution, as suggested by Kim *et al.* [84BER/KIM, 86AVO/BIL]. In a later publication, Ewart *et al.* [92EWA/SMI] stated that the americium concentrations could equally well be described with a model containing instead the bicarbonate complexes $AmHCO_3^{2+}$ and $Am(HCO_3)_2^+$ suggested by Bidoglio [82BID] and adopted by Phillips *et al.* [88PHI/HAL].

Figure A.7 compares the americium concentrations reported by Ewart *et al.* [92EWA/SMI, Figure 6] with the calculated solubility curve for $Am(OH)_3(cr)$ using the equilibrium constants selected in this review (*cf.* Table III.2). The calculations illustrated in Figure A.7 show that with a few exceptions, specially at pH = 10.5, the americium(III) levels can be described by the solubility of $Am(OH)_3(cr)$, and that hydrolysis complexes of Am(III) are predominant. The discrepancy around pH = 10.5 might be due to an unknown experimental artifact, or to some process like a change in the solid phase present in the experiments (change in chemical composition or crystallinity), or to a change in the kinetics of the solid-solution processes which regulate the concentration of americium(III). Due to the lack of characterisation of the solid phase and the short equilibration times in these experiments, is not possible to reach any definite conclusion from the data reported by Ewart *et al.*

[86RAO/MAH]

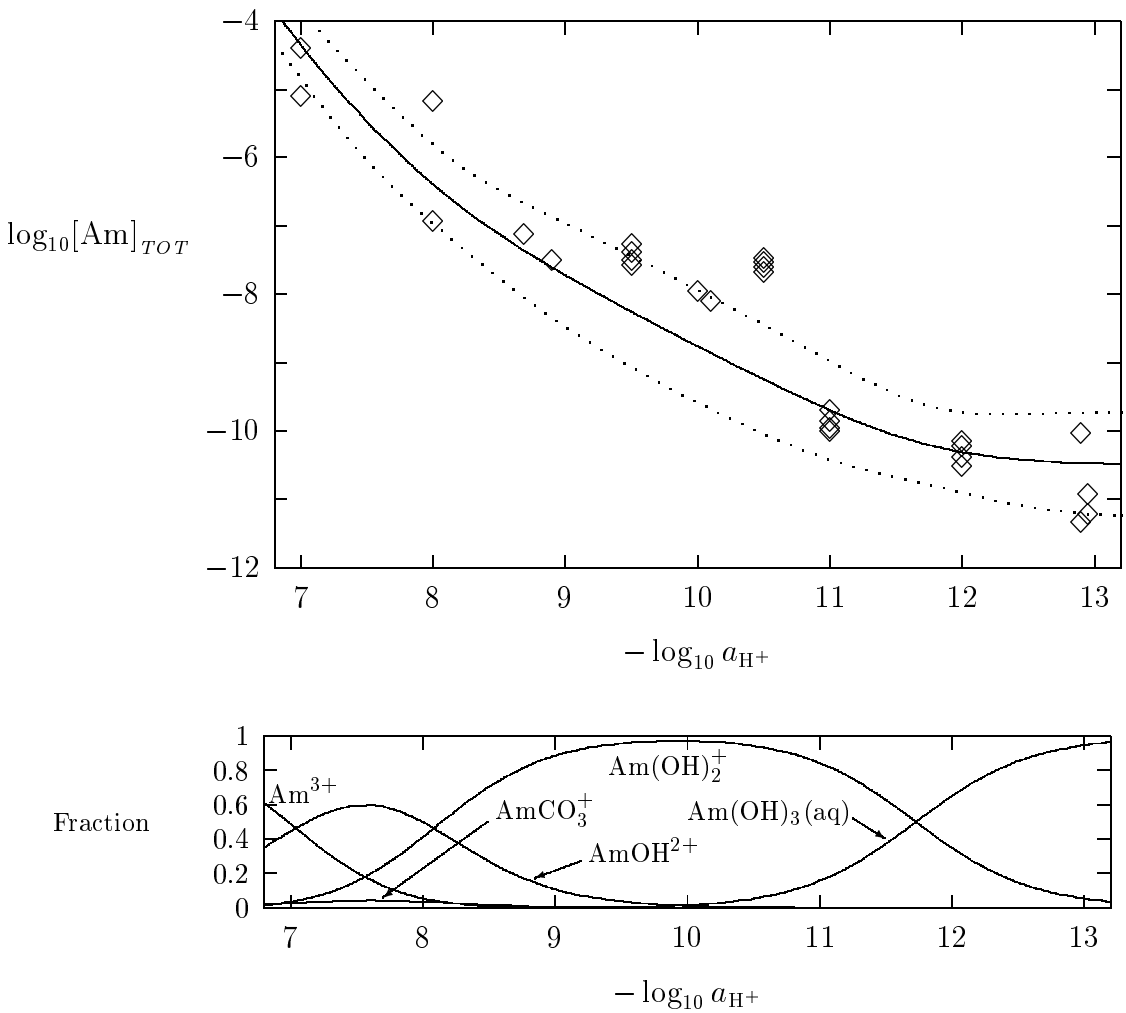
Rao, V.K., Mahajan, G.R., Natarajan, P.R., Phosphate complexation of americium(III), Radiochim. Acta, **40** (1986) 145–149.

The authors studied the complexation of americium(III) by phosphate using a solvent extraction technique (dinonylnaphthalene sulphonic acid in benzene, and an aqueous phase containing 0.5 M $NH_4^+/H_2PO_4^-/ClO_4^-$) at 30°C and pH = 2, 3, 7 and 8. The data was interpreted assuming the formation of $AmH_2PO_4^{2+}$ and $Am(HPO_4)^+$. This review calculates $[H_iPO_4^{(i-3)}]$ from the tabulated $[H_3PO_4]_{TOT}$, using the selected dissociation constants of phosphoric acid extrapolated to 0.5 M NH_4ClO_4 with the specific ion interaction equations of Appendix B ($\log_{10} K_i = -11.28$; -6.53 and -1.81, at 30°C and $I = 0.5$ M). The distribution coefficient data at pH = 2 and 3 show that $H_2PO_4^-$ is the complexing ligand, and reanalysis of these data according to reaction

$$Am^{+3} + H_2PO_4^- \rightleftharpoons AmH_2PO_4^{2+} \qquad (A.7)$$

gives $\log_{10} \beta_1(A.7) = (1.97 \pm 0.43)$ which is in agreement with the results of Rao *et*

Figure A.7: Americium concentrations determined by Ewart *et al.* [86EWA/HOW, 92EWA/SMI] in "concrete equilibrated water". The continuous curve shows the solubility of $Am(OH)_3(cr)$ calculated with the equilibrium constants selected by this review (*cf.* Table III.2), and the dotted curves display the associated uncertainty. The lower diagram shows the calculated acidity ranges of predominance for each Am(III) species under the same conditions as the upper plot.



al. (*cf.* Table V.15). This value, extrapolated to $I = 0$, is selected in this review as described in Section V.6.2.1.1.

The experimental data obtained at pH = 7 and 8 might be inaccurate because the activity of the aqueous phase was obtained from the difference of activities in the organic phase before and after equilibration. Since Am^{3+} is known to be absorbed on glass walls at neutral pH values [83CAC/CHO], the americium activity in the aqueous phase obtained in this way may be incorrect, resulting in erroneous distribution coefficients. The available experimental data indicate the presence of a new complex ($AmHPO_4^+$ or $AmPO_4$(aq)) but are insufficient to determine either its stoichiometry or its stability constant. Thus, the value of $\log_{10}\beta_1(AmHPO_4^+)$ reported by Rao, Mahajan and Natarajan (*cf.* Table V.15) is disregarded by this review.

[87CRO/EWA]
Cross, J.E., Ewart, F.T., Tweed, C.J., Thermochemical modelling with application to nuclear waste processing and disposal, Report AERE-R12324, UK Atomic Energy Authority, Harwell, UK, 1987, 45p.

See comments under [86EWA/HOW].

[87PER/LEB]
Perevalov, S.A., Lebedev, I.A., Myasoedov, B.F., Complex formation of Am(III) and Am(IV) with phosphate ions in acetonitrile solutions, Sov. Radiochem., **29** (1987) 572–577.

Perevalov *et al.* [87PER/LEB] investigated the complex formation of Am(III) in acetonitrile solutions containing 0.05 to 2.0 M H_3PO_4 using a spectrophotometric technique. The spectral shift and the broadening of the 503 nm peak was interpreted by the formation of $AmH_2PO_4^{2+}$ and $Am(H_2PO_4)_2^+$ in the organic solvent. The corresponding stability constants are: $\log_{10}\beta_1 = 12.0$ and $\log_{10}\beta_2 = 24.6$. The stability constants are many orders of magnitude larger than the ones obtained in aqueous solutions.

The authors investigated also the complex formation of Am(IV) in the same non-aqueous media. The decrease of the formal potential for the couple Am(IV)/Am(III) with increasing H_3PO_4 concentration was interpreted by the presence of the complex $Am(IV)(H_2PO_4)_3^+$, for which the stability constant was calculated to be:

$$Am^{4+} + 3\,H_2PO_4^- \rightleftharpoons Am(H_2PO_4)_3^+ \qquad \log_{10}\beta_3 = 46.4 \pm 0.2$$

These results obtained in acetonitrile solutions have an informative value, but will not be included in this review.

[87RAO/MAH]
Rao, V.K., Mahajan, G.R., Natarajan, P.R., Hydrolysis and carboxylate complexation of trivalent americium, Inorg. Chim. Acta, **128** (1987) 131–134.

The authors investigated the complexation of Am(III) with acetate and tartrate ions in 0.5 M $NaClO_4$ solutions at pH = 4 and pH = 8. Solvent extraction with dinonylnaphthalene sulphonic acid in benzene was used as the experimental technique.

The tartrate (L^{2-}) ions were considered to be the only complexing agents in the system, even though almost equal concentrations of HL^- and L^{2-} are present at pH = 4, as calculated with the values of the dissociation constants of tartaric acid, H_2L, used by the authors. Moreover, a disagreement exists between free ligand concentrations estimated from total tartrate concentrations, and those used in the regression analysis of the experimental data (see Table 1 and Figure 2 of the original paper).

The value of the first hydrolysis constant, $\log_{10}{}^*\beta_1 = -(6.80 \pm 0.30)$ was derived from the data for the tartrate system at pH = 8. However, by using the values of the complexation constants reported by Rao, Mahajan and Natarajan, the Am(III) speciation is calculated to be largely dominated by AmL^{2+} and AmL_2^- at pH = 8 and at the relatively high concentrations of tartrate ions used throughout the experiments (from 5×10^{-3} M to 8×10^{-2} M). Therefore, the derived value of ${}^*\beta_1$ may only be an artifact of the curve fitting procedure.

[88KIM/BUC]

Kim, J.I., Buckau, G., Büppelmann, K., Klenze, R., Lierse, Ch., Stadler, S. Chemisches verhalten von Np, Pu und Am unter natürlichen aquatischen bedingungen. Hydrolyse, carbonat-komplexierung, a-radiolyse, kolloidbildung, huminstoff-charakterisierung und speziation, Report RCM-00988, Inst. für Radiochemie, Techn. Univers. München, 1988, 134p., in German.

The information in this report on the hydrolysis of americium is also given in Refs. [88STA/KIM, 88STA/KIM2], see the comments in this Appendix on the corresponding references. The results of Bernkopf and Kim on the carbonate complexation of Am(III) are also summarised in this report, *cf.* the discussion of [84BER/KIM] in this Appendix.

[88RAO/MAH]

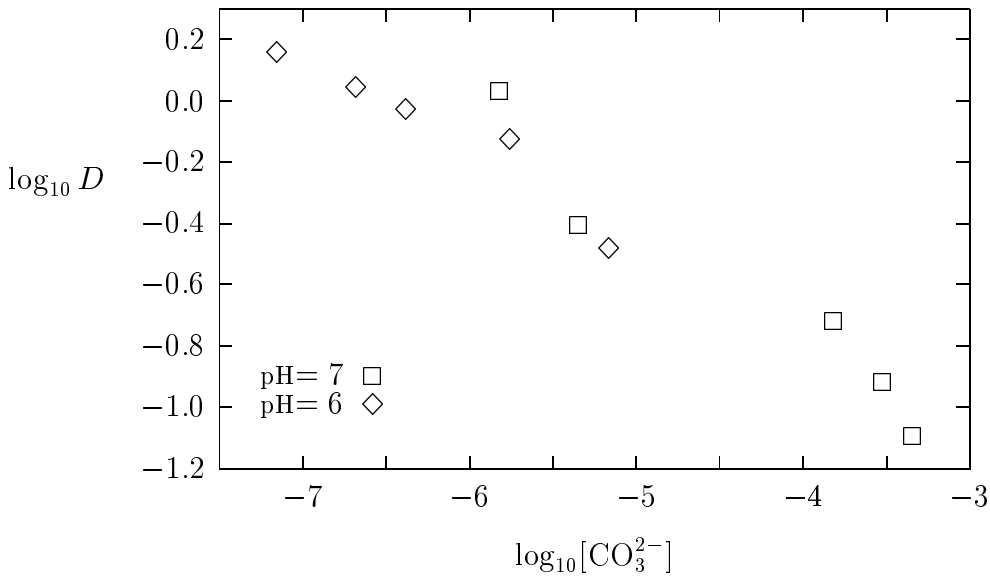
Rao, V.K., Mahajan, G.R., Natarajan, P.R., The thermodynamics of complexation of trivalent americium by phosphate and carbonate in neutral aqueous solutions, Lanthanide and Actinide Research, **2** (1988) 347–361.

Rao, Mahajan and Natarajan carried out solvent extraction experiments as a function of temperature to investigate the Am(III) carbonate system at $I = 0.5$ M $NaClO_4$, pH = 6 and 7. The results presented in Figures 3 and 4 of Ref. [88RAO/MAH] were interpreted by Rao, Mahajan and Natarajan assuming the formation of the $AmHCO_3^{2+}$ complex. This review uses the experimental data at 25°C, which consists of the total carbonate concentrations, pH and distribution coefficients [88RAO/MAH, Table 3], to check the chemical model. The following values were used for the first and second acidity constants in the carbonate system,

$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \qquad \log_{10} K_1(I = 0.5\ \text{M}) = 6.074 \pm 0.027$$
$$CO_3^{2-} + 2\,H^+ \rightleftharpoons CO_2(aq) + H_2O(l) \qquad \log_{10} K_2(I = 0.5\ \text{M}) = 15.731 \pm 0.035$$

Figure A.8 shows that the distribution coefficients measured at different pH values fall on the same curve ($\log_{10} D$ *versus* $\log_{10}[CO_3^{2-}]$) in contradiction with the calculations and with the conclusions of Rao, Mahajan and Natarajan [88RAO/MAH, Figure 3].

Figure A.8: Distribution coefficients of Am(III), D, measured by Rao, Mahajan and Natarajan [88RAO/MAH] in aqueous solutions containing carbonate at $I = 0.5$ M $NaClO_4$, pH = 6 and 7, and at 25°C.



The points in Figure A.8 indicate the formation of americium carbonate complexes (rather than bicarbonate). As no solvent extraction was measured in the absence of ligand in order to ascertain the extraction mechanism, it is not possible to determine the stoichiometry of the predominant americium complex in the aqueous phase, or its stability constant. This review rejects the chemical model proposed by Rao, Mahajan and Natarajan and considers that the bicarbonate complex, $AmHCO_3^{2+}$, is not evidenced by this experimental work.

Rao, Mahajan and Natarajan also studied the temperature dependence of Am(III) complexation by phosphate ions using a solvent extraction technique at $I = 0.5$ M $NH_4^+/H_2PO_4^-/ClO_4^-$, pH = 2 and 7, and at temperatures of 10, 20 and 41°C. The experimental results were interpreted assuming the formation of $AmH_2PO_4^{2+}$ and $AmHPO_4^+$. These species were previously suggested by Rao, Mahajan and Natarajan in a previous study [86RAO/MAH]. The reported equilibrium constants are reproduced in Table V.15. The authors calculated enthalpy changes from the variation of the equilibrium constants with temperature, and reported $\Delta_r H_m = 2.37$ and $1.34\ \mathrm{kJ \cdot mol^{-1}}$ for the formation of $AmH_2PO_4^{2+}$ and $AmHPO_4^+$ respectively. However, from the values of $\log_{10} \beta_1$ given in Table 2 of [88RAO/MAH], the values $\Delta_r H_m = (40 \pm 18)$ and $(24 \pm 4)\ \mathrm{kJ \cdot mol^{-1}}$ are instead obtained for $AmH_2PO_4^{2+}$ and $AmHPO_4^+$ respectively. There is no apparent reason for such a large discrepancy.

The experimental data obtained at pH = 7 are not considered sufficient for the determination of either the stoichiometry or the stability constant of the predominant americium species at neutral pH (*cf.* discussion of Ref. [86RAO/MAH] in this Appendix), and therefore, the corresponding $\log_{10} \beta_1(AmHPO_4^+)$ values (at 10 and 20°C, Table V.15) are not accepted by this review. This review calculates

$[H_2PO_4^-]$, from the tabulated $[H_3PO_4]_{TOT}$ at pH =2 using the selected dissociation constant of phosphoric acid extrapolated to $I = 0.5$ M NH_4ClO_4 with the specific ion interaction equations in Appendix B ($\log_{10} K_3 = -1.71$; -1.76 and -1.86, at 10, 20 and 41°C, respectively). The variation of the distribution coefficient *vs.* $[H_2PO_4^-]$ indicates the formation of $AmH_2PO_4^{2+}$ (pH = 2 and 3). Reanalysis of these data gives $\log_{10} \beta_1(A.7) = (1.74 \pm 0.30)$, (1.80 ± 0.16), and (1.97 ± 0.28) at 10, 20 and 41°C, respectively. These equilibrium constants and that obtained from the reevaluation of Ref. [86RAO/MAH] may be used to determine the enthalpy and entropy changes from a weighted linear regression "$\ln \beta_1(A.7)$ *vs.* $1/T$ (K^{-1})", yielding $\Delta_r H_{m,1} = (14 \pm 6)$ kJ · mol^{-1} and $\Delta_r S_{m,1} = (82 \pm 19)$ J · K^{-1} · mol^{-1} at 25° and $I = 0.5$ M. Extrapolation of the equilibrium constants to $I = 0$ with the aim of obtaining the reaction enthalpy in standard conditions is not attempted because it would require the extra assumption that $\Delta\varepsilon$ is constant with temperature, introducing an error of unknown magnitude. Furthermore, the small variation of $\log_{10} \beta_1$ with temperature is similar in value to the uncertainty in the individual values of the equilibrium constants.

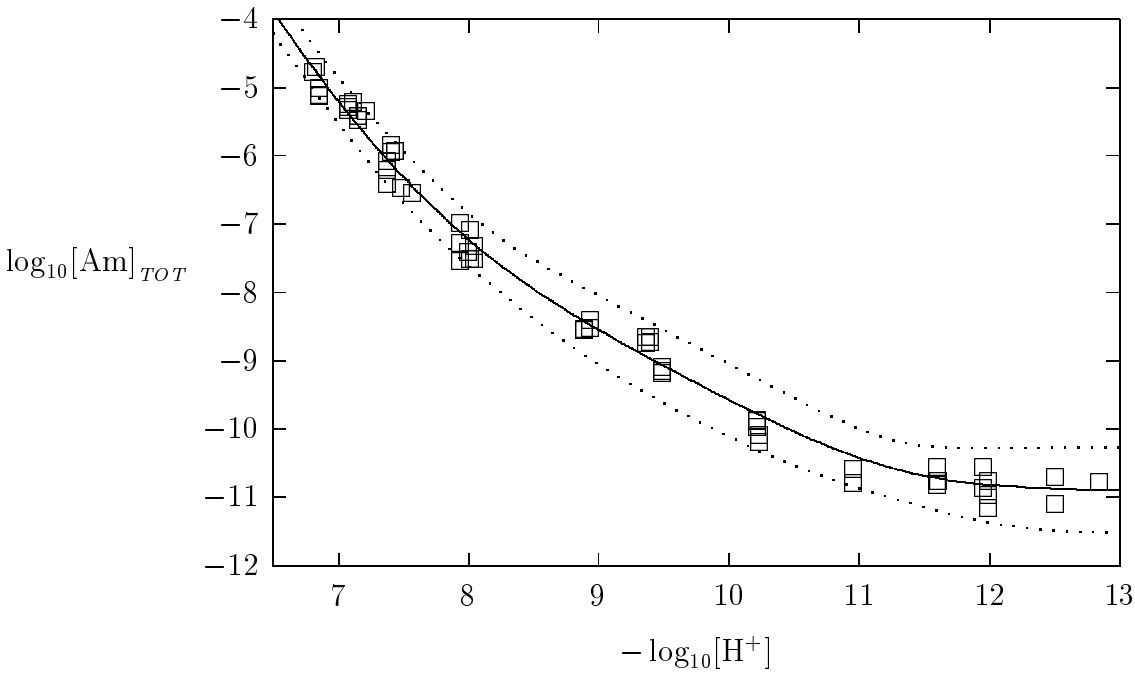
[88STA/KIM]
Stadler, S., Kim, J.I., Chemisches Verhalten von Americium in natürlichen wässrigen Lösungen: Hydrolyse, Radiolyse und Redox-Reaktionen, Report RCM-01188, Institute für Radiochemie der Technischen Universität, München, 1988, 141p., in German.

The authors investigated the pH dependence of $Am(OH)_3(s)$ solubility in the following solutions at (25±0.5)°C: 0.1 M $NaClO_4$ (*cf.* Figures A.9 and A.3), 0.1 M NaCl, 0.6 M NaCl, 3 M NaCl and 5 M $NaClO_4$. The effect of α-induced radiolysis on solubility was studied using different total concentrations of ^{241}Am. This is a reasonably careful work, but no attempts were made to characterise the solid phase. Precipitation of trivalent lanthanides with OH^- from solutions containing Cl^-, SO_4^{2-}, NO_3^- was found to form basic salts of composition depending both on the bulk anion concentration and on the age of the system [61AKS/ERM, 70MIR/POL]. It is possible that formation of mixed-anion precipitates might occur also in the $Am/H_2O/NaCl$ system studied by Stadler and Kim.

The reported solubility products are concordant with the value measured by Silva [82SIL] for $^{243}Am(OH)_3(cr)$. It is unclear, however, if the same phase controls the americium solubility in the two cases, because of the markedly different conditions of preparation of the starting solids. Parallel shift of solubility curves occurred by increasing total americium activity, with no further change above 44 MBq/ml. As suggested by the authors, the higher values determined for the solubility product probably results from an increase of available surface area of the solid phase due to radiation damage.

This review recalculates hydrolysis constants from the experimental data (plotted in Figures A.9 and A.3) in 0.1 M $NaClO_4$ with low radiation effect (≤ 3.7 MBq/ml). The experimental pH-values reported in [88STA/KIM, Table 7.3] are converted to $\log_{10}[H^+]$ values by introducing a correction factor accounting for the liquid junction potential (measured by this review using the same experimental setup as Stadler and Kim) and the value of the activity coefficient of H^+ recalculated for internal

Figure A.9: Solubility measurements of Am(III) hydroxide in 0.1 M $NaClO_4$ and 25°C from Stadler and Kim [88STA/KIM]. The continuous curve represents the solubility values calculated with the set of equilibrium constants re-estimated by this review from experimental data in Ref. [88STA/KIM] and the dotted curves show the associated uncertainties.



consistency with the equations given in Appendix B. The correction found by this review is: $-\log_{10}[\mathrm{H}^+] = (\mathrm{pH}_{exp.} - 0.0522)$. The least-squares Marquardt computation gives

$$\begin{aligned}
\log_{10}{}^{*}K_{\mathrm{s},0} &= 15.5 \pm 0.4 \\
\log_{10}{}^{*}\beta_1 &= -7.0 \pm 0.4 \\
\log_{10}{}^{*}\beta_2 &= -15.1 \pm 0.4 \\
\log_{10}{}^{*}\beta_3 &= -26.4 \pm 0.5
\end{aligned}$$

This review increases the estimated uncertainties because of the scarce information available on the composition of the solid phase. The thermodynamic constants are calculated using the $\Delta\varepsilon_n$ values reported in Section V.3.2.4 obtaining $\log_{10}{}^{*}\beta_1^\circ = -(6.6 \pm 0.4)$, $\log_{10}{}^{*}\beta_2^\circ = -(14.4 \pm 0.4)$, $\log_{10}{}^{*}\beta_3^\circ = -(25.7 \pm 0.5)$.

The solubility measurements in 5 M $NaClO_4$ are too few to derive reliable information on equilibrium constants.

Solubility experiments of $Am(OH)_3(s)$ in 3 M NaCl at 74 Bq/ml resulted in much higher americium concentrations, because of radiolytic oxidation of Am(III) to Am(V). Stadler and Kim fitted these experimental data with a model assuming AmO_2^+ and $AmO_2OH(aq)$ as main soluble species, and $AmO_2OH(s)$ as solubility-controlling solid

phase. Although no characterisation was made of the $Am(OH)_3(s)$ solid/liquid interface where Am(III) oxidation to Am(V) should occur, spectrophotometric evidence of Am(V) species in solution was reported. According to the calculated formation constant, $\log_{10} \beta_1 = (1.7 \pm 0.6)$, only 2% of $AmO_2OH(aq)$ should be present in solution at pH = 13, the highest pH value investigated. This review considers the experimental procedure not precise enough to obtain a reliable value of the hydrolysis constant for $AmO_2OH(aq)$. The order of magnitude of the solubility product of $AmO_2OH(s)$ is in agreement with other studies on different pentavalent actinides. The authors reported the value of $\log_{10} K_{s,0} = -(9.3 \pm 0.5)$ for the reaction

$$AmO_2OH(s) \rightleftharpoons AmO_2^+ + OH^-. \tag{A.8}$$

Stadler and Kim mentioned an ionic strength effect on pH measurements. It is not clear, however, if these were corrected for the liquid junction potential. If this is not the case, a displacement of the Am(V) solubility curve along the X-axis of about +0.7 pH units (as experimentally measured by this review) would occur at 3 M NaCl. Least-squares fit of the corrected data with a model neglecting $AmO_2OH(aq)$ would then give $\log_{10} K_{s,0}(A.8) = -(9.8 \pm 0.5)$, *i.e.*, $\log_{10}{}^*K_{s,0} = (4.2 \pm 0.5)$. Because of the high concentration of Cl^- ions, formation of mixed precipitates and soluble americium chloro complexes may not be disregarded. However, no characterisation of the solid phase was reported, and therefore this solubility constant for $AmO_2OH(s)$ is not recommended by this review.

[88STA/KIM2]
Stadler, S., Kim, J.I., Hydrolysis reactions of Am(III) and Am(V), Radiochim. Acta, **44/45** (1988) 39–44.

This appears to be the same study reported as Ref. [88STA/KIM] where more experimental details are given.

[89NIT/STA]
Nitsche, H., Standifer, E.M., Silva, R.J., Americium(III) carbonate complexation in aqueous perchlorate solution, Radiochim. Acta, **46** (1989) 185–189.

The authors determined the formation constant of $AmCO_3^+$ in 0.1 M $NaClO_4$ solutions by absorption spectrophotometry [89NIT/STA]. The shift in the absorption band at 502.8 nm (to longer wavelength with increasing $[CO_3^{2-}]$) was analysed by a non-linear least-squares method to estimate the first stability constant (β_1). By conducting the measurements at two different $CO_2(g)$ partial pressures (0.1 and 1.0 atm), it was possible to differentiate between carbonate and bicarbonate complexation. No evidence was found for the existence of americium bicarbonate complexes. The authors applied the specific ion interaction equations (*cf.* Appendix B) on the available literature data [82LUN, 84BER/KIM, 89ROB, 89NIT/STA] and extrapolated the value of the equilibrium constant to zero ionic strength. The results $\log_{10} \beta_1^\circ = (8.16 \pm 0.10)$ and $\Delta\varepsilon = -(0.11 \pm 0.07)\,kg \cdot mol^{-1}$ are in agreement with selected values in the present review.

[89PAZ/KOC]

Pazukhin, E.M., Kochergin, S.M. Stability constants of hydrolysed forms of americium(III) and solubility product of its hydroxide, Sov. Radiochem., **31** (1989) 430–436.

Pazukhim and Kochergin reported americium solubilities as a function of $[H^+]$ in 3 M $NaClO_4$ at (25 ± 0.5)°C. Most of the measurements were performed with ^{241}Am, but some experiments were duplicated with ^{243}Am. Contamination by atmospheric $CO_2(g)$ was prevented. The authors reported values for the formation constants of americium hydroxo species using a value for the ionic product of water $\log_{10} K_w = -14.0$. On this basis we calculate the following values for the solubility and hydrolysis constants at $I = 3$ M: $\log_{10}{}^*\beta_1 = -(6.40 \pm 0.11)$, $\log_{10}{}^*\beta_2 = -(13.40 \pm 0.16)$, $\log_{10}{}^*\beta_3 = -(20.30 \pm 0.17)$ and $\log_{10}{}^*K_{s,0} = (14.60 \pm 0.11)$. Extrapolation to $I = 0$ using the specific ion interaction equations of Appendix B gives: $\log_{10}{}^*\beta_1^\circ = -(5.1 \pm 0.2)$, $\log_{10}{}^*\beta_2^\circ = -(12.1 \pm 0.2)$, $\log_{10}{}^*\beta_3^\circ = -(19.2 \pm 0.2)$ and $\log_{10}{}^*K_{s,0}^\circ = (13.1 \pm 0.2)$.

The most striking difference between the solubility curves reported by other authors [83RAI/STR, 82SIL, 84BER/KIM, 84KIM/BER, 88STA/KIM] and the experimental results of [89PAZ/KOC] is the much higher solubility values reported in this work. This results in a very high value for $\log_{10}({}^*K_{s,0} \times {}^*\beta_3)$, suggesting the presence of a highly soluble $Am(OH)_3(s)$. However, this is in contradiction with the value of $\log_{10}{}^*K_{s,0}$ obtained in the regression analysis which points to a solid of high crystallinity. Indeed, the $\log_{10}{}^*K_{s,0}$ is two orders of magnitude lower than that reported by other authors who carefully characterised the solid phase.

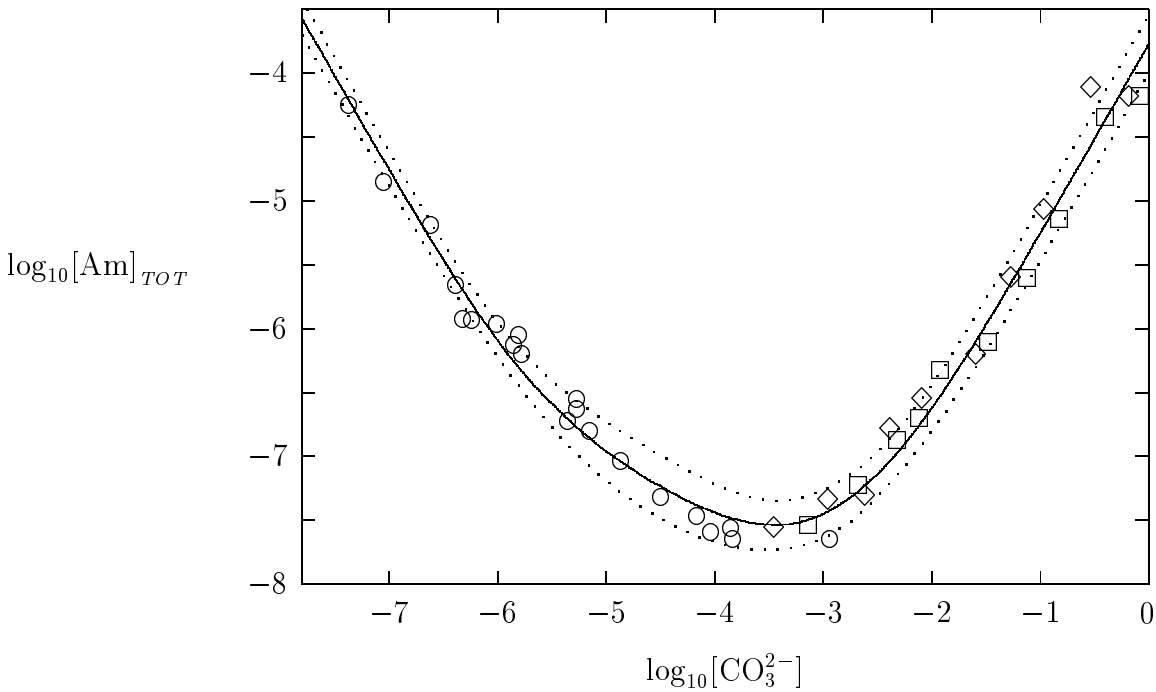
The method used by Pazukhin and Kochergin for the preparation of solid $Am(OH)_3(s)$ changed with the pH-range. Moreover, no characterisation of the solid was made, the equilibration time was very short (1 to 2 hours), and the centrifugation procedure used (10000 rpm during 25 min) may have not differentiated between smaller americium colloids and true dissolved americium species. The consequence of this last consideration would be a much higher apparent solubility. Based on these factors, the measurements reported by Pazukhin and Kochergin are disregarded in this review.

[89ROB]

Robouch, P., Contribution à la prévision du comportement de l'américium, du plutonium et du neptunium dans la géosphère; données chimiques, Ph.D. thesis, presented in Strasbourg, 13 Nov. 1987, Report CEA-R-5473, Commissariat à l'Energie Atomique, Gif-sur-Yvette, France, 1989, 216p., partly in French.

The solubility of $Am_2(CO_3)_3(s)$ as a function of the concentration of carbonate in solution was studied at 3 M $NaClO_4$ ionic strength and (20 ± 1)°C, *cf.* Figure A.10. X-ray diffraction studies were made of the solid phase, and the solid was identified as the normal carbonate of americium(III) by analogy of the X-ray diffraction pattern with that of lanthanides. Two sets of experiments were performed: the first one with known total carbonate concentration ($3 \times 10^{-4} \leq [CO_3^{2-}]_{TOT} \leq 1.0$ M and $\sim 7 \leq$ pH ≤ 10.5); the second one under controlled $CO_2(g)$ partial pressure ($p_{CO_2} = 0.1, 0.3$ and 1.0 atm and $5.1 \leq$ pH ≤ 7.8). The solubility data were analysed in terms of carbonate complexes ($Am(CO_3)_n^{(3-2n)}$ $n = 1, 2, 3$) and a solubility product for $Am_2(CO_3)_3(s)$. No evidence of $Am(CO_3)_4^{5-}$ formation was found by spectrophotometry in the 0.1 to

Figure A.10: Solubility measurements of Am(III) at 3 M $NaClO_4$ and 20°C from Robouch [89ROB]. The diagram shows experimental points (○) obtained under controlled CO_2(g) partial pressure (0.1, 0.3 and 1.0 atm) and data from batch experiments sampled after 10 and 20 weeks of equilibration time (◇ and □ respectively). The continuous curve represents the solubility of $Am_2(CO_3)_3$(cr) calculated with the set of equilibrium constants re-estimated by this review from data in Ref. [89ROB], and the dotted curves show the associated uncertainty.



3.0 M Na_2CO_3 range, which is in agreement with the observations of Shiloh *et al.* and Bourges *et al.* (*cf.* discussion of Refs. [69SHI/GIV, 83BOU/GUI] in this Appendix). The reported thermodynamic constants are presented in Table V.16.

This review re-evaluates the experimental data as follows. The acid equilibrium constants for the carbonate system given in Table IV.2 are extrapolated first to 20°C and then to 3.49 m $NaClO_4$ (using however ε-values valid at 25°) and converted to molar units:

$$CO_3^{2-} + 2\,H^+ \rightleftharpoons CO_2(g) + H_2O(l) \qquad \log_{10} K_{p,2}(I = 3\ \mathrm{M}, 20°\mathrm{C}) = 17.81 \pm 0.05$$
$$CO_3^{2-} + 2\,H^+ \rightleftharpoons CO_2(aq) + H_2O(l) \qquad \log_{10} K_2(I = 3\ \mathrm{M}, 20°\mathrm{C}) = 16.21 \pm 0.05$$
$$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^- \qquad \log_{10} K_1(I = 3\ \mathrm{M}, 20°\mathrm{C}) = 9.62 \pm 0.04$$

These equilibrium constants differ slightly from the values used by Robouch. Therefore the "pH" ($= \log_{10}[H^+]$) measurements reported in Tables 2a and 2b of [89ROB] were adjusted to the different $\log_{10}[H^+]$ values of the solutions used to calibrate his glass electrode. These corrected values, were used with p_{CO_2} (in bar units) or $[CO_3^{2-}]_{TOT}$ data to obtain revised values of $\log_{10}[CO_3^{2-}]$ which are shown in Fig-

ure A.10. An unweighted least squares fitting of the data yielded the following equilibrium constants (at $I = 3.0$ M): $\log_{10}\beta_1 = (5.73 \pm 0.24)$, $\log_{10}\beta_2 = (9.09 \pm 0.25)$, $\log_{10}\beta_3 = (11.50 \pm 0.18)$, and $\log_{10}K_{s,0} = -(15.27 \pm 0.14)$ for reaction:

$$0.5\,Am_2(CO_3)_3(cr) \rightleftharpoons Am^{3+} + 1.5\,CO_3^{2-}. \qquad (V.36)$$

These values, converted to molal units, are extrapolated to zero ionic strength (using however the ion interaction coefficients in Appendix B which are valid at 25°C). This yields: $\log_{10}\beta_1^\circ = (7.80 \pm 0.32)$, $\log_{10}\beta_2^\circ = (11.60 \pm 0.38)$, $\log_{10}\beta_3^\circ = (12.88 \pm 0.42)$ and $\log_{10}K_{s,0}^\circ(V.36) = -(17.54 \pm 0.24)$.

There is however an alternative interpretation for the data obtained with the batch experiments. The calculated partial pressures of $CO_2(g)$ in these solutions is in general much lower (8×10^{-3} bar in average) than in the experiments at constant p_{CO_2}. This would favor the transformation of $Am_2(CO_3)_3(s)$ into $AmCO_3OH(s)$ according to:

$$\frac{1}{2}Am_2(CO_3)_3(s) + \frac{1}{2}H_2O(l) \rightleftharpoons AmCO_3OH(s) + \frac{1}{2}CO_2(g)$$

as outlined by Vitorge [92VIT]. Under the conditions studied by Robouch the solubilities of these two solids are of the same order of magnitude, and because Robouch only determined the nature of the solid phase by X-ray analysis on experiments at controlled p_{CO_2}, it is possible that the hydroxy-carbonate was present in the batch experiments. If that is the case, the solubility of americium at high values of $[CO_3^{2-}]$ should be described with the following reactions:

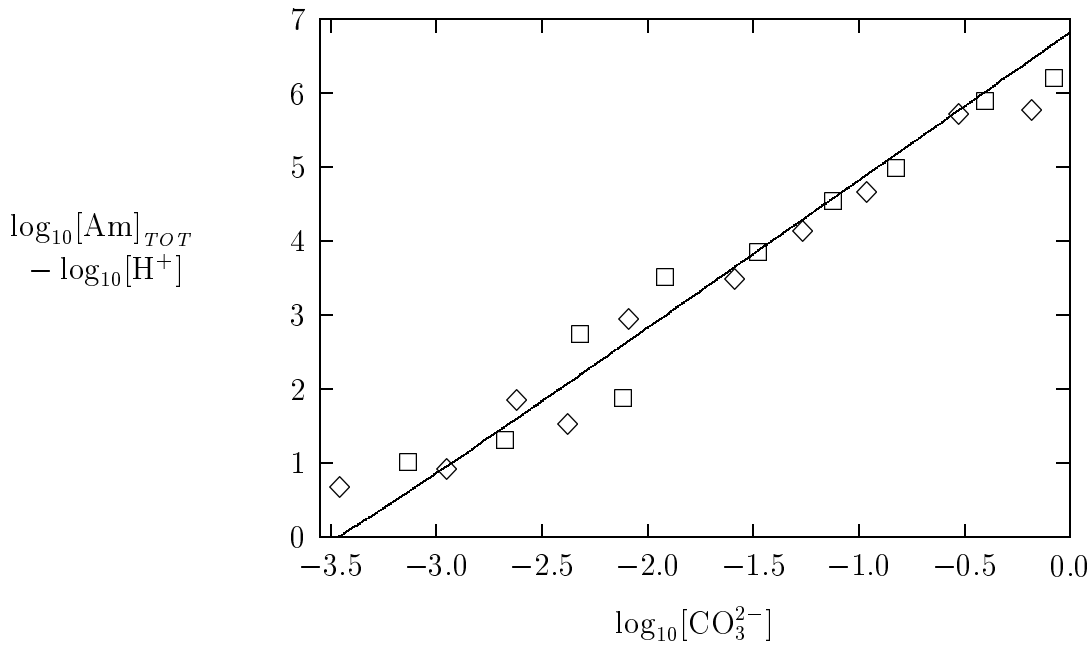
$$AmCO_3OH(s) + H^+ + CO_3^{2-} \rightleftharpoons Am(CO_3)_2^- \qquad (A.9)$$
$$AmCO_3OH(s) + H^+ + 2\,CO_3^{2-} \rightleftharpoons Am(CO_3)_3^{3-} \qquad (A.10)$$

(see also Ref. [94GIF]). Figure A.11 shows that indeed the data obtained in the batch experiments can be explained with the solubility of $AmCO_3OH(s)$. The values of the equilibrium constants, $K_{s,i} = (K_{s,0}(V.33) \times K_{H_2O} \times \beta_i)$, used to draw the continuous curve in Figure A.11 correspond to 3.33 and 6.23 at $I = 0$ for reactions (A.9) and (A.10). These values are similar to the equilibrium constants obtained from the data in Refs. [85SIL, 90FEL/RAI], but differ from the values given in Refs. [84BER/KIM, 92RUN/MEI].

As the data obtained by Robouch [89ROB] in batch experiments ($\log_{10}[CO_3^{2-}] \geq -3.5$) can equally well be described with the solubility of both $Am_2(CO_3)_3(s)$ and $AmCO_3OH(s)$, only the equilibrium constants unequivocally resulting from the measurements at constant p_{CO_2}, *i.e.* $\log_{10}\beta_1^\circ$ and $\log_{10}K_{s,0}^\circ(V.36)$, are used in the selection procedure described in Sections V.7.1.2.1.a and V.7.1.2.2.b.

Robouch mentioned [89ROB, *pp.*57–58] that the solid americium carbonate in contact for more than 8 months with solutions containing $[Na_2CO_3] \geq 1$ M was converted to $NaAm(CO_3)_2(cr)$. However, it is not clear for which experimental points [89ROB, Table 2b, page 60] the X-ray diffraction pattern was obtained. Furthermore, the reported solubilities are too few to permit an accurate determination of the solubility

Figure A.11: Americium(III) solubility measurements at 3 M $NaClO_4$ and 20°C from Robouch [89ROB]. The diagram shows only experimental data from batch experiments sampled after 10 and 20 weeks of equilibration time (◇ and □ respectively). The curve shows the values calculated assuming equilibrium with $AmCO_3OH(s)$ and the following equilibrium constants: $\log_{10} K_{s,2}(A.9) = 2.79$ and $\log_{10} K_{s,3}(A.10) = 6.82$.



product for this mixed-carbonate compound.

[89ROS/REI]

Rösch, F., Reimann, T., Buklanov, G.V., Milanov, M., Khalkin, V.A., Dreyer, R., Electromigration of carrier-free radionuclides. 13. Ion mobilities and hydrolysis of ^{241}Am-Am(III) in aqueous inert electrolytes, J. Radioanal. Nucl. Chem., **134** (1989) 109–128.

Rösch *et al.* present an electromigration study of ^{241}Am at $[ClO_4^-] = 0.1$ M and 25°C. The electromigration method used does not suffer from the possible artifacts of other electromigration methods using solid stationary phases (see considerations under Refs. [69MAR/KIK, 72SHA/STE, 73KOR2] in this Appendix). The ion mobilities of the americium(III) aqua ion were found to be pH-dependent even in the acidic pH region where Am(III) hydrolysis does not occur. The authors proposed a change in the hydration sphere to explain these observations. On the other hand, they assumed that this effect was negligible in the pH range 5.5 – 7.9, and ascribed only to hydrolysis the observed variations in the overall americium mobility. These data were fitted with a model assuming the presence of Am^{3+} and $AmOH^{2+}$ only, obtaining a value of $\log_{10}{}^*\beta_1 = -(6.9 \pm 0.2)$. No attempts were made to test alternative hydrolysis schemes. A dramatic drop of the overall americium mobility was observed above pH = 9. This was interpreted as the formation of the hydroxide $Am(OH)_3$, and

a value of $\log_{10}{}^{*}\beta_3 = -(23.8 \pm 0.9)$ was reported. It is not clear how this calculation was made. No indication was given on the nature of this hydroxide, either solid or a soluble species. Indeed the experiments were made by injecting 1 – 2 μl of an americium stock solution into the starting position of the migration tube, but no data are given on the total americium concentration involved. We expect that to cope with detection limits, quite high americium concentrations were used, and therefore local precipitation may have occurred. Rösch *et al.* also proposed an upper limit $\log_{10}{}^{*}K_4 \leq -12.9$ for the fourth hydrolysis complex, even though no experimental evidence for this complex was found.

Based on the above considerations the data of Rösch *et al.* [89ROS/REI] have not been credited by this review.

[90FEL/RAI]
Felmy, A.R., Rai, D., Fulton, R.W., The solubility of $AmOHCO_3$(c) and the aqueous thermodynamics of the system Na^+–Am^{3+}–HCO_3^-–CO_3^{2-}–OH^-–H2O, Radiochim. Acta, **50** (1990) 193–204.

Felmy, Rai and Fulton investigated the solubility of ^{243}Am in carbonate media over wide ranges of CO_3^{2-}/HCO_3^- concentrations and pH values:

- at $p_{CO_2} = 0.001$ atm and $5.2 < \text{pH} < 9.3$
- at $10.6 < \text{pH} < 11.3$ and $0.03 < [Na_2CO_3] < 0.1$ M
- at $11.7 < \text{pH} < 13.0$ and $[Na_2CO_3] = 0.07$ M.

The ionic strength of the solutions was not kept constant. Although the temperature at which the experiments were performed was not mentioned by Felmy, Rai and Fulton, this review assumes it to be close to 25°C. The authors presented X-ray pattern similar to the one presented by Silva and Nitsche [84SIL/NIT] and identified the precipitate as $AmCO_3OH$(s). The solubility data were then interpreted assuming the formation of $Am(CO_3)_i^{(3-2i)}$ (i = 1, 2, 3) complexes, which is in agreement with other experimental observations (*cf.* Section V.7.1.2.1). Felmy, Rai and Fulton used the Pitzer virial coefficient approach [79PIT] together with a nonlinear least-squares technique to calculate standard equilibrium constants (*cf.* Table V.16). The authors did not include their solubility results at pH ≤ 6.5 in the least-squares fit, because they suspected that the solutions were undersaturated. These experimental points were instead replaced with the solubility results of Silva and Nitsche [84SIL/NIT, 85SIL]. If only solubility measurements at pH > 6.5 are considered, it is only possible to obtain values for the equilibrium constants involving the predominant aqueous americium complexes in this pH range. Assuming, as Felmy, Rai and Fulton did, that $Am(CO_3)_i^{(3-2i)}$ (i = 1, 2, 3) are the predominant complexes, it is possible to use reactions like:

$$AmCO_3OH(cr) + H^+ + (i-1)\,CO_3^{2-} \rightleftharpoons Am(CO_3)_i^{(3-2i)} + H_2O(l) \quad (A.11)$$

or:

$$\mathrm{AmCO_3OH(cr)} + (i-2)\,\mathrm{H_2O(l)} + (i-1)\,\mathrm{CO_2(g)} \rightleftharpoons \mathrm{Am(CO_3)}_i^{(3-2i)} + (2i-3)\,\mathrm{H^+}$$

etc., to fit the data at pH > 6.5. This review digitises the solubilities at fixed p_{CO_2} (converted from atm to bar units) [90FEL/RAI, Figure 8] and at varying concentrations of Na_2CO_3 for 78 day equilibration [90FEL/RAI, Figure 9 and Table 1], and performs a least-squares fit of these solubilities, all of them measured at 6.5 < pH < 11. The measurements on 0.07 M Na_2CO_3 solutions with added NaOH [90FEL/RAI, Figure 5] at 11.7 ≤ pH ≤ 13.0 were not included in our re-evaluation because not enough experimental details are provided in the publication. The fitting procedure involved the calculation of $[H^+]$ from reported pH-values, and of the ionic strength and the activity coefficients (using the specific ion interaction equations in Appendix B) by an iteration procedure. Owing to the low ionic strengths of these solutions, the results of the calculations are not sensitive to the method used to obtain single ion activity coefficients. The calculations show that a systematic error of ±0.05 in the pH-values, for example from junction potentials, would result in errors between ±0.05 and ±0.1 in the fitted equilibrium constants.

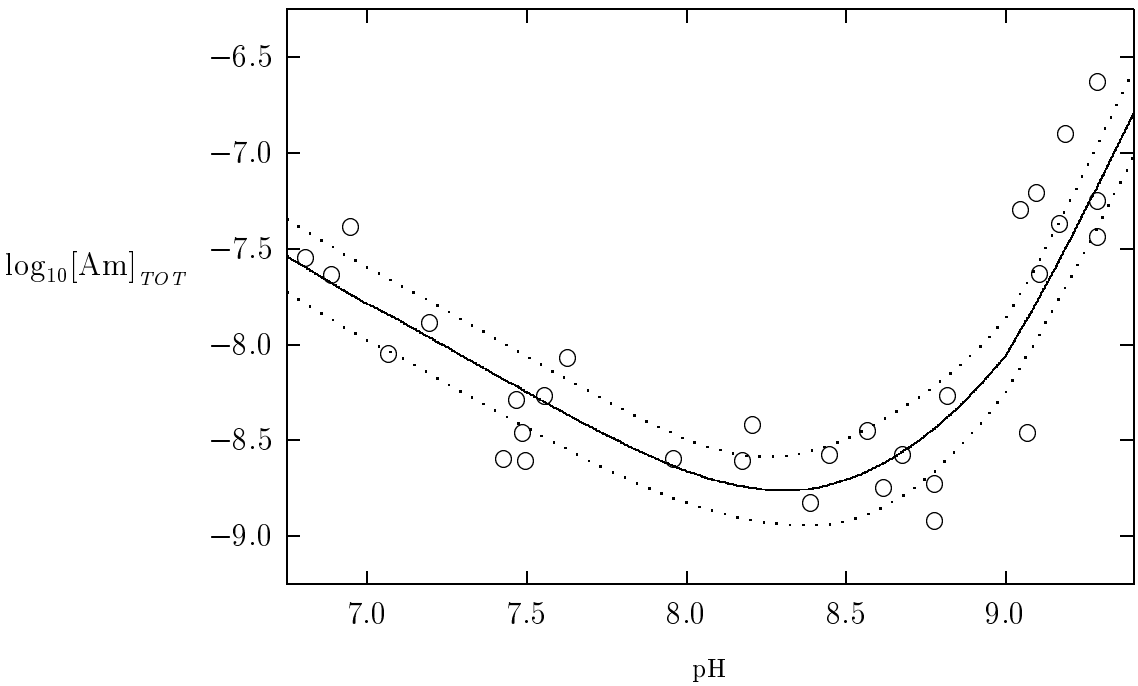
Our calculations yield values for $\log_{10}{}^{*}K^{\circ}_{s,i}$(A.11) of $-(0.8 \pm 0.2)$, (3.7 ± 0.4) and (6.4 ± 0.5) for $i = 1$, 2 and 3 respectively. These values can be compared with those calculated from the equilibrium constants reported by Felmy, Rai and Fulton [90FEL/RAI]: −0.9, 3.8 and 6.7 respectively. The experimental data at constant p_{CO_2} for pH > 6.5 are compared in Figure A.12 with the computed solubilities. Combining the recalculated values with $\log_{10} K^{\circ}_{s,0}$(V.33) $= -(22.3 \pm 0.3)$, from the reinterpretation of the experiments reported by Silva [85SIL], and the ionic product of water results in $\log_{10}\beta^{\circ}_1 = (7.5 \pm 0.4)$, $\log_{10}\beta^{\circ}_2 = (12.0 \pm 0.5)$ and $\log_{10}\beta^{\circ}_3 = (14.7 \pm 0.5)$. It should be noted that while the constants for the first and second complex agree with the values reported by Felmy, Rai and Fulton: 7.6 and 12.3 respectively, there is some discrepancy between the value of β°_3 given by Felmy, Rai and Fulton (15.2) and our results. This difference arises from the fact that the measurements in 0.07 M Na_2CO_3 at 11.7 ≤ pH ≤ 13.0 could not be included in our evaluation. Therefore, the equilibrium constants at $I = 0$ for the formation of $AmCO_3^+$, $Am(CO_3)_2^-$ and $Am(CO_3)_3^{3-}$ reported by Felmy, Rai and Fulton are included in the selection procedure of Section V.7.1.2.1.a with the uncertainties obtained in our recalculation.

On the basis of the solubility data above pH = 12.5, Rai *et al.* revised the upper limit proposed in a former paper [83RAI/STR] for the $Am(OH)_3$(aq) complex, *cf.* Table V.4.

[90PER/SAP]
Pershin, A.S., Sapozhnikova, T.V., Hydrolysis of Am(III), J. Radioanal. Nucl. Chem., **143** (1990) 455–462.

The authors performed two potentiometric titrations. No information was given on ionic strength or temperature for the pH measurements. The solubility product was

Figure A.12: Solubility measurements of $AmCO_3OH(cr)$ from Felmy, Rai and Fulton [90FEL/RAI] at $p_{CO_2} = 0.001$ atm. The continuous curve represents the values calculated with the set of equilibrium constants re-evaluated by this review from experimental data in [90FEL/RAI], and the dotted curves show the associated uncertainty.



derived from a jump on the titration curves associated by the authors to the onset of precipitation. Pershin and Sapozhnikova report the following value for the solubility product: $\log_{10}{}^{*}K_{s,0} = -27.3$. For lack of information on how the experiments were conducted this constant is disregarded in this review.

[90ROS/REI]

Rösch, F., Reimann, T., Buklanov, V., Milanov, M., Khalkin, V.A., Dreyer, R., Electromigration of carrier-free radionuclides. XIV. Complex formation of ^{241}Am–Am(III) with oxalate and sulphate in aqueous solution, J. Radioanl. Nucl. Chem., **140** (1990) 159–169.

Rösch *et al.* [90ROS/REI] investigated the formation of americium sulphato complexes using an electromigration technique at 298.15 K and $I = 0.1$ M, in $HClO_4$/-Na_2SO_4 (pH = 2.8) and $NaClO_4/Na_2SO_4$ (pH = 5.5) media. The decrease of the americium mobility with increasing $[SO_4^{2-}]$ was interpreted by the formation of $AmSO_4^+$ as the predominant species. The corresponding stability constant was found to be $\log_{10}\beta_1 = (2.5\pm0.3)$, and this value is used in the selection procedure described in Section V.5.1.2.1. Extrapolation to $I = 0$ (*cf.* Appendix B) yields $\log_{10}\beta_1^\circ = (3.8 \pm 0.6)$. This review considers that the experimental data presented by Rösch *et al.* are insufficient to prove the existence of $Am(SO_4)_2^-$, and therefore rejects the reported value of $\log_{10} K_2$.

[90TAN]
Tananaev, I.G., Hydroxides of pentavalent americium, Sov. Radiochem., **32** (1990) 305–307.

The procedure for the synthesis and the X-ray characterisation of several double hydroxides of americium(V) ($M\mathrm{AmO_2(OH)_2} \cdot x\mathrm{H_2O(cr)}$, M = Li, Na, K; and $M_2\mathrm{AmO_2(OH)_3} \cdot x\mathrm{H_2O(cr)}$, M = Na, K) were reported in this paper. The existence of these solid phases was taken as an evidence for the presence in basic media of the corresponding aqueous Am(V) hydroxo complexes. No values for equilibrium constants were reported.

[90TAN2]
Tananaev, I.G., Forms of Np(V) and Am(V) in basic aqueous media, Sov. Radiochem., **32** (1990) 476–479.

From spectrophotometric measurements Tananaev concluded that in alkaline solutions of Am(V), the dominant hydroxo complexes are $\mathrm{AmO_2(OH)}_n^{1-n}$, with $n = 1 \ldots 4$. No values for the equilibrium constants are reported in this work.

[91MEI/KIM]
Meinrath, G., Kim, J.I., The carbonate complexation of the Am(III) ion, Radiochim. Acta, **52/53** (1991) 29–34.

The authors investigated the americium complexation in carbonate media, performing solubility and spectroscopic experiments. The data were collected in a ionic media of 0.1 M $\mathrm{NaClO_4}$ (at $6 \leq \mathrm{pH} < 8$) and 0.3 M $\mathrm{NaClO_4}$ (at $8 < \mathrm{pH} < 9$), under a controlled $\mathrm{CO_2(g)}$ partial pressure ($p_{\mathrm{CO_2}} = 0.01$ atm), and at 25°C [91MEI/KIM, Table 4], *cf.* Figure A.13. The results were interpreted by the formation of $\mathrm{AmCO_3^+}$ and $\mathrm{Am(CO_3)_2^-}$. The precipitate, analysed by X-ray diffraction, thermogravimetry and differential thermal analysis, was characterised as $\mathrm{Am_2(CO_3)_3(cr)}$. The equilibrium constant, for the reaction

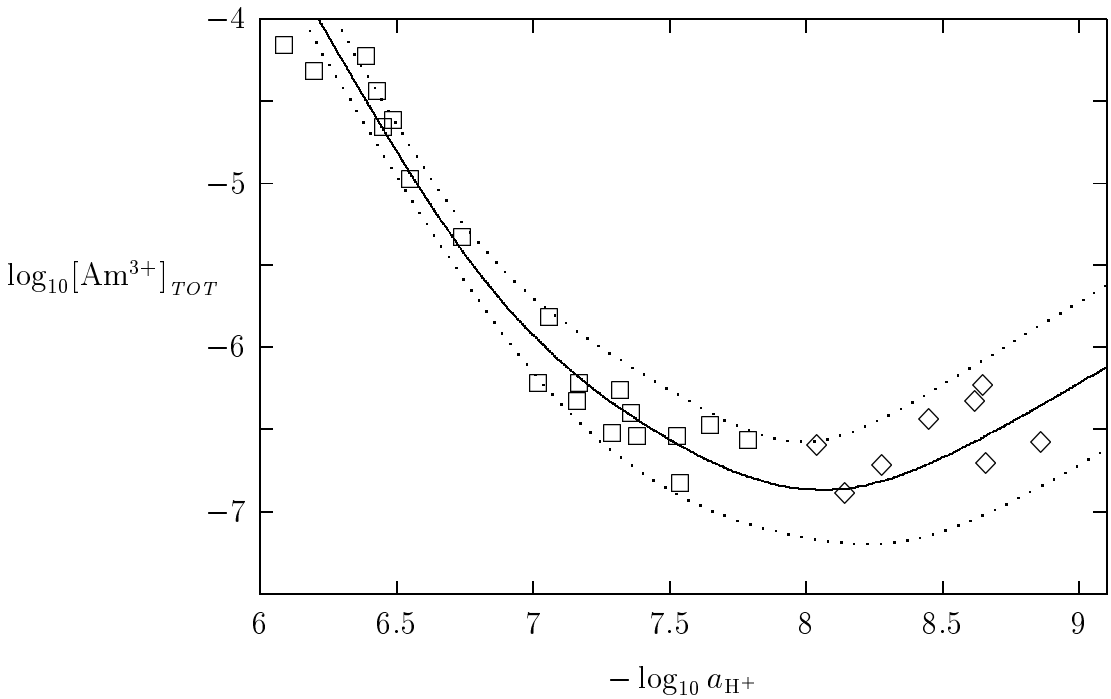
$$\mathrm{CO_2(g) + H_2O(l)} \rightleftharpoons \mathrm{2\,H^+ + CO_3^{2-}}, \tag{A.12}$$

was experimentally determined in 0.1 M $\mathrm{NaClO_4}$ as $\log_{10} K = -(17.62 \pm 0.10)$. For this very simple equilibrium the uncertainty at the 95% level (± 0.2 $\log_{10}$-units) seems to be considerable, and may indicate that the electrode measurements perhaps were not very accurate.

The spectrophotometric and photoacoustic results are essentially based on four spectra measured in carbonate media. The second formation constant, determined only from one spectrum at pH = 8.7 in combination with the solubility results, is to be disregarded due to insufficient accuracy of the collected data. The value of $\log_{10} \beta_1(0.1\ \mathrm{M}) = (6.48 \pm 0.03)$ determined spectrophotometrically is in good agreement with previous results by Nitsche, Standifer and Silva [89NIT/STA] and is selected by this review.

The solubilities presented in Figure 3 or Ref. [91MEI/KIM] were digitised by this review, and the data were re-analysed as follows. Activity coefficient corrections,

Figure A.13: Solubility measurements of $Am_2(CO_3)_3$(cr) from Meinrath and Kim [91MEI/KIM] at 0.1 M $NaClO_4$ and pH < 8 (□) and 0.3 M $NaClO_4$ and pH ≥ 8 (◇), and at $p_{CO_2} = 0.01$ atm and 25°C. The continuous curve represents the values calculated with the set of equilibrium constants determined by Meinrath and Kim [91MEI/KIM], and the dotted curves show the associated uncertainty.



using the specific ion interaction equations of Appendix B, were used to obtain $[H^+]$ from the reported pH-values and to calculate americium(III)-carbonate equilibrium constants at $I = 0.3$ M (for the points at pH > 8) from the fitted equilibrium constants at $I = 0.1$ M. The reported value of p_{CO_2} was converted from atm to bar units, and then used to calculate values of $[CO_3^{2-}]$ using $\log_{10} K(\text{A.12}) = -17.53$ and -17.28 at $I = 0.1$ and 0.3 M respectively (experimental points at pH < 8 and > 8). The calculations show that a systematic error of ± 0.05 in the pH-values, for example from junction potentials, would result in errors between ± 0.1 and ± 0.2 in the fitted equilibrium constants.

Our least-squares fitting yields the following values at $I = 0.1$ M $NaClO_4$: $\log_{10} \beta_1 = (6.1 \pm 0.3)$, $\log_{10} \beta_2 = (9.5 \pm 0.3)$, and $\log_{10} K_{s,0} = -(15.0 \pm 0.2)$, where the solubility constant refers to the reaction:

$$0.5\, Am_2(CO_3)_3(\text{cr}) \rightleftharpoons Am^{3+} + 1.5\, CO_3^{2-}. \qquad \text{(V.36)}$$

These values are in agreement with the ones reported by Meinrath and Kim (*cf.* Table V.16) which are consequently included in the selection procedure described in Section V.7.1.2. The complexation constants (solubility method) and the solubility products (solubility and spectrophotometric methods) given by Meinrath and Kim

are converted to molal units and extrapolated to $I = 0$ with the specific ion interaction model of Appendix B to yield: $\log_{10} \beta_1^\circ = (7.26 \pm 0.30)$ $\log_{10} \beta_2^\circ = (11.29 \pm 0.47)$, $\log_{10} K_{s,0}^\circ(\text{V.36}) = -(16.54 \pm 0.18)$ and $-(16.45 \pm 0.10)$ (solubility and spectrometry experiments, respectively).

[91MEI/KIM2]
Meinrath, G., Kim, J.I., Solubility products of different Am(III) and Nd(III) carbonates, Eur. J. Solid State Inorg. Chem., **28** (1991) 383–388.

Meinrath and Kim investigated the formation of $Am_2(CO_3)_3(s)$, $NdCO_3OH(s)$ and $Nd_2(CO_3)_3(s)$ under different $CO_2(g)$ partial pressures in the pH range of 4.1 to 6.2 at (22±1)°C. The chemical composition of the Nd(III) precipitates were characterised by X-ray diffraction measurements, FTIR spectroscopy and thermogravimetry together with differential thermal analysis.

$Nd_2(CO_3)_3(s)$ was found to be formed at $p_{CO_2} \geq 0.01$ atm, while at $p_{CO_2} = 0.031\%$ (*i.e.* atmospheric conditions) the Nd precipitate appears to be at first a mixture of $Nd_2(CO_3)_3(s)$ and $NdCO_3OH(s)$, with a steady increase of the amount of the hydroxy carbonate solid with time.

The solubility of $^{241}Am(III)$, obtained for $p_{CO_2} = 1\%$ and 100%, were interpreted assuming — by analogy — the formation of $Am_2(CO_3)_3(s)$. The equilibrium constant for the reaction $CO_2(g) + H_2O(l) \rightleftharpoons 2\,H^+ + CO_3^{2-}$, was experimentally determined in 0.1 M $NaClO_4$ as $\log_{10} K = -(17.62 \pm 0.07)$, and used by Meinrath and Kim for the data treatment. There are no graphs or tables in the paper presenting the experimental measurements on americium, and therefore it is not possible to judge the uncertainty in the results. The solubility product reported by Meinrath and Kim (*cf.* Table V.16) converted to molal units, is extrapolated to zero ionic strength using the specific ion interaction equations (*cf.* Appendix B) yielding $\log_{10} K_{s,0}^\circ(\text{V.36}) = -(16.38 \pm 0.10)$ (*cf.* Section V.7.1.2.2).

[91VIT/TRA]
Vitorge, P., Tran The, P., Solubility limits of radionuclides in interstitial water – Americium in cement. Task 3 – Characterization of radioactive waste forms. A series of final reports (1985–89) – No. 34, Report EUR 13664, 1991, Commission of the European Communities, Luxembourg, 39p.

Vitorge and Tran The investigated the solubility of ^{241}Am in cement leachates and in KOH solutions of variable concentration ($0 < [KOH] < 10$ M) in the presence of 0.04 M $Ca(OH)_2(s)$. No precautions were taken to avoid contact with atmospheric $CO_2(g)$, even though the addition of $Ca(OH)_2(s)$ was contributing to the removal of dissolved CO_2 by precipitation of solid calcium carbonate. The measurement of americium concentrations in the supernatant showed that equilibrium was attained in about 100 days. No characterisation of the solubility limiting solid phase was made. Incorporation of americium(III) in precipitating $CaCO_3(s)$ might have also occurred. The temperature of the solubility experiments is not mentioned in [91VIT/TRA].

The solubility of americium in alkaline solutions in the presence of excess $Ca(OH)_2(s)$ was found to be in agreement with the values given by Bernkopf and Kim [84BER/KIM], Ewart *et al.* [86EWA/HOW] and Stadler and Kim [88STA/KIM]. Vitorge and Tran The

reported $\log_{10} K_{s,3} = -11.1$ for reaction:

$$\mathrm{Am(OH)_3(s)} \rightleftharpoons \mathrm{Am(OH)_3(aq)} \tag{A.13}$$

This is in agreement with the equilibrium constant selected in this review (*cf.* Table III.2) for crystalline americium hydroxide, *i.e.* $\log_{10} K^{\circ}_{s,3} = -(10.5 \pm 0.8)$ (ionic strength effects are negligible for reaction (A.13) which does not involve charged aqueous species).

The observed increase in americium concentration with increasing concentration of KOH was interpreted assuming the formation of $\mathrm{Am(OH)_4^-}$:

$$\mathrm{Am(OH)_3(aq) + OH^-} \rightleftharpoons \mathrm{Am(OH)_4^-}$$

with $\log_{10} K_4 = -0.2$. This value, however, is disregarded because of variations in ionic strength and the lack of characterisation of the solid phase.

[92EWA/SMI]
Ewart, F.T., Smith-Briggs, J.L., Thomason, H.P., Williams, S.J., The solubility of actinides in a cementitious near-field environment, Waste Management, **12** (1992) 241–252.

See comments under [86EWA/HOW].

[92RAI/FEL]
Rai, D., Felmy, A.R., Fulton, R.W., Solubility and ion activity product of $\mathrm{AmPO_4} \cdot x\mathrm{H_2O(am)}$, Radiochim. Acta, **56** (1992) 7–14.

Rai, Felmy and Fulton investigated the americium solubility in phosphate media, from over- and under-saturation, for phosphate concentrations ranging from 10^{-3} to $10^{-5.2}$ M.

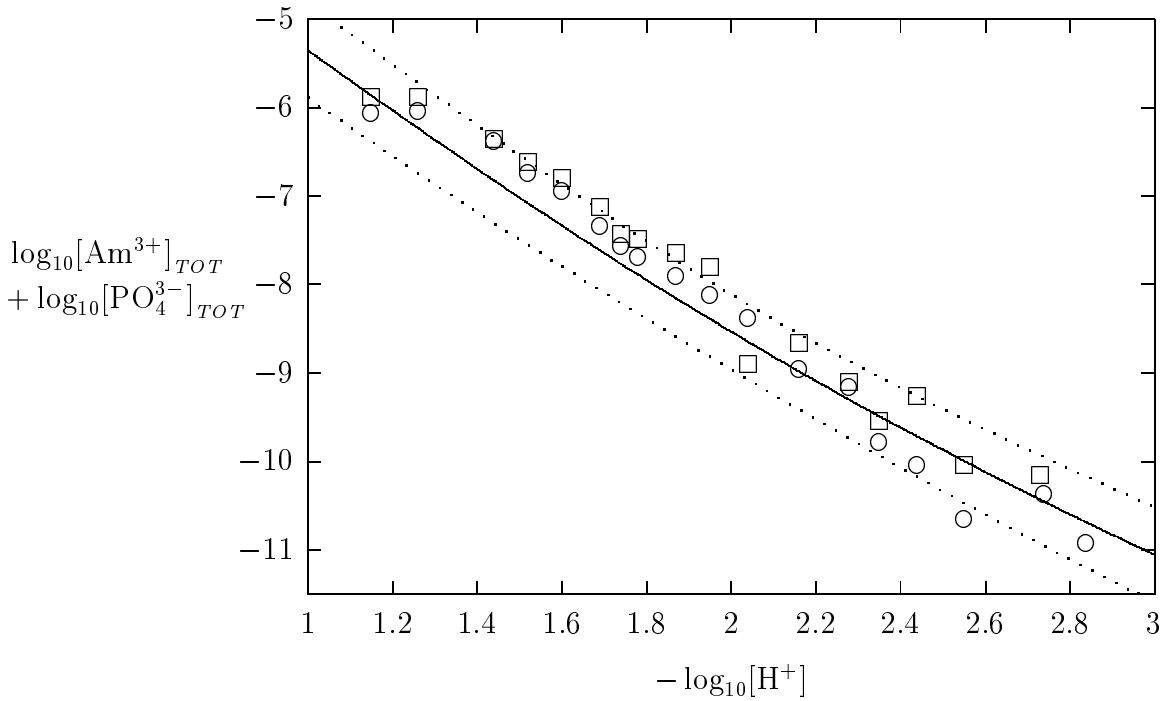
A pink americium phosphate solid was prepared by adding 5 mg ^{243}Am in a stock solution to 30 ml of 0.1 M $\mathrm{NaH_2PO_4}$ (pH = 4.5). After a few days of equilibration, the precipitate was filtered, washed, suspended in deaerated water samples (the pH was varied in the range 3 to 1 by adding HCl), and shaken continuously for 50 days. ^{243}Am was then added to half of the batches to increase the americium concentration in the solution (*i.e.* oversaturation). The samples were shaken again and analysed after different equilibration times.

Chemical and X-ray diffraction analysis show the presence of an amorphous americium phosphate solid: $\mathrm{AmPO_4} \cdot x\mathrm{H_2O(am)}$. The solubility data may be summarised as follows:

- at pH ≥ 3, the americium concentration is very low ($\sim 10^{-9}$ M) and close to the analytical detection limit of the equipment used by the authors. No reliable information on the complex formation can be therefore obtained in this pH region.

- at $2 <$ pH ≤ 3 the americium concentration decreases by two orders of magnitude with one pH unit. This is in disagreement with the expected trend. An inspection of Table 5 in [92RAI/FEL] shows that phosphate concentrations are systematically larger than the corresponding americium solubilities in the pH range ~ 2 to ~ 3. There is no clear reason for this imbalance.

Figure A.14: Solubility measurements of $AmPO_4 \cdot xH_2O$(am) from Rai, Felmy and Fulton [92RAI/FEL] (at 21 days, □, and 86 days, ○, equilibration time). The continuous curve represents the values calculated with the solubility product reported in [92RAI/FEL] (*i.e.* $\log_{10} K^\circ_{s,0} = -24.79$) in combination with the selected acidity constants for phosphoric acid given in Table IV.2 and the specific ion interaction equations in Appendix B. The dotted curves show the calculated uncertainty on the solubility when the uncertainty in the value of $\log_{10} K^\circ_{s,0}$ is set to ±0.6.



The authors used both Davies equation [62DAV] and the Pitzer virial coefficient approach [73PIT, 79PIT] to calculate the standard solubility product:

$$AmPO_4 \cdot xH_2O(am) \rightleftharpoons Am^{3+} + PO_4^{3-} + x\,H_2O(l)$$
$$\log_{10} K^\circ_{s,0} = -24.79 \pm 0.18.$$

The temperature was not mentioned by Rai, Felmy and Fulton, but this review assumes it to be close to 25°C.

A plot of the product of the americium and phosphate solubilities measured by Rai, Felmy and Fulton [92RAI/FEL, Table 5] *vs.* the corresponding acidities [92RAI/FEL, Table 1], is compared in Figure A.14 with the corresponding calculated values.

[92RUN/MEI]

Runde, W., Meinrath, G., Kim, J.I., A study of solid-liquid phase equilibria of trivalent lanthanide and actinide ions in carbonate systems, Radiochim. Acta, **58/59** (1992) 93–100.

Runde, Meinrath and Kim investigated the solubility of ^{241}Am in carbonate media at 0.1 M $NaClO_4$ and (25.0±0.2)°C using the methodology described in [91MEI/KIM].

The results are interpreted assuming the formation of $Am_2(CO_3)_3(s)$ (at $p_{CO_2} > 0.01$ atm), and $AmCO_3OH(s)$ (at $p_{CO_2} = 3 \times 10^{-4}$ atm). There are no graphs or tables in the paper presenting the experimental measurements on americium, and therefore it is not possible to judge the uncertainty in the results. The solubility products reported by Runde, Meinrath and Kim, presented in Table V.16, are converted to molal units and extrapolated to zero ionic strength using the specific ion interaction equations (*cf.* Appendix B) yielding $\log_{10} K^\circ_{s,0}(V.33) = -(20.18 \pm 0.24)$ and $\log_{10} K^\circ_{s,0}(V.36) = -(16.32 \pm 0.18)$ (*cf.* Section V.7.1.2.2).

[92VIT]
Vitorge, P., $Am(OH)_{3(s)}$, $AmOHCO_{3(s)}$ and $Am_2(CO_3)_{3(s)}$ stabilities in environmental conditions, Radiochim. Acta, **58/59** (1992) 105–107.

The author describes the equilibria between the americium solids present in the water-bicarbonate-carbonate system, as follows:

$$\begin{aligned} Am(OH)_3(s) + CO_2(g) &\rightleftharpoons AmCO_3OH(s) + H_2O(l) \\ AmCO_3OH(s) + \frac{1}{2}CO_2(g) &\rightleftharpoons \frac{1}{2}Am_2(CO_3)_3(s) + \frac{1}{2}H_2O(l) \end{aligned}$$

By combining the acid constants of $H_2CO_3(aq)$ and the solubility products of the different solids, Vitorge concludes that $Am_2(CO_3)_3(s)$ is stable at $p_{CO_2} > 0.1$ atm, while at $p_{CO_2} \leq 10^{-13}$ atm the solid that precipitates is $Am(OH)_3(s)$, and the mixed solid $AmCO_3OH(s)$ should be predominant under atmospheric conditions ($p_{CO_2} \approx 0.001$ atm). These thermodynamic considerations are in good agreement with experimental evidence as well as with the calculations performed in this review (*cf.* Section V.7.1.2.2).

[93GIF/VIT]†
Giffaut, E., Vitorge, P. Evidence of radiolytic oxidation of ^{241}Am in Na^+ / Cl^- / HCO_3^- / CO_3^{2-} media, Sci. Basis Nucl. Waste Management XVI (Interrante, C.G., Pabalan, R.T., *eds.*), Mat. Res. Soc. Symp. Proc., **294** (1993) 747–751.

Giffaut and Vitorge measured americium concentrations in 0.1 and 4 M NaCl solutions with added $Am_2(CO_3)_3(cr)$. The solutions contained known amounts of

† Additional experimental details and data are given in a doctoral thesis [94GIF] published after this volume had been sent for independent peer-reviewing.

In his thesis, Giffaut claims that the Am(III) solid phase in his experiments, performed at $p_{CO_2} < 10^{-2}$ atm, was in fact $AmCO_3OH(s)$ instead of $Am_2(CO_3)_3(s)$ as stated in [93GIF/VIT]. Owing to this, the results at 21°C for the Am(III) system reported in Giffaut's thesis ($\log_{10} \beta^\circ_1 = 8.9$, $\log_{10} \beta^\circ_2 = 13.5$, $\log_{10} \beta^\circ_3 = 14.8$ and $\log_{10} K^\circ_{s,0}(V.33) = -22.5$) [94GIF, *pp.* 155 and 159] differ considerably from the equilibrium constants given in [93GIF/VIT]. But the values reported for Am(V) [94GIF, *p.*147] do not differ significantly from the the equilibrium constants in [93GIF/VIT]. Giffaut extrapolated the equilibrium constants for Am(V) to $I = 0$, obtaining: $\log_{10} \beta^\circ_n = 4.7$, 7.0 and 5.6 for $AmO_2(CO_3)_n^{1-2n}$ with $n = 1$ to 3, and $\log_{10} K^\circ_{s,0}(NaAmO_2CO_3(s)) = -11.4$ [94GIF, *p.*148].

This work also presents americium solubility curves in 4 M NaCl and reducing conditions in the temperature range 20 to 70°C. Giffaut interpreted these experimental data assuming the formation of either $AmCO_3OH(s)$ or $NaAm(CO_3)_2(s)$.

total sodium carbonate/bicarbonate. Free carbonate concentrations were calculated from glass electrode measurements of $\log_{10}[H^+]$. All measurements were performed at 21°C, except for a few 4 M NaCl solutions which were equilibrated at 70°C.

Higher solubilities in concentrated chloride media were interpreted as the radiolytic oxidation of Am(III) to Am(V). This was consistent with the fact that addition of metallic iron, which imposed reducing conditions, resulted in solubilities at 4 M NaCl similar to the solubilities in 0.1 M NaCl media. This also showed that, in 4 M NaCl, chloride complex formation was negligible compared with carbonate complexing. The results in 4 M NaCl media were interpreted with the formation of $AmO_2CO_3^-$ and $AmO_2(CO_3)_2^{3-}$ in equilibrium with $NaAmO_2CO_3(s)$, while in dilute chloride media the formation of $Am(CO_3)_n^{(3-2n)}$ ($n = 1$ to 3) and $Am_2(CO_3)_3(s)$ was assumed, *cf.* Table V.16 and Section V.7.1.2.1.d.

The equilibrium constants are extrapolated here to $I = 0$ with the specific ion interaction equations of Appendix B, and the uncertainties are adjusted to a 95% level assuming that the reported uncertainties are $\pm\sigma$. The results for the americium(III) system in 0.1 M NaCl give (assuming that chloride complex formation is negligible and that $\varepsilon_{(Am^{3+},Cl^-)} \approx \varepsilon_{(Am^{3+},ClO_4^-)}$, *etc.*): $\log_{10}\beta_1^\circ = (9.0\pm0.4)$, $\log_{10}\beta_2^\circ = (12.9\pm0.4)$, $\log_{10}\beta_3^\circ = (14.1 \pm 0.5)$ and $\log_{10}K_{s,0}^\circ(V.36) = -(18.7 \pm 0.3)$. The extrapolation of the americium(V) results in 4 M NaCl to $I = 0$ is performed using the $\Delta\varepsilon_n$ values for the analogous neptunium(V) system [86GRE/ROB], again assuming that the complex formation between AmO_2^+ and Cl^- is negligible, even in these concentrated chloride solutions. These assumptions yield: $\log_{10}\beta_1^\circ(AmO_2CO_3^-) = (4.6 \pm 0.7)$, $\log_{10}\beta_2^\circ(AmO_2(CO_3)_2^{3-}) = (7.3 \pm 0.8)$, and $\log_{10}K_{s,0}^\circ = -(11.0 \pm 0.6)$, where the solubility constant refers to reaction:

$$NaAmO_2CO_3(s) \rightleftharpoons Na^+ + AmO_2^+ + CO_3^{2-}$$

However, no solid phase characterisation is reported in [93GIF/VIT], and no experimental details are given which would allow the estimation of p_{CO_2}. Due to lack of information, the equilibrium constants reported in [93GIF/VIT] can not be credited in this review.

Appendix B

Ionic strength corrections†

Thermodynamic data always refer to a selected standard state. The definition given by IUPAC [82LAF] 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 $m_{\mathrm{B}} = m^{\circ} = 1\,\mathrm{mol} \cdot \mathrm{kg}^{-1}$, 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, ensuring that 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 standard 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 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 introducing ionic pairing between the medium ions and the species involved in

† This Appendix contains essentially the text written by Grenthe and Wanner [92GRE/WAN] which was also printed in the uranium NEA–TDB review as Appendix B [92GRE/FUG]. The equations presented here are an essential part to the review procedure and are required to use the selected thermodynamic values. Main differences between this Appendix and the one in Grenthe *et al.* [92GRE/FUG] are: Table B.1, Eq. (B.11) and Sections B.1.2 and B.1.4. The contents of Tables B.3 and B.4 has also been revised.

the equilibrium reactions. Earlier, this approach has been used extensively in marine chemistry, *cf.* Refs. [79JOH/PYT, 79MIL, 79PYT, 79WHI].

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 [62DAV]. However, the Davies equation should in general not be used at ionic strengths larger than 0.1 mol·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" [61LEW/RAN] and the Pitzer virial coefficient method [79PIT]) are described in the NEA Guidelines for the extrapolation to zero ionic strength [92GRE/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 [92GRE/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, 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 are 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.

It should be emphasised that the specific ion interaction model is *approximate*. Modifying it, for example by introducing the equations suggested by Ciavatta [90CIA, Eqs. (8–10)] (*cf.* Section B.1.4), would result in slightly different ion interaction coefficients and equilibrium constants. Both methods provide an internally consistent set of values. However, their absolute values may differ somewhat. Grenthe *et al.* [92GRE/FUG] estimate that these differences in general are less than 0.2 units in $\log_{10} K^\circ$, *i.e.*, approximately 1 kJ · mol^{-1} in derived $\Delta_f G^\circ_m$ values.

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 [22BRO, 22BRO2], and elaborated by Scatchard [36SCA] and Guggenheim [66GUG]. 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).

$$\log_{10}\gamma_j = -z_j^2 D + \sum_k \varepsilon_{(j,k,I_m)} m_k \tag{B.1}$$

D is the Debye-Hückel term:

$$D = \frac{A\sqrt{I_m}}{1 + Ba_j\sqrt{I_m}} \tag{B.2}$$

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 $(0.509 \pm 0.001)\,\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$ 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 $Ba_j = 1.5\,\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$ at 25°C and 1 bar, as proposed by Scatchard [76SCA] and accepted by Ciavatta [80CIA]. 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 $Ba_j = 1.0$ [35GUG] to $Ba_j = 1.6$ [62VAS]. However, the parameter Ba_j is empirical and as such 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 Tables B.3 through B.5 have thus to be used with $Ba_j = 1.5\,\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$.

The summation in Eq. (B.1) extends over all ions k present in solution. Their molality is denoted 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 is 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.4) to (B.8).

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.

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 [66GUG], 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 accurately reproduce their activity coefficient data, concentration dependent ion interaction coefficients have to be used, *cf.* Lewis, Randall, Pitzer and Brewer [61LEW/RAN], Baes and Mesmer [76BAE/MES], or Ciavatta [80CIA]. By using a more elaborate virial expansion, Pitzer and co-workers [73PIT, 73PIT/MAY, 74PIT/KIM, 74PIT/MAY, 75PIT, 76PIT/SIL, 78PIT/PET, 79PIT] 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 no 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 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, ${}^*\beta^\circ_{q,n,m}$, by Eq. (B.3).

$$\begin{aligned}\log_{10}{}^*\beta_{q,n,m} &= \log_{10}{}^*\beta^\circ_{q,n,m} + m\log_{10}\gamma_\mathrm{M} + q\log_{10}\gamma_\mathrm{L} + n\log_{10}a_{\mathrm{H_2O}} \\ &\quad - \log_{10}\gamma_{q,n,m} - n\log_{10}\gamma_{\mathrm{H^+}} \qquad \text{(B.3)}\end{aligned}$$

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 $\mathrm{H^+}$, 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.4) is obtained at 25°C and 1 bar.

$$\log_{10}\gamma_\mathrm{M} = \frac{-z_\mathrm{M}^2 0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}} + \varepsilon_{(\mathrm{M,X},I_m)}m_\mathrm{X} \qquad \text{(B.4)}$$

Under these conditions, $I_m \approx m_{\mathrm{X}} = m_{\mathrm{N}}$. Substituting the $\log_{10}\gamma_j$ values in Eq. (B.3) with the corresponding forms of Eq. (B.4) and rearranging leads to

$$\log_{10}{}^{*}\beta_{q,n,m} - \Delta z^2 D - n\log_{10} a_{\mathrm{H_2O}} \;=\; \log_{10}{}^{*}\beta^{\circ}_{q,n,m} - \Delta\varepsilon I_m \tag{B.5}$$

where, at 25°C and 1 bar:

$$\Delta z^2 \;=\; (mz_{\mathrm{M}} - qz_{\mathrm{L}} - n)^2 + n - mz_{\mathrm{M}}^2 - qz_{\mathrm{L}}^2 \tag{B.6}$$

$$D \;=\; \frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \tag{B.7}$$

$$\Delta\varepsilon \;=\; \varepsilon_{(q,n,m,\mathrm{N\ or\ X})} + n\varepsilon_{(\mathrm{H,X})} - q\varepsilon_{(\mathrm{N,L})} - m\varepsilon_{(\mathrm{M,X})} \tag{B.8}$$

Here $(mz_{\mathrm{M}} - qz_{\mathrm{L}} - n)$, z_{M} and z_{L} are the charges of the complex $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$, the metal ion M and the ligand L, respectively.

Equilibria involving $\mathrm{H_2O(l)}$ as a reactant or product require a correction for the activity of water, $a_{\mathrm{H_2O}}$. The activity of water in an electrolyte mixture can be calculated as

$$\log_{10} a_{\mathrm{H_2O}} \;=\; \frac{-\Phi \sum_k m_k}{\ln(10) \times 55.51} \tag{B.9}$$

where Φ is the osmotic coefficient of the mixture 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 in dominant concentration, Eq. (B.9) 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 $I_m \approx m_{\mathrm{NX}}$, Eq. (B.9) becomes

$$\log_{10} a_{\mathrm{H_2O}} \;=\; \frac{-2m_{\mathrm{NX}}\Phi}{\ln(10) \times 55.51}. \tag{B.10}$$

Values of osmotic coefficients for single electrolytes have been compiled by various authors, *e.g.*, Robinson and Stokes [59ROB/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 $\mathrm{N}_{\nu_+}\mathrm{X}_{\nu_-}$ of a concentration much larger than those of the reacting ions, the osmotic coefficient can be calculated according to Eq. (B.11) (*cf.* Eqs. (23-39), (23-40) and (A4-2) in [61LEW/RAN]).

$$\begin{aligned} 1 - \Phi \;=\; & \frac{A\ln(10)|z_+z_-|}{I_m(Ba_j)^3}\left[1 + Ba_j\sqrt{I_m} - 2\log_{10}(1 + Ba_j\sqrt{I_m}) - \frac{1}{1 + Ba_j\sqrt{I_m}}\right] \\ & - \ln(10)\,\varepsilon_{(\mathrm{N,X})} m_{\mathrm{NX}}\left(\frac{\nu_+\nu_-}{\nu_+ + \nu_-}\right) \end{aligned} \tag{B.11}$$

were ν_+ and ν_- are the number of cations and anions in the salt formula ($\nu_+ z_+ = \nu_- z_-$), and in this case

$$I_m \;=\; \frac{1}{2}|z_+z_-|m_{\mathrm{NX}}(\nu_+ + \nu_-)$$

The activity of water is obtained by inserting Eq. (B.11) into Eq. (B.10). It should be mentioned that in mixed electrolytes with several components at high concentrations, it is necessary to use Pitzer's equation to calculate the activity of water. On the other hand, a_{H_2O} is near constant (and equal to 1) 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.* [92GRE/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 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.11) are listed in Table B.1 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.1 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. [74HEL/KIR2, 79BRA/PIT, 81HEL/KIR, 84ANA/ATK, 90ARC/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 $1.5\,\mathrm{kg}^{1/2} \cdot \mathrm{mol}^{-1/2}$ 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.1.

- The value of Ba_j is kept constant at $1.5\,\mathrm{kg}^{1/2} \cdot \mathrm{mol}^{-1/2}$. Due the variation of B with temperature, *cf.* Table B.1, this implies a temperature dependence for ion size parameters. Assuming that ion sizes are 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).

Table B.1: 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 $(\mathrm{kg \cdot mol^{-1}})^{\frac{1}{2}}$	$B \times 10^{-10}$ $(\mathrm{kg^{\frac{1}{2}} \cdot mol^{-\frac{1}{2}} \cdot m^{-1}})$
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

- 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.1. For example, in the aqueous ionic model of Helgeson *et al.* [88TAN/HEL, 88SHO/HEL, 89SHO/HEL, 89SHO/HEL2] ionic sizes follow the relation: $a_j(T) = a_j(298.15\ \mathrm{K}, 1\ \mathrm{bar}) + |z_j| g(T,p)$ [90OEL/HEL], where $g(T,p)$ is a temperature and pressure function which is tabulated in [88TAN/HEL, 92SHO/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 $Ba_j = 1.5\,\mathrm{kg}^{1/2} \cdot \mathrm{mol}^{-1/2}$ is the simplest one and is recommended by this review.

The variation of $\varepsilon_{(j,k,I_m)}$ with temperature is discussed by Lewis, Randall, Pitzer and Brewer [61LEW/RAN], Millero [79MIL], Helgeson *et al.* [81HEL/KIR, 90OEL/HEL], Giffaut *et al.* [93GIF/VIT2] and Grenthe and Plyasunov [94GRE/PLY]. The absolute values for the reported ion interaction parameters differ in these studies due to the fact that the Debye-Hückel term used by these authors is not exactly the

same. Nevertheless, common to all these studies is the fact that values of $(\partial\varepsilon/\partial T)_p$ are usually $\leq 0.005\,\mathrm{kg\cdot mol^{-1}\cdot K^{-1}}$ 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 on solubility calculations at $t \neq 25°$, studies on the variation of $\varepsilon_{(j,k,I_m)}$-values with temperature should be undertaken.

B.1.3. Estimation of ion interaction coefficients

B.1.3.1. Estimation from mean activity coefficient data

Example B.1:

The ion interaction coefficient $\varepsilon_{(\mathrm{H^+,Cl^-})}$ can be obtained from published values of $\gamma_{\pm,\mathrm{HCl}}$ *vs.* m_{HCl}.

$$\begin{aligned} 2\log_{10}\gamma_{\pm,\mathrm{HCl}} &= \log_{10}\gamma_{+,\mathrm{H^+}} + \log_{10}\gamma_{-,\mathrm{Cl^-}} \\ &= -D + \varepsilon_{(\mathrm{H^+,Cl^-})}m_{\mathrm{Cl^-}} - D + \varepsilon_{(\mathrm{Cl^-,H^+})}m_{\mathrm{H^+}} \\ \log_{10}\gamma_{\pm,\mathrm{HCl}} &= -D + \varepsilon_{(\mathrm{H^+,Cl^-})}m_{\mathrm{HCl}} \end{aligned}$$

By plotting $\log_{10}\gamma_{\pm,\mathrm{HCl}} + D$ *vs.* m_{HCl} a straight line with the slope $\varepsilon_{(\mathrm{H^+,Cl^-})}$ 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.2 for the reaction

$$\mathrm{UO_2^{2+}} + \mathrm{Cl^-} \rightleftharpoons \mathrm{UO_2Cl^+}. \tag{B.12}$$

The following formula is deduced from Eq. (B.5) for the extrapolation to $I = 0$:

$$\log_{10}\beta_1 + 4D = \log_{10}\beta_1^\circ - \Delta\varepsilon I_m \tag{B.13}$$

The linear regression is done as described in Appendix C. The following results are obtained:

$$\begin{aligned} \log_{10}\beta_1^\circ &= 0.170 \pm 0.021 \\ \Delta\varepsilon(\mathrm{B.12}) &= -(0.248 \pm 0.022)\,\mathrm{kg\cdot mol^{-1}} \end{aligned}$$

The experimental data are depicted in Figure B.1, where the dashed area represents the uncertainty range that is obtained by using the results in $\log_{10}\beta_1^\circ$ and $\Delta\varepsilon$ and correcting back to $I \neq 0$.

Example B.3:

When using the specific ion interaction theory, the relationship between the redox potential of the couple $\mathrm{UO_2^{2+}/U^{4+}}$ in a medium of ionic strength I_m and the corresponding quantity at $I = 0$ should be calculated in the following way. The reaction

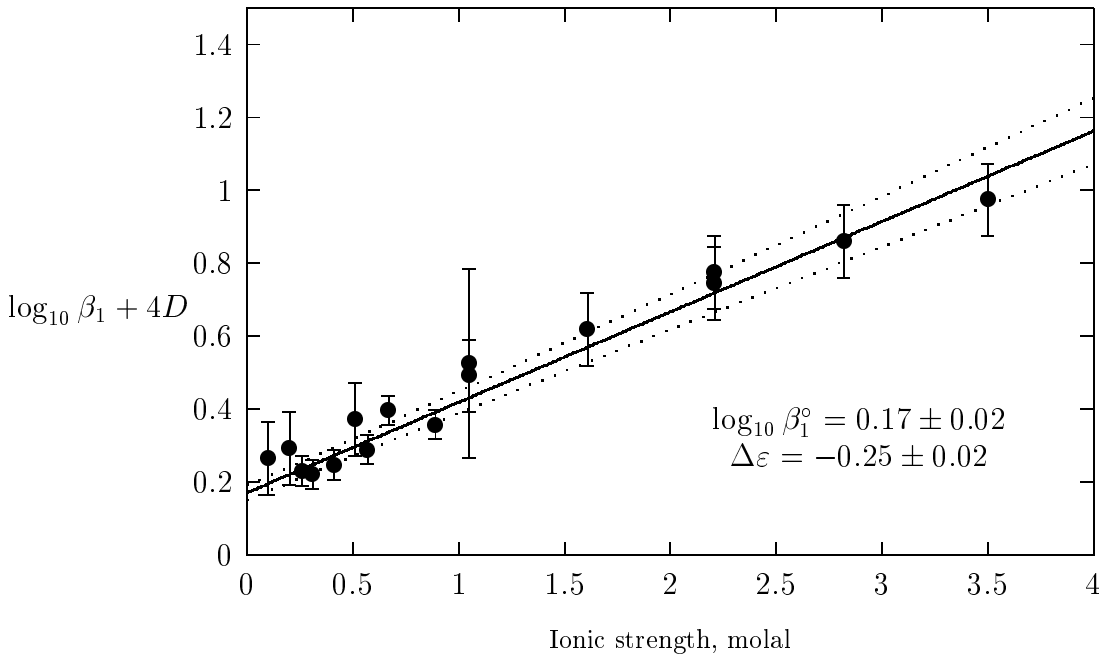
Table B.2: The preparation of the experimental equilibrium constants for the extrapolation to $I = 0$ with the specific ion interaction method at 25°C and 1 bar, according to Reaction (B.12). The linear regression of this set of data is shown in Figure B.1.

I_m	$\log_{10}\beta_1(\text{exp})^{(a)}$	$\log_{10}\beta_{1,m}^{(b)}$	$\log_{10}\beta_{1,m} + 4D$
0.1	-0.17 ± 0.10	-0.174	0.264 ± 0.100
0.2	-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	-0.021	0.860 ± 0.100
3.5	0.04 ± 0.10	-0.021	0.974 ± 0.100

(a) Equilibrium constants for Reaction (B.12) with assigned uncertainties, corrected to 25°C where necessary.

(b) Equilibrium constants corrected from molarity to molarity units, as described in Section II.2.

Figure B.1: Plot of $\log_{10}\beta_1+4D$ *vs.* I_m for Reaction (B.12), $UO_2^{2+}+Cl^- \rightleftharpoons UO_2Cl^+$ 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.



in the galvanic cell

$$\mathrm{Pt} \mid \mathrm{H_2(g)} \mid \mathrm{H^+} \parallel \mathrm{UO_2^{2+}, U^{4+}} \mid \mathrm{Pt}$$

is

$$\mathrm{UO_2^{2+} + H_2(g) + 2\,H^+ \rightleftharpoons U^{4+} + 2\,H_2O(l)}. \tag{B.14}$$

For this reaction

$$\begin{aligned}
\log_{10} K^\circ &= \log_{10}\left(\frac{a_{\mathrm{U^{4+}}} \times a^2_{\mathrm{H_2O}}}{a_{\mathrm{UO_2^{2+}}} \times a^2_{\mathrm{H^+}} \times f_{\mathrm{H_2}}}\right), \\
\log_{10} K^\circ &= \log_{10} K + \log_{10}\gamma_{\mathrm{U^{4+}}} - \log_{10}\gamma_{\mathrm{UO_2^{2+}}} - 2\log_{10}\gamma_{\mathrm{H^+}} \\
&\quad - \log_{10}\gamma_{f,\mathrm{H_2}} + 2\log_{10} a_{\mathrm{H_2O}},
\end{aligned}$$

$f_{\mathrm{H_2}} \approx p_{\mathrm{H_2}}$ at reasonably low partial pressure of $H_2(g)$, $a_{\mathrm{H_2O}} \approx 1$, and

$$\begin{aligned}
\log_{10}\gamma_{\mathrm{U^{4+}}} &= -16D + \varepsilon_{(\mathrm{U^{4+}},\mathrm{ClO_4^-})} m_{\mathrm{ClO_4^-}} \\
\log_{10}\gamma_{\mathrm{UO_2^{2+}}} &= -4D + \varepsilon_{(\mathrm{UO_2^{2+}},\mathrm{ClO_4^-})} m_{\mathrm{ClO_4^-}} \\
\log_{10}\gamma_{\mathrm{H^+}} &= -D + \varepsilon_{(\mathrm{H^+},\mathrm{ClO_4^-})} m_{\mathrm{ClO_4^-}}\,.
\end{aligned}$$

Hence,

$$\begin{aligned}\log_{10} K^\circ &= \log_{10} K - 10D \\ &\quad + \left(\varepsilon_{(U^{4+},ClO_4^-)} - \varepsilon_{(UO_2^{2+},ClO_4^-)} - 2\varepsilon_{(H^+,ClO_4^-)}\right) m_{ClO_4^-} \,. \end{aligned} \tag{B.15}$$

The relationship between the equilibrium constant and the redox potential is

$$\ln K = \frac{nF}{RT} E \tag{B.16}$$

$$\ln K^\circ = \frac{nF}{RT} E^\circ . \tag{B.17}$$

E 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.15), (B.16) and (B.17) and rearranging them leads to Eq. (B.18).

$$E - 10D\left(\frac{RT\ln(10)}{nF}\right) = E^\circ - \Delta\varepsilon m_{ClO_4^-}\left(\frac{RT\ln(10)}{nF}\right) \tag{B.18}$$

For $n = 2$ in the present example and $T = 298.15\,\mathrm{K}$, Eq. (B.18) becomes

$$E[\mathrm{mV}] - 295.8D = E^\circ[\mathrm{mV}] - 29.58\Delta\varepsilon m_{ClO_4^-}$$

where

$$\Delta\varepsilon = \left(\varepsilon_{(U^{4+},ClO_4^-)} - \varepsilon_{(UO_2^{2+},ClO_4^-)} - 2\varepsilon_{(H^+,ClO_4^-)}\right).$$

In general however, 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 [92GRE/FUG]. In that case, the H^+ appearing in the reduction reaction might already be in standard conditions. For example, experimental data are available on the formal potentials for reactions

$$UO_2^{2+} + 4\,H^+ + 2\,e^- \rightleftharpoons U^{4+} + 2\,H_2O(l) \tag{B.19}$$

and

$$UO_2^{2+} + e^- \rightleftharpoons UO_2^+ \tag{B.20}$$

While reaction (B.19) corresponds to (B.14), reaction (B.20) is equivalent to

$$UO_2^{2+} + \frac{1}{2}H_2(g) \rightleftharpoons UO_2^+ + H^+ \tag{B.21}$$

The cations in reaction (B.14) represent aqueous species in the ionic media used during the experiments. However, in reaction (B.21) 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.20).

B.1.4. On the magnitude of ion interaction coefficients

Ciavatta [80CIA] made a compilation of ion interaction coefficients for a large number of electrolytes. Similar data for complexations of various kinds were reported by Spahiu [83SPA] and Ferri, Grenthe and Salvatore [83FER/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 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.* [92GRE/FUG] proposed that it is possible to estimate, with an error of at most ± 0.1 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 ± 0.1 in $\Delta\varepsilon$ in most cases, based on comparison with $\Delta\varepsilon$ values of various reactions of the same charge type.

Since there are no interaction coefficient data for americium species, using the arguments presented in the previous paragraph, this review estimates the following interaction coefficients at 25°C and 1 bar,

$$\begin{aligned}
\varepsilon_{(\mathrm{Am^{3+}},\mathrm{ClO_4^-})} &\approx \varepsilon_{(\mathrm{Nd^{3+}},\mathrm{ClO_4^-})} &&= (0.49 \pm 0.03)\,\mathrm{kg \cdot mol^{-1}} \\
\varepsilon_{(\mathrm{AmOH^{2+}},\mathrm{ClO_4^-})} &\approx \varepsilon_{(\mathrm{YHCO_3^{2+}},\mathrm{ClO_4^-})} &&= (0.39 \pm 0.04)\,\mathrm{kg \cdot mol^{-1}} \\
\varepsilon_{(\mathrm{Am(OH)_2^+},\mathrm{ClO_4^-})} &\approx \varepsilon_{(\mathrm{YCO_3^+},\mathrm{ClO_4^-})} &&= (0.17 \pm 0.04)\,\mathrm{kg \cdot mol^{-1}}
\end{aligned}$$

Estimates of ion interaction coefficients for other americium complexes were also made from ions of the same charge, *i.e.*

$$\begin{aligned}
\varepsilon_{(\mathrm{AmOH^{2+}},\mathrm{ClO_4^-})} &\approx \varepsilon_{(\mathrm{AmF^{2+}},\mathrm{ClO_4^-})} &&\approx \varepsilon_{(\mathrm{AmCl^{2+}},\mathrm{ClO_4^-})} &&\approx \varepsilon_{(\mathrm{AmN_3^{2+}},\mathrm{ClO_4^-})} \\
&\approx \varepsilon_{(\mathrm{AmNO_2^{2+}},\mathrm{ClO_4^-})} &&\approx \varepsilon_{(\mathrm{AmNO_3^{2+}},\mathrm{ClO_4^-})} &&\approx \varepsilon_{(\mathrm{AmH_2PO_4^{2+}},\mathrm{ClO_4^-})} \\
&\approx \varepsilon_{(\mathrm{AmSCN^{2+}},\mathrm{ClO_4^-})} \\
\varepsilon_{(\mathrm{Am(OH)_2^+},\mathrm{ClO_4^-})} &\approx \varepsilon_{(\mathrm{AmF_2^+},\mathrm{ClO_4^-})} &&\approx \varepsilon_{(\mathrm{AmCO_3^+},\mathrm{ClO_4^-})}
\end{aligned}$$

etc. Similarly, for negatively charged aqueous complexes of americium this review estimates:

$$\begin{aligned}
\varepsilon_{(\mathrm{Am(CO_3)_2^-},\mathrm{Na^+})} &\approx \varepsilon_{(\mathrm{Am(SO_4)_2^-},\mathrm{Na^+})} &&= -(0.05 \pm 0.05)\,\mathrm{kg \cdot mol^{-1}} \\
\varepsilon_{(\mathrm{Am(CO_3)_3^{3-}},\mathrm{Na^+})} &= &&-(0.15 \pm 0.05)\,\mathrm{kg \cdot mol^{-1}}
\end{aligned}$$

Ciavatta [90CIA] has proposed an alternative method to estimate values of ε for a first or second complex, ML or ML_2, in an ionic media NX, according to the following relationships,

$$\varepsilon_{(ML,\ N\,\mathrm{or}\,X)} \approx (\varepsilon_{(M,X)} + \varepsilon_{(L,N)})/2 \tag{B.22}$$

$$\varepsilon_{(ML_2,\ N\,\mathrm{or}\,X)} \approx (\varepsilon_{(M,X)} + 2\varepsilon_{(L,N)})/3 \tag{B.23}$$

Ciavatta obtained [90CIA] an average deviation of $\pm 0.05\,\mathrm{kg{\cdot}mol^{-1}}$ between ε-estimates according to Eqs. (B.22) and (B.23) and the ε-values at 25°C obtained from ionic strength dependency of equilibrium constants.

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 [80CIA] 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.3. 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 $\varepsilon_{(M^{n+},\mathrm{ClO}_4^-)}$ as a substitute for $\varepsilon_{(M^{n+},\mathrm{Cl}^-)}$ and $\varepsilon_{(M^{n+},\mathrm{NO}_3^-)}$. 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 negatively charged complexes and the cation of the ionic medium. An example is the stabilisation of the complex ion $UO_2(CO_3)_3^{5-}$ at high ionic strength, see for example Section V.7.1.2.1.d (page 322) in the uranium review [92GRE/FUG].

B.3. Tables of ion interaction coefficients

Tables B.3 through B.5 contain the selected specific ion interaction coefficients used in this review, according to the specific ion interaction theory described. Table B.3 contains cation interaction coefficients with Cl^-, ClO_4^- and NO_3^-, Table B.4 anion interaction coefficients with Li^+, with Na^+ or NH_4^+ and with K^+. The coefficients have the units of $\mathrm{kg \cdot mol^{-1}}$ (m) and are valid for 298.15 K and 1 bar. The species are ordered by charge and appear, within each charge class, in standard order of arrangement, *cf.* Section II.1.8.

In some cases, the ionic interaction can be better described by assuming ion interaction coefficients as functions of the ionic strength rather than as constants. Ciavatta [80CIA] proposed the use of Eq. (B.24) for cases where the uncertainties in Tables B.3 and B.4 are $\pm 0.03\,\mathrm{kg \cdot mol^{-1}}$ or greater.

$$\varepsilon \;=\; \varepsilon_1 + \varepsilon_2 \log_{10} I_m$$

For these cases, and when the uncertainty can be improved with respect to the use of a constant value of ε, the values ε_1 and ε_2 given in Table B.5 should be used.

It should be noted that ion interaction coefficients tabulated in Tables B.3 through B.5 may also involve ion pairing effects, as described in Section B.3. In direct com-

parisons of ion interaction coefficients, or when estimates are made by analogy, this aspect must be taken into account.

Table B.3: Ion interaction coefficients $\varepsilon_{j,k}$ $(kg \cdot mol^{-1})$ at 25°C and 1 bar for cations j with $k = Cl^-$, ClO_4^- and NO_3^-, taken from Ciavatta [80CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level, most of them were estimated by Ciavatta [88CIA]. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B.5. As discussed in Section B.2, care should be taken when using the coefficients $\varepsilon_{(M^{n+},Cl^-)}$ and $\varepsilon_{(M^{n+},NO_3^-)}$ reported by Ciavatta [80CIA], which were evaluated without taking chloride and nitrate complexation into account.

j $k \rightarrow$ ↓	Cl^-	ClO_4^-	NO_3^-
H^+	0.12 ± 0.01	0.14 ± 0.02	0.07 ± 0.01
NH_4^+	-0.01 ± 0.01	$-0.08 \pm 0.04^{\dagger}$	$-0.06 \pm 0.03^{\dagger}$
H_2gly^+	-0.06 ± 0.02		
Tl^+		$-0.21 \pm 0.06^{\dagger}$	
$ZnHCO_3^+$	$0.2^{(h)}$		
$CdCl^+$		0.25 ± 0.02	
CdI^+		0.27 ± 0.02	
$CdSCN^+$		0.31 ± 0.02	
$HgCl^+$		0.19 ± 0.02	
Cu^+		0.11 ± 0.01	
Ag^+		0.00 ± 0.01	$-0.12 \pm 0.05^{\dagger}$
YCO_3^+		$0.17 \pm 0.04^{(d)}$	
UO_2^+		$0.26 \pm 0.03^{(c)}$	
UO_2OH^+		$-0.06 \pm 3.7^{(c)}$	$0.51 \pm 1.4^{(c)}$
$(UO_2)_3(OH)_5^+$	$0.81 \pm 0.17^{(c)}$	$0.45 \pm 0.15^{(c)}$	$0.41 \pm 0.22^{(c)}$
UF_3^+	$0.1 \pm 0.1^{(f)}$	$0.1 \pm 0.1^{(f)}$	
UO_2F^+	$0.04 \pm 0.07^{(b)}$	$0.29 \pm 0.05^{(c)}$	
UO_2Cl^+		$0.33 \pm 0.04^{(c)}$	
$UO_2ClO_3^+$		$0.33 \pm 0.04^{(f)}$	
UO_2Br^+		$0.24 \pm 0.04^{(f)}$	
$UO_2BrO_3^+$		$0.33 \pm 0.04^{(f)}$	
$UO_2IO_3^+$		$0.33 \pm 0.04^{(f)}$	
$UO_2N_3^+$		$0.3 \pm 0.1^{(f)}$	
$UO_2NO_3^+$		$0.33 \pm 0.04^{(f)}$	
UO_2SCN^+		$0.22 \pm 0.04^{(f)}$	
NpO_2^+		$0.25 \pm 0.05^{(b)}$	
PuO_2^+		$0.17 \pm 0.05^{(b)}$	
$Am(OH)_2^+$		$0.17 \pm 0.04^{(j)}$	
AmF_2^+		$0.17 \pm 0.04^{(j)}$	

Table B.3 (continued)

j $k \rightarrow$ $\downarrow$	Cl^-	ClO_4^-	NO_3^-
$AmSO_4^+$		$0.22 \pm 0.08^{(k)}$	
$AmCO_3^+$		$0.17 \pm 0.04^{(j)}$	
$AlOH^{2+}$	$0.09^{(a)}$	$0.31^{(a)}$	
$Al_2CO_3(OH)_2^{2+}$	$0.26^{(a)}$		
Pb^{2+}		0.15 ± 0.02	$-0.20 \pm 0.12^{\dagger}$
Zn^{2+}		0.33 ± 0.03	0.16 ± 0.02
$ZnCO_3^{2+}$	$0.35 \pm 0.05^{(h)}$		
Cd^{2+}			0.09 ± 0.02
Hg^{2+}		0.34 ± 0.03	$-0.1 \pm 0.1^{\dagger}$
Hg_2^{2+}		0.09 ± 0.02	$-0.2 \pm 0.1^{\dagger}$
Cu^{2+}	0.08 ± 0.01	0.32 ± 0.02	0.11 ± 0.01
Ni^{2+}	0.17 ± 0.02		
Co^{2+}	0.16 ± 0.02	0.34 ± 0.03	0.14 ± 0.01
$FeOH^{2+}$		$0.38^{(d)}$	
$FeSCN^{2+}$		$0.45^{(d)}$	
Mn^{2+}	0.13 ± 0.01		
$YHCO_3^{2+}$		$0.39 \pm 0.04^{(d)}$	
UO_2^{2+}	$0.21 \pm 0.02^{(i)}$	0.46 ± 0.03	$0.24 \pm 0.03^{(i)}$
$(UO_2)_2(OH)_2^{2+}$	$0.69 \pm 0.07^{(c)}$	$0.57 \pm 0.07^{(c)}$	$0.49 \pm 0.09^{(c)}$
$(UO_2)_3(OH)_4^{2+}$	$0.50 \pm 0.18^{(c)}$	$0.89 \pm 0.23^{(c)}$	$0.72 \pm 1.0^{(c)}$
UF_2^{2+}		$0.3 \pm 0.1^{(f)}$	
USO_4^{2+}		$0.3 \pm 0.1^{(f)}$	
$U(NO_3)_2^{2+}$		$0.49 \pm 0.14^{(g)}$	
$AmOH^{2+}$		$0.39 \pm 0.04^{(j)}$	
AmF^{2+}		$0.39 \pm 0.04^{(j)}$	
$AmCl^{2+}$		$0.39 \pm 0.04^{(j)}$	
AmN_3^{2+}		$0.39 \pm 0.04^{(j)}$	
$AmNO_2^{2+}$		$0.39 \pm 0.04^{(j)}$	
$AmNO_3^{2+}$		$0.39 \pm 0.04^{(j)}$	
$AmH_2PO_4^{2+}$		$0.39 \pm 0.04^{(j)}$	
$AmSCN^{2+}$		$0.39 \pm 0.04^{(j)}$	
Mg^{2+}	0.19 ± 0.02	0.33 ± 0.03	0.17 ± 0.01
Ca^{2+}	0.14 ± 0.01	0.27 ± 0.03	0.02 ± 0.01
Ba^{2+}	0.07 ± 0.01	0.15 ± 0.02	-0.28 ± 0.03

Table B.3 (continued)

j $k \rightarrow$ $\downarrow$	Cl^-	ClO_4^-	NO_3^-
Al^{3+}	0.33 ± 0.02		
Fe^{3+}		0.56 ± 0.03	0.42 ± 0.08
Cr^{3+}	0.30 ± 0.03		0.27 ± 0.02
La^{3+}	0.22 ± 0.02	0.47 ± 0.03	
$La^{3+} \rightarrow Lu^{3+}$		$0.47 \rightarrow 0.52^{(d)}$	
UOH^{3+}		$0.48 \pm 0.08^{(g)}$	
UF^{3+}		$0.48 \pm 0.08^{(f)}$	
UCl^{3+}		$0.59 \pm 0.10^{(g)}$	
UBr^{3+}		$0.52 \pm 0.10^{(f)}$	
UI^{3+}		$0.55 \pm 0.10^{(f)}$	
UNO_3^{3+}		$0.62 \pm 0.08^{(g)}$	
Am^{3+}		$0.49 \pm 0.03^{(j)}$	
Be_2OH^{3+}		$0.50 \pm 0.05^{(e)}$	
$Be_3(OH)_3^{3+}$	$0.30 \pm 0.05^{(e)}$	$0.51 \pm 0.05^{(e)}$	$0.29 \pm 0.05^{(e)}$
$Al_3CO_3(OH)_4^{4+}$	$0.41^{(a)}$		
$Fe_2(OH)_2^{4+}$		$0.82^{(d)}$	
$Y_2CO_3^{4+}$		$0.80 \pm 0.04^{(d)}$	
Pu^{4+}		$1.03 \pm 0.05^{(b)}$	
Np^{4+}		$0.82 \pm 0.05^{(b)}$	
U^{4+}		$0.76 \pm 0.06^{(f)}$	
Th^{4+}	0.25 ± 0.03		0.11 ± 0.02
$Al_3(OH)_4^{5+}$	$0.66^{(a)}$	$1.30^{(a)}$	

Table B.3 (continued)

Footnotes:

(a) Taken from Hedlund [88HED].

(b) Taken from Riglet, Robouch and Vitorge [89RIG/ROB], where the following assumptions were made : $\varepsilon_{(Np^{3+},ClO_4^-)} \approx \varepsilon_{(Pu^{3+},ClO_4^-)} = 0.49\,kg \cdot mol^{-1}$ as for other (M^{3+}, ClO_4^-) interactions, and $\varepsilon_{(NpO_2^{2+},ClO_4^-)} \approx \varepsilon_{(PuO_2^{2+},ClO_4^-)} \approx \varepsilon_{(UO_2^{2+},ClO_4^-)} = 0.46\,kg \cdot mol^{-1}$.

(c) Evaluated in NEA-TDB review on uranium thermodynamics [92GRE/FUG], using $\varepsilon_{(UO_2^{2+},X)} = (0.46 \pm 0.03)\,kg \cdot mol^{-1}$, where $X = Cl^-$, ClO_4^- and NO_3^-, *cf.* Section B.2.

(d) Taken from Spahiu [83SPA].

(e) Taken from Bruno [86BRU], where the following assumptions were made: $\varepsilon_{(Be^{2+},ClO_4^-)} = 0.30\,kg \cdot mol^{-1}$ as for other $\varepsilon_{(M^{2+},ClO_4^-)}$, $\varepsilon_{(Be^{2+},Cl^-)} = 0.17\,kg \cdot mol^{-1}$ as for other $\varepsilon_{(M^{2+},Cl^-)}$, and $\varepsilon_{(Be^{2+},NO_3^-)} = 0.17\,kg \cdot mol^{-1}$ as for other $\varepsilon_{(M^{2+},NO_3^-)}$.

(f) Estimated in NEA-TDB review on uranium thermodynamics [92GRE/FUG].

(g) Evaluated in NEA-TDB review on uranium thermodynamics [92GRE/FUG] using $\varepsilon_{(U^{4+},ClO_4^-)} = (0.76 \pm 0.06)\,kg \cdot mol^{-1}$.

(h) Taken from Ferri *et al.* [85FER/GRE].

(i) It is recalled that these coefficients were not used in the NEA-TDB review on uranium thermodynamics [92GRE/FUG] because they were evaluated by Ciavatta [80CIA] without taking chloride and nitrate complexation into account. Instead, Grenthe *et al.* used $\varepsilon_{(UO_2^{2+},X)} = (0.46 \pm 0.03)\,kg \cdot mol^{-1}$, for $X = Cl^-$, ClO_4^- and NO_3^-.

(j) Estimated in this review (*p.*322).

(k) Evaluated in this review (*p.*130).

Table B.4: Ion interaction coefficients $\varepsilon_{j,k}$ ($\mathrm{kg \cdot mol^{-1}}$) at 25°C and 1 bar for anions j with $k = \mathrm{Li^+}, \mathrm{Na^+}$ and $\mathrm{K^+}$, taken from Ciavatta [80CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level, most of them were estimated by Ciavatta [88CIA]. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B.5.

j $k \rightarrow$ ↓	Li^+	Na^+	K^+
OH^-	$-0.02 \pm 0.03^{\dagger}$	0.04 ± 0.01	0.09 ± 0.01
F^-		$0.02 \pm 0.02^{(a)}$	0.03 ± 0.02
HF_2^-		$-0.11 \pm 0.06^{(a)}$	
Cl^-	0.10 ± 0.01	0.03 ± 0.01	0.00 ± 0.01
ClO_3^-		-0.01 ± 0.02	
ClO_4^-	0.15 ± 0.01	0.01 ± 0.01	
Br^-	0.13 ± 0.02	0.05 ± 0.01	0.01 ± 0.02
BrO_3^-		-0.06 ± 0.02	
I^-	0.16 ± 0.01	0.08 ± 0.02	0.02 ± 0.01
IO_3^-		$-0.06 \pm 0.02^{(b)}$	
HSO_4^-		-0.01 ± 0.02	
N_3^-		$0.0 \pm 0.1^{(b)}$	
NO_2^-	$0.06 \pm 0.04^{\dagger}$	0.00 ± 0.02	-0.04 ± 0.02
NO_3^-	0.08 ± 0.01	$-0.04 \pm 0.03^{\dagger}$	$-0.11 \pm 0.04^{\dagger}$
$H_2PO_4^-$		$-0.08 \pm 0.04^{\dagger}$	$-0.14 \pm 0.04^{\dagger}$
HCO_3^-		$-0.00 \pm 0.02^{(c)}$	
SCN^-		0.05 ± 0.01	-0.01 ± 0.01
$HCOO^-$		0.03 ± 0.01	
CH_3COO^-	0.05 ± 0.01	0.08 ± 0.01	0.09 ± 0.01
$SiO(OH)_3^-$		$-0.08 \pm 0.03^{(a)}$	
$Si_2O_2(OH)_5^-$		$-0.08 \pm 0.04^{(b)}$	
$B(OH)_4^-$		$-0.07 \pm 0.05^{\dagger}$	
$UO_2(OH)_3^-$		$-0.09 \pm 0.05^{(b)}$	
$UO_2F_3^-$		$0.00 \pm 0.05^{(b)}$	
$UO_2(N_3)_3^-$		$0.0 \pm 0.1^{(b)}$	
$(UO_2)_2CO_3(OH)_3^-$		$0.00 \pm 0.05^{(b,d)}$	
$Am(SO_4)_2^-$		$-0.05 \pm 0.05^{(e)}$	
$Am(CO_3)_2^-$		$-0.05 \pm 0.05^{(e)}$	
SO_3^{2-}		$-0.08 \pm 0.05^{\dagger}$	
SO_4^{2-}	$-0.03 \pm 0.04^{\dagger}$	$-0.12 \pm 0.06^{\dagger}$	-0.06 ± 0.02

Table B.4 (continued)

j $k \rightarrow$ $\downarrow$	Li^+	Na^+	K^+
$S_2O_3^{2-}$		$-0.08 \pm 0.05^{\dagger}$	
HPO_4^{2-}		$-0.15 \pm 0.06^{\dagger}$	$-0.10 \pm 0.06^{\dagger}$
CO_3^{2-}		$-0.08 \pm 0.03^{(c)}$	0.02 ± 0.01
$SiO_2(OH)_2^{2-}$		$-0.10 \pm 0.07^{(a)}$	
$Si_2O_3(OH)_4^{2-}$		$-0.15 \pm 0.06^{(b)}$	
CrO_4^{2-}		$-0.06 \pm 0.04^{\dagger}$	$-0.08 \pm 0.04^{\dagger}$
$UO_2F_4^{2-}$		$-0.08 \pm 0.06^{(b)}$	
$UO_2(SO_4)_2^{2-}$		$-0.12 \pm 0.06^{(b)}$	
$UO_2(N_3)_4^{2-}$		$-0.1 \pm 0.1^{(b)}$	
$UO_2(CO_3)_2^{2-}$		$-0.02 \pm 0.09^{(d)}$	
PO_4^{3-}		$-0.25 \pm 0.03^{\dagger}$	-0.09 ± 0.02
$Si_3O_6(OH)_3^{3-}$		$-0.25 \pm 0.03^{(b)}$	
$Si_3O_5(OH)_5^{3-}$		$-0.25 \pm 0.03^{(b)}$	
$Si_4O_7(OH)_5^{3-}$		$-0.25 \pm 0.03^{(b)}$	
$Am(CO_3)_3^{3-}$		$-0.15 \pm 0.05^{(e)}$	
$P_2O_7^{4-}$		-0.26 ± 0.05	-0.15 ± 0.05
$Fe(CN)_6^{4-}$			-0.17 ± 0.03
$U(CO_3)_4^{4-}$		$-0.09 \pm 0.10^{(b,d)}$	
$UO_2(CO_3)_3^{4-}$		$-0.01 \pm 0.11^{(d)}$	
$UO_2(CO_3)_3^{5-}$		$-0.62 \pm 0.15^{(d)}$	
$U(CO_3)_5^{6-}$		$-0.30 \pm 0.15^{(d)}$	
$(UO_2)_3(CO_3)_6^{6-}$		$0.37 \pm 0.11^{(d)}$	

(a) Evaluated in NEA-TDB review on uranium thermodynamics [92GRE/FUG].
(b) Estimated in NEA-TDB review on uranium thermodynamics [92GRE/FUG].
(c) From [80CIA]. These values differ from those reported in the NEA-TDB uranium review [92GRE/FUG]. See the discussion in Section D.4.
(d) See the discussion in Section D.4.
(e) Estimated in this review (*p*.322).

Table B.5: Ion interaction coefficients $\varepsilon_{(1,j,k)}$ and $\varepsilon_{(2,j,k)}$ (in units of $\mathrm{kg \cdot mol^{-1}}$) for cations j with $k = \mathrm{Cl^-}$, $\mathrm{ClO_4^-}$ and $\mathrm{NO_3^-}$ (first part), and for anions j with $k = \mathrm{Li^+}$, $\mathrm{Na^+}$ and $\mathrm{K^+}$ (second part), according to the relationship $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_\mathrm{m}$. The data are from Ciavatta [80CIA] and valid at 25°C and 1 bar. The uncertainties represent the 95% confidence level, and most of them were estimated by Ciavatta [88CIA].

j $k \rightarrow$ ↓	$\mathrm{Cl^-}$		$\mathrm{ClO_4^-}$		$\mathrm{NO_3^-}$	
	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
$\mathrm{NH_4^+}$			-0.088 ± 0.002	0.095 ± 0.012	-0.075 ± 0.001	0.057 ± 0.004
$\mathrm{Ag^+}$					-0.1432 ± 0.0002	0.0971 ± 0.0009
$\mathrm{Tl^+}$			-0.18 ± 0.02	0.09 ± 0.02		
$\mathrm{Hg_2^{2+}}$					-0.2300 ± 0.0004	0.194 ± 0.002
$\mathrm{Hg^{2+}}$					-0.145 ± 0.001	0.194 ± 0.002
$\mathrm{Pb^{2+}}$					-0.329 ± 0.007	0.288 ± 0.018

j $k \rightarrow$ ↓	$\mathrm{Li^+}$		$\mathrm{Na^+}$		$\mathrm{K^+}$	
	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
$\mathrm{OH^-}$	-0.039 ± 0.002	0.072 ± 0.006				
$\mathrm{NO_2^-}$	0.02 ± 0.01	0.11 ± 0.01				
$\mathrm{NO_3^-}$			-0.049 ± 0.001	0.044 ± 0.002	-0.131 ± 0.002	0.082 ± 0.006
$\mathrm{B(OH)_4^-}$			-0.092 ± 0.002	0.103 ± 0.005		
$\mathrm{H_2PO_4^-}$			-0.109 ± 0.001	0.095 ± 0.003	-0.1473 ± 0.0008	0.121 ± 0.004
$\mathrm{SO_3^{2-}}$			-0.125 ± 0.008	0.106 ± 0.009		
$\mathrm{SO_4^{2-}}$	-0.068 ± 0.003	0.093 ± 0.007	-0.184 ± 0.002	0.139 ± 0.006		
$\mathrm{S_2O_3^{2-}}$			-0.125 ± 0.008	0.106 ± 0.009		
$\mathrm{HPO_4^{2-}}$			-0.19 ± 0.01	0.11 ± 0.03	-0.152 ± 0.007	0.123 ± 0.016
$\mathrm{CrO_4^{2-}}$			-0.090 ± 0.005	0.07 ± 0.01	-0.123 ± 0.003	0.106 ± 0.007
$\mathrm{PO_4^{3-}}$			-0.29 ± 0.02	0.10 ± 0.01		

Appendix C

Assigned uncertainties†

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, 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.1. 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 the selected value is based on allows the use of the "root mean square" [82TAY] deviation of the data points X_i to describe the standard deviation s_X associated with

† This Appendix contains essentially the text written by Wanner [94WAN] which was also printed in the uranium NEA–TDB review as Appendix C [92GRE/FUG]. 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 after some minor revision.

the average $\overline{X}$:

$$s_X = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(X_i - \overline{X})^2} \; . \tag{C.1}$$

The standard deviation s_X is thus calculated from the dispersion of the equally weighted data points X_i around the average $\overline{X}$, and the probability is 95% that an X_i is within $\overline{X} \pm 1.96\, s_X$, see Taylor [82TAY, *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.1) (but often not multiplied by 1.96), but these do not represent the quality of the reported values in absolute terms. It is thus important not to confuse the standard deviation s 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.2), assuming that the systematic errors are independent.

$$\sigma_{\overline{X}} = \sqrt{s_X^2 + \textstyle\sum_j (s_j^2)} \tag{C.2}$$

The estimation of the systematic errors s_j (which, of course, have to relate to $\overline{X}$ and be expressed in the same unit) 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 C.4.2.

More often, the determination of s_X is not possible 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.2) assuming that s_X^2 is much smaller than $\sum_j (s_j^2)$, which is usually the case anyway.

C.2. 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.1. The weighted mean $\overline{X}$ and its uncertainty $\sigma_{\overline{X}}$ are then calculated according to Eqs. (C.3) and (C.4).

$$\overline{X} \equiv \frac{\sum_{i=1}^{N}\left(\frac{X_i}{\sigma_i^2}\right)}{\sum_{i=1}^{N}\left(\frac{1}{\sigma_i^2}\right)} \tag{C.3}$$

$$\sigma_{\overline{X}} = \sqrt{\frac{1}{\sum_{i=1}^{N}\left(\frac{1}{\sigma_i^2}\right)}} \tag{C.4}$$

Eqs. (C.3) and (C.4) 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.2.1. It can be seen from Eq. (C.4) 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.3) and (C.4) reduce to Eqs. (C.5) and (C.6).

$$\overline{X} = \frac{1}{N}\sum_{i=1}^{N} X_i \tag{C.5}$$

$$\sigma_{\overline{X}} = \frac{\sigma}{\sqrt{N}} \tag{C.6}$$

Example C.1:

Five data sources report values for the thermodynamic quantity X. The reviewer has assigned uncertainties that represent the 95% confidence level as described in Section C.1.

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.3) and (C.4), the following result is obtained:

$$\overline{X} = 25.3 \pm 0.2.$$

The calculated uncertainty $\sigma_{\overline{X}} = 0.2$ appears relatively small but is statistically correct, for the values are assumed to follow a Gaussian distribution. As a consequence of Eq. (C.4), $\sigma_{\overline{X}}$ will always come out smaller than the smallest σ_i. Assuming $\sigma_4 = 0.10$ instead of 0.25 would yield $\overline{X} = (25.0 \pm 0.1)$, and $\sigma_4 = 0.60$ would result in $\overline{X} = (25.6 \pm 0.2)$. In fact, the values $(X_i \pm \sigma_i)$ in this example are at the limit of consistency, that is, 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 alternatives 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 $\overline{X} = (25.3 \pm 0.3)$.

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 $X_A(i = 1, 4, 5) = (24.95 \pm 0.21)$ and of those in Group B $X_B(i = 2, 3) = (26.06 \pm 0.31)$, the second digit after the decimal point being carried over to avoid loss of information. The selected value is now determined as described below under "Discrepancies" (Section C.2.1), 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 $\overline{X} = (25.5 \pm 0.9)$.

iii Another explanation could be that unidentified systematic errors are associated with some values. If this seems likely to be the case, there is no reason for splitting the values up into two groups. The correct way of proceeding would be to calculate the unweighted average of all the five points and assign an uncertainty that covers the whole range of expectancy of the five values. The resulting value is then $\overline{X} = (25.45 \pm 1.05)$, which is rounded according to the rules in Section C.4.3 to $\overline{X} = (25.4 \pm 1.1)$.

C.2.1. 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 unrecognized 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.7),

$$\sigma_{\overline{X}} = \left| X_i - \overline{X} \right| + \sigma_{\max}, \tag{C.7}$$

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:

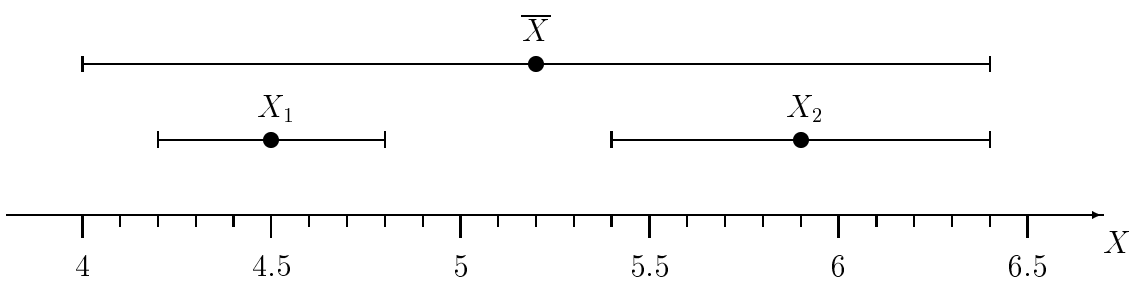
The following credible source data are given:

$$\begin{aligned} X_1 &= 4.5 \pm 0.3 \\ X_2 &= 5.9 \pm 0.5. \end{aligned}$$

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:

$$\overline{X} = 5.2 \pm 1.2.$$

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 sets of data that, statistically, belong to different parent distributions A and B. According to Eqs. (C.3) and (C.4), 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:

$$\overline{X} \;=\; 5.0 \pm 0.9.$$

C.3. Several data at different ionic strengths

The extrapolation procedure 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 is listed in the corresponding table of Appendix B.

The available source data may sometimes be sparse or may not cover a sufficient range of ionic strengths to allow a proper linear regression. In this case, the correction to $I = 0$ should be carried out according to the procedure described in Section C.4.1.

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 $I = 0$, $\overline{X}^\circ$, and $\Delta\varepsilon$. The first step is the conversion of the ionic strength from the frequently used molar ($\mathrm{mol \cdot dm^{-3}}$, M) to the molal ($\mathrm{mol \cdot kg^{-1}}$, 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 C.1. A large number of commercial and public domain computer programs and routines exist for weighted linear regressions. The subroutine published by Bevington [69BEV, *pp.*104-105] has been used for the calculations in the examples of this appendix. Eqs. (C.8) through (C.12) present the equations that are used for the calculation of the intercept $\overline{X}^\circ$ and the slope $-\Delta\varepsilon$:

$$\overline{X}^\circ \;=\; \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2}\right) \tag{C.8}$$

$$-\Delta\varepsilon \;=\; \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2}\right) \tag{C.9}$$

$$\sigma_{\overline{X}^\circ} \;=\; \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}} \tag{C.10}$$

$$\sigma_{\Delta\varepsilon} \;=\; \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}}\,, \tag{C.11}$$

where

$$\Delta \;=\; \sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2} - \left(\sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\right)^2. \tag{C.12}$$

In this way, the uncertainties σ_i are not only used for the weighting of the data in Eqs. (C.8) and (C.9), but also for the calculation of the uncertainties $\sigma_{\overline{X}^\circ}$ and $\sigma_{\Delta\varepsilon}$ in Eqs. (C.10) and (C.11). If the σ_i represent the 95% confidence level, $\sigma_{\overline{X}^\circ}$ and $\sigma_{\Delta\varepsilon}$ will also do so. In other words, the uncertainties of the intercept and the slope do not depend on the dispersion of the data points around the straight line but rather directly on their absolute uncertainties σ_i.

Example C.4:

Ten independent determinations of the equilibrium constant $\log_{10}{}^*\beta$ for the reaction

$$UO_2^{2+} + HF(aq) \rightleftharpoons UO_2F^+ + H^+ \qquad \text{(C.13)}$$

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, $(\log_{10}{}^*\beta + 2D)$ *vs.* m_k, according to the formula $\log_{10}{}^*\beta(\text{C.13}) + 2D = \log_{10}{}^*\beta^\circ(\text{C.13}) - \Delta\varepsilon\, m_k$, will yield the correct values for the intercept $\log_{10}{}^*\beta^\circ(\text{C.13})$ 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	$m_{ClO_4^-,i}$	$\log_{10}{}^*\beta_i(\text{C.13}) + 2D$	σ
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:

$$\begin{aligned} \text{intercept} &= 1.837 \pm 0.054 = \log_{10}{}^*\beta^\circ(\text{C.13}) \\ \text{slope} &= 0.029 \pm 0.036 = -\Delta\varepsilon. \end{aligned}$$

Calculation of the ion interaction coefficient $\varepsilon_{(UO_2F^+,ClO_4^-)} = \Delta\varepsilon + \varepsilon_{(UO_2^{2+},ClO_4^-)} - \varepsilon_{(H^+,ClO_4^-)}$: From $\varepsilon_{(UO_2^{2+},ClO_4^-)} = (0.46 \pm 0.03)\,\text{kg}\cdot\text{mol}^{-1}$, $\varepsilon_{(H^+,ClO_4^-)} = (0.14 \pm 0.02)\,\text{kg}\cdot\text{mol}^{-1}$ (see Appendix B) and the slope of the linear regression, $\Delta\varepsilon = -(0.03 \pm 0.04)\,\text{kg}\cdot\text{mol}^{-1}$, it follows that $\varepsilon_{(UO_2F^+,ClO_4^-)} = (0.29 \pm 0.05)\,\text{kg}\cdot\text{mol}^{-1}$. Note that the uncertainty $(\pm 0.05)\,\text{kg}\cdot\text{mol}^{-1}$ is obtained based on the rules of error propagation as described in Section C.4.2:

$$\sigma = \sqrt{(0.04)^2 + (0.03)^2 + (0.02)^2}\,.$$

The resulting selected values are thus

$$\begin{aligned} \log_{10}{}^{*}\beta^{\circ}(\mathrm{C.13}) &= 1.84 \pm 0.05 \\ \varepsilon_{(\mathrm{UO_2F^+},\mathrm{ClO_4^-})} &= (0.29 \pm 0.05)\,\mathrm{kg \cdot mol^{-1}}. \end{aligned}$$

C.3.1. Discrepancies or insufficient number of data points

Discrepancies are principally treated as described in Section C.2. Again, two cases can be defined. Case I: Only two data 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.4 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 obtained by this procedure, and its uncertainty must cover the entire range of expectancy of the two values, analogous to Case I in Section C.2. It should be mentioned that the ranges of expectancy of the corrected values at $I = 0$ are given by their uncertainties which are based on the uncertainties of the source data at $I \neq 0$ and the uncertainty in the slope of the straight line. The latter uncertainty is not an estimate but is calculated from the uncertainties in the ion interaction coefficients involved, according to the rules of error propagation outlined in Section C.4.2. 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 judgement 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 judgement 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

$$UO_2^{2+} + SCN^- \rightleftharpoons UO_2SCN^+ \tag{C.14}$$

are available in different electrolyte media:

$$\begin{array}{ll}
I_c = 0.1\ \mathrm{M}\ (KNO_3): & \log_{10}\beta(\mathrm{C.14}) = 1.19 \pm 0.03 \\
I_c = 0.33\ \mathrm{M}\ (KNO_3): & \log_{10}\beta(\mathrm{C.14}) = 0.90 \pm 0.10 \\
I_c = 1.0\ \mathrm{M}\ (NaClO_4): & \log_{10}\beta(\mathrm{C.14}) = 0.75 \pm 0.03 \\
I_c = 1.0\ \mathrm{M}\ (NaClO_4): & \log_{10}\beta(\mathrm{C.14}) = 0.76 \pm 0.03 \\
I_c = 1.0\ \mathrm{M}\ (NaClO_4): & \log_{10}\beta(\mathrm{C.14}) = 0.93 \pm 0.03 \\
I_c = 2.5\ \mathrm{M}\ (NaNO_3): & \log_{10}\beta(\mathrm{C.14}) = 0.72 \pm 0.03
\end{array}$$

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 like in Example C.4 would not be appropriate. 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 cancelling 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.14, and for which $\Delta\varepsilon$ is well known, is

$$UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+ \tag{C.15}$$

The value of $\Delta\varepsilon(C.15) = -(0.25 \pm 0.02)$ was obtained from a linear regression using 16 experimental data between $I_c = 0.1$ M and $I_c = 3$ M $Na(Cl,ClO_4)$ [92GRE/FUG]. It is thus assumed that

$$\Delta\varepsilon(\mathrm{C.14}) \quad = \quad \Delta\varepsilon(\mathrm{C.15}) \quad = \quad -0.25 \pm 0.02$$

The correction of $\log_{10}\beta(C.14)$ to $I_c = 0$ is done using the specific ion interaction equation, *cf.* TDB-2, which uses molal units:

$$\log_{10}\beta + 4D \quad = \quad \log_{10}\beta^\circ - \Delta\varepsilon I_\mathrm{m} \tag{C.16}$$

D is the Debye-Hückel term in molal units and I_m the ionic strength converted to molal units by using the conversion factors listed in [76BAE/MES, *p*.439]. The following list gives the details of this calculation. The resulting uncertainties in $\log_{10}\beta$ are obtained based on the rules of error propagation as described in Section C.4.2.

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	$1.68 \pm 0.03^{(a)}$
0.335	KNO_3	0.90 ± 0.10	0.617	-0.084	$1.65 \pm 0.10^{(a)}$
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	$1.82 \pm 0.13^{(a)}$

(a) These values were corrected for the formation of the nitrate complex $UO_2NO_3^+$ by using $\log_{10} K(UO_2NO_3^+) = (0.30 \pm 0.15)$ [92GRE/FUG].

As was expected, the resulting values $\log_{10}\beta^\circ$ are inconsistent and have therefore to be treated as described in Case I of Section C.2. 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.4. Procedures for data handling

C.4.1. 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.3, B.4 and B.5 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

$$M^{3+} + 2\,H_2O(l) \;\rightleftharpoons\; M(OH)_2^+ + 2\,H^+ \qquad (C.17)$$

only one credible determination in 3 M $NaClO_4$ solution is known, $\log_{10}{}^*\beta(C.17) = -6.31$, to which an uncertainty of ± 0.12 has been assigned. The ion interaction coefficients are as follows:

$$\begin{aligned}
\varepsilon_{(M^{3+},ClO_4^-)} &= (0.56 \pm 0.03)\,kg \cdot mol^{-1} \\
\varepsilon_{(M(OH)_2^+,ClO_4^-)} &= (0.26 \pm 0.11)\,kg \cdot mol^{-1} \\
\varepsilon_{(H^+,ClO_4^-)} &= (0.14 \pm 0.02)\,kg \cdot mol^{-1}.
\end{aligned}$$

The values of $\Delta\varepsilon$ and $\sigma_{\Delta\varepsilon}$ can be obtained readily (*cf.* Eq. C.19):

$$\begin{aligned}
\Delta\varepsilon &= \varepsilon_{(M(OH)_2^+,ClO_4^-)} + 2\varepsilon_{(H^+,ClO_4^-)} - \varepsilon_{(M^{3+},ClO_4^-)} = -0.02\,kg \cdot mol^{-1} \\
\sigma_{\Delta\varepsilon} &= \sqrt{(0.11)^2 + (2 \times 0.02)^2 + (0.03)^2} = 0.12\,kg \cdot mol^{-1}.
\end{aligned}$$

The two variables are thus:

$$\begin{aligned}
\log_{10}{}^*\beta(C.17) &= -6.31 \pm 0.12 \\
\Delta\varepsilon &= -(0.02 \pm 0.13)\,kg \cdot mol^{-1}
\end{aligned}$$

According to the specific ion interaction model the following equation is used to correct for ionic strength for the reaction considered here:

$$\log_{10}{}^*\beta(C.17) + 6D = \log_{10}{}^*\beta^\circ(C.17) - \Delta\varepsilon\, m_{ClO_4^-}$$

D is the Debye-Hückel term: $D = 0.509\sqrt{I_m}/(1 + 1.5\sqrt{I_m})$. 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

$$\log_{10}{}^*\beta^\circ(C.17) = -4.88.$$

The uncertainty in $\log_{10}{}^*\beta^\circ$ is calculated from the uncertainties in $\log_{10}{}^*\beta$ and $\Delta\varepsilon$ (*cf.* Eq. C.19):

$$\sigma_{\log_{10}{}^*\beta^\circ} = \sqrt{\sigma^2_{\log_{10}{}^*\beta} + \left(m_{ClO_4^-}\,\sigma_{\Delta\varepsilon}\right)^2} = \sqrt{(0.12)^2 + (3.5 \times 0.12)^2} = 0.44.$$

The selected, rounded value is

$$\log_{10}{}^*\beta^\circ(C.17) = -4.9 \pm 0.4.$$

C.4.2. 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 [69BEV]. A simplified form of the general formula for error propagation is given by Eq. (C.18), supposing that X is a function of $Y_1, Y_2, \ldots, Y_N$.

$$\sigma_X^2 = \sum_{i=1}^{N} \left(\frac{\partial X}{\partial Y_i} \sigma_{Y_i} \right)^2 \tag{C.18}$$

Eq. (C.18) can be used only if the variables $Y_1, Y_2, \ldots, Y_N$ are independent or if their uncertainties are small, that is the covariances can be disregarded. One of these two assumptions can almost always be made in chemical thermodynamics, and Eq. (C.18) can thus almost universally be used in this review. Eqs. (C.19) through (C.23) present explicit formulas for a number of frequently encountered algebraic expressions, where c, c_1, c_2 are constants.

$$X = c_1 Y_1 \pm c_2 Y_2 : \qquad \sigma_X^2 = (c_1 \sigma_{Y_1})^2 + (c_2 \sigma_{Y_2})^2 \tag{C.19}$$

$$X = \pm c Y_1 Y_2 \text{ and } X = \pm \frac{c Y_1}{Y_2} : \qquad \left(\frac{\sigma_X}{X}\right)^2 = \left(\frac{\sigma_{Y_1}}{Y_1}\right)^2 + \left(\frac{\sigma_{Y_2}}{Y_2}\right)^2 \tag{C.20}$$

$$X = c_1 Y^{\pm c_2} : \qquad \frac{\sigma_X}{X} = c_2 \frac{\sigma_Y}{Y} \tag{C.21}$$

$$X = c_1 \, e^{\pm c_2 Y} : \qquad \frac{\sigma_X}{X} = c_2 \sigma_Y \tag{C.22}$$

$$X = c_1 \, \ln(\pm c_2 Y) : \qquad \sigma_X = c_1 \frac{\sigma_Y}{Y} \tag{C.23}$$

Example C.7:

A few simple calculations illustrate how these formulas are used. The values have not been rounded.

$$\text{Eq. (C.19)}: \quad \Delta_r G_m = 2[-(277.4 \pm 4.9)]\,\mathrm{kJ \cdot mol^{-1}} - [-(467.3 \pm 6.2)]\,\mathrm{kJ \cdot mol^{-1}} = -(87.5 \pm 11.6)\,\mathrm{kJ \cdot mol^{-1}}$$

$$\text{Eq. (C.20)}: \quad K = \frac{(0.038 \pm 0.002)}{(0.0047 \pm 0.0005)} = (8.09 \pm 0.92)$$

$$\text{Eq. (C.21)}: \quad K = 4(3.75 \pm 0.12)^3 = (210.9 \pm 20.3)$$

$$\text{Eq. (C.22)}: \quad K^\circ = e^{\frac{-\Delta_r G_m^\circ}{RT}}; \qquad \begin{aligned} \Delta_r G_m^\circ &= -(2.7 \pm 0.3)\ \mathrm{kJ \cdot mol^{-1}} \\ R &= 8.3145\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \\ T &= 298.15\,\mathrm{K} \end{aligned}$$

$$K^\circ = 2.97 \pm 0.36$$

Note that powers of 10 have to be reduced to powers of e, *i.e.*, the variable has to be multiplied by $\ln(10)$, *e.g.*,

$$\log_{10} K = (2.45 \pm 0.10); \quad K = 10^{\log_{10} K} = e^{(\ln(10)\ \log_{10} K)} = (282 \pm 65).$$

$$\text{Eq. (C.23)}: \quad \Delta_r G^\circ_m = -RT \ln K^\circ ; \qquad \begin{aligned} K^\circ &= (8.2 \pm 1.2) \times 10^6 \\ R &= 8.3145\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}} \\ T &= 298.15\,\mathrm{K} \end{aligned}$$

$$\begin{aligned} \Delta_r G^\circ_m &= -(39.46 \pm 0.36)\,\mathrm{kJ \cdot mol^{-1}} \\ \ln K^\circ &= 15.92 \pm 0.15 \\ \log_{10} K^\circ &= \ln K^\circ / \ln(10) = 6.91 \pm 0.06 \end{aligned}$$

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.4.3. 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 set of data is developed, and only then are data rounded.

C.4.4. Significant digits

The uncertainty of a value basically defines the number of significant digits a value should be given.

$$\text{Examples:} \quad \begin{aligned} &3.478 \pm 0.008 \\ &3.48 \pm 0.01 \\ &2.8 \pm 0.4 \end{aligned}$$

In the case of auxiliary data or values that are used for later calculations, it is often not convenient 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

Corrections to the Uranium NEA-TDB review†

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D.1. Introduction

Readers of the uranium review [92GRE/FUG] have pointed out to us several minor problems and misprints.

- The labels "$U(OH)_4(aq)$" and "$UO_2CO_3(aq)$" should be interchanged in Figure V.19, *p*.325.
- In Section V.3.3.1.4, *p*.136, the reference in the first line should be "Cordfunke [66COR]", while in the second line after Eq. (V.22), the reference [66COR] should read [63COR/ALI].
- The value of $\Delta_f H^\circ_m(UO_4 \cdot 4H_2O, cr, 298.15\,K)$ should be $-(2384.7 \pm 2.1)$ kJ $\cdot$ mol^{-1} (instead of -2394.8 kJ $\cdot$ mol^{-1}), both in Table III.1, *p*.32, and in Section V.3.3.1.4, *p*.136.

† Although this text has been prepared by the authors listed, most of the corrections mentioned in it have been pointed out by various observant readers: D. Cubicciotti, J. Fuger, R.J. Lemire, P. Vitorge and others. It must be stressed that this Appendix *has not been submitted to independent peer-review*. Judgement should be used when applying the comments and values given in this and following pages.

- The title and the last page number for Ref. [63COR/ALI], which were omitted in the uranium book can be found in the Reference list of this Appendix.
- In Figures V.7, V.8, V.19 and V.20, the variable "pe", which denotes the Y-axis, is not defined anywhere in the uranium review. The definition of this variable is given in Section II.1.6.5 of this volume.
- Several errors in Appendices B and C of [92GRE/FUG] have been corrected and reprinted in this volume, for example, Eqs. (B.11) and (C.9). Likewise, footnotes "(c)" and "(i)" in Table B.3 of [92GRE/FUG] have been revised.
- In the first line of Section V.9.5.2.3, *p*.347, the compound should be Ba_2SrUO_6(cr) and not Ba_2CaUO_6(cr).

The authors of the uranium volume agreed that updates of the review to include later publications would not be made, but that the selected values could be revised if errors were discovered. Problems brought to our attention with the selected uranium thermodynamic data in Chapter III and with the specific ion interaction coefficients in Appendix B of Ref. [92GRE/FUG] are dealt with in the following Sections.

D.2. Uranium trichloride

The value of $C^\circ_{p,\mathrm{m}}(\mathrm{UCl_3, cr}, 298.15\,\mathrm{K})$ in Table III.1 of the uranium NEA-TDB review [92GRE/FUG, *p*.36] is erroneous. Grenthe *et al.* [92GRE/FUG, *pp*.200–202] adopted the values reported by Cordfunke, Konings and Westrum [89COR/KON], but the numbers were mistyped. The correct value is $C^\circ_{p,\mathrm{m}}(\mathrm{UCl_3, cr}, 298.15\,\mathrm{K}) = (102.5 \pm 0.5)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, instead of $95.1\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and the thermal function quoted in Table III.3 [92GRE/FUG, *p*.61] should read

$$C^\circ_{p,\mathrm{m}}/(\,\mathrm{J \cdot K^{-1} \cdot mol^{-1}}) = 87.78 + 31.127 \times 10^{-3}\mathrm{T/K} + 4.853 \times 10^5(\mathrm{T/K})^{-2}.$$

We note however that this function has a minimum at $\sim 315\,\mathrm{K}$. In order to remove this artifact the original data [47GIN/COR] should be refitted.

D.3. Aqueous uranium hydroxide complexes

D.3.1. $UO_2(OH)_2(aq)$

Concerns have been expressed about the inadequacy of the selected values for this species, namely:

$$\mathrm{UO_2^{2+} + 2\,H_2O(l) \rightleftharpoons UO_2(OH)_2(aq) + 2\,H^+} \qquad \log_{10} {}^*\beta^\circ_2(298.15\,\mathrm{K}) \leq -10.3$$

which corresponds to $\Delta_\mathrm{f}G^\circ_\mathrm{m}(\mathrm{UO_2(OH)_2, aq}, 298.15\,\mathrm{K}) \geq -1368\ \mathrm{kJ \cdot mol^{-1}}$. This upper stability limit would suggest that this complex is not a predominating hydrolysis species in the uranium(VI) system. However, Figures V.4 to V.5, V.7 and V.18 in pages 115, 116, 128 and 322 of Ref. [92GRE/FUG] show that this species predominates over a large range of conditions. Most of these Figures might be misleading,

because for the sake of clarity they were constructed suppressing the precipitation of solid phases. Nevertheless, Figure V.5 in [92GRE/FUG] shows that $UO_2(OH)_2(aq)$ can reach concentrations approaching 10^{-5} M in equilibrium with schoepite if the selected upper limit for $\log_{10} {}^*\beta_2^\circ$ is used. It appears therefore, that some additional comments are required for this complex.

The selected values expressed the knowledge on this system by the date the draft was sent for peer-review. Later publications (for example [91CHO/MAT, 92BIS/KRA, 92SIL, 94TOR/CAS]) have shown that the actual value of $\Delta_f G_m^\circ$ for this complex is probably larger than the lower limit set by Grenthe *et al.* by about 8 $kJ \cdot mol^{-1}$, *cf.* the footnote in *p.*113 of Ref. [92GRE/FUG]. Nevertheless, a revised value for this complex is not offered because of the decision taken that the uranium book would not be updated in the near future to take account of subsequent publications.

D.3.2. U(IV) hydroxide complexes

Users of the selected data set for this system should be aware of the caveats expressed in section "A potential inconsistency" in [92GRE/FUG, *pp.*129–131]. Although it appears that the stability of $U(OH)_4(aq)$ has been overestimated by orders of magnitude in [92GRE/FUG], the inconsistencies mentioned by Grenthe *et al.* still remain unresolved, and a re-examination of this system is being undertaken simultaneously with the neptunium and plutonium NEA-reviews.

D.4. Uranium carbonate complexes and compounds

Although no remarks have been made on the selected thermodynamic values concerning this chemical system, a re-adjustment of the method for ionic strength corrections has taken place within the NEA-TDB project as discussed below. This has insignificant consequences on the selected thermodynamic values, but might have non-negligible effects on the ionic strength extrapolations in carbonate solutions for users of the specific ion interaction equations discussed in Appendix B.

More important is the fact that the thermodynamic data selected by Grenthe *et al.* [92GRE/FUG] are not likely to reflect the behaviour of U(IV) at pH < 7, because mixed hydroxide carbonate/bicarbonate complexes of U(IV) are probably formed in those aqueous solutions (*cf.* [92GRE/FUG, *p.*323]). Experimental information on the complexes formed and their stability is still badly needed 3 years after the publication of the NEA review.

The grounds for the change in the parameters of the ionic strength correction method for carbonate solutions, and its effects on the selected uranium values, are presented in the following discussions.

For consistency, the auxiliary data presented in Chapter IV have to be used with the values selected in the NEA-TDB reviews. For the aqueous carbonate system, the equilibrium constants are calculated from the CODATA Key Values [89COX/WAG] with the uncertainties re-evaluated in Chapter VI of [92GRE/FUG]. For example for the reaction

$$CO_3^{2-} + 2\,H^+ \rightleftharpoons CO_2(g) + H_2O(l) \qquad \text{(D.1)}$$

$\log_{10} K^{\circ}_{\mathrm{p}} = (18.15 \pm 0.04)$ is obtained combining the values given in Table IV.2.

The selected data in the NEA-TDB project should be used in combination with the specific ion interaction equations (*cf.* Appendix B). This will ensure consistency between the ionic strength corrections used in the modelling calculations and during the NEA review procedure.

However, a member of the team for the Np/Pu review (Dr. Vitorge, CEA, France) has pointed out that for the aqueous carbonate system the experimental equilibrium constants in $NaClO_4$ media are poorly represented by the combination of CODATA Key Values and the specific ion interaction equations (using the values of $\varepsilon_{(Na^+,CO_3^{2-})}$ and $\varepsilon_{(Na^+,HCO_3^-)}$ adopted in [92GRE/FUG]). Nevertheless, it must be stated that the calculated and experimental values do agree within the uncertainty of the extrapolations. A better agreement between the CODATA Key Values and the experimental measurements is obtained using the ε-values reported by Ciavatta [80CIA]. Apparently the values of $\varepsilon_{(Na^+,CO_3^{2-})}$ and $\varepsilon_{(Na^+,HCO_3^-)}$ adopted in [92GRE/FUG] were obtained from a fitting of activity (or osmotic) coefficient data for Na_2CO_3 and $NaHCO_3$ solutions. However, Dr. Vitorge pointed out that this procedure is inadequate, because hydrolysis will take place in these solutions of the "pure" salts, introducing a systematic error in the ε-values obtained by the fitting procedure. These arguments weighted against the policy of keeping the values of the specific ion interaction parameters constant throughout the NEA-TDB reviews, and it was finally decided that it would be reasonable to change the values of the two key ε-values to those given in [80CIA]:

$$\varepsilon_{(Na^+,CO_3^{2-})} = -(0.08 \pm 0.03)\,\mathrm{kg \cdot mol^{-1}}, \tag{D.2}$$

$$\varepsilon_{(Na^+,HCO_3^-)} = (0.00 \pm 0.02)\,\mathrm{kg \cdot mol^{-1}}. \tag{D.3}$$

In order to keep internal consistency among the NEA-TDB reviews, this change of ε-values requires a re-evaluation of the values selected in the NEA review on uranium thermodynamics [92GRE/FUG]. Grenthe *at al.* selected data for 10 aqueous carbonate/bicarbonate complexes of uranium, including mixed complexes with hydroxo or oxo groups. Furthermore, the uranium review contains selected values for two complexes containing both dioxouranium(VI) and either dioxoplutonium(VI) or dioxoneptunium(VI). Two solid phases have selected values: UO_2CO_3(cr) and $Na_4UO_2(CO_3)_3$(cr).

In addition to formation and reaction data 7 specific ion interaction coefficients were selected by Grenthe *et al.* [92GRE/FUG, Table B.4] for aqueous complexes of uranium and carbonate (including a mixed carbonate-hydroxo complex).

The selection procedure followed by Grenthe *et al.* is repeated here using the new ε-values as described in the following Sections. As expected, the effect of the new ε-values (*cf.* Eqs. (D.2) and (D.3)) in the selected thermodynamic data for uranium complexes and compounds is quite small, but the changes are larger on the values of the specific ion interaction coefficients of uranium carbonate complexes. The results of these re-evaluations are summarized in Tables D.1, D.2 and D.3.

Table D.1: Specific ion interaction coefficients (ε, in units of $\mathrm{kg \cdot mol^{-1}}$) for uranium carbonate complexes revised for the changed ε-values given in Eqs. (D.2) and (D.3). The value in *emphasized* typeface is taken directly from Ref. [92GRE/FUG] and is not affected by this re-evaluation. All ionic species listed in this table are aqueous species. All data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa. The uncertainties listed represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval.

$\varepsilon_{((UO_2)CO_3(OH)_3^-,Na^+)}$	=	*0.00±0.05*
$\varepsilon_{(UO_2(CO_3)_2^{2-},Na^+)}$	=	-0.02 ± 0.09
$\varepsilon_{(U(CO_3)_4^{4-},Na^+)}$	=	-0.09 ± 0.10
$\varepsilon_{(UO_2(CO_3)_3^{4-},Na^+)}$	=	-0.01 ± 0.11
$\varepsilon_{(UO_2(CO_3)_3^{5-},Na^+)}$	=	-0.62 ± 0.15
$\varepsilon_{(U(CO_3)_5^{6-},Na^+)}$	=	-0.30 ± 0.15
$\varepsilon_{((UO_2)_3(CO_3)_6^{6-},Na^+)}$	=	0.37 ± 0.11

D.4.1. U(VI) carbonate complexes

D.4.1.1. $UO_2CO_3(aq)$

The two values of the equilibrium constants for reaction

$$UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2CO_3(aq) \tag{D.4}$$

from Refs. [72SER/NIK, 91GRE/LAG] and the four values obtained from reinterpretations of the data in Refs. [69TSY, 79CIA/FER, 84GRE/FER] are corrected to $I = 0$ using $\Delta\varepsilon(\mathrm{D.4}) = -(0.38 \pm 0.04)\,\mathrm{kg \cdot mol^{-1}}$ instead of $-(0.41 \pm 0.04)\,\mathrm{kg \cdot mol^{-1}}$. The revised values are given in Table D.4.

Note that the values of $\log_{10}\beta_1$ for Refs. [79CIA/FER, 84GRE/FER, 91GRE/LAG] have been recalculated from the corresponding equilibrium constants of reactions involving $CO_2(g)$:

$$UO_2^{2+} + H_2O(l) + CO_2(g) \rightleftharpoons UO_2CO_3(aq)$$

combined with values of $\log_{10} K_p(\mathrm{D.1})$ calculated from the CODATA Key Values (*cf.* Table IV.2) and the specific ion interaction equations (*cf.* Appendix B) using $\varepsilon_{(Na^+,CO_3^{2-})} = -(0.08 \pm 0.03)\,\mathrm{kg \cdot mol^{-1}}$.

The weighted average of the values extrapolated to $I = 0$ and listed in Table D.4 is:

$$\log_{10}\beta_1^\circ(\mathrm{D.4}, 298.15\,\mathrm{K}) = 9.67 \pm 0.05$$

which is essentially equal to the value obtained by Grenthe *et al.* [92GRE/FUG]: $\log_{10}\beta_1^\circ = (9.68 \pm 0.04)$.

Table D.2: Thermodynamic data for uranium carbonate complexes and compounds from Ref. [92GRE/FUG] revised for the changed ε-values given in Eqs. (D.2) and (D.3). Values in *emphasized* typeface are taken directly from Ref. [92GRE/FUG] and are not affected by this re-evaluation. 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 Chapter V of [92GRE/FUG]. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits.

Compound	$\Delta_f G^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^\circ_m$ ($kJ \cdot mol^{-1}$)	S°_m ($J \cdot K^{-1} \cdot mol^{-1}$)	$C^\circ_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
$UO_2CO_3(aq)$	$-1535.650^{(b)}$ ± 1.813	$-1689.230^{(b)}$ ± 2.512	$53.710^{(a)}$ ± 10.394	
$UO_2CO_3(cr)$	$-1563.160^{(b)}$ ± 1.805	$-1689.760^{(a)}$ ± 1.808	*144.200* *±0.300*	*120.100* *±0.100*
$U(CO_3)_5^{6-}$	$-3362.860^{(b)}$ ± 6.285	$-3987.350^{(b)}$ ± 5.334	$-84.970^{(a)}$ ± 27.654	
$(UO_2)_2(PuO_2)(CO_3)_6^{6-}$ (c)				
$(UO_2)_2(NpO_2)(CO_3)_6^{6-}$ (c)				

(a) Value calculated internally with the Gibbs-Helmholtz equation, $\Delta_f G^\circ_m = \Delta_f H^\circ_m - T\Delta_f S^\circ_m$.
(b) Value calculated internally from reaction data (see Table D.3).
(c) Only reaction data are selected for this compound, *cf.* Table D.3.

Table D.3: Thermodynamic data for reactions involving uranium compounds and complexes revised for the changed ε-values given in Eqs. (D.2) and (D.3). Values in *emphasized* typeface are taken directly from Ref. [92GRE/FUG] and are not affected by this re-evaluation. 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.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapter V of [92GRE/FUG]. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits.

Species	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})
UO_2CO_3(aq)	$CO_3^{2-} + UO_2^{2+} \rightleftharpoons UO_2CO_3$(aq)				
		9.670	−55.197	*5.000*	201.901[(a)]
		±0.050	±0.285	*±2.000*	±6.776
UO_2CO_3(cr)	$CO_3^{2-} + UO_2^{2+} \rightleftharpoons UO_2CO_3$(cr)				
		14.490	−82.710		
		±0.040	±0.228		
$U(CO_3)_5^{6-}$	$5\ CO_3^{2-} + U^{4+} \rightleftharpoons U(CO_3)_5^{6-}$				
		33.900	−193.503	*−20.000*	581.931[(a)]
		±1.000	±5.708	*±4.000*	±23.378
$(UO_2)_2(PuO_2)(CO_3)_6^{6-}$	$PuO_2(CO_3)_3^{4-} + 2\ UO_2(CO_3)_3^{4-} \rightleftharpoons (UO_2)_2(PuO_2)(CO_3)_6^{6-} + 3\ CO_3^{2-}$				
		−8.200	46.806		
		±1.300	±7.420		
$(UO_2)_2(NpO_2)(CO_3)_6^{6-}$	$NpO_2(CO_3)_3^{4-} + 2\ UO_2(CO_3)_3^{4-} \rightleftharpoons (UO_2)_2(NpO_2)(CO_3)_6^{6-} + 3\ CO_3^{2-}$				
		−9.400	53.656		
		±1.300	±7.420		

(a) Value calculated internally with the Gibbs-Helmholtz equation, $\Delta_r G_m^\circ = \Delta_r H_m^\circ - T\Delta_r S_m^\circ$.

Table D.4: Experimental equilibrium data for reaction: $UO_2^{2+} + CO_3^{2-} \rightleftharpoons UO_2CO_3(aq)$. This table supersedes the corresponding values in Table V.42, *p*.309 of Ref. [92GRE/FUG].

Method	Ionic Medium	t (°C)	$\log_{10}\beta_1^{(a)}$	$\log_{10}\beta_1^{\circ(a)}$	Reference
emf, gl	0.1 M ($NaClO_4$)	25	$9.30 \pm 0.20^{(b,d)}$	10.13 ± 0.20	[69TSY]
sol, sp	≤ 0.03 M	25		$9.87 \pm 0.30^{(d)}$	[72SER/NIK]
emf, gl	3.0 M ($NaClO_4$)	25	$8.60 \pm 0.18^{(b,c)}$	9.14 ± 0.23	[79CIA/FER]
sol	0.5 M ($NaClO_4$)	25	$8.38 \pm 0.10^{(b,c)}$	9.57 ± 0.11	[84GRE/FER]
	3.0 M ($NaClO_4$)	25	$8.89 \pm 0.10^{(b,c)}$	9.43 ± 0.18	
emf, gl	0.5 m ($NaClO_4$)	25	8.54 ± 0.05	9.73 ± 0.07	[91GRE/LAG]

(a) $\log_{10}\beta_1$ refers to equilibrium constant in the ionic medium and at the temperature given in the table, $\log_{10}\beta_1^\circ$ (in molal units) at $I = 0$ and 298.15 K.
(b) Re-evaluated by Grenthe *et al.* [92GRE/FUG, Appendix A].
(c) The reported constant is corrected for the different protonation constant of carbonate used in the NEA reviews (*cf.* Table IV.2) corrected for medium effects with the specific ion interaction equations (*cf.* Appendix B), using the same procedure as Grenthe *et al.* [92GRE/FUG, Appendix A].
(d) Uncertainties estimated by Grenthe *et al.* [92GRE/FUG].

D.4.1.2. $UO_2(CO_3)_2^{2-}$ and $UO_2(CO_3)_3^{4-}$

The selection procedure for the values of $\log_{10}\beta_2^\circ$ and $\log_{10}\beta_3^\circ$ is not affected by the change in the key ε-values. However, from the values of $\Delta\varepsilon_2$ and $\Delta\varepsilon_3$ the two selected ion interaction coefficients are instead:

$$\varepsilon_{(UO_2(CO_3)_2^{2-},Na^+)} = -(0.02 \pm 0.09)\,\mathrm{kg \cdot mol^{-1}} \quad (D.5)$$

$$\varepsilon_{(UO_2(CO_3)_3^{4-},Na^+)} = -(0.01 \pm 0.11)\,\mathrm{kg \cdot mol^{-1}}. \quad (D.6)$$

D.4.1.3. $(UO_2)_3(CO_3)_6^{6-}$

The selection procedure for the value of the standard equilibrium constant of formation of this complex, $\log_{10}\beta_{6,3}^\circ$, is not affected by the change in the key ε-values. However, the value of the selected ion interaction coefficient is derived to be:

$$\varepsilon_{((UO_2)_3(CO_3)_6^{6-},Na^+)} = (0.37 \pm 0.11)\,\mathrm{kg \cdot mol^{-1}}.$$

D.4.2. Mixed U(VI) hydroxide-carbonate complexes

The selection procedure for the value of the standard equilibrium constant of formation of these complexes ($(UO_2)_{11}(CO_3)_6(OH)_{12}^{2-}$, $(UO_2)_3O(OH)_2(HCO_3)^+$ and $(UO_2)_2CO_3(OH)_3^-$) is not affected by the change in the key ε-values, because the reactions considered by by Grenthe *et al.* [92GRE/FUG] did involve $CO_2(g)$ as

a component, rather than carbonate or bicarbonate ions, *cf.* reactions (V.164) to (V.167) and Table III.2 in Ref. [92GRE/FUG]. For the same reason, the value of $\varepsilon_{((UO_2)_2CO_3(OH)_3^-,Na^+)}$ selected by Grenthe *et al.* remains unchanged.

D.4.3. Mixed U(VI), Np(VI) and Pu(VI) carbonate complexes

The equilibrium constants at (22 ± 1)°C in 3 M $NaClO_4$ reported in [86GRE/RIG] for the reactions

$$2\,UO_2(CO_3)_3^{4-} + MO_2(CO_3)_3^{4-} \rightleftharpoons (UO_2)_2(MO_2)(CO_3)_6^{6-} + 3\,CO_3^{2-} \qquad M = \mathrm{Np,\ Pu} \tag{D.7}$$

are extrapolated to $I = 0$ assuming that ε-values are the same for the complexes with M = U, Np and Pu, *i.e.* using $\Delta\varepsilon = (0.16 \pm 0.36)\,\mathrm{kg \cdot mol^{-1}}$, obtaining

$$\log_{10} K^\circ(\mathrm{D.7},\ M = \mathrm{Np}, 298.15\,\mathrm{K}) = -9.4 \pm 1.3$$
$$\log_{10} K^\circ(\mathrm{D.7},\ M = \mathrm{Pu}, 298.15\,\mathrm{K}) = -8.2 \pm 1.3$$

The standard Gibbs energies of formation for $(UO_2)_2(NpO_2)(CO_3)_6^{6-}$ and $(UO_2)_2(PuO_2)(CO_3)_6^{6-}$ will be selected in the forthcoming NEA review on the chemical thermodynamics of neptunium and plutonium.

D.4.4. U(V) carbonate complexes

The selection procedure used by Grenthe *et al.* to obtain the value for the standard redox potential for reaction

$$UO_2(CO_3)_3^{4-} + e^- \rightleftharpoons UO_2(CO_3)_3^{5-} \tag{D.8}$$

is not affected by the change in the key ε-values, because no carbonate or bicarbonate ions are involved in this reaction. However, from the value of $\Delta\varepsilon(\mathrm{D.8}) = -(0.61 \pm 0.10)$ obtained by Riglet [90RIG, *p.*105], the selected ion interaction coefficient is:

$$\varepsilon_{(UO_2(CO_3)_3^{5-},Na^+)} = -(0.62 \pm 0.15)\,\mathrm{kg \cdot mol^{-1}}.$$

Note that at each of the $NaClO_4$ concentrations studied by Riglet, she measured apparent normal potentials relative to the *standard* hydrogen electrode and, therefore, activity coefficient corrections for H^+ according to the reaction: $\frac{1}{2}H_2(g) \rightleftharpoons H^+ + e^-$ are not included in the value of $\Delta\varepsilon$.

D.4.5. U(IV) carbonate complexes

D.4.5.1. $U(CO_3)_4^{4-}$

The selected stepwise equilibrium constant for reaction

$$U(CO_3)_4^{4-} + CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-} \tag{D.9}$$

is not affected by the ε-values given in Eqs. (D.2) and (D.3). Grenthe *et al.* estimated † $\varepsilon_{(U(CO_3)_4^{4-},Na^+)} = -(0.09 \pm 0.10)\,kg \cdot mol^{-1}$ [92GRE/FUG, *p*.324], which is combined with the experimental value of $\Delta\varepsilon(D.9) = -(0.13 \pm 0.11)\,kg \cdot mol^{-1}$ to yield $\varepsilon_{(U(CO_3)_5^{6-},Na^+)} = -(0.30 \pm 0.15)\,kg \cdot mol^{-1}$. The selected ε-values are

$$\begin{aligned} \varepsilon_{(U(CO_3)_4^{4-},Na^+)} &= -(0.09 \pm 0.10)\,kg \cdot mol^{-1}, \\ \varepsilon_{(U(CO_3)_5^{6-},Na^+)} &= -(0.30 \pm 0.15)\,kg \cdot mol^{-1}. \end{aligned}$$

The value of $\varepsilon_{(U(CO_3)_5^{6-},Na^+)}$, which is derived from the estimate of $\varepsilon_{(U(CO_3)_4^{4-},Na^+)}$, is used in next Section to extrapolate the value of $\log_{10}\beta_5$ to $I = 0$.

D.4.5.2. $U(CO_3)_5^{6-}$

The normal redox potential of the reaction

$$UO_2(CO_3)_3^{4-} + 2\,e^- + 2\,CO_2(g) \rightleftharpoons U(CO_3)_5^{6-} \qquad (D.10)$$

was determined in 3 M $NaClO_4$ solutions at 25°C by Ciavatta *et al.* [83CIA/FER]: $E^\circ = -(0.279 \pm 0.001)$ V, *i.e.*, $\log_{10} K(D.10) = -(9.432 \pm 0.034)$. The procedure indicated in Grenthe *et al.* [92GRE/FUG, Appendix A], will also be followed here. Reaction (D.10) is combined with the equilibria

$$UO_2^{2+} + 2\,e^- + 4\,H^+ \rightleftharpoons U^{4+} + 2\,H_2O(l) \qquad (D.11)$$

$$UO_2^{2+} + 3\,CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \qquad (D.12)$$

$$CO_2(g) + H_2O(l) \rightleftharpoons CO_3^{2-} + 2\,H^+ \qquad (D.13)$$

whose selected constants are extrapolated to $I = 3$ M $NaClO_4$ using the specific ion interaction equations of Appendix B (with the ε-values given by Eqs. (D.2) and (D.3)), obtaining, $\log_{10} K(D.11) = (11.96 \pm 0.37)$, $\log_{10} K(D.12) = (22.61 \pm 0.51)$ and $\log_{10} K(D.13) = -(17.61 \pm 0.18)$. Finally, for reaction

$$U^{4+} + 5\,CO_3^{2-} \rightleftharpoons U(CO_3)_5^{6-} \qquad (D.14)$$

the equilibrium constant is calculated to be $\log_{10}\beta_5 = (36.44 \pm 0.68)$. The value of $\varepsilon_{(U(CO_3)_5^{6-},Na^+)} = -(0.30 \pm 0.15)\,kg \cdot mol^{-1}$, estimated in the previous section following the procedure of Grenthe *et al.* (*cf.* pages 660 and 324 in Ref. [92GRE/FUG]), is used to obtain $\Delta\varepsilon(D.14) = -(0.66 \pm 0.22)\,kg \cdot mol^{-1}$, which allows us to calculate:

$$\log_{10}\beta_5^\circ(298.15\,K) = 34.1 \pm 1.0,$$

which is essentially the same value as that reported by Grenthe *et al.*, (34.0 ± 0.9) [92GRE/FUG, *p*.324]. The large uncertainty is due to the accumulation of uncertainties for the extrapolation of the equilibrium constants for reactions (D.11) to (D.13) from $I = 0$ to $I = 3$ M, and then for the extrapolation of $\log_{10}\beta_5$ back to $I = 0$.

† Grenthe *et al.* consistently listed $\varepsilon_{(U(CO_3)_4^{4-},Na^+)} = (0.09 \pm 0.10)$ both in *p*.324 and in *p*.697 [92GRE/FUG]. This appears to be a misprint, and the value should in fact have a negative sign.

D.4.6. Solid uranium carbonates

D.4.6.1. $UO_2CO_3(cr)$

The four reliable values of the equilibrium constants for reaction

$$UO_2CO_3(cr) \rightleftharpoons UO_2^{2+} + CO_3^{2-} \tag{D.15}$$

from Refs. [72SER/NIK, 76NIK2, 84GRE/FER] are corrected to $I = 0$ using $\Delta\varepsilon(\text{D.15}) = -(0.38 \pm 0.04)\,\text{kg}\cdot\text{mol}^{-1}$. The revised values are listed in Table D.5. The weighted average of the values extrapolated to $I = 0$ is:

$$\log_{10} K^{\circ}_{s,0}(\text{D.15}, 298.15\,\text{K}) = -14.49 \pm 0.04$$

which is essentially equal to the value obtained by Grenthe *et al.* [92GRE/FUG]: $\log_{10} K^{\circ}_{s,0} = -(14.47 \pm 0.04)$.

Table D.5: Experimental equilibrium data for reaction: $UO_2CO_3(cr) \rightleftharpoons UO_2^{2+} + CO_3^{2-}$. This table supersedes the corresponding values in Table V.42, *p*.311 of Ref. [92GRE/FUG].

Method	Ionic Medium	t (°C)	$\log_{10} K^{(a)}_{s,0}$	$\log_{10} K^{\circ(a)}_{s,0}$	Reference
sol	0.0002 to 0.02 M	25	$-14.26^{(j)}$	$-14.26 \pm 0.30^{(d)}$	[72SER/NIK]
sol	0.01 M$^{(h)}$	25	-14.15 ± 0.08	$-14.50 \pm 0.17^{(d)}$	[76NIK2]
sol	0.5 M ($NaClO_4$)	25	$-13.31 \pm 0.03^{(b,c)}$	-14.49 ± 0.04	[84GRE/FER]
	3.0 M ($NaClO_4$)	25	$-13.94 \pm 0.03^{(b,c)}$	-14.48 ± 0.15	

(a) $\log_{10} K_{s,0}$ refers to equilibrium constant in the ionic medium and at the temperature given in the table, $\log_{10} K^{\circ}_{s,0}$ (in molal units) at $I = 0$ and 298.15 K.
(b) Re-evaluated by Grenthe *et al.* [92GRE/FUG, Appendix A].
(c) The reported constant is corrected for the different protonation constant of carbonate used in this review (*cf.* Table IV.2) corrected for medium effects with the specific ion interaction equations (*cf.* Appendix B), following the procedure of Grenthe *et al.* [92GRE/FUG, Appendix A].
(d) Uncertainties estimated by Grenthe *et al.* [92GRE/FUG].
(h) Ionic strength assumed to be similar to that reported in Ref. [72SER/NIK].
(j) Value refers to $I = 0$.

D.4.6.2. $Na_4UO_2(CO_3)_3(cr)$

The extrapolation to $I = 0$ of the measurements [56BLA/COL] of the equilibrium constant for

$$Na_4UO_2(CO_3)_3(cr) \rightleftharpoons 4\,Na^+ + UO_2(CO_3)_3^{4-} \tag{D.16}$$

is not affected by the new ε-values defined in Eqs. (D.2) and (D.3). The value of $\Delta\varepsilon(\text{D.16}) = -(0.09 \pm 0.06)\,\text{kg}\cdot\text{mol}^{-1}$ obtained by Grenthe *et al.* [92GRE/FUG,

p.328] now leads to $\varepsilon_{(UO_2(CO_3)_3^{4-},Na^+)} = -(0.13 \pm 0.07)\,\mathrm{kg \cdot mol^{-1}}$, which still differs significantly from the value given in Eq. (D.6) and Table D.1.

D.5. Uranium minerals

The thermodynamic data for uranium minerals have been the subject of some expressed criticism regarding the NEA-TDB review for uranium. Taking into account the complex chemistry of these solid phases, it is to be expected that the number of publications with experimental determinations of thermodynamic parameters for uranium minerals is low. The existing literature on this subject was reviewed by Grenthe *et al.*, [92GRE/FUG], and we are not aware of any other experimental work which escaped the attention of the NEA-review team and that could have been used to recommend thermodynamic data on uranium minerals.

Nevertheless, a few publications have been found [81OBR/WIL, 81VOC/PIR, 83OBR/WIL, 83VOC/PEL, 84VOC/GRA, 84VOC/GOE, 86VOC/GRA, 88ATK/BEC, 90VOC/HAV] which by mistake were not included in the discussions of Chapter V in Ref. [92GRE/FUG]. As the quality of the experimental data given in these references is not adequate to include them in a selection procedure, it is important to note that this omission does not really affect the set of selected thermodynamic uranium data given in the NEA review.

Two studies presented by O'Brien and Williams in [81OBR/WIL, 83OBR/WIL] deal with the stabilities of different secondary uranyl minerals. These references are Parts 3 and 4 of a series of papers. Parts 1 and 2 [79HAA/WIL, 80ALW/WIL] in the same series were reviewed and discussed by Grenthe *et al.* [92GRE/FUG] (Sections V.5.1.3.2.c and V.7.1.2.2.b, *pp.* 254–255 and 328, and the comments on [79HAA/WIL] in Appendix A, *pp.* 646–648).

O'Brien and Williams [81OBR/WIL] reported the Gibbs energies of formation of sodium, potassium, and ammonium zippeites, (basic dioxouranium(VI) sulphates). There are almost no experimental details on the technique and data analysis used in this work as well as no information about the auxiliary data used. In Part 4, [83OBR/WIL], O'Brien and Williams reported the thermodynamic stabilities, *i.e.*, Gibbs energies of formation, of schröckingerite, $Ca_3NaUO_2(CO_3)_3FSO_4 \cdot 10H_2O$(cr), and grimselite, $K_3NaUO_2(CO_3)_3 \cdot H_2O$(cr), calculated from solubility experiments. The method used for these measurements is essentially the same as was previously used by Haacke *et al.*, [79HAA/WIL] in Part 1 of this series. The authors performed corrections for ionic strength effects to the equilibrium constants for the aqueous complexes, but the data suffer from the same flaw as previous studies, *i.e.*, neglect of the formation of hydrolysis species, which in the investigated pH range (7.69 to 10.00) is expected to be important for the uranium system, introducing a large uncertainty in the calculated solubility products, and therefore on the resulting values of the thermodynamic data.

The solubility products of cobalt, nickel, and copper uranylphosphate, (metatorbenite) were measured by Vochten *et al.*, [81VOC/PIR]. The solid compounds were synthesised and adequately characterised. However, the solubility experiments

and the corresponding data analysis have serious limitations, *e.g.*, lack of uranium and phosphorous analysis, standardisation of the pH electrode with buffer solutions which were out of the pH range under investigation, no correction for ionic strength effects on the auxiliary thermodynamic data (which were taken from Sillén *et al.* [64SIL/MAR], and only included uranyl phosphorus complexes), *etc.* Furthermore, the authors did not specify in which ionic medium the solubility experiments were done. It might be assumed that this was just pure water. No enough details were given for a thorough evaluation.

Sabugalite is a hydrated acid aluminium uranylphosphate which crystal chemical formula corresponds to $HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O(cr)$. The study performed by Vochten and Pelsmaekers, [83VOC/PEL], gives some information on the solubility of this compound under conditions not well defined, in two ionic media, phosphoric and hydrochloric acid. The lack of experimental details along with the absence of the raw data does not allow further calculations of thermodynamic values.

Bassetite is a secondary uranyl phosphate and has the crystal chemical formula $Fe(UO_2)_2(PO_4)_2 \cdot 8H_2O(cr)$. This compound together with its fully oxidised form were synthesised and extensively investigated by Vochten *et al.* [84VOC/GRA], using various techniques, *i.e.*, powder diffraction, Mössbauer and infrared spectroscopy, zeta- potential measurements and thermal analysis. The authors also measured the solubility of this solid as a function of the acidity, at $2.4 < pH < 6.0$ in HCl medium under nitrogen atmosphere. They reported solubility values based only on the total iron concentration in solution. The ionic strength of the experiments is unknown. The experimental details are so scarce that it is not possible to obtain any further information.

The synthesis and properties of several uranyl arsenates have been reported in [84VOC/GOE, 86VOC/GRA]. Vochten and Goeminne [84VOC/GOE] measured the solubility of copper (meta-zeunerite), cobalt (meta-kirchheimerite) and nickel uranyl arsenates at room temperature. The corresponding ionic medium was not specified. The experimental methodology and data analysis were basically the same as previously described in other publications by the same authors (see the comments on [81VOC/PIR] given previously in this section). Therefore, all the data exhibit analogous limitations. A similar study on manganese and iron (meta-kahlerite and its fully oxidised form) uranyl arsenates was reported by Vochten *et al.* [86VOC/GRA]. Again, the same procedures were used which render the measurements unsuitable for the extraction of additional thermodynamic data.

The stability field of becquerelite, $CaU_6O_{19} \cdot 11H_2O(cr)$, was reported as a function of temperature and calcium concentration by Atkins *et al.* [88ATK/BEC]. They also measured the solubility of this solid and $Ca_2UO_5 \cdot (1.3–1.7)H_2O(cr)$, at 20°C in two ionic media, pure water and a 0.5 M NaOH solution. Very few details about the experimental procedure are given. Thus, these solubility values do not provide sufficient information to extract thermodynamic data.

Vochten and Van Haverbeke, [90VOC/HAV], investigated the transformation of schoepite, chemically equivalent to $UO_3 \cdot 2H_2O(cr)$, into becquerelite, billietite and wölsendorfite, which correspond to $CaU_6O_{19} \cdot 11H_2O(cr)$, $BaU_6O_{19} \cdot 11H_2O(cr)$, and $PbU_2O_7 \cdot 2H_2O(cr)$, respectively. These transformation reactions were obtained at

60°C. The solubilities of these compounds were also measured at 25°C in water as a function of the pH. Care was taken to avoid the presence of CO_2(g). However, the stability of these solids at room temperature in the absence of calcium, barium, and lead, in the aqueous solution at the pH values investigated was not addressed. Based on the solubilities measured under these experimental conditions, the authors calculated the solubility products for becquerelite and billietite. They claimed to use auxiliary data from various sources of published thermodynamic data for the uranyl hydroxo species, but the set of complexes along with the corresponding thermodynamic values used are not reported. Moreover, they presented two distribution diagrams for the aqueous uranyl species involved in these two systems, which are clearly incorrect (for example, the complex UO_2OH^+ predominates at pH ≥ 9 in their figures). Therefore, all the thermodynamic data derived from this study will be strongly affected by these uncertainties.

To facilitate the task of geochemists searching for thermodynamic data to model uranium migration in aquatic environments, the tables in Chapters IX and X of Ref. [92GRE/FUG] have been combined, re-organised, updated with new references and purged of aqueous complexes. Furthermore, only solid phases which are believed (perhaps arbitrarily) to be important for modelling radionuclide migration were left in the table. Thus, solids containing alkali metals other than sodium, and potassium have not been included. For the same reason, intermetallic compounds and alloys, halides, nitrates, *etc.*, have been excluded. Other systems have also been excluded because they have been thoroughly discussed in [92GRE/FUG], like simple oxides, hydroxides, sulphides, sulphites, sulphates, arsenates and their hydrates, *etc.* Solid phases for which there is only stoichiometric or structural information have also been excluded (*e.g.*, those having only Ref. [83FLE] in Chapter IX of [92GRE/FUG]) in order to present the reader with a table containing literature sources of thermodynamic and/or solubility data of uranium minerals. The solid phases have been rearranged into families (phosphates, sulphates *etc.*). The result of all these changes is given in Table D.6. It is stressed that this table does not bring new information to the reader, but it is provided only as a convenience to geochemical modellers. Table D.6 in combination with Chapter IX in 92GRE/FUG constitute a convenient way of obtaining bibliographic information. It must be noted that it is intended that these tables should be as comprehensive as possible, but any errors or omission will be gladly received by the NEA secretariat.

Table D.6: Minerals of uranium and related solid phases of interest for geochemical modeling. The inclusion of these formulae in this Table is to be understood as information on the existence of published material. It does not imply that the authors of this Appendix give any credit to either the thermodynamic data or the chemical composition or existence of these species. The compounds for which selected data are presented in Chapter III of [92GRE/FUG], as well as those which are discussed but for which no data are recommended in Ref. [92GRE/FUG], are marked correspondingly.

Formula	Name	References
Ternary and quaternary oxides and hydroxides[(a)]*:*		
$PbU_2O_7 \cdot 2H_2O$(cr)	wölsendorfite	[90VOC/HAV]
$Ni(UO_2)_3O_3(OH)_2 \cdot 4\text{-}6H_2O$(cr)		[91VOC/HAV]
$Mn(UO_2)_3O_3(OH)_2 \cdot 4\text{-}6H_2O$(cr)		[91VOC/HAV]
$MgUO_4$(cr)		**data selected** in [92GRE/FUG]
MgU_2O_6(cr)		[81GOL/TRE2]
MgU_2O_7(cr)		[81GOL/TRE2]
MgU_3O_{10}(cr)		**data selected** in [92GRE/FUG]
$Mg(UO_2)_6O_4(OH)_6 \cdot 10\text{-}13H_2O$(cr)		[91VOC/HAV]
$Mg_3U_3O_{10}$(cr)		[83FUG]
$CaUO_4$(cr)		**data selected** in [92GRE/FUG]
$\alpha - CaUO_4$		**data selected** in [71NAU/RYZ]
$\beta - CaUO_4$		**data selected** in [92GRE/FUG]
Ca_3UO_6(cr)		**data selected** in [92GRE/FUG]
CaU_2O_6(cr)		[81GOL/TRE, 82MOR, 83FUG, 85PHI/PHI, 86MOR, 88PHI/HAL]
CaU_2O_7(cr)	calciouranoite, anhydr.	[81GOL/TRE, 82MOR, 83FUG, 85PHI/PHI, 86MOR, 88PHI/HAL]
$CaU_6O_{19} \cdot 11H_2O$(cr)	becquerelite	[88ATK/BEC, 90VOC/HAV, 94CAS/BRU, 94SAN/GRA]
$\alpha - SrUO_4$(cr)		**data selected** in [92GRE/FUG]
$\beta - SrUO_4$(cr)		**data selected** in [92GRE/FUG] [79TAG/FUJ, 86MOR]
$SrUO_4$(cr)		[83KOH]
Sr_2UO_5(cr)		**data selected** in [92GRE/FUG]
Sr_3UO_6(cr)		**data selected** in [92GRE/FUG]
$Sr_2U_3O_{11}$(cr)		**data selected** in [92GRE/FUG]
SrU_4O_{13}(cr)		**data selected** in [92GRE/FUG]
$BaUO_3$(cr)		**data selected** in [92GRE/FUG]
$BaUO_4$(cr)		**data selected** in [92GRE/FUG]
Ba_3UO_6(cr)		**data selected** in [92GRE/FUG]
BaU_2O_7(cr)	bauranoite, anhydr.	**data selected** in [92GRE/FUG]
$Ba_2U_2O_7$(cr)		**data selected** in [92GRE/FUG]
$Ba_6Dy_2(UO_6)_3$(cr)		[82MOR]

Table D.6 (continued)

Formula	Name	References
Ternary and quaternary oxides and hydroxides (continued):		
Ba_2MgUO_6(cr)		**data selected** in [92GRE/FUG]
Ba_2CaUO_6(cr)		**data selected** in [92GRE/FUG]
Ba_2SrUO_6(cr)		**data selected** in [92GRE/FUG]
$BaU_6O_{19} \cdot 11H_2O$(cr)	billietite	[90VOC/HAV]
$NaUO_3$(cr)		**data selected** in [92GRE/FUG]
$\alpha - Na_2UO_4$		**data selected** in [92GRE/FUG]
$\beta - Na_2UO_4$		**data selected** in [92GRE/FUG]
Na_3UO_4(cr)		**data selected** in [92GRE/FUG]
Na_4UO_5(cr)		**data selected** in [92GRE/FUG] [71COR/LOO, 78COR/OHA, 81LIN/BES, 82HEM, 82WAG/EVA, 83FUG, 85PHI/PHI, 85TSO/BRO, 86MOR, 88PHI/HAL]
$Na_2U_2O_7$(cr)		**data selected** in [92GRE/FUG]
$Na_6U_7O_{21}$(cr)		[78COR/OHA]
$Na_6U_7O_{24}$(cr)		**data selected** in [92GRE/FUG] [71COR/LOO, 81LIN/BES, 82HEM, 82MOR, 82WAG/EVA, 83FUG, 86MOR]
$Na_4O_4UO_4 \cdot 9H_2O$(cr)		[82WAG/EVA]
$Na_2U_2O_7 \cdot 1.5H_2O$(cr)		[65MUT, 82WAG/EVA]
KUO_3(cr)		**data selected** in [92GRE/FUG] [81COR/OUW, 81LIN/BES, 82HEM, 82MOR, 83FUG, 83KAG/KYS, 85PHI/PHI, 86MOR, 88PHI/HAL]
K_2UO_4(cr)		**data selected** in [92GRE/FUG]
K_4UO_5(cr)		[81LIN/BES]
$K_2U_2O_7$(cr)		**data selected** in [92GRE/FUG] [75OHA/HOE2, 81LIN/BES, 85FUG, 86MOR]
$K_2U_4O_{13}$(cr)		[81LIN/BES]
$K_2U_6O_{19} \cdot 11H_2O$(cr)	compreignacite	[94SAN/GRA]
$K_2U_7O_{22}$(cr)		[81LIN/BES]

Table D.6 (continued)

Formula	Name	References
Sulphates[b,c]*:*		
$Ca_3NaUO_2(CO_3)_3FSO_4 \cdot 10H_2O(cr)$	schroeckingerite	[82HEM, 83OBR/WIL]
$Zn_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O(cr)$	Zn-zippeite	[79HAA/WIL, 81OBR/WIL, 82HEM][d]
$Co_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O(cr)$	Co-zippeite	[79HAA/WIL, 81OBR/WIL, 82HEM][d]
$Ni_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O(cr)$	Ni-zippeite	[79HAA/WIL, 81OBR/WIL, 82HEM][d]
$Mg_2(UO_2)_6(SO_4)_3(OH)_{10} \cdot 8H_2O(cr)$	Mg-zippeite	[79HAA/WIL, 81OBR/WIL, 82HEM][d]
$Na_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot 4H_2O(cr)$	Na-zippeite	[81OBR/WIL, 82HEM]
$K_4(UO_2)_6(SO_4)_3(OH)_{10} \cdot 4H_2O(cr)$	zippeite	[81OBR/WIL, 82HEM]
Phosphates:		
$U_3(PO_4)_4(cr)$		[73MOS, 78ALL/BEA][e]
$U(HPO_4)_2 \cdot 4H_2O(cr)$		**data selected** in [92GRE/FUG]
$U(HPO_4)_2(cr)$		[71MOS, 84VIE/TAR, 86WAN][f]
$U(HPO_4)_2H_3PO_4 \cdot H_2O(cr)$		[55SCH][g]
$UO_2HPO_4 \cdot 4H_2O(cr)$	H-autunite	**data selected** in [92GRE/FUG]
$UO_2HPO_4(cr)$		See footnote (h)
$(UO_2)_2(HPO_4)_2(cr)$		See footnote (h)
$H_2(UO_2)_2(PO_4)_2(cr)$		See footnote (h)
$H_2(UO_2)_2(PO_4)_2 \cdot 10H_2O(cr)$		See footnotes (h) and (i)
$UO_2(H_2PO_4)_2 \cdot 3H_2O(cr)$		[54SCH/BAE][j]
$(UO_2)_3(PO_4)_2(cr)$		**data selected** in [92GRE/FUG]
$(UO_2)_3(PO_4)_2 \cdot 4H_2O(cr)$		**data selected** in [92GRE/FUG] [92SAN/BRU]
$(UO_2)_3(PO_4)_2 \cdot 6H_2O(cr)$		**data selected** in [92GRE/FUG]
$NH_4UO_2PO_4 \cdot 3H_2O(cr)$	uramphite	[61KAR, 71NAU/RYZ, 84VIE/TAR, 88PHI/HAL]
$NH_4UO_2PO_4(cr)$	NH_4-autunite, anhydr.	[56CHU/STE, 65VES/PEK, 84VIE/TAR, 85PHI/PHI, 86WAN][k]
$(NH_4)_2(UO_2)_2(PO_4)_2(cr)$		[78LAN, 88PHI/HAL]
$HAl(UO_2)_4(PO_4)_4 \cdot 16H_2O(cr)$	sabugalite	[83VOC/PEL]
$HAl(UO_2)_4(PO_4)_4(cr)$	sabugalite, anhydr.	[84GEN/WEI]
$Pb_2UO_2(PO_4)_2 \cdot 2H_2O(cr)$	parsonsite	[84NRI2]
$Pb_2UO_2(PO_4)_2(cr)$	parsonsite, anhydr.	[84GEN/WEI]
$Pb(UO_2)_2(PO_4)_2 \cdot 10H_2O(cr)$		[65MUT/HIR]
$Pb(UO_2)_2(PO_4)_2 \cdot 2H_2O(cr)$	przhevalskite	[84NRI2][l]
$Pb(UO_2)_2(PO_4)_2(cr)$	przhevalskite, anhydr.	[78LAN, 85PHI/PHI, 88PHI/HAL]

Table D.6 (continued)

Formula	Name	References
Phosphates (continued):		
$Pb(UO_2)_3(PO_4)_2(OH)_2$(cr)		[84GEN/WEI]
$Pb_2(UO_2)_3(PO_4)_2(OH)_4 \cdot 3H_2O$(cr)	dumontite	[84NRI2]
$Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 7H_2O$(cr)	renardite[(m)]	[84NRI2]
$Pb(UO_2)_4(PO_4)_2(OH)_4 \cdot 8H_2O$(cr)		[84NRI2]
$Cu(UO_2)_2(PO_4)_2 \cdot$ 8-12H_2O(cr)	torbernite	[65MUT/HIR, 84NRI2]
$Cu(UO_2)_2(PO_4)_2 \cdot 8H_2O$(cr)	meta-torbernite	[81VOC/PIR, 84NRI2, 84VIE/TAR]
$Cu(UO_2)_2(PO_4)_2$(cr)	torbernite, anhydr.	[78LAN, 85PHI/PHI, 88PHI/HAL]
$Ni(UO_2)_2(PO_4)_2 \cdot 7H_2O$(cr)		[81VOC/PIR, 84VIE/TAR]
$Co(UO_2)_2(PO_4)_2 \cdot 7H_2O$(cr)		[81VOC/PIR, 84VIE/TAR]
$Fe(UO_2)_2(PO_4)_2OH \cdot 6H_2O$(cr)		[84VOC/GRA]
$Fe(UO_2)_2(PO_4)_2 \cdot 8H_2O$(cr)	bassetite	[65MUT/HIR, 84VOC/GRA][(n)]
$Fe(UO_2)_2(PO_4)_2$(cr)	bassetite, anhydr.	[78LAN, 85PHI/PHI, 86WAN, 88PHI/HAL]
$Mg(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)	saleeite	[65MUT/HIR]
$Mg(UO_2)_2(PO_4)_2$(cr)	saleeite, anhydr.	[78LAN, 85PHI/PHI, 86WAN, 88PHI/HAL]
$CaU(PO_4)_2 \cdot 2H_2O$(cr)	ningyoite	[65MUT, 65MUT/HIR, 78LAN, 84VIE/TAR, 88PHI/HAL][(i)]
$CaU(PO_4)_2$(cr)		[86WAN]
$Ca(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)	autunite	[65MUT, 65MUT/HIR, 84VIE/TAR][(i)]
$Ca(UO_2)_2(PO_4)_2$(cr)	autunite, anhydr.	[78LAN, 85PHI/PHI, 86WAN, 88PHI/HAL]
$Ca(UO_2)_4(PO_4)_2(OH)_4$(cr)		[84GEN/WEI]
$Sr(UO_2)_2(PO_4)_2$(cr)	Sr-autunite, anhydr.	[78LAN, 85PHI/PHI, 86WAN, 88PHI/HAL]
$Sr(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)		[65MUT/HIR]
$Ba(UO_2)_2(PO_4)_2$(cr)	uranocircite, anhydr.	[78LAN, 84GEN/WEI, 85PHI/PHI, 86WAN, 88PHI/HAL]
$Ba(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)	uranocircite II	[65MUT/HIR]
$NaUO_2PO_4$(cr)	Na-autunite, anhydr.	[65VES/PEK, 85PHI/PHI, 86WAN][(k)]
$Na_2(UO_2)_2(PO_4)_2$(cr)		[78LAN, 88PHI/HAL][(k)]
$Na_2(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)		[65MUT/HIR]
KUO_2PO_4(cr)	K-autunite, anhydr.	[56CHU/STE, 65VES/PEK, 82WAG/EVA, 84VIE/TAR, 85PHI/PHI, 86WAN][(k)]
$K_2(UO_2)_2(PO_4)_2$(cr)		[78LAN, 88PHI/HAL][(k)]
$KUO_2PO_4 \cdot 3H_2O$(cr)	See footnote (o)	[61KAR, 71NAU/RYZ, 84VIE/TAR, 85PHI/PHI, 88PHI/HAL]
$K_2(UO_2)_2(PO_4)_2 \cdot 10H_2O$(cr)		[65MUT/HIR]

Table D.6 (continued)

Formula	Name	References
Pyrophosphates:		
UPO_5(cr)		**data selected** in [92GRE/FUG]
$UP_2O_7 \cdot xH_2O$(cr)		[67MER/SKO][(p)]
UP_2O_7(cr)		**data selected** in [92GRE/FUG]
$(UO_2)_2P_2O_7$(cr)		**data selected** in [92GRE/FUG]
Arsenates:		
$(UO_2)_3(AsO_4)_2$(cr)	troegerite, anhydr.	**data selected** in [92GRE/FUG]
UO_2HAsO_4(cr)	hydrogen spinite	[56CHU/SHA, 84GEN/WEI]
$NH_4UO_2AsO_4$(cr)		[56CHU/SHA]
$Pb_2UO_2(AsO_4)_2$(cr)	hallimondite	[84GEN/WEI]
$Zn(UO_2)_2(AsO_4)_2$(cr)	meta-lodevite, anhydr.	[84GEN/WEI]
$Cu(UO_2)_2(AsO_4)_2$(cr)	meta-zeunerite, anhydr.	[84GEN/WEI]
$Cu(UO_2)_2(AsO_4)_2 \cdot 8H_2O$(cr)	meta-zeunerite	[84VOC/GOE]
$Ni(UO_2)_2(AsO_4)_2 \cdot 7H_2O$(cr)		[84VOC/GOE]
$Co(UO_2)_2(AsO_4)_2$(cr)	meta-kirchheimerite, anhydr.	[84GEN/WEI]
$Co(UO_2)_2(AsO_4)_2 \cdot 7H_2O$(cr)	meta-kirchheimerite, heptahydrate	[84VOC/GOE]
$Fe(UO_2)_2(AsO_4)_2$(cr)	kahlerite, anhydr.	[84GEN/WEI]
$Fe(UO_2)_2(AsO_4)_2 \cdot 8H_2O$(cr)	meta-kahlerite	[86VOC/GRA]
$Mn(UO_2)_2(AsO_4)_2 \cdot 8H_2O$(cr)		[86VOC/GRA]
$Mg(UO_2)_2(AsO_4)_2$(cr)	novacekite, anhydr.	[84GEN/WEI]
$Ca(UO_2)_2(AsO_4)_2$(cr)	uranospinite, anhydr.	[84GEN/WEI, 91FAL/HOO]
$Ca(UO_2)_4(AsO_4)_2(OH)_4$(cr)	arsenuranylite, anhydr.	[84GEN/WEI]
$Ba(UO_2)_2(AsO_4)_2$(cr)	meta-heinrichite, anhydr.	[84GEN/WEI]
$NaUO_2AsO_4 \cdot 4H_2O$(cr)	Na-uranospinite	[71NAU/RYZ]
$NaUO_2AsO_4$(cr)		[56CHU/SHA, 91FAL/HOO]
KUO_2AsO_4(cr)	abernathyite, anhydr.	[56CHU/SHA, 71NAU/RYZ, 82WAG/EVA]
Carbonates:		
UO_2CO_3(cr)	rutherfordine	**data selected** in [92GRE/FUG]
$UO_2CO_3 \cdot H_2O$(cr)		[82HEM][(q)]
$UO_2(HCO_3)_2 \cdot H_2O$(cr)		[76BOU/BON, 78COR/OHA, 82WAG/EVA, 83FUG, 86MOR]
$Ca_3NaUO_2(CO_3)_3FSO_4 \cdot 10H_2O$(cr)	schroeckingerite	[82HEM, 83OBR/WIL]
$Ca_2UO_2(CO_3)_3 \cdot 10\text{-}11H_2O$(cr)	liebigite	[80BEN/TEA, 80ALW/WIL, 82HEM, 83OBR/WIL][(r)]

Table D.6 (continued)

Formula	Name	References
Carbonates (continued):		
$CaMgUO_2(CO_3)_3 \cdot 12H_2O(cr)$	swartzite	[80ALW/WIL, 80BEN/TEA, 82HEM][(r)]
$Mg_2UO_2(CO_3)_3 \cdot 18H_2O(cr)$	bayleyite	[80ALW/WIL, 80BEN/TEA, 82HEM][(r)]
$CaNa_2UO_2(CO_3)_3 \cdot 6H_2O(cr)$	andersonite	[80ALW/WIL, 80BEN/TEA, 83OBR/WIL][(r)]
$Ca_2CuUO_2(CO_3)_4 \cdot 6H_2O(cr)$	voglite	[82HEM]
$Ca_3Mg_3(UO_2)_2(CO_3)_6(OH)_4 \cdot 18H_2O(cr)$	rabbittite	[82HEM]
$Na_4UO_2(CO_3)_3(cr)$		**data selected** in [92GRE/FUG]
$K_3NaUO_2(CO_3)_3 \cdot H_2O(cr)$	grimselite	[83OBR/WIL]
Silicates:		
$USiO_4(cr)$	coffinite	**data selected** in [92GRE/FUG]
$(UO_2)_2SiO_4 \cdot 2H_2O(cr)$	soddyite	[82HEM, 92NGU/SIL, 94CAS/BRU]
$PbUO_2SiO_4 \cdot H_2O(cr)$	kasolite	[82HEM]
$(H_3O)KUO_2SiO_4(cr)$	boltwoodite[(s)]	[82HEM]
$Na_{0.7}K_{0.3}(H_3O)UO_2SiO_4 \cdot H_2O(cr)$	Na-boltwoodite[(s)]	[82HEM, 92NGU/SIL]
$Cu(UO_2)_2(SiO_3OH)_2 \cdot 6H_2O(cr)$	cupro sklodowskite	[82HEM]
$Mg(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O(cr)$	sklodowskite	[82HEM][(t)]
$Ca(UO_2)_2(SiO_3OH)_2(cr)$	uranophane, anhydr.	[78LAN, 80BEN/TEA, 86WAN, 88LEM, 88PHI/HAL]
$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O(cr)$	uranophane	[82HEM, 92NGU/SIL, 94CAS/BRU]
$Ca(UO_2)_2Si_6O_{15} \cdot 5H_2O(cr)$	haiweeite	[82HEM]
$Na_2(UO_2)_2Si_6O_{15} \cdot 4H_2O(cr)$	Na-weeksite	[92NGU/SIL]
$K_2(UO_2)_2Si_6O_{15} \cdot 4H_2O(cr)$	weeksite	[82HEM]
Vanadates:		
$Pb(UO_2)_2(VO_4)_2(cr)$	curienite, anhydr.	[84GEN/WEI]
$Al(UO_2)_2(VO_4)_2OH(cr)$	vanuralite, anhydr.	[84GEN/WEI]
$CuUO_2VO_4(cr)$	sengierite, anhydr.	[84GEN/WEI]
$Ca(UO_2)_2(VO_4)_2(cr)$	tyuyamunite, anhydr.	[78LAN, 80BEN/TEA, 85PHI/PHI, 88PHI/HAL]
$Ba(UO_2)_2(VO_4)_2(cr)$	francevillite, anhydr.	[84GEN/WEI]
$NaUO_2VO_4(cr)$	strelkinite, anhydr.	[84GEN/WEI]
$K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O(cr)$	carnotite	[62HOS/GAR]
$K_2(UO_2)_2(VO_4)_2(cr)$	carnotite, anhydr.	[78LAN, 80BEN/TEA, 85PHI/PHI, 88PHI/HAL]

Table D.6 (continued)

Footnotes:

(a) Simple oxides and hydroxides of uranium are discussed in Section V.3.3 (*pp.*131–148) of [92GRE/FUG].

(b) Only binary and ternary sulphates are listed. Simple uranium sulphates are discussed in Section V.5.1.3.2 (*pp.*249–254) of [92GRE/FUG].

(c) It should be noted that there is some disagreement in the literature on the number of water molecules in the formulae of the zippeite family.

(d) See Section V.5.1.3.2.c (*pp.*254–255) and the discussion of Ref. [79HAA/WIL] in Appendix A (*p.*646) of [92GRE/FUG].

(e) See the discussion in Section V.6.2.2.5.b (*p.*294) of [92GRE/FUG].

(f) See the discussion in Section V.6.2.2.7.b (*p.*297) of [92GRE/FUG].

(g) See the discussion in Section V.6.2.2.9 (*p.*298) of [92GRE/FUG].

(h) Compounds with formula $H_2(UO_2)_2(PO_4)_2 \cdot xH_2O$(cr) ($x = 0$ to 10) are discussed in Sections V.6.2.1.1.b and V.6.2.2.10.c (*pp.* 284–286 and 299–300 respectively) of [92GRE/FUG]. Grenthe *et al.* selected thermodynamic data for $UO_2HPO_4 \cdot 4H_2O$(cr), *cf.* Table III.1 in [92GRE/FUG].

(i) See the discussion of Ref. [65MUT] in Appendix A (*p.*599) of Ref. [92GRE/FUG].

(j) See the discussions in Sections V.6.2.1.1.b and V.6.2.2.8 (*pp.* 284–286 and 298) and the comments on [54SCH/BAE] in Appendix A (*p.*564) of Ref. [92GRE/FUG].

(k) Veselý *et al.* [65VES/PEK] reported solubility products for *hydrated* alkali phosphates. Grenthe *et al.* [92GRE/FUG] reinterpreted the results of Ref. [65VES/PEK], *cf.* Table V.40 (*p.*283), Section V.6.2.1.1.b (*pp.*286), and Appendix A (*pp.*600–601) of [92GRE/FUG]. It should be noted that Langmuir [78LAN] incorrectly referred as sodium and potassiun autunite the anhydrous compounds.

(l) Nriagu gives 4 waters of hydration for this mineral [84NRI2, Table 1].

(m) The stoichiometry of the mineral renardite is not clear, and it is related to dewindtite: $Pb_3(IO_2)_6(PO_4)_4O_2(OH)_2 \cdot 12H_2O$(s) (see [91FIN/EWI]).

(n) Muto, Hirono and Kurata give 10 molecules of water of hydration for this mineral [65MUT/HIR].

(o) This formula is related to meta-ankoleite: $K_2(UO_2)_2(PO_4)_2 \cdot 6H_2O$(cr).

(p) See the discussion of Ref. [67MER/SKO] in Appendix A (*p.*603) of [92GRE/FUG].

(q) Hemingway [82HEM] incorrectly assigned the name of sharpite to this solid.

(r) Discussed in Section V.7.1.2.2.b (*pp.*327–328) of [92GRE/FUG].

(s) There is some uncertainty in the composition of boltwoodite and Na-boltwoodite, *cf.* [81STO/SMI, 91FIN/EWI, 92NGU/SIL].

(t) Hemingway [82HEM] reports estimated data for a solid with 6 water molecules.

D.6. References to Appendix D

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