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**CHEMICAL
THERMODYNAMICS
OF NEPTUNIUM
AND PLUTONIUM**

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**CHEMICAL THERMODYNAMICS
OF
NEPTUNIUM AND PLUTONIUM**

CHEMICAL THERMODYNAMICS

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- Vol. 2. Chemical Thermodynamics of Americium (R.J. Silva et al.)
- Vol. 3. Chemical Thermodynamics of Technetium (M.C.A. Sandino and E. Östhols, eds.)
- Vol. 4. Chemical Thermodynamics of Neptunium and
Plutonium (OECD Nuclear Energy Agency, ed.)

CHEMICAL THERMODYNAMICS 4

Chemical Thermodynamics of Neptunium and Plutonium

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NUCLEAR ENERGY AGENCY
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT



2001

ELSEVIER

AMSTERDAM • LONDON • NEW YORK • OXFORD • PARIS • SHANNON • TOKYO

Published under the imprint NORTH-HOLLAND by
ELSEVIER SCIENCE B.V.
Sara Burgerhartstraat 25
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

Library of Congress Cataloging-in-Publication Data
A catalog record from the Library of Congress has been applied for.

ISBN: 0-444-50379-X

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Printed in The Netherlands

Preface

Unlike earlier books in this series, this review describes the selection of chemical thermodynamic data for species of two elements, neptunium and plutonium. Although this came about more by circumstance than design, it has allowed for a more consistent approach to chemical interpretations than might have occurred in two separate treatments. It has also drawn attention to cases where the available data do not show expected parallels, and where further work may be useful to confirm or refute apparent differences in the behaviour of neptunium and plutonium.

This volume has taken more than ten years to compile. The combined neptunium and plutonium groups, selected by Anthony Muller, the originator of the TDB project, first met at Saclay, France in April 1988. Subsequent meetings were held at Pinawa, Canada in September 1990, at Saclay in February 1992, and at Issy-les-Moulineaux, France in March 1994 and December 1997. Smaller working sub-groups met in Chicago (1994 and 1996) and Issy-les-Moulineaux (1995 and 1996). The logistics and financing of the TDB project has meant the NEA itself has had difficulties in editorial preparation of more than one volume at a time, and the current volume has passed through the hands of four successive TDB co-ordinators, Hans Wanner (who later joined the neptunium/plutonium TDB team as a reviewer), Ignasi Puigdomenech, Amaia Sandino and Erik Östholts. The latter two have done the bulk of the work in combining the reviewers' drafts and seeing the book through to its final form. Several of the reviewers worked on other elements for the TDB; this overlap delayed work on neptunium and plutonium, but has enhanced the consistency of the TDB as a whole.

Despite the extended time-frame, most of the original participants in the project have persisted through to its completion - perhaps an indication of the importance the authors have attached to the review. During the time the work was being done, a large number of excellent, relevant studies have been reported in the literature, many based in the world-wide efforts directed toward management of nuclear fuel waste. These papers have helped strengthen, but have to some extent delayed this publication. Any chemical thermodynamic database does no more than represent a survey of what is known at a particular time. The time required to carefully compile and consider data dictates that any database is at least slightly "out-of-date" by the time it appears in print. The current review is no exception. Although an arbitrary "cut-off" date of mid-1996 was set for papers used in this review, a few later papers have been included.

The large number of co-authors has resulted in less consistency in style and depth of discussion than in some previous volumes. We hope readers do not find this unduly distracting. Although almost all of the authors contributed text and comments to many of the chapters, primary responsibility for the different chapters was divided as follows. William Ullman and Jim Sullivan prepared the sections on sulphato complexes and on plutonium carbonates, Hans Wanner the sections on aqueous halide and thiocyanate complexes, Kastriot Spahiu the sections on nitrate and phosphato complexes, Pierre Vitorge the extensive section on neptunium carbonates (he also extensively re-

viewed several of the other sections), Heino Nitsche the initial drafts of the aqua-ion sections, and Paul Potter the sections on nitrides. Malcolm Rand prepared the sections on carbides and, with Jean Fuger, the sections on solid and gas phase halides. He and the chairman drafted the sections on oxides, and the chairman prepared the sections on hydrolysis with help from Jan Rydberg (who also provided his expertise in extraction techniques to the other reviewers as required).

Experimental chemical thermodynamics is not a particularly popular topic in modern scientific circles. Because of safety and regulatory constraints, work on the chemistry of transuranium elements is particularly slow, and therefore costly. Fewer and fewer laboratories are capable of carrying out such measurements, and of having the luxury of time to check and recheck their values. It was therefore distressing to find that much of the work that has been done was incompletely documented. Often the reviewers have had to pass over what were probably good studies because interpretations had been used that are now known to be incorrect, and the raw data were unavailable for reinterpretation (sadly, this was the case even for several studies done in the late 1980s). As is the case for databases for many other elements, “key” values often are based on a single experiment or even more tenuously on a chain of uncorroborated experimental values. Some of the values for the plutonium aqua ions are particularly glaring examples. Although we have assigned uncertainties, there is no satisfactory way of dealing quantitatively with this problem.

Chalk River, Canada, November 2000

Robert Lemire, Chairman

Acknowledgements

Contributions of Robert Lemire were prepared under the auspices of Atomic Energy of Canada Limited at the Whiteshell Laboratories from 1988-1992 and at the Chalk River Laboratories from 1992 onwards. Support was provided by Atomic Energy of Canada (until 1996 this support came under the auspices of the CANDU Owners Group). Some additional support was provided by the NEA in 1998 and 2000.

Early contributions of the review work by Malcolm Rand were funded from the Corporate Research Programme of AEA Technology, Harwell, while he was employed by the U.K. Atomic Energy Authority.

Contributions of Hans Wanner were supported by the Swiss Federal Nuclear Safety Inspectorate (HSK).

Contributions of Kastriot Spahiu were supported by SKB.

Contributions of Jan Rydberg were supported financially by SKB.

Jean Fuger acknowledges the financial support of the Inter-University Institute for Nuclear Sciences (Brussels) to the Laboratory of Coordination Chemistry and Radiochemistry of University of Liège.

Support for the U.S. participation in this project (William J. Ullman, James C. Sullivan and Heino Nitsche) was provided by the U.S. Department of Energy through the Yucca Mountain Project Office at Lawrence Livermore National Laboratory and Argonne National Laboratory.

Much of the work on which the reviews by Paul Potter are based was supported, several years ago, by the Fast Breeder Reactor and Underlying Research Programmes of the U.K. Atomic Energy Authority of which he was an employee.

The authors wish to express their gratitude to Ingmar Grenthe for his continuing interest in the project, and especially for his help in providing a preliminary review of the book. Dr. Dhanpat Rai assisted by providing preprints of several of his publications on neptunium and plutonium thermodynamics. We also thank Thomas Fanghänel and Volker Neck for their comments on several draft sections before these were sent to peer review. Their remarks led us to rethink several points, and we feel this has resulted in substantial improvements. Useful comments were also received from Wolfgang Hummel and Tres Thoenen.

The tireless efforts of Erik Östhols and Amaia Sandino, co-ordinators for the TDB project during the time the main part of the draft of this book was assembled, are greatly appreciated. Their work built on the earlier efforts of Ignasi Puigdomenèch and Hans Wanner.

Also at the NEA, Stina Lundberg has diligently shepherded the draft into its final form over the last year of the project, and Cecile Lotteau deserves credit for much of the layout work for the volume done between 1995 and 1997. Claes Nordborg has helped maintain support for the project through many personnel changes at the NEA. Pierre Vitorge wishes to express his appreciation to Helena Capdevila of the CEA for many helpful discussions. Robert Lemire thanks the library staff at both Chalk River

and Whiteshell Laboratories of AECL for their literature searches and assistance in obtaining copies of many references.

The entire manuscript of this book has undergone a peer review by an independent international group of reviewers, according to the procedures in the TDB-6 guidelines, available from the NEA. The peer reviewers have viewed and approved the modifications made by the authors in response to their comments. The peer review comment records may be obtained on request from the OECD Nuclear Energy Agency. The peer reviewers are:

Dr. Jacques Bourges	Verrières-le-Buisson, France
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Dr. Dhanpat Rai	Battelle, Pacific Northwest National Laboratory, Richland, Washington, U.S.A.

Their contributions are gratefully acknowledged.

Foreword

This is the fourth volume of a series of expert reviews of the chemical thermodynamics of key chemical elements in nuclear technology and waste management. 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 2.6, ensures consistency not only within the recommended data sets on neptunium and plutonium, but also among all the data sets to be published in the 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 via Internet directly from the NEA Data Bank.
- 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.

We'd like to hear from you!

If you have comments on the NEA TDB reviews, please contact us and tell us what you liked, what you didn't like, and of course about any errors you find in the reviews. See below for information on where to find us.

How to contact the NEA TDB project

Information on the NEA and the TDB project, on-line access to selected data, computer programs *etc.*, as well as many documents in electronic format, is available at <http://www.nea.fr>.

For contact with the TDB project coordinator and the authors of the review reports,

sending comments on the TDB reviews, or if you wish to request further information, please send mail to tdb@nea.fr. If this is not possible, write to

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Part I

Introductory material

Chapter 1

Introduction

1.1 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 ground water, and the surrounding rock material, in order to estimate the quantities of waste that can be transported in the aqueous phase. It is thus essential to know the relative stabilities of the compounds and complexes that may form under the relevant conditions. This information is often provided by speciation calculations using chemical thermodynamic data. The local conditions, such as ground water and rock composition or temperature, may not be constant along the migration paths of hazardous materials, and fundamental thermodynamic data are the indispensable basis for dynamic modelling of the chemical behaviour of hazardous waste components.

In the field of radioactive waste management, the hazardous material consists to a large extent of actinides and fission products from nuclear reactors. 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 special issues with compilations of physicochemical properties of compounds and alloys of elements important in reactor technology: Pu, Nb, Ta, Be, Th, Zr, Mo, Hf and Ti between 1966 and 1983. 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) is lacking in the IAEA series.

The Radioactive Waste Management Committee (RWMC) of the OECD Nuclear Energy Agency recognized 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 [85MUL, 88WAN, 91WAN]. 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 books on chemical thermodynamics of uranium [92GRE/FUG], americium [95SIL/BID] and technetium [99RAR/RAN], the present report on thermodynamics neptunium and plutonium is the fourth 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/KON2], 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], and Part 12 by Fuger *et al.* [92FUG/KHO] within the IAEA reviews series 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.

1.2 Focus of the review

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

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

The present review therefore puts much weight on the assessment of the low-temperature thermodynamics of neptunium and plutonium in aqueous solution and makes independent analyses of the available literature in this area. 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 ground water, within the ionic strength limits given by the experimental data used for the data analyses in the present review.

The interactions between solid compounds, such as the rock materials, and the aqueous solution and its components are as important as the interactions within the aqueous solution, because the solid materials in the geosphere control the chemistry of the ground water, and they also contribute to the overall solubilities of key elements. The present review therefore also considers the chemical behaviour of solid compounds that are likely to occur, or to be formed, under geological and environmental conditions. It is, however, difficult to assess the relative importance of the solid phases for performance assessment purposes, particularly since their interactions with the aqueous phase are in many cases known to be subject to quantitatively unknown kinetic constraints. Furthermore, in some circumstances sorption of aqueous ions at mineral-water interfaces may be a more important factor in determining migration of neptunium and plutonium than dissolution and precipitation phenomena.

This book contains a summary and a critical review of the thermodynamic data on compounds and complexes containing neptunium (*cf.* Part III) and plutonium (*cf.* Part IV), as reported in the available chemical literature up to mid-1996, but a few more recent references are also included. A comparatively large number of primary references are discussed separately in Appendix A.

Although the focus of this review is on neptunium and plutonium, 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 and other volumes of this series [92GRE/FUG, 95SIL/BID, 99RAR/RAN], and their use is recommended by this review. Care has been taken that all the selected thermodynamic data at standard conditions (*cf.* Section 2.3) and 298.15 K are internally consistent. For this purpose, special software has been developed at the NEA Data Bank that is operational in conjunction with the NEA-TDB data base system, *cf.* Section 2.6. 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 neptunium and plutonium compounds and complexes.

The present review does not include any compounds or complexes containing organic ligands. This class of compounds is planned to be the subject of a later review in the NEA-TDB series.

1.3 Review procedure and results

The objective of the present review is to present an assessment of the sources of published thermodynamic data in order to decide on the most reliable values 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 neg-

lected, 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 re-interpreted 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 ion interaction (SIT) equations (*cf.* Appendix B). For convenience, these SIT equations are referred to in some places in the text as “the SIT”.

In order to ensure that consistent procedures are used for the evaluation of primary data, a number of guidelines have been developed. They have been updated and improved since 1987, and their most recent versions are available at the NEA [2000ÖST/WAN, 2000GRE/WAN, 99WAN/ÖST, 2000WAN/ÖST, 99WAN]. Some of these procedures are also outlined in this volume, *cf.* Chapter 2, Appendix B, and Appendix C. Parts of these sections, which were also published in earlier volumes [92GRE/FUG, 95SIL/BID, 99RAR/RAN], have been revised in this review. For example, in Chapter 2, the section on “Redox equilibria” has been revised.

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 [99WAN]. 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 3, 4 and 5) refer to the reference temperature of 298.15 K and to standard conditions, *cf.* Section 2.3. 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 (SIT) for the extrapolation of experimental data to the standard state in the data evaluation process, and in some cases this requires the re-evaluation of original experimental values (solubilities, emf data, *etc.*). For maximum consistency, 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 (Chapters 3 and 4) may not be “complete” with respect to all the conceivable systems and conditions; there are gaps in the information. The gaps are pointed out in the various sections of Parts III and IV, and this information may be used as a basis for the assignment of research priorities.

Chapter 2

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.

2.1 Symbols, terminology and nomenclature

2.1.1 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 2.2.

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”, and this is a term which is often used to refer 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.

2.1.2 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 [79WHI, 88MIL/CVI]. They are summarised in Table 2.1.

Table 2.1: Symbols and terminology.

Symbols and terminology	
length	l
height	h
radius	r
diameter	d

(Continued on next page)

Table 2.1: (continued)

Symbols and terminology	
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: $A/(c_B l)$	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	$C_{p,m}$
(molar) heat capacity of a solute at constant pressure	$C_{p,m,2}$
(molar) enthalpy	H_m
(molar) Gibbs energy	G_m
chemical potential of substance B	μ_B
pressure	p
partial pressure of substance B: $x_B p$	p_B
fugacity of substance B	f_B
fugacity coefficient: f_B/p_B	$\gamma_{f,B}$
amount of substance ^(b)	n
mole fraction of substance B: $n_B/\sum_i n_i$	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) , $m_{\pm}^{(v_+ + v_-)} = m_+^{v_+} m_-^{v_-}$	m_{\pm}
activity of substance B	a_B

(Continued on next page)

Table 2.1: (continued)

Symbols and terminology	
activity coefficient, molality basis: a_B/m_B	γ_B
activity coefficient, concentration basis: a_B/c_B	y_B
mean ionic activity ^(e) , $a_{\pm}^{(\nu_+ + \nu_-)} = a_B = a_+^{\nu_+} a_-^{\nu_-}$	a_{\pm}
mean ionic activity coefficient ^(e) , $\gamma_{\pm}^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$	γ_{\pm}
osmotic coefficient, molality basis	ϕ
ionic strength: $I_m = \frac{1}{2} \sum_i m_i z_i^2$ or $I_c = \frac{1}{2} \sum_i c_i z_i^2$	I
SIT ion interaction coefficient between substance B ₁ and substance B ₂	$\varepsilon_{(B_1, B_2)}$
stoichiometric coefficient of substance B (negative for reactants, positive for products)	ν_B
general equation for a chemical reaction	$0 = \sum_B \nu_B B$
equilibrium constant ^(f)	K
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
pH = $-\log_{10}[a_{H^+}/(\text{mol} \cdot \text{kg}^{-1})]$	
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}C .

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

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

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

^(e)For an electrolyte $N_{\nu_+} X_{\nu_-}$ which dissociates into ν_{\pm} ($= \nu_+ + \nu_-$) ions, in an aqueous solution with concentration m , the individual cationic molality and activity coefficient are m_+ ($= \nu_+ m$) and γ_+ ($= a_+/m_+$). 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 2.1.6. 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 2.3.1.

Table 2.2: 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

2.1.3 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:

- 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 $\text{UF}_2\text{O}(\text{cr})$.

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, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ is standard, $(\text{UO}_2)_2(\text{OH})_3\text{CO}_3^-$ 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^- , $\text{Am}(\text{Hedta})(\text{s})$ (where edta stands for ethylenediaminetetraacetate).

2.1.4 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.*, $\text{H}_2\text{O}(\text{l})$.
- The designator (aq) is used for undissociated, uncharged aqueous species, *e.g.*, $\text{U}(\text{OH})_4(\text{aq})$, $\text{CO}_2(\text{aq})$. 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 H₂O in Eqs. (2.2) and (2.3). H₂O(l) in Reaction (2.2) indicates that H₂O is present as a pure liquid, *i.e.*, no solutes are present, whereas Reaction (2.3) involves a HCl solution, in which the thermodynamic properties of H₂O(sln) may not be the same as those of the pure liquid H₂O(l). In dilute solutions, however, this difference in the thermodynamic properties of H₂O can be neglected, and H₂O(sln) may be regarded as pure H₂O(l).

Example:



- The designators (cr), (am), (vit), and (s) are used for solid substances. (cr) is used when it is known that the compound is crystalline, (am) when it is known that it is amorphous, and (vit) for glassy substances. Otherwise, (s) is used.
- In some cases, more than one crystalline form of the same chemical composition may exist. In such a case, the different forms are distinguished by separate designators that describe the forms more precisely. If the crystal has a mineral name, the designator (cr) is replaced by the first four characters of the mineral name in parentheses, *e.g.*, SiO₂(quar) for quartz and SiO₂(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 -UF₅, β -UF₅.

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.

Example:

$\Delta_f G_m^\circ(\text{Na}^+, \text{aq}, 298.15 \text{ K})$	standard molar Gibbs energy of formation of aqueous Na ⁺ at 298.15 K
$S_m^\circ(\text{UO}_2\text{SO}_4 \cdot 2.5\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$	standard molar entropy of UO ₂ SO ₄ · 2.5H ₂ O(cr) at 298.15 K
$C_{p,m}^\circ(\text{UO}_3, \alpha, 298.15 \text{ K})$	standard molar heat capacity of α -UO ₃ at 298.15 K
$\Delta_f H_m(\text{HF}, \text{sln}, \text{HF} \cdot 7.8\text{H}_2\text{O})$	enthalpy of formation of HF diluted 1:7.8 with water

Table 2.3: 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

2.1.5 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 2.1.6. The nature of the process is denoted by annotation of the Δ , *e.g.*, the Gibbs energy of formation, $\Delta_f G_m$, the enthalpy of sublimation, $\Delta_{\text{sub}} H_m$, *etc.* The abbreviations of chemical processes are summarised in Table 2.3.

The most frequently used symbols for processes are $\Delta_f G$ and $\Delta_f H$, the Gibbs energy and the enthalpy of formation of a compound or complex from the elements in their reference states (*cf.* Table 2.6).

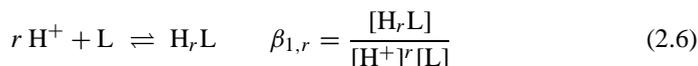
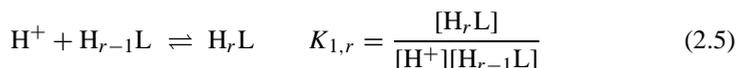
2.1.6 Equilibrium constants

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



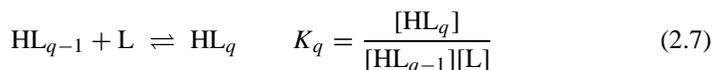
both $\beta_{q,m}$ and $\beta(2.4)$ would be appropriate, and $\beta_{q,m}(2.4)$ is accepted, too. Note that, in general, K is used for the consecutive or stepwise formation constant, and β is used for the cumulative or overall formation constant. In the following outline, charges are only given for actual chemical species, but are omitted for species containing general symbols (M, L). The ionization constant for water is designated by K_w .

2.1.6.1 Protonation of a ligand

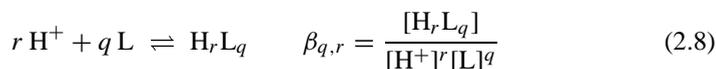


This notation has been proposed and used by Sillén and Martell [64SIL/MAR], but it has been simplified later by the same authors [71SIL/MAR] from $K_{1,r}$ to K_r . This review retains, for the sake of consistency, *cf.* Eqs. (2.7) and (2.8), the older formulation of $K_{1,r}$.

For the addition of a ligand, the notation shown in Eq.(2.7) is used.

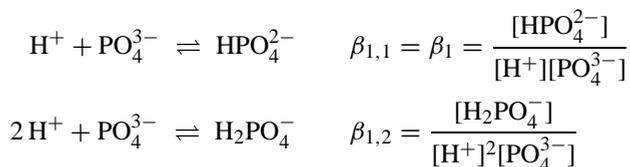


Eq. (2.8) refers to the overall formation constant of the species H_rL_q .

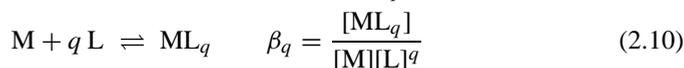
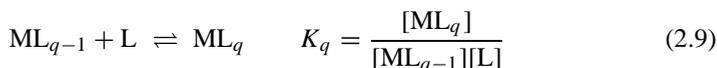


In Eqs. (2.5), (2.6) and (2.8), the second subscript r can be omitted if $r = 1$, as shown in Eq. (2.7).

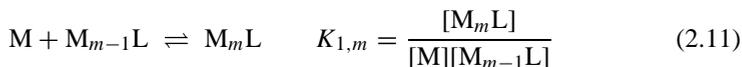
Example:



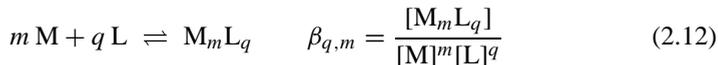
2.1.6.2 Formation of metal ion complexes



For the addition of a metal ion, *i.e.*, the formation of polynuclear complexes, the following notation is used, analogous to Eq.(2.5):

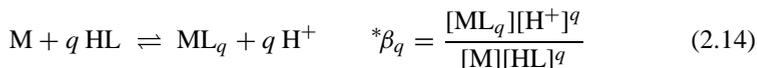
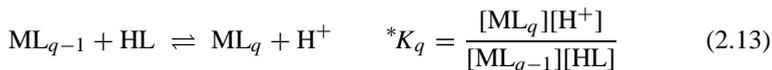


Eq. (2.12) refers to the overall formation constant of a complex M_mL_q .

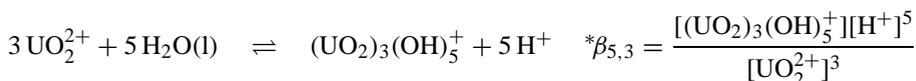


The second index can be omitted if it is equal to 1, *i.e.*, $\beta_{q,m}$ becomes β_q if $m = 1$. The formation constants of mixed ligand complexes are not indexed. In this case, it is necessary to list the chemical reactions considered and to refer the constants to the corresponding reaction numbers.

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. (2.13) to (2.15) 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. (2.13) and (2.14) for mononuclear and in Eq. (2.15) for polynuclear complexes.

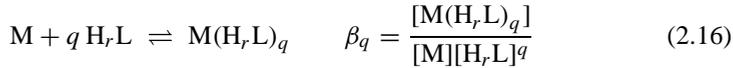


Example:

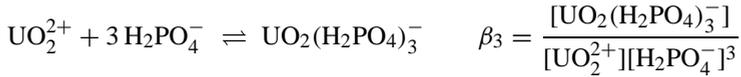


Note that an asterisk is only assigned to the formation constant if the protonated ligand that is added is deprotonated during the reaction. If a protonated ligand is added

and coordinated as such to the metal ion, the asterisk is to be omitted, as shown in Eq. (2.16).

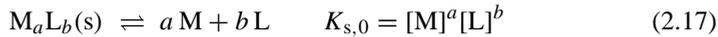


Example:

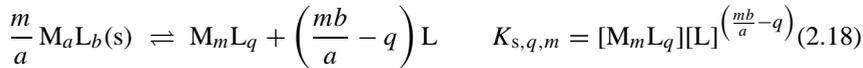


2.1.6.3 Solubility constants

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. (2.17) to (2.19).



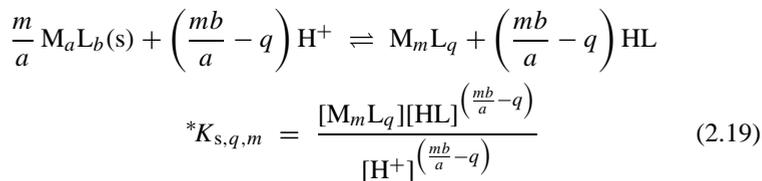
$K_{s,0}$ is the conventional solubility product, and the subscript “0” indicates that the equilibrium reaction involves only uncomplexed aqueous species. If the solubility constant includes the formation of aqueous complexes, a notation analogous to that of Eq. (2.12) is used:



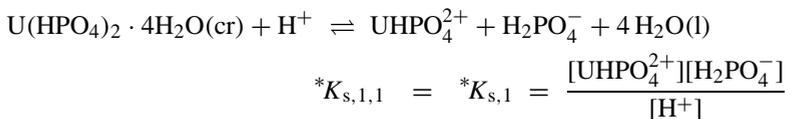
Example:



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

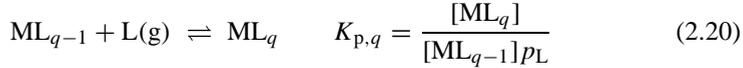


Example:



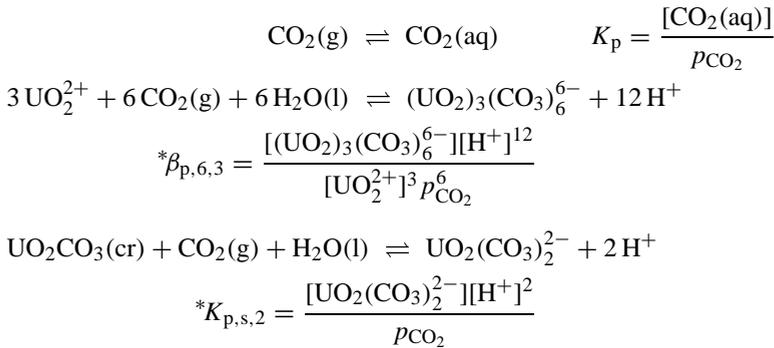
2.1.6.4 Equilibria involving the addition of a gaseous ligand

A special notation is used for constants describing equilibria that involve the addition of a gaseous ligand, as outlined in Eq. (2.20).



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

Example:



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.

2.1.6.5 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, SHE¹, 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, $\text{H}_2(\text{g})$ is at unit fugacity (an ideal gas at unit pressure, 0.1 MPa), and H^+ is at unit activity. The sign of the electrode potential, E , is that of the observed sign of its polarity when coupled with the standard hydrogen electrode. The standard electrode potential, E° , *i.e.* the potential of a standard galvanic cell relative to the standard hydrogen electrode (all components in their standard state, *cf.* Section 2.3.1, and with no liquid junction potential) is related to the standard Gibbs energy change $\Delta_{\text{r}}G_{\text{m}}^\circ$ and the standard (or thermodynamic) equilibrium constant K° as outlined in Eq. (2.21).

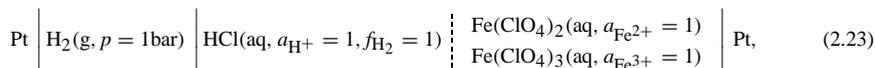
$$E^\circ = -\frac{1}{nF} \Delta_{\text{r}}G_{\text{m}}^\circ = \frac{RT}{nF} \ln K^\circ \quad (2.21)$$

¹The definitions of SHE and NHE are given in Section 2.1.1.

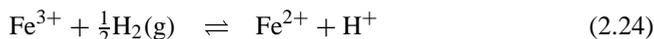
and the potential, E , is related to E° by

$$E = E^\circ - (RT/nF) \sum v_i \ln a_i \quad (2.22)$$

For example, for the hypothetical galvanic cell:



where “|” denotes a liquid junction and “|” a phase boundary, the cell reaction is:



For convenience Reaction (2.24) can be represented by half cell reactions, each involving an equal number of “electrons” (designated “ e^- ”), as shown in the following equations



The terminology is useful, though it must be emphasized that “ e^- ” here does not represent the hydrated electron.

Equilibrium 2.26 and Nernst law can be used to introduce a_{e^-} :

$$E = E^\circ(2.26) + \frac{RT}{F} \ln(\sqrt{f_{\text{H}_2}} / (a_{\text{H}^+} a_{e^-})) \quad (2.27)$$

According to the SHE convention $E^\circ(2.26) = 0$, $f_{\text{H}_2} = 1$, $a_{\text{H}^+} = 1$, hence

$$E = -\frac{RT}{F} \ln a_{e^-} \quad (2.28)$$

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

$$K^\circ(2.25) = \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}} \times a_{e^-}} \quad (2.29)$$

$$K^\circ(2.26) = \frac{a_{\text{H}^+} \times a_{e^-}}{\sqrt{f_{\text{H}_2}}} = 1 \quad (\text{by definition}) \quad (2.30)$$

In addition, $\Delta_r G_m^\circ(2.26) = 0$, $\Delta_r H_m^\circ(2.26) = 0$, $\Delta_r S_m^\circ(2.26) = 0$ by definition, at all temperatures, and therefore $\Delta_r G_m^\circ(2.25) = \Delta_r G_m^\circ(2.24)$. From $\Delta_r G_m^\circ(2.26)$ and the values given at 298.15 K in Table 5.1 for $\text{H}_2(\text{g})$ and H^+ , the corresponding values for e^- can be calculated to be used in thermodynamic cycles involving half cell reactions. The following equations describe the change in the redox potential of Reaction (2.24), if p_{H_2} and a_{H^+} are equal to unity (*cf.* Eq. (2.22)):

$$E(2.24) = E^\circ(2.24) - \frac{RT}{nF} \ln \left(\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} \right) \quad (2.31)$$

For the standard hydrogen electrode $a_{e^-} = 1$ (by the convention expressed in Eq. (2.30)), while rearrangement of Eq. (2.29) for the half-cell containing the iron perchlorates in cell 2.23 gives:

$$-\log_{10} a_{e^-} = \log_{10} K^\circ(2.25) - \log_{10} \left(\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} \right)$$

and from Eq. (2.27):

$$-\log_{10} a_{e^-} = \log_{10} K^\circ(2.24) - \log_{10} \left(\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}} \right) \quad (2.32)$$

and

$$-\log_{10} a_{e^-} = \frac{F}{RT \ln(10)} E(2.24) \quad (2.33)$$

which is a specific case of the general equation 2.28.

The splitting of redox reactions into two half cell reactions by introducing the symbol “ e^- ”, which according to Eq. 2.27 is related to the standard electrode potential, is arbitrary, but useful (this e^- notation does not in any way refer to solvated electrons). When calculating the equilibrium composition of a chemical system, both “ e^- ” and H^+ can be chosen as components and they can be treated numerically in a similar way: equilibrium constants, mass balance, *etc.* may be defined for both. However, while H^+ represents the hydrated proton in aqueous solution, the above equations use only the activity of e^- , and never the concentration of e^- . Concentration to activity conversions (or activity coefficients) are never needed for the electron (*cf.* Appendix B, Example B.3).

In the literature on geochemical modelling of natural waters, it is customary to represent the “electron activity” of an aqueous solution with the symbol “pe” or “pe ϵ ” ($= -\log_{10} a_{e^-}$) by analogy with pH ($= -\log_{10} a_{\text{H}^+}$), 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]).

In this review, the symbol $E^{\circ'}$ is used to denote the so-called “formal potential” [74PAR]. The formal (or “conditional”) potential can be regarded as a standard potential for a particular medium in which the activity coefficients are independent (or approximately so) of the reactant concentrations [85BAR/PAR] (the definition of $E^{\circ'}$ parallels that of “concentration quotients” for equilibria). Therefore, from

$$E = E^{\circ'} - \frac{RT}{nF} \sum v_i \ln c_i \quad (2.34)$$

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

$$E^{\circ'} = E^\circ - \frac{RT}{nF} \sum v_i \ln \varrho \gamma_i = -\Delta_r G_m / nF \quad (2.35)$$

where the γ_i are the molality activity coefficients and ϱ is (m_i/c_i) , the ratio of molality to molarity (*cf.* Section 2.2). The medium must be specified.

2.1.7 pH

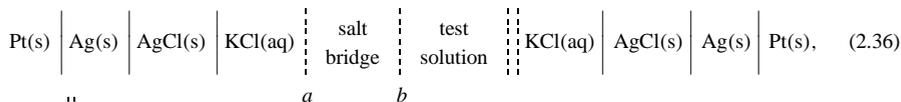
Because of the importance that potentiometric methods have in the determination of equilibrium constants in aqueous solutions, a short discussion on the definition of “pH” and a simplified description of the experimental techniques used to measure pH will be given here.

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

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

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):



where “ $\begin{array}{c} \vdots \\ \vdots \\ \vdots \\ \vdots \\ \vdots \end{array}$ ” stands for a glass membrane (permeable to hydrogen ions). The emf of such a cell is given by

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

where E^* is a constant, and E_j is the 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 ² 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 NaClO₄). 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 [ClO₄⁻] = 0.1 M as background electrolyte, the dependence of the liquid junction at “*b*” on acidity is $E_j \approx -440 \times [\text{H}^+] \text{ mV} \cdot \text{dm}^3 \cdot \text{mol}^{-1}$ at 25°C [69ROS, p.110], which corresponds to an error at pH= 2 of ≥ 0.07 pH units.

²KClO₄(cr) has a solubility of ≈ 0.15 M in pure water at 25°C.

Because of the problems in eliminating the liquid junction potentials and in defining individual ionic activity coefficients, an “operational” definition of pH is given by IUPAC [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 subtracted).

2.1.8 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 2.1 below which shows the sequence of the ranks of the elements in this convention. The order follows the ranks of the elements.

For example, for uranium, this means that, after elemental uranium and its monoatomic ions (*e.g.*, U^{4+}), the uranium compounds and complexes with oxygen would be listed, then those with hydrogen, then those with oxygen and hydrogen, and so on, with decreasing rank of the element and combinations of the elements. Within a class, increasing coefficients of the higher rank elements go before increasing coefficients of the lower rank elements. For example, in the U-O-F class of compounds and complexes, a typical sequence would be $\text{UOF}_2(\text{cr})$, $\text{UOF}_4(\text{cr})$, $\text{UOF}_4(\text{g})$, $\text{UO}_2\text{F}(\text{aq})$, UO_2F^+ , $\text{UO}_2\text{F}_2(\text{aq})$, $\text{UO}_2\text{F}_2(\text{cr})$, $\text{UO}_2\text{F}_2(\text{g})$, UO_2F_3^- , $\text{UO}_2\text{F}_4^{2-}$, $\text{U}_2\text{O}_3\text{F}_6(\text{cr})$, *etc.* [92GRE/FUG]. Formulae with identical stoichiometry are in alphabetical order of their designators.

2.1.9 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 surnames of the first two authors, separated by a slash.

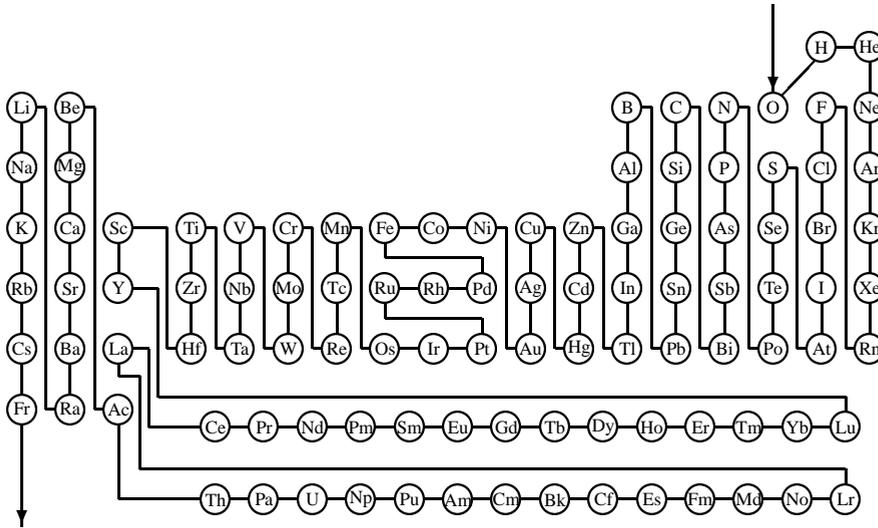
If there are multiple reference codes, a “2” will be added to the second one, a “3” to the third one, and so forth. Reference codes are always enclosed in square brackets.

2.2 Units and conversion factors

Thermodynamic data are given according to the *Système International d’unités* (SI units). The unit of energy is the joule. Some basic conversion factors, also for non-thermodynamic units, are given in Table 2.4.

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 “ $\text{mol} \cdot \text{dm}^{-3}$ ” for molarity, *c*, and, in Appendices B and C, “m” as an abbreviation of “ $\text{mol} \cdot \text{kg}^{-1}$ ”

Figure 2.1: Standard order of arrangement of the elements and compounds based on the periodic classification of the elements (from Ref. [82WAG/EVA]).



for molality, m . It is often necessary to convert concentration data from molarity to molality and vice versa. This conversion is used for the correction and extrapolation of equilibrium data to zero ionic strength by the specific ion interaction theory which works in molality units (*cf.* Appendix B). This conversion is made in the following way. Molality is defined as m_B moles of substance B dissolved in 1000 grams of pure water. Molarity is defined as c_B moles of substance B dissolved in $(1000\rho - c_B M)$ 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

$$m_B = \frac{1000c_B}{1000\rho - c_B M}$$

Table 2.4: 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. $\hat{=}$ cal \cdot K $^{-1}$ \cdot mol $^{-1}$)	J \cdot K $^{-1}$ \cdot mol $^{-1}$	4.184 (exactly)

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 [85SÖH/NOV], are reported in Table 2.5.

Table 2.5: 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 [85SÖH/NOV]).

c (M)	$\varrho = m_B/c_B$ (dm ³ of solution per kg of H ₂ O)							
	HClO ₄	NaClO ₄	LiClO ₄	NH ₄ ClO 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 ₄ Cl	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 ₄ NO ₃	H ₂ SO ₄	Na ₂ SO ₄	(NH ₄) ₂ SO ₄	H ₃ PO ₄	Na ₂ CO ₃	K ₂ CO 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

Example:

$$\begin{aligned}
 1.00 \text{ M NaClO}_4 &\stackrel{\wedge}{=} 1.05 \text{ m NaClO}_4 \\
 1.00 \text{ M NaCl} &\stackrel{\wedge}{=} 1.02 \text{ m NaCl} \\
 4.00 \text{ M NaClO}_4 &\stackrel{\wedge}{=} 4.95 \text{ m NaClO}_4 \\
 6.00 \text{ M NaNO}_3 &\stackrel{\wedge}{=} 7.55 \text{ m NaNO}_3
 \end{aligned}$$

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

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

With $(m_{\text{B}}/c_{\text{B}}) = \varrho$, or $(\log_{10} m_{\text{B}} - \log_{10} c_{\text{B}}) = \log_{10} \varrho$, the relationship between K_c and K_m becomes very simple, as shown in Eq. (2.37).

$$\log_{10} K_m = \log_{10} K_c + \sum_{\text{B}} \nu_{\text{B}} \log_{10} \varrho \quad (2.37)$$

$\sum_{\text{B}} \nu_{\text{B}}$ is the sum of the stoichiometric coefficients of the reaction, *cf.* Eq. (2.53), and the values of ϱ are the factors for the conversion of molarity to molality as tabulated in Table 2.5 for several electrolyte media at 298.15 K. The differences between the values in Table 2.5 and the values listed in the uranium NEA-TDB review [92GRE/FUG, p.23] are found at the highest concentrations, and are no larger than $\pm 0.003 \text{ dm}^3/\text{kg}$, reflecting the accuracy expected in this type of conversions. The uncertainty introduced by the use of Eq. (2.37) in the values of $\log_{10} K_m$ will be then no larger than $\pm 0.001 \sum_{\text{B}} \nu_{\text{B}}$.

2.3 Standard and reference conditions

2.3.1 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, $p^\circ = 0.1 \text{ MPa}$ (1 bar), has therefore also been adopted, *cf.* Section 2.3.2. 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 2.3.3.

- 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 $m_B = m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$, and in which the activity coefficient γ_B is unity.

It should be emphasised that the use of $^\circ$, *e.g.*, in $\Delta_f H_m^\circ$, implies that the compound in question is in the standard state and that the elements are in their reference states. The reference states of the elements at the reference temperature (*cf.* Section 2.3.3) are listed in Table 2.6.

Table 2.6: Reference states for some elements at the reference temperature of 298.15 K and standard pressure of 0.1 MPa [[82WAG/EVA](#), [89COX/WAG](#), [91DIN](#)].

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

2.3.2 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 pressure of 1 “standard atmosphere” (= 0.101325 MPa). The difference between the thermodynamic data for the two standard state pressures is not large and lies in most cases within the uncertainty limits. It is nevertheless essential to make the corrections for the change in the standard state pressure in order to avoid inconsistencies and propagation of errors. In practice the parameters affected by the change between these two standard state pressures are the Gibbs energy and entropy changes of all processes that involve gaseous species. Consequently, changes occur also in the Gibbs energies of formation of species that consist of elements whose reference state is gaseous (H, O, F, Cl, N, and the noble gases). No other thermodynamic quantities are affected significantly. A large part of the following discussion has been taken from the NBS tables of chemical thermodynamic properties [82WAG/EVA], see also Freeman [84FRE].

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

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p = V(1 - \alpha T) \quad (2.38)$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T \left(\frac{\partial^2 V}{\partial T^2}\right)_p \quad (2.39)$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\alpha = -\left(\frac{\partial V}{\partial T}\right)_p \quad (2.40)$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad (2.41)$$

$$\text{where} \quad \alpha \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p \quad (2.42)$$

For ideal gases, $V = \frac{RT}{p}$ and $\alpha = \frac{R}{pV} = \frac{1}{T}$. The conversion equations listed below (Eqs. (2.43) to (2.50)) apply to the small pressure change from 1 atm to 1 bar (0.1 MPa). The quantities that refer to the old standard state pressure of 1 atm are assigned the superscript ^(atm) here, the ones that refer to the new standard state pressure of 1 bar the superscript ^(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.

$$\Delta_f H^{(\text{bar})}(T) - \Delta_f H^{(\text{atm})}(T) = 0 \quad (2.43)$$

$$C_p^{(\text{bar})}(T) - C_p^{(\text{atm})}(T) = 0 \quad (2.44)$$

For gaseous substances, the entropy difference is

$$\begin{aligned} S^{(\text{bar})}(T) - S^{(\text{atm})}(T) &= R \ln \left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) \\ &= R \ln 1.01325 \\ &= 0.1094 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned} \quad (2.45)$$

This is exactly true for ideal gases, as follows from Eq. (2.40) with $\alpha = \frac{R}{pV}$. The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

$$\begin{aligned} \Delta_r S^{(\text{bar})} - \Delta_r S^{(\text{atm})} &= \delta \times R \ln \left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) \\ &= \delta \times 0.1094 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned} \quad (2.46)$$

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

$$\begin{aligned} \Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})} &= -\delta \times RT \ln \left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) \\ &= -\delta \times 0.03263 \text{ kJ} \cdot \text{mol}^{-1} \text{ at } 298.15 \text{ K}. \end{aligned} \quad (2.47)$$

Eq. (2.47) applies also to $\Delta_f G^{(\text{bar})} - \Delta_f G^{(\text{atm})}$, since the Gibbs energy of formation describes the formation process of a compound or complex from the reference states of the elements involved:

$$\Delta_f G^{(\text{bar})} - \Delta_f G^{(\text{atm})} = -\delta \times 0.03263 \text{ kJ} \cdot \text{mol}^{-1} \text{ at } 298.15 \text{ K} \quad (2.48)$$

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. (2.47):

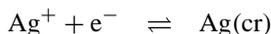
$$\begin{aligned} \log_{10} K^{(\text{bar})} - \log_{10} K^{(\text{atm})} &= -\frac{\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})}}{RT \ln 10} \\ &= \delta \times \frac{\ln \left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right)}{\ln 10} = \delta \times \log_{10} \left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) \\ &= \delta \times 0.005717 \end{aligned} \quad (2.49)$$

$$\begin{aligned} E^{(\text{bar})} - E^{(\text{atm})} &= -\frac{\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})}}{nF} \\ &= \delta \times \frac{RT \ln \left(\frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right)}{nF} \\ &= \delta \times \frac{0.0003382}{n} \text{ V at } 298.15 \text{ K} \end{aligned} \quad (2.50)$$

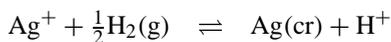
It should be noted that the standard potential of the hydrogen electrode is equal to 0.00 V exactly, by definition.



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

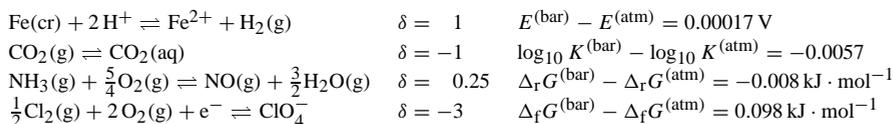


should thus be calculated from the balanced reaction that includes the hydrogen electrode,



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

Example:



2.3.3 Reference temperature

The definitions of standard states given in Section 2.3 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 $T = 298.15 \text{ K}$ or $t = 25.00^\circ\text{C}$. 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 ($^\circ\text{C}$) is defined by $t = (T - T_0)$ where $T_0 = 273.15 \text{ K}$.

2.4 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 2.7.

Table 2.7: 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	$\text{m} \cdot \text{s}^{-1}$
permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ $= 12.566\,370\,614 \dots$	$10^{-7} \text{N} \cdot \text{A}^{-2}$
permittivity of vacuum	ϵ_0	$1/\mu_0 c^2$ $= 8.854\,187\,817 \dots$	$10^{-12} \text{C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$
Planck constant	h	6.626 0755(40)	$10^{-34} \text{J} \cdot \text{s}$
elementary charge	e	1.602 177 33(49)	10^{-19}C
Avogadro constant	N_A	6.022 1367(36)	10^{23}mol^{-1}
Faraday constant, $N_A \times e$	F	96 485.309(29)	$\text{C} \cdot \text{mol}^{-1}$
molar gas constant	R	8.314 510(70)	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
Boltzmann constant, R/N_A	k	1.380 658(12)	$10^{-23} \text{J} \cdot \text{K}^{-1}$
Non-SI units used with SI:			
electron volt, $(e/C) \text{J}$	eV	1.602 177 33(49)	10^{-19}J
atomic mass unit, $1\text{u} = m_{\text{u}} = \frac{1}{12}m(^{12}\text{C})$	u	1.660 5402(10)	10^{-27}kg

2.5 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.

2.6 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. 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 also stored in the data base.

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

$\Delta_f G_m^\circ$	the standard molar Gibbs energy of formation from the elements in their reference state	(kJ · mol ⁻¹)
$\Delta_f H_m^\circ$	the standard molar enthalpy of formation from the elements in their reference state	(kJ · mol ⁻¹)
S_m°	the standard molar entropy	(J · K ⁻¹ · mol ⁻¹)
$C_{p,m}^\circ$	the standard molar heat capacity	(J · K ⁻¹ · mol ⁻¹)

For aqueous neutral species and ions, the values of $\Delta_f G_m^\circ$, $\Delta_f H_m^\circ$, S_m° and $C_{p,m}^\circ$ correspond to the standard partial molar quantities, and for individual aqueous ions they are relative quantities, defined with respect to the aqueous hydrogen ion, according to the convention [89COX/WAG] that $\Delta_f H_m^\circ(\text{H}^+, \text{aq}, T) = 0$, and that $S_m^\circ(\text{H}^+, \text{aq}, T) = 0$. Furthermore, for an *ionised solute* B containing any number of different cations and anions:

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

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

$$\begin{aligned}F(T) &= a + b \times T + c \times T^2 + d \times T^{-1} + e \times T^{-2} + f \times \ln T + g \times T \ln T \\ &+ h \times \sqrt{T} + \frac{i}{\sqrt{T}} + j \times T^3 + k \times T^{-3}.\end{aligned}\quad (2.52)$$

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 $C_{p,m}^\circ(T)$, *i.e.*, the thermal functions of the heat capacities of individual species, are considered and stored in the data base. They refer to the relation

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

and are listed in Tables 3.3 and 4.3.

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 are also compiled in the data base. A chemical reaction “*r*”, involving reactants and products “*B*”, can be abbreviated as

$$0 = \sum_{\text{B}} \nu_{\text{B}}^r \text{B} \quad (2.53)$$

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
$\Delta_r G_m^\circ$	the molar Gibbs energy of reaction (kJ · mol ⁻¹)
$\Delta_r H_m^\circ$	the molar enthalpy of reaction (kJ · mol ⁻¹)
$\Delta_r S_m^\circ$	the molar entropy of reaction (J · K ⁻¹ · mol ⁻¹)
$\Delta_r C_{p,m}^\circ$	the molar heat capacity of reaction (J · K ⁻¹ · mol ⁻¹)

The temperature functions of these data, if available, are stored according to Eq. (2.52).

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

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

and can be calculated from the individual values of $\Delta_r G_m^\circ(\text{B})$ (for example, those given in Tables 3.3 and 4.3 and in table 5.1), according to

$$\log_{10} K_r^\circ = -\frac{1}{RT \ln(10)} \sum_{\text{B}} \nu_{\text{B}}^r \Delta_r G_m^\circ(\text{B}) \quad (2.54)$$

2.7 Presentation of the selected data

The selected data are presented in Chapters 3, 4 and 5. Unless otherwise indicated, they refer to standard conditions (*cf.* Section 2.3) and 298.15 K (25°C) and are provided with an uncertainty which should correspond to the 95% confidence level (see Appendix C).

Chapters 3 and 4 contain tables of selected thermodynamic data for individual compounds and complexes of neptunium and plutonium (Tables 3.1 and 4.1 respectively), tables of selected reaction data (Tables 3.2 and 4.2) for reactions concerning neptunium and plutonium species respectively, and tables containing selected thermal functions of the heat capacities of individual species of neptunium and plutonium (Tables 3.3 and 4.3 respectively). The selection of these data is discussed in Parts III and IV.

Chapter 5 contains, for auxiliary compounds and complexes that do not contain neptunium or plutonium, a table of the thermodynamic data for individual species (Table 5.1) and a table of reaction data (Table 5.2). 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 3.1, 3.2, 4.1, 4.2, 5.1 and 5.2 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 2.6. Therefore, when using the selected data for either neptunium or plutonium species, the auxiliary data of Chapter 5 must be used together with the data in Chapters 3 and 4 to ensure internal consistency of the data set.

It is important to note that Tables 3.2, 4.2 and 5.2 include only those species of which the primary selected data are reaction data. The formation data derived therefrom and listed in Tables 3.1 and 4.1 are obtained using auxiliary data, and their uncertainties are propagated accordingly. In order to maintain the uncertainties originally assigned to the selected data in this review, the user is advised to make direct use of the reaction data presented in Tables 3.2, 4.2 and 5.2, rather than taking the derived values in Tables 3.1, 4.1 and 5.1 to calculate the reaction data with Eq. (2.54). The latter approach would imply a twofold propagation of the uncertainties and result in reaction data whose uncertainties would be considerably larger than those originally assigned.

The thermodynamic data in the selected set refer to a temperature of 298.15 K (25.00°C), but they can be recalculated to other temperatures if the corresponding data (enthalpies, entropies, heat capacities) are available [97PUI/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:

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

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

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

where R is the gas constant (*cf.* Table 2.7).

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. The user may find information on various procedures to estimate the temperature dependence of these thermodynamic parameters in [97PUI/RAR]. The thermodynamic data in the selected set refer to infinite dilution for soluble species. Extrapolation of an equilibrium constant K , usually measured at high ionic strength, to K° at $I = 0$ using activity coefficients γ , is explained in Appendix B. The corresponding Gibbs energy of dilution is

$$\Delta_{\text{dil}}G_{\text{m}} = \Delta_{\text{r}}G_{\text{m}}^{\circ} - \Delta_{\text{r}}G_{\text{m}} \quad (2.55)$$

$$= -RT \Delta_{\text{r}} \ln \gamma_{\pm} \quad (2.56)$$

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

$$\Delta_{\text{dil}}H_{\text{m}} = RT^2 \frac{\partial}{\partial T} (\Delta_{\text{r}} \ln \gamma_{\pm})_p \quad (2.57)$$

depends only on the variation of γ with T , which are neglected in this review, when no data on the temperature dependence of γ 's are available. In this case the Gibbs energy of dilution $\Delta_{\text{dil}}G_{\text{m}}$ is entirely assigned to entropy difference. This entropy of reaction is calculated using the Gibbs-Helmholtz equation, the above assumption $\Delta_{\text{dil}}H_{\text{m}} = 0$, and $\Delta_{\text{dil}}G_{\text{m}}$.

Part II

Tables of selected data

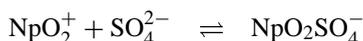
Chapter 3

Selected neptunium data

This chapter presents the chemical thermodynamic data set for neptunium species which has been selected in this review. Table 3.1 contains the recommended thermodynamic data of the neptunium compounds and complexes, Table 3.2 the recommended thermodynamic data of chemical equilibrium reactions by which the neptunium compounds and complexes are formed, and Table 3.3 the temperature coefficients of the heat capacity data of Table 3.1 where available.

The species and reactions in Tables 3.1, 3.2 and 3.3 appear in standard order of arrangement (*cf.* Figure 2.1). Table 3.2 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 neptunium species (for example Np^{4+}) and auxiliary data listed in Table 5.1, to derive the corresponding formation quantities in Table 3.1. The uncertainties associated with values for the key neptunium species and for some of the auxiliary data are substantial, leading to comparatively large uncertainties in the formation quantities derived in this manner.

However, then the fact remains that for many reactions uncertainties in quantities such as $\Delta_r G_m^\circ$ are known more accurately than would be calculated directly from the uncertainties of the $\Delta_f G_m^\circ$ values for species listed in Table 3.1 and the auxiliary data in Table 5.1. The uncertainties in, for example, the value of $\Delta_f G_m^\circ(\text{NpO}_2\text{SO}_4^-)$ incorporates not only the uncertainty in $\Delta_r G_m^\circ$ for the complexation reaction from which it is derived,



but also the uncertainties in $\Delta_f G_m^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K})$ and $\Delta_f G_m^\circ(\text{SO}_4^{2-}, \text{aq}, 298.15 \text{ K})$. Thus, back-calculation from the uncertainties of the separate species overestimates the uncertainty in the Gibbs energy of reaction and the uncertainty in the corresponding equilibrium constant. The inclusion of a table for reaction data (Table 3.2) in this report allows the use of equilibrium constants with total uncertainties that are directly based on the experimental accuracies. This is the main reason for including both the table for reaction data (Table 3.2) and the table of $\Delta_f G_m^\circ$, $\Delta_f H_m^\circ$, S_m° and $C_{p,m}^\circ$ values (Table 3.1). In a few cases, correlation of small uncertainties in values for ligands has been neglected in calculations of uncertainty values for species in Table 3.1 from uncertainty values in Table 3.2. However, for those species the effects are less than 2% of the stated uncertainties.

Furthermore, for some reactions that involve concurrent ligand protonation or deprotonation (e.g., in certain neptunium-carbonate, -sulphate or -phosphate systems) the uncertainties in equilibrium constants are less than would have been calculated directly

using the uncertainties in the Gibbs energy values for the specific ligands (*cf.* the introductory paragraphs in Chapter 5). This occurs because the Gibbs energy change for a particular deprotonation equilibrium (*cf.* Table 5.2) may be known more accurately than the Gibbs energy of formation of the ligand.

The selected thermal functions of the heat capacities, listed in Table 3.3, refer to the relation

$$C_{p,m}^{\circ}(T) = a + b \times T + c \times T^2 + d \times T^{-1} + e \times T^{-2} \quad (3.1)$$

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 Part III.

A warning: The addition of any aqueous species and its 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 Part III.

Table 3.1: Selected thermodynamic data for neptunium 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 Part III. 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	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
Np(cr)	0.000	0.000	50.460 ±0.800	29.620 ^(c) ±0.800
$\beta - \text{Np}^{(d)}$				
$\gamma - \text{Np}^{(d)}$				
Np(g)	421.195 ^(a) ±3.009	465.100 ^(b) ±3.000	197.719 ±0.005	20.824 ^(c) ±0.020
Np ³⁺	-512.866 ^(b) ±5.669	-527.184 ±2.092	-193.584 ±20.253	
Np ⁴⁺	-491.774 ^(a) ±5.586	-556.022 ±4.185	-426.390 ^(b) ±12.386	
NpO ₂ (am, hyd)	-957.321 ^(b) ±7.987			
NpO ₂ (cr)	-1021.731 ^(a) ±2.514	-1074.000 ±2.500	80.300 ±0.400	66.200 ^(c) ±0.500
NpO ₂ ⁺	-907.765 ^(a) ±5.628	-978.181 ±4.629	-45.904 ±10.706	-4.000 ±25.000
NpO ₂ ²⁺	-795.939 ±5.615	-860.733 ±4.662	-92.387 ^(b) ±10.464	
Np ₂ O ₅ (cr)	-2031.574 ^(a) ±11.227	-2162.700 ±9.500	174.000 ±20.000	128.600 ^(c) ±5.000
NpOH ²⁺	-711.191 ^(b) ±5.922			
NpOH ³⁺	-727.259 ^(b) ±7.987			
NpO ₂ OH(am, aged)	-1118.078 ^(b) ±6.310	-1222.900 ±5.500	71.952 ^(a) ±28.087	86.000 ±20.000
NpO ₂ OH(am, fresh)	-1114.652 ^(b) ±5.743	-1222.900 ±5.500	60.456 ^(a) ±26.682	86.000 ±20.000
NpO ₂ OH(aq)	-1080.405 ^(b) ±6.902	-1199.226 ^(a) ±19.176	25.000 ±60.000	

(Continued on next page)

Table 3.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
NpO ₂ OH ⁺	-1003.968 ^(b) ±6.062			
NpO ₂ (OH) ₂ (cr)	-1239.000 ±6.400	-1377.000 ±5.000	128.590 ^(a) ±27.252	120.000 ±20.000
NpO ₂ (OH) ₂ ⁻	-1247.336 ^(b) ±6.311	-1431.230 ^(a) ±30.476	40.000 ±100.000	
NpO ₃ ·H ₂ O(cr)	-1238.997 ^(b) ±6.062			
Np(OH) ₄ (aq)	-1384.225 ^(b) ±8.482			
(NpO ₂) ₂ (OH) ₂ ²⁺	-2030.369 ^(b) ±11.294			
(NpO ₂) ₃ (OH) ₅ ⁺	-3475.795 ^(b) ±16.893			
NpF(g)	-111.560 ^(a) ±30.038	-82.000 ±30.000	251.000 ±5.000	33.800 ^(c) ±3.000
NpF ³⁺	-824.441 ^(b) ±5.686	-889.872 ^(b) ±4.684	-263.621 ^(b) ±14.361	
NpF ₂ (g)	-585.131 ^(a) ±50.089	-570.000 ±50.000	304.000 ±10.000	55.900 ^(c) ±5.000
NpF ₂ ²⁺	-1144.436 ^(b) ±6.005			
NpF ₃ (cr)	-1460.501 ^(a) ±8.325	-1529.000 ±8.300	124.900 ±2.000	94.200 ^(c) ±3.000
NpF ₃ (g)	-1104.801 ^(a) ±20.222	-1112.000 ±20.000	330.500 ±10.000	72.200 ^(c) ±5.000
NpF ₄ (cr)	-1783.797 ^(a) ±16.046	-1874.000 ±16.000	153.500 ±4.000	116.100 ^(c) ±4.000
NpF ₄ (g)	-1535.287 ^(a) ±22.202	-1561.000 ±22.000	369.800 ±10.000	95.300 ^(c) ±5.000
NpF ₅ (cr)	-1834.430 ^(a) ±25.398	-1941.000 ±25.000	200.000 ±15.000	132.800 ^(c) ±8.000
NpF ₆ (cr)	-1841.872 ^(a) ±20.002	-1970.000 ±20.000	229.090 ±0.500	167.440 ^(c) ±0.400
NpF ₆ (g)	-1837.525 ^(a) ±20.002	-1921.660 ±20.000	376.643 ±0.500	129.072 ^(c) ±1.000
NpF ₆ (l) ^(d)				
NpO ₂ F(aq)	-1196.138 ^(b) ±5.923			
NpO ₂ F ⁺	-1103.548 ^(b) ±5.672			
NpO ₂ F ₂ (aq)	-1402.366 ^(b) ±5.801			

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Table 3.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
NpO ₂ F ₂ (cr) ^(d)				
NpCl ³⁺	-631.553 ^(b) ±5.844			
NpCl ₃ (cr)	-829.811 ^(a) ±3.237	-896.800 ±3.000	160.400 ±4.000	101.850 ^(c) ±4.000
NpCl ₃ (g)	-582.357 ^(a) ±10.822	-589.000 ±10.400	362.800 ±10.000	78.500 ^(c) ±5.000
NpCl ₄ (cr)	-895.562 ^(a) ±2.998	-984.000 ±1.800	200.000 ±8.000	122.000 ^(c) ±6.000
NpCl ₄ (g)	-765.050 ^(a) ±5.487	-787.000 ±4.600	423.000 ±10.000	105.000 ^(c) ±5.000
NpCl ₄ (l) ^(d)				
NpOCl ₂ (cr)	-960.645 ^(a) ±8.141	-1030.000 ±8.000	143.500 ±5.000	95.000 ^(c) ±4.000
NpO ₂ Cl ⁺	-929.440 ^(b) ±5.699			
NpO ₂ ClO ₄ (aq)				-32.000 ^(c) ±25.000
NpBr ₃ (cr, hex)	-705.521 ^(a) ±3.765	-730.200 ±2.900	196.000 ±8.000	103.800 ^(c) ±6.000
NpBr ₄ (cr)	-737.843 ^(a) ±3.495	-771.200 ±1.800	243.000 ±10.000	128.000 ^(c) ±4.000
NpOBr ₂ (cr)	-906.933 ^(a) ±11.067	-950.000 ±11.000	160.800 ±4.000	98.200 ^(c) ±4.000
NpI ³⁺	-552.059 ^(b) ±6.036			
NpI ₃ (cr)	-512.498 ^(a) ±3.715	-512.400 ±2.200	225.000 ±10.000	110.000 ^(c) ±8.000
NpO ₂ IO ₃ (aq)	-1036.957 ^(b) ±5.934			
NpO ₂ IO ₃ ⁺	-929.126 ^(b) ±5.922			
NpSO ₄ ²⁺	-1274.887 ^(b) ±5.809	-1435.522 ^(b) ±9.796	-176.635 ^(b) ±32.277	
NpO ₂ SO ₄ (aq)	-1558.666 ^(b) ±5.641	-1753.373 ^(b) ±4.706	44.920 ^(b) ±10.667	
NpO ₂ SO ₄ ⁻	-1654.281 ^(b) ±5.850	-1864.321 ^(b) ±8.569	58.833 ^(b) ±26.920	
Np(SO ₄) ₂ (aq)	-2042.873 ^(b) ±6.360	-2319.322 ^(b) ±5.871	7.964 ^(b) ±18.924	
NpO ₂ (SO ₄) ₂ ²⁻	-2310.775 ^(b) ±5.705	-2653.413 ^(b) ±4.880	121.798 ^(b) ±11.402	

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Table 3.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
NpN(cr)	-270.043 ^(a) ±5.026	-294.600 ±5.000	63.900 ±1.500	48.700 ^(c) ±0.900
NpNO ₃ ³⁺	-613.413 ^(b) ±5.667			
NpO ₂ (NO ₃) ₂ ·6H ₂ O(s)	-2428.069 ^(a) ±5.565	-3008.241 ±5.022	516.306 ±8.000	
NpO ₂ HPO ₄ (aq)	-1927.314 ^(b) ±7.067			
NpO ₂ HPO ₄ ⁻	-2020.589 ^(b) ±5.870			
NpO ₂ H ₂ PO ₄ ⁺	-1952.042 ^(b) ±6.491			
NpO ₂ (HPO ₄) ₂ ²⁻	-3042.135 ^(b) ±8.598			
NpC _{0.91} (cr)	-76.024 ^(a) ±10.028	-71.100 ±10.000	72.200 ±2.400	50.000 ^(c) ±1.000
Np ₂ C ₃ (cr)	-192.427 ±19.436	-187.400 ±19.200	135.000 ±10.000	110.000 ±8.000
NpO ₂ CO ₃ (aq)	-1377.040 ^(b) ±6.617			
NpO ₂ CO ₃ (s)	-1407.156 ^(b) ±6.233			
NpO ₂ CO ₃ ⁻	-1463.988 ^(b) ±5.652			
NpO ₂ (CO ₃) ₂ ²⁻	-1946.015 ^(b) ±7.033			
NpO ₂ (CO ₃) ₂ ³⁻	-2000.861 ^(b) ±5.685			
Np(CO ₃) ₃ ³⁻	-2185.949 ^(b) ±15.451			
NpO ₂ (CO ₃) ₃ ⁴⁻	-2490.208 ^(b) ±5.759	-2928.323 ±6.254	-12.070 ±17.917	
NpO ₂ (CO ₃) ₃ ⁵⁻	-2522.859 ^(b) ±5.733	-3017.120 ±6.893	-135.050 ±20.467	
Np(CO ₃) ₄ ⁴⁻	-2812.775 ^(b) ±8.240			
Np(CO ₃) ₅ ⁶⁻	-3334.567 ^(b) ±8.425			
(NpO ₂) ₃ (CO ₃) ₆ ⁶⁻	-5839.709 ^(b) ±19.185			
NpO ₂ (CO ₃) ₂ OH ⁴⁻	-2170.417 ^(b) ±8.785			
(NpO ₂) ₂ CO ₃ (OH) ₃ ⁻	-2814.914 ^(b) ±14.665			

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Table 3.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
(NH ₄) ₄ NpO ₂ (CO ₃) ₃ (s)	-2850.284 ^(b) ±6.106			
Np(SCN) ³⁺	-416.198 ^(b) ±7.081	-486.622 ^(b) ±6.520	-248.165 ^(b) ±25.449	
Np(SCN) ₂ ²⁺	-329.777 ^(b) ±10.166	-412.222 ^(b) ±12.748	-89.545 ^(b) ±50.953	
Np(SCN) ₃ ⁺	-241.072 ^(b) ±13.541	-339.822 ^(b) ±15.573	54.707 ^(b) ±66.304	
(UO ₂) ₂ NpO ₂ (CO ₃) ₆ ⁶⁻	-6174.307 ^(b) ±16.981			
Sr ₃ NpO ₆ (cr)		-3125.800 ±5.900		
Ba ₃ NpO ₆ (cr)		-3085.600 ±9.600		
Ba ₂ MgNpO ₆ (cr)		-3096.900 ±8.200		
Ba ₂ CaNpO ₆ (cr)		-3159.300 ±7.900		
Ba ₂ SrNpO ₆ (cr)		-3122.500 ±7.800		
Li ₂ NpO ₄ (cr)		-1828.200 ±5.800		
α – Na ₂ NpO ₄		-1763.800 ±5.700		
β – Na ₂ NpO ₄		-1748.500 ±6.100		
β – Na ₄ NpO ₅		-2315.400 ±5.700		
Na ₂ Np ₂ O ₇ (cr)		-2894.000 ±11.000		
Na ₃ NpF ₈ (cr)	-3521.239 ^(a) ±21.305	-3714.000 ±21.000	369.000 ±12.000	272.250 ^(c) ±12.000
NaNpO ₂ CO ₃ (s, aged)	-1764.157 ^(b) ±6.326			
Na ₃ NpO ₂ (CO ₃) ₂ (s)	-2833.333 ^(b) ±6.839			
NaNpO ₂ CO ₃ ·3.5H ₂ O(s, fresh)	-2591.287 ^(b) ±5.991			
K ₂ NpO ₄ (cr)		-1784.300 ±6.400		
K ₂ Np ₂ O ₇ (cr)		-2932.000 ±11.000		
K ₄ NpO ₂ (CO ₃) ₃ (s)	-3660.395 ^(b) ±7.641			

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Table 3.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
Rb ₂ Np ₂ O ₇ (cr)		-2914.000 ±12.000		
Cs ₂ NpO ₄ (cr)		-1788.100 ±5.700		
Cs ₂ NpCl ₆ (cr)	-1833.039 ^(a) ±4.871	-1976.200 ±1.900	410.000 ±15.000	
Cs ₂ NpO ₂ Cl ₄ (cr)		-2056.100 ±5.400		
Cs ₃ NpO ₂ Cl ₄ (cr)		-2449.100 ±4.800		
Cs ₂ NpBr ₆ (cr)	-1620.121 ^(a) ±3.616	-1682.300 ±2.000	469.000 ±10.000	
Cs ₂ NaNpCl ₆ (cr)		-2217.200 ±3.100		

^(a) Value calculated internally with the Gibbs-Helmholtz equation, $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T \sum_i S_{m,i}^\circ$.

^(b) Value calculated internally from reaction data (see Table 3.2).

^(c) Temperature coefficients of this function are listed in Table 3.3.

^(d) A temperature function for the heat capacity is given in Table 3.3.

Table 3.2: Selected thermodynamic data for reactions involving neptunium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principal to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part III. 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	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
			(kJ · mol ⁻¹)	(kJ · mol ⁻¹)	(J · K ⁻¹ · mol ⁻¹)
Np(g)	Np(cr) \rightleftharpoons Np(g)			465.100 ±3.000	
Np ³⁺	0.50H ₂ (g) + Np ⁴⁺ \rightleftharpoons H ⁺ + Np ³⁺	3.695 ^(b) ±0.169	-21.092 ±0.965		
Np ⁴⁺	3H ⁺ + 0.50H ₂ (g) + NpO ₂ ⁺ \rightleftharpoons 2H ₂ O(l) + Np ⁴⁺				-305.926 ±6.228
NpO ₂ (am, hyd)	2H ₂ O(l) + Np ⁴⁺ \rightleftharpoons 4H ⁺ + NpO ₂ (am, hyd)	-1.530 ±1.000	8.733 ±5.708		
NpO ₂ ⁺	0.50H ₂ (g) + NpO ₂ ²⁺ \rightleftharpoons H ⁺ + NpO ₂ ⁺				-18.857 ±2.264
NpO ₂ ²⁺	NpO ₂ (NO ₃) ₂ · 6H ₂ O(s) \rightleftharpoons 6H ₂ O(l) + 2NO ₃ ⁻ + NpO ₂ ²⁺				104.407 ±6.695
NpOH ²⁺	H ₂ O(l) + Np ³⁺ \rightleftharpoons H ⁺ + NpOH ²⁺	-6.800 ±0.300	38.815 ±1.712		
NpOH ³⁺	H ₂ O(l) + Np ⁴⁺ \rightleftharpoons H ⁺ + NpOH ³⁺	-0.290 ±1.000	1.655 ±5.708		
NpO ₂ OH(am, aged)	H ₂ O(l) + NpO ₂ ⁺ \rightleftharpoons H ⁺ + NpO ₂ OH(am, aged)	-4.700 ±0.500	26.828 ±2.854		
NpO ₂ OH(am, fresh)	H ₂ O(l) + NpO ₂ ⁺ \rightleftharpoons H ⁺ + NpO ₂ OH(am, fresh)	-5.300 ±0.200	30.253 ±1.142		

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Table 3.2: (continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
			(kJ · mol ⁻¹)	(kJ · mol ⁻¹)	(J · K ⁻¹ · mol ⁻¹)
NpO ₂ OH(aq)	H ₂ O(l) + NpO ₂ ⁺ ⇌ H ⁺ + NpO ₂ OH(aq)	-11.300 ±0.700	64.501 ±3.996		
NpO ₂ OH ⁺	H ₂ O(l) + NpO ₂ ²⁺ ⇌ H ⁺ + NpO ₂ OH ⁺	-5.100 ±0.400	29.111 ±2.283		
NpO ₂ (OH) ₂ ⁻	2H ₂ O(l) + NpO ₂ ⁺ ⇌ 2H ⁺ + NpO ₂ (OH) ₂ ⁻	-23.600 ±0.500	134.710 ±2.854		
NpO ₃ ·H ₂ O(cr)	2H ₂ O(l) + NpO ₂ ²⁺ ⇌ 2H ⁺ + NpO ₃ ·H ₂ O(cr)	-5.470 ±0.400	31.223 ±2.283		
Np(OH) ₄ (aq)	2H ₂ O(l) + NpO ₂ (am, hyd) ⇌ Np(OH) ₄ (aq)	-8.300 ±0.500	47.377 ±2.854		
(NpO ₂) ₂ (OH) ₂ ²⁺	2H ₂ O(l) + 2NpO ₂ ²⁺ ⇌ (NpO ₂) ₂ (OH) ₂ ²⁺ + 2H ⁺	-6.270 ±0.210	35.789 ±1.199		
(NpO ₂) ₃ (OH) ₅ ⁺	5H ₂ O(l) + 3NpO ₂ ²⁺ ⇌ (NpO ₂) ₃ (OH) ₅ ⁺ + 5H ⁺	-17.120 ±0.220	97.722 ±1.256		
NpF ³⁺	F ⁻ + Np ⁴⁺ ⇌ NpF ³⁺	8.960 ±0.140	-51.144 ±0.799	1.500 ±2.000	176.569 ^(a) ±7.224
NpF ₂ ²⁺	2F ⁻ + Np ⁴⁺ ⇌ NpF ₂ ²⁺	15.700 ±0.300	-89.616 ±1.712		
NpO ₂ F(aq)	F ⁻ + NpO ₂ ⁺ ⇌ NpO ₂ F(aq)	1.200 ±0.300	-6.850 ±1.712		
NpO ₂ F ⁺	F ⁻ + NpO ₂ ²⁺ ⇌ NpO ₂ F ⁺	4.570 ±0.070	-26.086 ±0.400		
NpO ₂ F ₂ (aq)	2F ⁻ + NpO ₂ ²⁺ ⇌ NpO ₂ F ₂ (aq)	7.600 ±0.080	-43.381 ±0.457		
NpCl ³⁺	Cl ⁻ + Np ⁴⁺ ⇌ NpCl ³⁺	1.500 ±0.300	-8.562 ±1.712		
NpO ₂ Cl ⁺	Cl ⁻ + NpO ₂ ²⁺ ⇌ NpO ₂ Cl ⁺	0.400 ±0.170	-2.283 ±0.970		

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Table 3.2: (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)
NpI ³⁺	$I^- + Np^{4+} \rightleftharpoons NpI^{3+}$	1.500	-8.562		
		±0.400	±2.283		
NpO ₂ IO ₃ (aq)	$IO_3^- + NpO_2^+ \rightleftharpoons NpO_2IO_3(aq)$	0.500	-2.854		
		±0.300	±1.712		
NpO ₂ IO ₃ ⁺	$IO_3^- + NpO_2^{2+} \rightleftharpoons NpO_2IO_3^+$	1.200	-6.850		
		±0.300	±1.712		
NpSO ₄ ²⁺	$HSO_4^- + Np^{4+} \rightleftharpoons H^+ + NpSO_4^{2+}$	4.870	-27.798	7.400	118.055 ^(a)
		±0.150	±0.856	±8.800	±29.655
NpO ₂ SO ₄ (aq)	$NpO_2^{2+} + SO_4^{2-} \rightleftharpoons NpO_2SO_4(aq)$	3.280	-18.722	16.700	118.807 ^(a)
		±0.060	±0.342	±0.500	±2.033
NpO ₂ SO ₄ ⁻	$NpO_2^+ + SO_4^{2-} \rightleftharpoons NpO_2SO_4^-$	0.440	-2.512	23.200	86.237 ^(a)
		±0.270	±1.541	±7.200	±24.696
Np(SO ₄) ₂ (aq)	$2HSO_4^- + Np^{4+} \rightleftharpoons 2H^+ + Np(SO_4)_2(aq)$	7.090	-40.470	10.500	170.954 ^(a)
		±0.250	±1.427	±3.600	±12.988
NpO ₂ (SO ₄) ₂ ²⁻	$NpO_2^{2+} + 2SO_4^{2-} \rightleftharpoons NpO_2(SO_4)_2^{2-}$	4.700	-26.828	26.000	177.185 ^(a)
		±0.100	±0.571	±1.200	±4.457
NpNO ₃ ³⁺	$NO_3^- + Np^{4+} \rightleftharpoons NpNO_3^{3+}$	1.900	-10.845		
		±0.150	±0.856		
NpO ₂ HPO ₄ (aq)	$HPO_4^{2-} + NpO_2^{2+} \rightleftharpoons NpO_2HPO_4(aq)$	6.200	-35.390		
		±0.700	±3.996		
NpO ₂ HPO ₄ ⁻	$HPO_4^{2-} + NpO_2^+ \rightleftharpoons NpO_2HPO_4^-$	2.950	-16.839		
		±0.100	±0.571		
NpO ₂ H ₂ PO ₄ ⁺	$H_2PO_4^- + NpO_2^{2+} \rightleftharpoons NpO_2H_2PO_4^+$	3.320	-18.951		
		±0.500	±2.854		
NpO ₂ (HPO ₄) ₂ ²⁻	$2HPO_4^{2-} + NpO_2^{2+} \rightleftharpoons NpO_2(HPO_4)_2^{2-}$	9.500	-54.226		
		±1.000	±5.708		
NpO ₂ CO ₃ (aq)	$CO_3^{2-} + NpO_2^{2+} \rightleftharpoons NpO_2CO_3(aq)$	9.320 ^(b)	-53.201		
		±0.610	±3.480		

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Table 3.2: (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)
NpO ₂ CO ₃ (s)	CO ₃ ²⁻ + NpO ₂ ²⁺ ⇌ NpO ₂ CO ₃ (s)	14.596 ^(b)	-83.317		
		±0.469	±2.678		
NpO ₂ CO ₃ ⁻	CO ₃ ²⁻ + NpO ₂ ⁺ ⇌ NpO ₂ CO ₃ ⁻	4.962	-28.323		
		±0.061	±0.348		
NpO ₂ (CO ₃) ₂ ²⁻	2CO ₃ ²⁻ + NpO ₂ ²⁺ ⇌ NpO ₂ (CO ₃) ₂ ²⁻	16.516 ^(b)	-94.276		
		±0.729	±4.162		
NpO ₂ (CO ₃) ₂ ³⁻	CO ₃ ²⁻ + NpO ₂ CO ₃ ⁻ ⇌ NpO ₂ (CO ₃) ₂ ³⁻	1.572	-8.973		
		±0.083	±0.474		
Np(CO ₃) ₃ ³⁻	Np(CO ₃) ₅ ⁶⁻ + e ⁻ ⇌ 2CO ₃ ²⁻ + Np(CO ₃) ₃ ³⁻	-16.261	92.818		
		±2.265	±12.929		
NpO ₂ (CO ₃) ₃ ⁴⁻	NpO ₂ (CO ₃) ₃ ⁵⁻ ⇌ NpO ₂ (CO ₃) ₃ ⁴⁻ + e ⁻	-5.720 ^(b)	32.651		
		±0.095	±0.540		
NpO ₂ (CO ₃) ₃ ⁴⁻	3CO ₃ ²⁻ + NpO ₂ ²⁺ ⇌ NpO ₂ (CO ₃) ₃ ⁴⁻			-41.900	
				±4.100	
NpO ₂ (CO ₃) ₃ ⁵⁻	CO ₃ ²⁻ + NpO ₂ (CO ₃) ₂ ³⁻ ⇌ NpO ₂ (CO ₃) ₃ ⁵⁻	-1.034	5.902		
		±0.110	±0.628		
NpO ₂ (CO ₃) ₃ ⁵⁻	NpO ₂ (CO ₃) ₃ ⁴⁻ + e ⁻ ⇌ NpO ₂ (CO ₃) ₃ ⁵⁻			-88.800	
				±2.900	
Np(CO ₃) ₄ ⁴⁻	4CO ₃ ²⁻ + 2H ₂ O(l) + NpO ₂ (am, hyd) ⇌ Np(CO ₃) ₄ ⁴⁻ + 4OH ⁻	-17.790	101.546		
		±0.220	±1.256		
Np(CO ₃) ₅ ⁶⁻	CO ₃ ²⁻ + Np(CO ₃) ₄ ⁴⁻ ⇌ Np(CO ₃) ₅ ⁶⁻	-1.070	6.108		
		±0.300	±1.712		
(NpO ₂) ₃ (CO ₃) ₆ ⁶⁻	3NpO ₂ (CO ₃) ₃ ⁴⁻ ⇌ (NpO ₂) ₃ (CO ₃) ₆ ⁶⁻ + 3CO ₃ ²⁻	-8.272 ^(b)	47.215		
		±1.447	±8.260		
NpO ₂ (CO ₃) ₂ OH ⁴⁻	NpO ₂ (CO ₃) ₃ ⁵⁻ + OH ⁻ ⇌ CO ₃ ²⁻ + NpO ₂ (CO ₃) ₂ OH ⁴⁻	3.195 ^(b)	-18.238		
		±1.164	±6.644		
(NpO ₂) ₂ CO ₃ (OH) ₃ ⁻	7H ⁺ + 2NpO ₂ (CO ₃) ₃ ⁴⁻ ⇌ (NpO ₂) ₂ CO ₃ (OH) ₃ ⁻ + 5CO ₂ (g) + 2H ₂ O(l)	49.166 ^(b)	-280.643		
		±1.586	±9.053		

(Continued on next page)

Table 3.2: (continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
			(kJ · mol ⁻¹)	(kJ · mol ⁻¹)	(J · K ⁻¹ · mol ⁻¹)
(NH ₄) ₄ NpO ₂ (CO ₃) ₃ (s)	4NH ₄ ⁺ + NpO ₂ (CO ₃) ₃ ⁴⁻ ⇌ (NH ₄) ₄ NpO ₂ (CO ₃) ₃ (s)	7.443 ^(b)	-42.485		
		±0.297	±1.698		
Np(SCN) ³⁺	Np ⁴⁺ + SCN ⁻ ⇌ Np(SCN) ³⁺	3.000	-17.124	-7.000	33.956 ^(a)
		±0.300	±1.712	±3.000	±11.586
Np(SCN) ₂ ²⁺	Np ⁴⁺ + 2SCN ⁻ ⇌ Np(SCN) ₂ ²⁺	4.100	-23.403	-9.000	48.308 ^(a)
		±0.500	±2.854	±9.000	±31.668
Np(SCN) ₃ ⁺	Np ⁴⁺ + 3SCN ⁻ ⇌ Np(SCN) ₃ ⁺	4.800	-27.399	-13.000	48.293 ^(a)
		±0.500	±2.854	±9.000	±31.668
(UO ₂) ₂ NpO ₂ (CO ₃) ₆ ⁶⁻	NpO ₂ (CO ₃) ₃ ⁴⁻ + 2UO ₂ (CO ₃) ₃ ⁴⁻ ⇌ (UO ₂) ₂ NpO ₂ (CO ₃) ₆ ⁶⁻ + 3CO ₃ ²⁻	-8.985	51.288		
		±2.690	±15.356		
Na ₃ NpF ₈ (cr)	3NaF(cr) + NpF ₆ (g) ⇌ 0.50F ₂ (g) + Na ₃ NpF ₈ (cr)	7.876 ^(b)	-44.954 ^(a)	-62.678	-59.447
		±1.350	±7.705	±6.900	±11.500
NaNpO ₂ CO ₃ (s, aged)	CO ₃ ²⁻ + Na ⁺ + NpO ₂ ⁺ ⇌ NaNpO ₂ CO ₃ (s, aged)	11.657 ^(b)	-66.539		
		±0.501	±2.860		
Na ₃ NpO ₂ (CO ₃) ₂ (s)	3Na ⁺ + NpO ₂ (CO ₃) ₃ ⁵⁻ ⇌ CO ₃ ²⁻ + Na ₃ NpO ₂ (CO ₃) ₂ (s)	9.200 ^(b)	-52.515		
		±0.648	±3.697		
NaNpO ₂ CO ₃ ·3.5H ₂ O(s, fresh)	CO ₃ ²⁻ + 3.5H ₂ O(l) + Na ⁺ + NpO ₂ ⁺ ⇌ NaNpO ₂ CO ₃ ·3.5H ₂ O(s, fresh)	11.156	-63.679		
		±0.352	±2.009		
K ₄ NpO ₂ (CO ₃) ₃ (s)	4K ⁺ + NpO ₂ (CO ₃) ₃ ⁴⁻ ⇌ K ₄ NpO ₂ (CO ₃) ₃ (s)	7.033 ^(b)	-40.147		
		±0.876	±5.001		

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

Table 3.3: Selected temperature coefficients for heat capacities functions for the values marked with ^(c) in Table 3.1, according to the form

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

The functions are valid between the temperatures T_{\min} and T_{\max} (in K). Units for $C_{p,m}^{\circ}$ are $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Compound	a	b	$c/d^{(a)}$	e	T_{\min}	T_{\max}
β -Np	$3.93300\cdot 10^1$				553	849
Np(cr)	-4.05430	$8.25545\cdot 10^{-2}$		$8.05714\cdot 10^5$	298	553
Np(g)	$1.77820\cdot 10^1$	$3.35250\cdot 10^{-3}$	$6.68071\cdot 10^{-6(c)}$	$1.28800\cdot 10^5$	298	800
	$1.41320\cdot 10^1$	$1.556770\cdot 10^{-2}$	$-1.59546\cdot 10^{-6(c)}$	$-3.98870\cdot 10^5$	800	2000
γ -Np	$3.64010\cdot 10^1$				849	912
NpO ₂ (cr)	$6.75110\cdot 10^1$	$2.65990\cdot 10^{-2}$		$-8.19000\cdot 10^5$	220	800
Np ₂ O ₅ (cr)	$9.92000\cdot 10^1$	$9.86000\cdot 10^{-2}$			298	750
NpF(g)	$3.59880\cdot 10^1$	$2.30310\cdot 10^{-3}$	$-7.30170\cdot 10^{-7(c)}$	$-2.50010\cdot 10^5$	298	1400
NpF ₂ (g)	$6.74740\cdot 10^1$	$5.56480\cdot 10^{-3}$	$-5.95158\cdot 10^{-6(c)}$	$-1.12930\cdot 10^6$	298	600
NpF ₃ (cr)	$1.05200\cdot 10^2$	$8.12000\cdot 10^{-4}$		$-1.00000\cdot 10^6$	298	1735
NpF ₃ (g)	$8.16540\cdot 10^1$	$1.20840\cdot 10^{-3}$	$-2.42780\cdot 10^{-7(c)}$	$-8.67160\cdot 10^5$	298	3000
NpF ₄ (cr)	$1.22635\cdot 10^2$	$9.68400\cdot 10^{-3}$		$-8.36465\cdot 10^5$	298	1305
NpF ₄ (g)	$1.05840\cdot 10^2$	$8.61400\cdot 10^{-4}$	$1.57427\cdot 10^{-6(c)}$	$-9.75640\cdot 10^5$	298	1500
NpF ₅ (cr)	$1.26000\cdot 10^2$	$3.00000\cdot 10^{-2}$		$-1.90000\cdot 10^5$	298	600
NpF ₆ (cr)	$6.23330\cdot 10^1$	$3.52547\cdot 10^{-1}$			298	328
NpF ₆ (g)	$1.43242\cdot 10^2$	$2.44158\cdot 10^{-2}$	$-1.13115\cdot 10^{-5(c)}$	$-1.81740\cdot 10^6$	298	1000
NpF ₆ (l)	$1.50344\cdot 10^2$	$1.10076\cdot 10^{-1}$			328	350
NpO ₂ F ₂ (cr)	$1.06238\cdot 10^2$	$2.83260\cdot 10^{-2}$		$-1.02080\cdot 10^6$	298	1000
NpCl ₃ (cr)	$8.96000\cdot 10^1$	$2.75000\cdot 10^{-2}$		$3.60000\cdot 10^5$	298	1075
NpCl ₃ (g)	$7.19890\cdot 10^1$	$2.47412\cdot 10^{-2}$	$-8.48423\cdot 10^{-6(c)}$	$-1.15000\cdot 10^4$	298	1000
NpCl ₄ (cr)	$1.12500\cdot 10^2$	$3.60000\cdot 10^{-2}$		$-1.10000\cdot 10^5$	298	811
NpCl ₄ (g)	$1.08768\cdot 10^2$	$-2.86580\cdot 10^{-3}$	$3.15883\cdot 10^{-6(c)}$	$-2.80770\cdot 10^5$	298	1800
NpCl ₄ (l)	$1.08000\cdot 10^2$	$6.00000\cdot 10^{-2}$			811	1000
NpOCl ₂ (cr)	$9.88000\cdot 10^1$	$2.20000\cdot 10^{-2}$		$-9.20000\cdot 10^5$	298	1000
NpO ₂ ClO ₄ (aq) ^(b)	$3.56770\cdot 10^3$	-4.95931	$-6.32344\cdot 10^5(d)$		291	398
NpBr ₃ (cr, hex)	$1.01230\cdot 10^2$	$2.06800\cdot 10^{-2}$		$-3.20000\cdot 10^5$	298	975
NpBr ₄ (cr)	$1.19000\cdot 10^2$	$3.00000\cdot 10^{-2}$			298	800
NpOBr ₂ (cr)	$1.11000\cdot 10^2$	$1.37000\cdot 10^{-2}$		$-1.50000\cdot 10^6$	298	800
NpI ₃ (cr)	$1.04000\cdot 10^2$	$2.00000\cdot 10^{-2}$			298	975
NpN(cr)	$4.76700\cdot 10^1$	$1.31740\cdot 10^{-2}$		$-2.57620\cdot 10^5$	298	2000
NpC _{0.91} (cr)	$6.12500\cdot 10^1$	$-3.52747\cdot 10^{-2}$	$3.62834\cdot 10^{-5(c)}$	$-3.48420\cdot 10^5$	298	1000
Na ₃ NpF ₈ (cr)	$2.70000\cdot 10^2$	$5.66000\cdot 10^{-2}$		$-1.30000\cdot 10^6$	298	800

^(a) One single column is used for the two coefficients c and d , because they never occur together in the thermal functions presented in this table. The coefficient concerned is indicated in parentheses after each value.

^(b) partial molar heat capacity of solute.

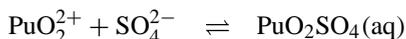
Chapter 4

Selected plutonium data

This chapter presents the chemical thermodynamic data set for plutonium species which has been selected in this review. Table 4.1 contains the recommended thermodynamic data of the plutonium compounds and complexes, Table 4.2 the recommended thermodynamic data of chemical equilibrium reactions by which the plutonium compounds and complexes are formed, and Table 4.3 the temperature coefficients of the heat capacity data of Table 4.1 where available.

The species and reactions in Tables 4.1, 4.2 and 4.3 appear in standard order of arrangement (*cf.* Figure 2.1). Table 4.2 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 plutonium species (for example Pu^{4+}) and auxiliary data listed in Table 5.1, to derive the corresponding formation quantities in Table 4.1. The uncertainties associated with values for the key plutonium species and for some of the auxiliary data are substantial, leading to comparatively large uncertainties in the formation quantities derived in this manner.

However, then the fact remains that for many reactions uncertainties in quantities such as $\Delta_r G_m^\circ$ are known more accurately than would be calculated directly from the uncertainties of the $\Delta_f G_m^\circ$ values for species listed in Table 4.1 and the auxiliary data in Table 5.1. The uncertainties in, for example, the value of $\Delta_r G_m^\circ(\text{PuO}_2\text{SO}_4(\text{aq}))$ incorporates not only the uncertainty in $\Delta_r G_m^\circ$ for the complexation reaction from which it is derived,



but also the uncertainties in $\Delta_f G_m^\circ(\text{PuO}_2^{2+}, \text{aq}, 298.15 \text{ K})$ and $\Delta_f G_m^\circ(\text{SO}_4^{2-}, \text{aq}, 298.15 \text{ K})$. Thus, back-calculation from the uncertainties of the separate species overestimates the uncertainty in the Gibbs energy of reaction and the uncertainty in the corresponding equilibrium constant. The inclusion of a table for reaction data (Table 4.2) in this report allows the use of equilibrium constants with total uncertainties that are directly based on the experimental accuracies. This is the main reason for including both the table for reaction data (Table 4.2) and the table of $\Delta_f G_m^\circ$, $\Delta_f H_m^\circ$, S_m° and $C_{p,m}^\circ$ values (Table 4.1).

Furthermore, for some reactions that involve concurrent ligand protonation or deprotonation (e.g., in certain plutonium-carbonate, -sulphate or -phosphate systems) the uncertainties in equilibrium constants are less than would have been calculated directly using the uncertainties in the Gibbs energy values for the specific ligands (*cf.* the introductory paragraphs in Chapter 5). This occurs because the Gibbs energy change for

a particular deprotonation equilibrium (*cf.* Table 5.2) may be known more accurately than the Gibbs energy formation of the ligand.

The selected thermal functions of the heat capacities, listed in Table 4.3, refer to the relation

$$C_{p,m}^{\circ}(T) = a + b \times T + c \times T^2 + d \times T^{-1} + e \times T^{-2} \quad (4.1)$$

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 Part IV.

A warning: The addition of any aqueous species and its 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 conceivable systems and conditions. Gaps are pointed out in the various sections of Part IV.

Table 4.1: Selected thermodynamic data for plutonium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principal to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* 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 Part IV. 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	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
Pu(cr)	0.000	0.000	54.460 ±0.800	31.490 ^(c) ±0.400
$\beta - \text{Pu}^{(e)}$				
$\gamma - \text{Pu}^{(e)}$				
$\delta - \text{Pu}^{(e)}$				
$\delta' - \text{Pu}^{(e)}$				
$\varepsilon - \text{Pu}^{(e)}$				
Pu(g)	312.415 ^(a) ±3.009	349.000 ^(b) ±3.000	177.167 ±0.005	20.854 ^(c) ±0.010
Pu ³⁺	-578.984 ±2.688	-591.790 ±1.964	-184.510 ^(b) ±6.154	
Pu ⁴⁺	-477.988 ±2.705	-539.895 ±3.103	-414.535 ±10.192	
PuO _{1.61} (cr, bcc)	-834.771 ^(a) ±10.113	-875.500 ±10.000	83.000 ±5.000	61.200 ^(c) ±5.000
PuO ₂ (cr)	-998.113 ^(a) ±1.031	-1055.800 ±1.000	66.130 ±0.260	66.250 ^(c) ±0.260
PuO ₂ (hyd, aged)	-963.654 ^(b) ±6.324			
PuO ₂ ⁺	-852.646 ^(b) ±2.868	-910.127 ^(a) ±8.920	1.480 ^(b) ±30.013	
PuO ₂ ²⁺	-762.353 ±2.821	-822.036 ±6.577	-71.246 ±22.120	
Pu ₂ O ₃ (cr)	-1580.375 ^(a) ±10.013	-1656.000 ±10.000	163.000 ±0.600	117.000 ^(c) ±0.500
PuOH ²⁺	-776.739 ^(b) ±3.187			

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Table 4.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
PuOH ³⁺	-710.676 ^(b) ±4.364	-789.725 ^(b) ±10.470	-238.773 ^(a) ±36.889	
PuO ₂ OH(am)	-1061.246 ^(b) ±4.046	-1159.793 ^(a) ±6.036	97.000 ±15.000	86.000 ±20.000
PuO ₂ OH(aq)	≥ -1034.247 ^(b)			
PuO ₂ OH ⁺	-968.099 ^(b) ±4.013	-1079.866 ^(b) ±16.378	-12.680 ^(b) ±55.786	
Pu(OH) ₃ (cr)	-1200.218 ^(b) ±8.975			
PuO ₂ (OH) ₂ (aq) ^(d)	-1161.287 ^(b) ±9.015			
PuO ₂ (OH) ₂ ·H ₂ O(cr)	-1442.379 ^(b) ±6.368	-1632.808 ^(a) ±13.522	190.000 ±40.000	170.000 ±20.000
(PuO ₂) ₂ (OH) ₂ ²⁺ ^(d)	-1956.176 ^(b) ±8.026			
PuF(g)	-140.967 ^(a) ±10.113	-112.600 ±10.000	251.000 ±5.000	33.500 ^(c) ±3.000
PuF ³⁺	-809.970 ^(b) ±2.850	-866.145 ^(b) ±3.859	-228.573 ^(b) ±12.753	
PuF ₂ (g)	-626.151 ^(a) ±6.704	-614.300 ±6.000	297.000 ±10.000	51.500 ^(c) ±5.000
PuF ₂ ²⁺	-1130.651 ^(b) ±3.246	-1199.595 ^(b) ±6.026	-104.666 ^(b) ±20.058	
PuF ₃ (cr)	-1517.369 ^(a) ±3.709	-1586.700 ±3.700	126.110 ±0.360	92.640 ^(c) ±0.280
PuF ₃ (g)	-1161.081 ^(a) ±4.758	-1167.800 ±3.700	336.110 ±10.000	72.240 ^(c) ±5.000
PuF ₄ (cr)	-1756.741 ^(a) ±20.002	-1850.000 ±20.000	147.250 ±0.370	116.190 ±0.290
PuF ₄ (g)	-1517.874 ^(a) ±22.202	-1548.000 ±22.000	359.000 ±10.000	92.400 ^(c) ±5.000
PuF ₆ (cr)	-1729.856 ^(a) ±20.174	-1861.350 ±20.170	221.800 ±1.100	168.100 ^(c) ±2.000
PuF ₆ (g)	-1725.064 ^(a) ±20.104	-1812.700 ±20.100	368.900 ±1.000	129.320 ^(c) ±1.000
PuOF(cr)	-1091.571 ^(a) ±20.222	-1140.000 ±20.000	96.000 ±10.000	69.400 ^(c) ±10.000
PuO ₂ F ⁺	-1069.905 ^(b) ±3.121			
PuO ₂ F ₂ (aq)	-1366.783 ^(b) ±4.059			
PuCl ²⁺	-717.051 ^(b) ±2.923			

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Table 4.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
PuCl ³⁺	-619.480 ^(b) ±3.204			
PuCl ₃ (cr)	-891.806 ^(a) ±2.024	-959.600 ±1.800	161.700 ±3.000	101.200 ^(c) ±4.000
PuCl ₃ (g)	-641.299 ^(a) ±3.598	-647.400 ±2.000	368.620 ±10.000	78.470 ^(c) ±5.000
PuCl ₄ (cr)	-879.368 ^(a) ±5.826	-968.700 ±5.000	201.000 ±10.000	121.400 ±4.000
PuCl ₄ (g)	-764.683 ^(a) ±10.438	-792.000 ±10.000	409.000 ±10.000	103.400 ^(c) ±5.000
PuOCl(cr)	-882.409 ^(a) ±1.936	-931.000 ±1.700	105.600 ±3.000	71.600 ^(c) ±4.000
PuO ₂ Cl ⁺	-897.566 ^(b) ±2.919			
PuO ₂ Cl ₂ (aq)	-1021.363 ^(b) ±3.052			
PuCl ₃ ·6H ₂ O(cr)	-2365.347 ^(a) ±2.586	-2773.400 ±2.100	420.000 ±5.000	
PuBr ³⁺	-590.971 ^(b) ±3.206			
PuBr ₃ (cr)	-767.324 ^(a) ±2.697	-792.600 ±2.000	198.000 ±6.000	101.800 ^(c) ±6.000
PuBr ₃ (g)	-529.808 ^(a) ±15.655	-488.000 ±15.000	423.000 ±15.000	81.600 ^(c) ±10.000
PuOBr(cr)	-838.354 ^(a) ±8.541	-870.000 ±8.000	127.000 ±10.000	73.000 ^(c) ±8.000
PuI ²⁺	-636.987 ^(b) ±3.529			
PuI ₃ (cr)	-579.000 ^(a) ±4.551	-579.200 ±2.800	228.000 ±12.000	110.000 ^(c) ±8.000
PuI ₃ (g)	-366.517 ^(a) ±15.655	-305.000 ±15.000	435.000 ±15.000	82.000 ^(c) ±5.000
PuOI(cr)	-776.626 ^(a) ±20.495	-802.000 ±20.000	130.000 ±15.000	75.600 ^(c) ±10.000
PuSO ₄ ⁺	-1345.315 ^(b) ±4.599	-1483.890 ^(b) ±2.976	-33.301 ^(b) ±15.108	
PuSO ₄ ²⁺	-1261.329 ^(b) ±3.270			
PuO ₂ SO ₄ (aq)	-1525.650 ^(b) ±3.072	-1715.276 ^(b) ±6.616	65.963 ^(b) ±22.543	
Pu(SO ₄) ₂ (aq)	-2029.601 ^(b) ±4.225			
Pu(SO ₄) ₂ ⁻	-2099.545 ^(b) ±5.766	-2398.590 ^(b) ±16.244	1.520 ^(b) ±56.262	

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Table 4.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
PuO ₂ (SO ₄) ₂ ²⁻	-2275.477 ^(b)	-2597.716 ^(b)	194.214 ^(b)	
	±3.156	±11.176	±37.627	
PuN(cr)	-273.719 ^(a)	-299.200	64.800	49.600
	±2.551	±2.500	±1.500	±1.000
PuNO ₃ ³⁺	-599.913 ^(b)			
	±2.868			
PuO ₂ (NO ₃) ₂ ·6H ₂ O(cr)	-2393.300			
	±3.200			
PuP(cr)	-313.757 ^(a)	-318.000	81.320	50.200
	±21.078	±21.000	±6.000	±4.000
PuPO ₄ (s, hyd)	-1744.893 ^(b)			
	±5.528			
PuH ₃ PO ₄ ⁴⁺	-1641.055 ^(b)			
	±3.569			
Pu(HPO ₄) ₂ (am, hyd)	-2843.768 ^(b)			
	±5.061			
PuAs(cr)	-241.413 ^(a)	-240.000	94.300	51.600
	±20.111	±20.000	±7.000	±4.000
PuSb(cr)	-152.063 ^(a)	-150.000	106.900	52.800
	±20.126	±20.000	±7.500	±3.500
PuBi(cr)	-119.624 ^(a)	-117.000	120.000	
	±20.223	±20.000	±10.000	
PuBi ₂ (cr)	-124.527 ^(a)	-126.000	163.000	
	±22.399	±22.000	±14.000	
PuC _{0.84} (cr)	-49.827 ^(a)	-45.200	74.800	47.100 ^(c)
	±8.028	±8.000	±2.100	±1.000
Pu ₃ C ₂ (cr)	-123.477 ^(a)	-113.000	210.000	136.800 ^(c)
	±30.046	±30.000	±5.000	±2.500
Pu ₂ C ₃ (cr)	-156.514 ^(a)	-149.400	150.000	114.000 ^(c)
	±16.729	±16.700	±2.900	±0.400
PuO ₂ CO ₃ (aq)	-1356.466 ^(b)			
	±17.359			
PuO ₂ CO ₃ (s)	-1371.307 ^(b)			
	±3.323			
PuO ₂ CO ₃ ⁻	-1409.771 ^(b)			
	±3.002			
PuO ₂ (CO ₃) ₂ ²⁻	-1900.920 ^(b)	-2199.496 ^(b)	15.796 ^(b)	
	±15.127	±7.714	±56.134	
PuO ₂ (CO ₃) ₃ ⁴⁻	-2447.085 ^(b)	-2886.326 ^(b)	-11.847 ^(b)	
	±5.977	±6.915	±28.986	
PuO ₂ (CO ₃) ₃ ⁵⁻	-2465.031 ^(b)	-2954.927 ^(b)	-116.406 ^(b)	
	±6.096	±12.344	±45.084	
(PuO ₂) ₃ (CO ₃) ₆ ^{6-(f)}	-5740.431 ^(b)			
	±16.755			

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Table 4.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
PuSCN ²⁺	-493.704 ^(b)	-515.390 ^(b)	-15.354 ^(a)	
	±5.333	±5.988	±25.229	
(UO ₂) ₂ PuO ₂ (CO ₃) ₆ ⁶⁻	-6135.666 ^(b)			
	±10.496			
Sr ₃ PuO ₆ (cr)		-3042.100		
		±7.900		
BaPuO ₃ (cr)		-1654.200		
		±8.300		
Ba ₃ PuO ₆ (cr)		-2997.000		
		±10.000		
Ba ₂ MgPuO ₆ (cr)		-2995.800		
		±8.800		
Ba ₂ CaPuO ₆ (cr)		-3067.500		
		±8.900		
Ba ₂ SrPuO ₆ (cr)		-3023.300		
		±9.000		
Cs ₂ PuCl ₆ (cr)	-1838.243 ^(a)	-1982.000	412.000	
	±6.717	±5.000	±15.000	
Cs ₃ PuCl ₆ (cr)	-2208.045 ^(b)	-2364.415 ^(b)	454.925 ^(b)	258.600 ^(c)
	±9.491	±9.040	±10.959	±10.000
CsPu ₂ Cl ₇ (cr)	-2235.119 ^(b)	-2399.380 ^(a)	424.000 ^(b)	254.900 ^(c)
	±5.284	±5.734	±7.281	±10.000
Cs ₂ PuBr ₆ (cr)	-1634.326 ^(a)	-1697.400	470.000	
	±6.150	±4.200	±15.000	
Cs ₂ NaPuCl ₆ (cr)	-2143.496 ^(a)	-2294.200	440.000	
	±5.184	±2.600	±15.000	

^(a) Value calculated internally with the Gibbs-Helmholtz equation, $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T \sum_i S_{m,i}^\circ$.

^(b) Value calculated internally from reaction data (see Table 4.2).

^(c) Temperature coefficients of this function are listed in Table 4.3.

^(d) Uncertainty is not symmetrical, see the discussion of plutonium data selection (Part IV).

^(e) A temperature function for the heat capacity is given in Table 4.3.

^(f) Reaction data are selected for this species at $I = 3$ M (NaClO₄) (cf. Section 21.1.2.1.1.d).

Table 4.2: Selected thermodynamic data for reactions involving plutonium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principal to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Part IV. 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)
Pu(g)	Pu(cr) \rightleftharpoons Pu(g)			349.000 ±3.000	
Pu ³⁺	PuCl ₃ ·6H ₂ O(cr) \rightleftharpoons 3Cl ⁻ + 6H ₂ O(l) + Pu ³⁺				-15.010 ±3.533
Pu ⁴⁺	H ⁺ + Pu ³⁺ \rightleftharpoons 0.50H ₂ (g) + Pu ⁴⁺				-164.685 ±8.124
PuO ₂ (hyd, aged)	4OH ⁻ + Pu ⁴⁺ \rightleftharpoons 2H ₂ O(l) + PuO ₂ (hyd, aged)	58.000 ±1.000	-331.066 ±5.708		
PuO ₂ ⁺	0.50H ₂ (g) + PuO ₂ ⁺ \rightleftharpoons H ⁺ + PuO ₂ ⁺	15.819 ^(b) ±0.090	-90.293 ±0.515	-88.091 ±6.026	7.386 ^(a) ±20.285
PuOH ²⁺	H ₂ O(l) + Pu ³⁺ \rightleftharpoons H ⁺ + PuOH ²⁺		-6.900 ±0.300	39.385 ±1.712	
PuOH ³⁺	H ₂ O(l) + Pu ⁴⁺ \rightleftharpoons H ⁺ + PuOH ³⁺		-0.780 ±0.600	4.452 ±3.425	36.000 ±10.000
PuO ₂ OH(am)	H ₂ O(l) + PuO ₂ ⁺ \rightleftharpoons H ⁺ + PuO ₂ OH(am)		-5.000 ±0.500	28.540 ±2.854	105.812 ^(a) ±35.453
PuO ₂ OH(aq)	H ₂ O(l) + PuO ₂ ⁺ \rightleftharpoons H ⁺ + PuO ₂ OH(aq)		≤ -9.730 ≥ 55.539		
PuO ₂ OH ⁺	H ₂ O(l) + PuO ₂ ²⁺ \rightleftharpoons H ⁺ + PuO ₂ OH ⁺		-5.500 ±0.500	31.394 ±2.854	28.000 ±15.000
					-11.384 ^(a) ±51.213

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Table 4.2: (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)
Pu(OH) ₃ (cr)	3H ₂ O(l) + Pu ³⁺ ⇌ 3H ⁺ + Pu(OH) ₃ (cr)	-15.800	90.187		
		±1.500	±8.562		
PuO ₂ (OH) ₂ (aq)	2H ₂ O(l) + PuO ₂ ²⁺ ⇌ 2H ⁺ + PuO ₂ (OH) ₂ (aq)	-13.200	75.346		
		±1.500 ^(c)	±8.562 ^(c)		
PuO ₂ (OH) ₂ ·H ₂ O(cr)	3H ₂ O(l) + PuO ₂ ²⁺ ⇌ 2H ⁺ + PuO ₂ (OH) ₂ ·H ₂ O(cr)	-5.500	31.394		
		±1.000	±5.708		
(PuO ₂) ₂ (OH) ₂ ²⁺	2H ₂ O(l) + 2PuO ₂ ²⁺ ⇌ (PuO ₂) ₂ (OH) ₂ ²⁺ + 2H ⁺	-7.500	42.810		
		±1.000 ^(c)	±5.708 ^(c)		
PuF ³⁺	F ⁻ + Pu ⁴⁺ ⇌ PuF ³⁺	8.840	-50.459	9.100	199.762 ^(a)
		±0.100	±0.571	±2.200	±7.623
PuF ₂ ²⁺	2F ⁻ + Pu ⁴⁺ ⇌ PuF ₂ ²⁺	15.700	-89.616	11.000	337.469 ^(a)
		±0.200	±1.142	±5.000	±17.202
PuO ₂ F ⁺	F ⁻ + PuO ₂ ²⁺ ⇌ PuO ₂ F ⁺	4.560	-26.029		
		±0.200	±1.142		
PuO ₂ F ₂ (aq)	2F ⁻ + PuO ₂ ²⁺ ⇌ PuO ₂ F ₂ (aq)	7.250	-41.383		
		±0.450	±2.569		
PuCl ²⁺	Cl ⁻ + Pu ³⁺ ⇌ PuCl ²⁺	1.200	-6.850		
		±0.200	±1.142		
PuCl ³⁺	Cl ⁻ + Pu ⁴⁺ ⇌ PuCl ³⁺	1.800	-10.274		
		±0.300	±1.712		
PuCl ₄ (g)	0.50Cl ₂ (g) + PuCl ₃ (cr) ⇌ PuCl ₄ (g)			167.600	
				±1.000	
PuO ₂ Cl ⁺	Cl ⁻ + PuO ₂ ²⁺ ⇌ PuO ₂ Cl ⁺	0.700	-3.996		
		±0.130	±0.742		
PuO ₂ Cl ₂ (aq)	2Cl ⁻ + PuO ₂ ²⁺ ⇌ PuO ₂ Cl ₂ (aq)	-0.600	3.425		
		±0.200	±1.142		
PuBr ³⁺	Br ⁻ + Pu ⁴⁺ ⇌ PuBr ³⁺	1.600	-9.133		
		±0.300	±1.712		

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Table 4.2: (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)
PuI ²⁺	I ⁻ + Pu ³⁺ ⇌ PuI ²⁺	1.100	-6.279		
		±0.400	±2.283		
PuSO ₄ ⁺	HSO ₄ ⁻ + Pu ³⁺ ⇌ H ⁺ + PuSO ₄ ⁺	1.930	-11.017	-5.200	19.509 ^(a)
		±0.610	±3.482	±2.000	±13.468
PuSO ₄ ²⁺	HSO ₄ ⁻ + Pu ⁴⁺ ⇌ H ⁺ + PuSO ₄ ²⁺	4.910	-28.026		
		±0.220	±1.256		
PuO ₂ SO ₄ (aq)	PuO ₂ ²⁺ + SO ₄ ²⁻ ⇌ PuO ₂ SO ₄ (aq)	3.380	-19.293	16.100	118.709 ^(a)
		±0.200	±1.142	±0.600	±4.326
Pu(SO ₄) ₂ (aq)	2HSO ₄ ⁻ + Pu ⁴⁺ ⇌ 2H ⁺ + Pu(SO ₄) ₂ (aq)	7.180	-40.984		
		±0.320	±1.827		
Pu(SO ₄) ₂ ⁻	2HSO ₄ ⁻ + Pu ³⁺ ⇌ 2H ⁺ + Pu(SO ₄) ₂ ⁻	1.740	-9.932	-33.000	-77.370 ^(a)
		±0.760	±4.338	±16.000	±55.602
PuO ₂ (SO ₄) ₂ ²⁻	PuO ₂ ²⁺ + 2SO ₄ ²⁻ ⇌ PuO ₂ (SO ₄) ₂ ²⁻	4.400	-25.115	43.000	228.460 ^(a)
		±0.200	±1.142	±9.000	±30.428
PuNO ₃ ³⁺	NO ₃ ⁻ + Pu ⁴⁺ ⇌ PuNO ₃ ³⁺	1.950	-11.131		
		±0.150	±0.856		
PuPO ₄ (s, hyd)	PO ₄ ³⁻ + Pu ³⁺ ⇌ PuPO ₄ (s, hyd)	24.600	-140.418		
		±0.800	±4.566		
PuH ₃ PO ₄ ⁴⁺	H ₃ PO ₄ (aq) + Pu ⁴⁺ ⇌ PuH ₃ PO ₄ ⁴⁺	2.400	-13.699		
		±0.300	±1.712		
Pu(HPO ₄) ₂ (am, hyd)	2HPO ₄ ²⁻ + Pu ⁴⁺ ⇌ Pu(HPO ₄) ₂ (am, hyd)	30.450	-173.810		
		±0.510	±2.911		
PuO ₂ CO ₃ (aq)	CO ₃ ²⁻ + PuO ₂ ²⁺ ⇌ PuO ₂ CO ₃ (aq)	11.600	-66.213		
		±3.000	±17.124		
PuO ₂ CO ₃ (s)	CO ₃ ²⁻ + PuO ₂ ²⁺ ⇌ PuO ₂ CO ₃ (s)	14.200	-81.054		
		±0.300	±1.712		
PuO ₂ CO ₃ ⁻	CO ₃ ²⁻ + PuO ₂ ⁺ ⇌ PuO ₂ CO ₃ ⁻	5.120	-29.225		
		±0.140	±0.799		

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Table 4.2: (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)
PuO ₂ (CO ₃) ₂ ²⁻	2CO ₃ ²⁻ + PuO ₂ ²⁺ ⇌ PuO ₂ (CO ₃) ₂ ²⁻	14.500	-82.767	-27.000	187.042 ^(a)
		±2.600	±14.841	±4.000	±51.553
PuO ₂ (CO ₃) ₃ ⁴⁻	3CO ₃ ²⁻ + PuO ₂ ²⁺ ⇌ PuO ₂ (CO ₃) ₃ ⁴⁻	17.700	-101.032	-38.600	209.399 ^(a)
		±0.900	±5.137	±2.000	±18.490
PuO ₂ (CO ₃) ₃ ⁵⁻	3CO ₃ ²⁻ + PuO ₂ ⁺ ⇌ PuO ₂ (CO ₃) ₃ ⁵⁻	5.025 ^(b)	-28.685	-19.110	32.115 ^(a)
		±0.920	±5.250	±8.500	±33.509
Pu(CO ₃) ₅ ⁶⁻	CO ₃ ²⁻ + Pu(CO ₃) ₄ ⁴⁻ ⇌ Pu(CO ₃) ₅ ⁶⁻	-1.360	7.763		
		±0.090	±0.514		
(PuO ₂) ₃ (CO ₃) ₆ ^{6-(d)}	6CO ₃ ²⁻ + 3PuO ₂ ²⁺ ⇌ (PuO ₂) ₃ (CO ₃) ₆ ⁶⁻	50.100	-285.973		
		±2.500	±14.270		
PuSCN ²⁺	Pu ³⁺ + SCN ⁻ ⇌ PuSCN ²⁺	1.300	-7.420	0.000	24.888 ^(a)
		±0.400	±2.283	±4.000	±15.448
(UO ₂) ₂ PuO ₂ (CO ₃) ₆ ⁶⁻	PuO ₂ (CO ₃) ₃ ⁴⁻ + 2UO ₂ (CO ₃) ₃ ⁴⁻ ⇌ (UO ₂) ₂ PuO ₂ (CO ₃) ₆ ⁶⁻ + 3CO ₃ ²⁻	-8.200	46.806		
		±1.300	±7.420		
Cs ₃ PuCl ₆ (cr)	CsCl(cr) + 0.20CsPu ₂ Cl ₇ (cr) ⇌ 0.40Cs ₃ PuCl ₆ (cr)	3.922 ^(b)	-22.387 ^(a)	-23.580	-4.000
		±0.638	±3.640	±3.426	±4.130
CsPu ₂ Cl ₇ (cr)	CsCl(cr) + 2PuCl ₃ (cr) ⇌ CsPu ₂ Cl ₇ (cr)	6.605 ^(b)	-37.700 ^(a)	-37.870	-0.570
		±0.594	±3.390	±3.160	±4.120

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

^(c) Uncertainty is not symmetrical, see the discussion of plutonium data selection (Part IV).

^(d) As discussed in Section 21.1.2.1.1.d, the value for (PuO₂)₃(CO₃)₆⁶⁻ is valid only for $I = 3$ M (NaClO₄).

Table 4.3: Selected temperature coefficients for heat capacities functions for the values marked with ^(c) in Table 4.1, according to the form

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

The functions are valid between the temperatures T_{\min} and T_{\max} (in K). Units for $C_{p,m}^{\circ}$ are $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

Compound	a	b	$c/d^{(a)}$	e	T_{\min}	T_{\max}
Pu(cr)	$1.81258\cdot 10^1$	$4.48200\cdot 10^{-2}$			298	398
β -Pu	$2.74160\cdot 10^1$	$1.30600\cdot 10^{-2}$			398	488
γ -Pu	$2.20233\cdot 10^1$	$2.29590\cdot 10^{-2}$			488	593
δ -Pu	$2.84781\cdot 10^1$	$1.08070\cdot 10^{-2}$			593	736
δ' -Pu	$3.55600\cdot 10^1$				736	756
ε -Pu	$3.37200\cdot 10^1$				756	913
Pu(g)	$2.05200\cdot 10^1$	$-9.39140\cdot 10^{-3}$	$2.57547\cdot 10^{-5(c)}$	$7.51200\cdot 10^4$	298	500
	$4.59200\cdot 10^0$	$3.31521\cdot 10^{-2}$	$-5.64466\cdot 10^{-6(c)}$	$7.01590\cdot 10^5$	500	1100
	$-9.58800\cdot 10^0$	$4.60885\cdot 10^{-2}$	$-8.63248\cdot 10^{-6(c)}$	$5.01446\cdot 10^5$	1100	2000
PuO _{1.61} (cr, bcc)	$6.59100\cdot 10^1$	$1.38500\cdot 10^{-2}$		$-8.75700\cdot 10^5$	298	2300
PuO ₂ (cr)	$8.44950\cdot 10^1$	$1.06390\cdot 10^{-2}$	$-6.11360\cdot 10^{-7(c)}$	$-1.90056\cdot 10^6$	298	2500
Pu ₂ O ₃ (cr)	$1.69466\cdot 10^2$	$-7.99800\cdot 10^{-2}$		$-2.54590\cdot 10^6$	298	350
	$1.22953\cdot 10^2$	$2.85480\cdot 10^{-2}$		$-1.50120\cdot 10^5$	350	2358
PuF(g)	$3.66410\cdot 10^1$	$9.20600\cdot 10^{-4}$	$-1.44430\cdot 10^{-7(c)}$	$-3.02540\cdot 10^5$	298	3000
PuF ₂ (g)	$5.73100\cdot 10^1$	$7.27000\cdot 10^{-4}$	$-1.47210\cdot 10^{-7(c)}$	$-5.38960\cdot 10^5$	298	3000
PuF ₃ (cr)	$1.04078\cdot 10^2$	$7.07000\cdot 10^{-4}$		$-1.03550\cdot 10^6$	298	1700
PuF ₃ (g)	$7.92670\cdot 10^1$	$5.60920\cdot 10^{-3}$	$-2.20239\cdot 10^{-6(c)}$	$-7.55940\cdot 10^5$	298	1300
PuF ₄ (g)	$1.05112\cdot 10^2$	$2.84120\cdot 10^{-3}$	$-6.88730\cdot 10^{-7(c)}$	$-1.19683\cdot 10^6$	298	2400
PuF ₆ (cr)	$7.23480\cdot 10^1$	$3.21296\cdot 10^{-1}$			298	325
PuF ₆ (g)	$1.43988\cdot 10^2$	$2.32109\cdot 10^{-2}$	$-1.07641\cdot 10^{-5(c)}$	$-1.83427\cdot 10^6$	298	1000
PuOF(cr)	$7.20000\cdot 10^1$	$1.60000\cdot 10^{-2}$	$-3.30000\cdot 10^{-6(c)}$	$-6.20000\cdot 10^5$	298	1500
PuCl ₃ (cr)	$9.13500\cdot 10^1$	$2.40000\cdot 10^{-2}$		$2.40000\cdot 10^5$	298	1041
PuCl ₃ (g)	$7.71030\cdot 10^1$	$1.29971\cdot 10^{-2}$	$-4.31251\cdot 10^{-6(c)}$	$-1.88730\cdot 10^5$	298	1100
PuCl ₄ (g)	$1.10428\cdot 10^2$	$4.08180\cdot 10^{-3}$	$-9.76160\cdot 10^{-7(c)}$	$-7.23430\cdot 10^5$	298	3000
PuOCl(cr)	$7.30300\cdot 10^1$	$1.71000\cdot 10^{-2}$		$-5.83000\cdot 10^5$	298	1100
PuBr ₃ (cr)	$1.04500\cdot 10^2$	$1.50000\cdot 10^{-2}$		$-6.38000\cdot 10^5$	298	935
PuBr ₃ (g)	$8.31350\cdot 10^1$	$3.90000\cdot 10^{-6}$		$-1.38320\cdot 10^5$	298	1500
PuOBr(cr)	$7.37000\cdot 10^1$	$1.70000\cdot 10^{-2}$		$-5.15000\cdot 10^5$	298	1100
PuI ₃ (cr)	$1.04000\cdot 10^2$	$2.00000\cdot 10^{-2}$			298	930
PuI ₃ (g)	$8.31500\cdot 10^1$	$1.40000\cdot 10^{-6}$		$-1.00000\cdot 10^5$	298	1500
PuOI(cr)	$6.70000\cdot 10^1$	$3.57000\cdot 10^{-2}$	$-1.20000\cdot 10^{-5(c)}$	$-9.00000\cdot 10^4$	298	1000
PuC _{0.84} (cr)	$7.15910\cdot 10^1$	$-5.95042\cdot 10^{-2}$	$4.94346\cdot 10^{-5(c)}$	$-9.93200\cdot 10^5$	298	1875
Pu ₃ C ₂ (cr)	$1.20670\cdot 10^2$	$4.68600\cdot 10^{-2}$		$1.94560\cdot 10^5$	298	850
Pu ₂ C ₃ (cr)	$1.56000\cdot 10^2$	$-7.98726\cdot 10^{-2}$	$7.04170\cdot 10^{-5(c)}$	$-2.17570\cdot 10^6$	298	2285
Cs ₃ PuCl ₆ (cr)	$2.56600\cdot 10^2$	$3.46000\cdot 10^{-2}$		$-7.40000\cdot 10^5$	298	900
CsPu ₂ Cl ₇ (cr)	$2.37800\cdot 10^2$	$5.15000\cdot 10^{-2}$		$1.55000\cdot 10^5$	298	900

^(a) One single column is used for the two coefficients c and d , because they never occur together in the thermal functions presented in this table. The coefficient concerned is indicated in parentheses after each value.

Chapter 5

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 neptunium and plutonium data in Tables 3.1, 3.2, 4.1 and 4.2. It is therefore essential to always use these auxiliary data in conjunction with the selected data for neptunium and plutonium. 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 [89COX/WAG], or were evaluated within the NEA's TDB project, as described in Chapter VI of the uranium review [92GRE/FUG].

Table 5.1 contains the selected thermodynamic data of the auxiliary species and Table 5.2 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 Chapters 3 and 4, that uncertainties in reaction data are often smaller than the derived S_m° , $\Delta_f H_m^\circ$ and $\Delta_f G_m^\circ$, due to uncertainty accumulation during the calculations.

All data in Tables 5.1 and 5.2 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 5.2 are total uncertainties, and correspond mainly to the statistically defined 95% confidence interval. The uncertainties listed below each value in Table 5.1 have the following significance:

- for CODATA values from [89COX/WAG], the \pm terms have the meaning: "it is probable, but not at all certain, that the true values of the thermodynamic quantities differ from the recommended values given in this report by no more than twice the \pm terms attached to the recommended values".
- for values from [92GRE/FUG], the \pm terms are derived from total uncertainties in the corresponding equilibrium constant of reaction (*cf.* Table 5.2), and from the \pm terms listed for the necessary CODATA key values.

CODATA [89COX/WAG] values are available for $\text{CO}_2(\text{g})$, HCO_3^- , CO_3^{2-} , H_2PO_4^- and HPO_4^{2-} . From the values given for $\Delta_f H_m^\circ$ and S_m° the values of $\Delta_f G_m^\circ$ and, consequently, all the relevant equilibrium constants and enthalpy changes can be calculated. The propagation of errors during this procedure, however, leads to uncertainties in the resulting equilibrium constants that are significantly higher than those obtained from experimental determination of the constants. Therefore, reaction data for $\text{CO}_2(\text{g})$,

HCO_3^- , CO_3^{2-} and H_2PO_4^- , which were absent from the corresponding Table 5.2 in [92GRE/FUG], are included in this volume to provide the user of selected data for species of neptunium and plutonium (*cf.* Chapters 3 and 4) with the data needed to obtain the lowest possible uncertainties on reaction properties.

Note that the values in Tables 5.1 and 5.2 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 computerized data base and rounded to three digits after the decimal point throughout.

Table 5.1: 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 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a reference state or standard state of infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values in **bold** typeface are CODATA Key Values and are taken directly from 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	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · 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 ₂ O(g)	-228.582 ^(a) ±0.040	-241.826 ±0.040	188.835 ±0.010	33.609 ±0.030
H ₂ O(l)	-237.140 ^(a) ±0.041	-285.830 ±0.040	69.950 ±0.030	75.351 ±0.080
H ₂ O ₂ (aq)		-191.170 ^(c) ±0.100		

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
He(g)	0.000	0.000	126.153	20.786
			± 0.002	± 0.001
Ne(g)	0.000	0.000	146.328	20.786
			± 0.003	± 0.001
Ar(g)	0.000	0.000	154.846	20.786
			± 0.003	± 0.001
Kr(g)	0.000	0.000	164.085	20.786
			± 0.003	± 0.001
Xe(g)	0.000	0.000	169.685	20.786
			± 0.003	± 0.001
F(g)	62.280^(a)	79.380	158.751	22.746
	± 0.300	± 0.300	± 0.004	± 0.002
F ⁻	-281.523^(a)	-335.350	-13.800	
	± 0.692	± 0.650	± 0.800	
F ₂ (g)	0.000	0.000	202.791	31.304
			± 0.005	± 0.002
HF(aq)	-299.675^(b)	-323.150^(b)	88.000^(a)	
	± 0.702	± 0.716	± 3.362	
HF(g)	-275.400^(a)	-273.300	173.779	29.137
	± 0.700	± 0.700	± 0.003	± 0.002
HF ₂ ⁻	-583.709^(b)	-655.500^(b)	92.683^(a)	
	± 1.200	± 2.221	± 8.469	
Cl(g)	105.305^(a)	121.301	165.190	21.838
	± 0.008	± 0.008	± 0.004	± 0.001
Cl ⁻	-131.217^(a)	-167.080	56.600	
	± 0.117	± 0.100	± 0.200	
Cl ₂ (g)	0.000	0.000	223.081	33.949
			± 0.010	± 0.002
ClO ⁻	-37.669^(b)			
	± 0.962			
ClO ₂ ⁻	10.250^(b)			
	± 4.044			
ClO ₃ ⁻	-7.903^(a)	-104.000	162.300	
	± 1.342	± 1.000	± 3.000	
ClO ₄ ⁻	-7.890^(a)	-128.100	184.000	
	± 0.600	± 0.400	± 1.500	
HCl(g)	-95.298^(a)	-92.310	186.902	29.136
	± 0.100	± 0.100	± 0.005	± 0.002
HClO(aq)	-80.023^(b)			
	± 0.613			
HClO ₂ (aq)	-0.938^(b)			
	± 4.043			
Br(g)	82.379^(a)	111.870	175.018	20.786
	± 0.128	± 0.120	± 0.004	± 0.001

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
Br ⁻	-103.850 ^(a)	-121.410	82.550	
	±0.167	±0.150	±0.200	
Br ₂ (aq)	4.900			
	±1.000			
Br ₂ (g)	3.105 ^(a)	30.910	245.468	36.057
	±0.142	±0.110	±0.005	±0.002
Br ₂ (l)	0.000	0.000	152.210	
			±0.300	
BrO ⁻	-32.095 ^(b)			
	±1.537			
BrO ₃ ⁻	19.070 ^(a)	-66.700	161.500	
	±0.634	±0.500	±1.300	
HBr(g)	-53.361 ^(a)	-36.290	198.700	29.141
	±0.166	±0.160	±0.004	±0.003
HBrO(aq)	-81.356			
	±1.527			
I(g)	70.172 ^(a)	106.760	180.787	20.786
	±0.060	±0.040	±0.004	±0.001
I ⁻	-51.724 ^(a)	-56.780	106.450	
	±0.112	±0.050	±0.300	
I ₂ (cr)	0.000	0.000	116.140	
			±0.300	
I ₂ (g)	19.323 ^(a)	62.420	260.687	36.888
	±0.120	±0.080	±0.005	±0.002
IO ₃ ⁻	-126.338 ^(a)	-219.700	118.000	
	±0.779	±0.500	±2.000	
HI(g)	1.700 ^(a)	26.500	206.590	29.157
	±0.110	±0.100	±0.004	±0.003
HIO ₃ (aq)	-130.836 ^(b)			
	±0.797			
S(cr) ^(d)	0.000	0.000	32.054	22.750
			±0.050	±0.050
S(g)	236.689 ^(a)	277.170	167.829	23.674
	±0.151	±0.150	±0.006	±0.001
S ²⁻	120.695 ^(b)			
	±11.610			
S ₂ (g)	79.686 ^(a)	128.600	228.167	32.505
	±0.301	±0.300	±0.010	±0.010
SO ₂ (g)	-300.095 ^(a)	-296.810	248.223	39.842
	±0.201	±0.200	±0.050	±0.020
SO ₃ ²⁻	-487.472 ^(b)			
	±4.020			
S ₂ O ₃ ²⁻	-519.291 ^(b)			
	±11.345			

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
SO ₄ ²⁻	-744.004^(a) ±0.418	-909.340 ±0.400	18.500 ±0.400	
HS ⁻	12.243^(a) ±2.115	-16.300 ±1.500	67.000 ±5.000	
H ₂ S(aq)	-27.648^(a) ±2.115	-38.600 ±1.500	126.000 ±5.000	
H ₂ S(g)	-33.443^(a) ±0.500	-20.600 ±0.500	205.810 ±0.050	34.248 ±0.010
HSO ₃ ⁻	-528.684 ^(b) ±4.046			
HS ₂ O ₃ ⁻	-528.366 ^(b) ±11.377			
H ₂ SO ₃ (aq)	-539.187 ^(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⁻	-361.597 ^(b) ±1.473			
HSeO ₃ ⁻	-409.544 ^(b) ±1.358			
H ₂ SeO 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
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 ±0.005
NH ₄ ⁺	-79.398^(a) ±0.278	-133.260 ±0.250	111.170 ±0.400	

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
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	316.500 ±1.000	163.199 ±0.003	20.786 ±0.001
P ₂ (g)	103.469^(a) ±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 ₂ O ₇ ⁴⁻	-1935.503 ^(b) ±4.563			
HPO ₄ ²⁻	-1095.985^(a) ±1.567	-1299.000 ±1.500	-33.500 ±1.500	
H ₂ PO ₄ ⁻	-1137.152^(a) ±1.567	-1302.600 ±1.500	92.500 ±1.500	
H ₃ PO ₄ (aq)	-1149.367 ^(b) ±1.576	-1294.120 ^(b) ±1.616	161.912 ^(b) ±2.575	
HP ₂ O ₇ ³⁻	-1989.158 ^(b) ±4.482			
H ₂ P ₂ O ₇ ²⁻	-2027.117 ^(b) ±4.445			
H ₃ P ₂ O ₇ ⁻	-2039.960 ^(b) ±4.362			
H ₄ P ₂ O 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	-888.140 ±4.000	-162.800 ±0.600	
As ₂ O ₅ (cr)	-782.449 ^(a) ±8.016	-924.870 ±8.000	105.400 ±1.200	116.520 ±0.800
As ₄ O ₆ (cubi) ^(f)	-1152.445 ^(a) ±16.032	-1313.940 ±16.000	214.200 ±2.400	191.290 ±0.800
As ₄ O 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 ₂ AsO ₃ ⁻	-587.078 ^(a) ±4.008	-714.790 ±4.000	110.500 ±0.600	

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
H ₃ AsO ₃ (aq)	-639.681 ^(a)	-742.200	195.000	
	±4.015	±4.000	±1.000	
HAsO ₄ ²⁻	-714.592 ^(a)	-906.340	-1.700	
	±4.008	±4.000	±0.600	
H ₂ AsO ₄ ⁻	-753.203 ^(a)	-909.560	117.000	
	±4.015	±4.000	±1.000	
H ₃ AsO ₄ (aq)	-766.119 ^(a)	-902.500	184.000	
	±4.015	±4.000	±1.000	
(As ₂ O ₅) ₃ ·5H ₂ O(cr)		-4248.400		
		±24.000		
Sb(cr)	0.000	0.000	45.520	25.260
			±0.210	±0.200
Bi(cr) ^(o)	0.0	0.0	56.740	25.520
			±0.840	
C(cr)	0.000	0.000	5.740	8.517
			±0.100	±0.080
C(g)	671.254^(a)	716.680	158.100	20.839
	±0.451	±0.450	±0.003	±0.001
CO(g)	-137.168 ^(a)	-110.530	197.660	29.141
	±0.173	±0.170	±0.004	±0.002
CO ₂ (aq)	-385.970 ^(a)	-413.260	119.360	
	±0.270	±0.200	±0.600	
CO ₂ (g)	-394.373 ^(a)	-393.510	213.785	37.135
	±0.133	±0.130	±0.010	±0.002
CO ₃ ²⁻	-527.900 ^(a)	-675.230	-50.000	
	±0.390	±0.250	±1.000	
HCO ₃ ⁻	-586.845 ^(a)	-689.930	98.400	
	±0.251	±0.200	±0.500	
SCN ⁻	92.700	76.400	144.268 ^(a)	
	±4.000	±4.000	±18.974	
Si(cr)	0.000	0.000	18.810	19.789
			±0.080	±0.030
Si(g)	405.525^(a)	450.000	167.981	22.251
	±8.000	±8.000	±0.004	±0.001
SiO ₂ (quar) ^(h)	-856.287 ^(a)	-910.700	41.460	44.602
	±1.002	±1.000	±0.200	±0.300
SiO ₂ (OH) ₂ ²⁻	-1175.651 ^(b)	-1381.960 ^(b)	-1.488 ^(b)	
	±1.265	±15.330	±51.592	
SiO(OH) ₃ ⁻	-1251.740 ^(b)	-1431.360 ^(b)	88.024 ^(b)	
	±1.162	±3.743	±13.144	
Si(OH) ₄ (aq)	-1307.735 ^(b)	-1456.960 ^(b)	189.973 ^(a)	
	±1.156	±3.163	±11.296	
Si ₂ O ₃ (OH) ₄ ²⁻	-2269.878 ^(b)			
	±2.878			

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
Si ₂ O ₂ (OH) ₅ ⁻	-2332.096 ^(b) ±2.878			
Si ₃ O ₆ (OH) ₃ ³⁻	-3048.536 ^(b) ±3.870			
Si ₃ O ₅ (OH) ₅ ³⁻	-3291.955 ^(b) ±3.869			
Si ₄ O ₈ (OH) ₄ ⁴⁻	-4075.179 ^(b) ±5.437			
Si ₄ O 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
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) ⁽ⁱ⁾	-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 ±1.000	
PbSO ₄ (cr)	-813.036 ^(a) ±0.447	-919.970 ±0.400	148.500 ±0.600	
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 ₂ O ₃ (cr)	-1194.324 ^(a) ±1.404	-1273.500 ±1.400	53.970 ±0.300	62.761 ±0.300

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
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
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 ₂ O 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
Tl ⁺	-32.400 ±0.300			
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) ±0.205	111.800 ±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 ·2.667H ₂ O(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	
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	

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
HgO(mont) ^(l)	-58.523 ^(a)	-90.790	70.250	
	±0.154	±0.120	±0.300	
Hg ₂ Cl ₂ (cr)	-210.725 ^(a)	-265.370	191.600	
	±0.471	±0.400	±0.800	
Hg ₂ SO ₄ (cr)	-625.780 ^(a)	-743.090	200.700	
	±0.411	±0.400	±0.200	
Cu(cr)	0.000	0.000	33.150	24.440
			±0.080	±0.050
Cu(g)	297.672 ^(a)	337.400	166.398	20.786
	±1.200	±1.200	±0.004	±0.001
Cu ²⁺	65.040 ^(a)	64.900	-98.000	
	±1.557	±1.000	±4.000	
CuSO ₄ (cr)	-662.185 ^(a)	-771.400	109.200	
	±1.206	±1.200	±0.400	
Ag(cr)	0.000	0.000	42.550	25.350
			±0.200	±0.100
Ag(g)	246.007 ^(a)	284.900	172.997	20.786
	±0.802	±0.800	±0.004	±0.001
Ag ⁺	77.096 ^(a)	105.790	73.450	
	±0.156	±0.080	±0.400	
AgCl(cr)	-109.765 ^(a)	-127.010	96.250	
	±0.098	±0.050	±0.200	
Ti(cr)	0.000	0.000	30.720	25.060
			±0.100	±0.080
Ti(g)	428.403 ^(a)	473.000	180.298	24.430
	±3.000	±3.000	±0.010	±0.030
TiO ₂ (ruti) ^(m)	-888.767 ^(a)	-944.000	50.620	55.080
	±0.806	±0.800	±0.300	±0.300
TiCl ₄ (g)	-726.324 ^(a)	-763.200	353.200	95.408
	±3.229	±3.000	±4.000	±1.000
Th(cr)	0.000	0.000	51.800	26.230
			±0.500	±0.050
Th(g)	560.745 ^(a)	602.000	190.170	20.789
	±6.002	±6.000	±0.050	±0.100
ThO ₂ (cr)	-1169.238 ^(a)	-1226.400	65.230	
	±3.504	±3.500	±0.200	
Be(cr)	0.000	0.000	9.500	16.443
			±0.080	±0.060
Be(g)	286.202 ^(a)	324.000	136.275	20.786
	±5.000	±5.000	±0.003	±0.001
BeO(brom) ⁽ⁿ⁾	-580.090 ^(a)	-609.400	13.770	25.565
	±2.500	±2.500	±0.040	±0.100
Mg(cr)	0.000	0.000	32.670	24.869
			±0.100	±0.020

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
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
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	194.600 ±2.100	
Ba(cr)	0.000	0.000	62.420 ±0.840	
Ba ²⁺	-557.656 ^(a) ±2.582	-534.800 ±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
Na(g)	76.964^(a) ±0.703	107.500 ±0.700	153.718 ±0.003	20.786 ±0.001

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Table 5.1: (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol ⁻¹)	$\Delta_f H_m^\circ$ (kJ · mol ⁻¹)	S_m° (J · K ⁻¹ · mol ⁻¹)	$C_{p,m}^\circ$ (J · K ⁻¹ · mol ⁻¹)
Na ⁺	-261.953 ^(a) ±0.096	-240.340 ±0.060	58.450 ±0.150	
NaF(cr) ^(p)	-546.327 ±0.704	-576.600 ±0.700	51.160 ±0.150	46.820
NaCl(cr) ^(p)	-384.221 ±0.147	-411.260 ±0.120	72.150 ±0.200	50.500
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	-251.120 ±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	
CsCl(cr)	-413.807 ^(a) ±0.208	-442.310 ±0.160	101.170 ±0.200	52.470
CsBr(cr) ^(p)	-391.171 ±0.305	-405.600 ±0.250	112.940 ±0.400	52.930

(a) Value calculated internally with the equation $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T \Delta_f S_m^\circ$.

(b) Value calculated internally from reaction data (see Table 5.2).

(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.

(o) Data from [82WAG/EVA, 73HUL/DES], with the uncertainty in S° from the latter.

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(footnotes continued)

^(P)Data from [82GLU/GUR], compatible with [89COX/WAG].

Table 5.2: Selected thermodynamic data for reactions involving auxiliary compounds and complexes used in the evaluation of thermodynamic data for the NEA TDB Project data. All ionic species listed in this table are aqueous species. The selection of these data is described in Chapter VI of the uranium review [92GRE/FUG]. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a reference state or standard state of infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The 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 ⁻	$HClO_2(aq) \rightleftharpoons ClO_2^- + H^+$	-1.960	11.188		
		±0.020	±0.114		
HClO(aq)	$Cl_2(g) + H_2O(l) \rightleftharpoons Cl^- + H^+ + HClO(aq)$	-4.537	25.900		
		±0.105	±0.600		
HClO ₂ (aq)	$H_2O(l) + HClO(aq) \rightleftharpoons 2H^+ + HClO_2(aq) + 2e^-$	-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
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		

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Table 5.2: (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)
SO_3^{2-}	$\text{H}_2\text{O}(\text{l}) + \text{SO}_4^{2-} + 2\text{e}^- \rightleftharpoons 2\text{OH}^- + \text{SO}_3^{2-}$	-31.400 ^(b) ±0.700	179.233 ±3.996		
$\text{S}_2\text{O}_3^{2-}$	$3\text{H}_2\text{O}(\text{l}) + 2\text{SO}_3^{2-} + 4\text{e}^- \rightleftharpoons 6\text{OH}^- + \text{S}_2\text{O}_3^{2-}$	-39.200 ^(b) ±1.400	223.755 ±7.991		
$\text{H}_2\text{S}(\text{aq})$	$\text{H}_2\text{S}(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HS}^-$	-6.990 ±0.170	39.899 ±0.970		
HSO_3^-	$\text{H}^+ + \text{SO}_3^{2-} \rightleftharpoons \text{HSO}_3^-$	7.220 ±0.080	-41.212 ±0.457	66.000 ±30.000	359.591 ^(a) ±100.632
HS_2O_3^-	$\text{H}^+ + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{HS}_2\text{O}_3^-$	1.590 ±0.150	-9.076 ±0.856		
$\text{H}_2\text{SO}_3(\text{aq})$	$\text{H}^+ + \text{HSO}_3^- \rightleftharpoons \text{H}_2\text{SO}_3(\text{aq})$	1.840 ±0.080	-10.503 ±0.457	16.000 ±5.000	88.891 ^(a) ±16.840
HSO_4^-	$\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^-$	1.980 ±0.050	-11.302 ±0.285		
SeO_3^{2-}	$\text{HSeO}_3^- \rightleftharpoons \text{H}^+ + \text{SeO}_3^{2-}$	-8.400 ±0.100	47.948 ±0.571	-5.020 ±0.500	-177.654 ^(a) ±2.545
$\text{H}_2\text{Se}(\text{aq})$	$\text{H}^+ + \text{HSe}^- \rightleftharpoons \text{H}_2\text{Se}(\text{aq})$	3.800 ±0.300	-21.691 ±1.712		
HSeO_3^-	$\text{H}_2\text{SeO}_3(\text{aq}) \rightleftharpoons \text{H}^+ + \text{HSeO}_3^-$	-2.800 ±0.200	15.983 ±1.142	-7.070 ±0.500	-77.319 ^(a) ±4.180
$\text{H}_2\text{SeO}_3(\text{aq})$	$3\text{H}_2\text{O}(\text{l}) + 2\text{I}_2(\text{cr}) + \text{Se}(\text{cr}) \rightleftharpoons 4\text{H}^+ + \text{H}_2\text{SeO}_3(\text{aq}) + 4\text{I}^-$	-13.840 ±0.100	78.999 ±0.571		
HSeO_4^-	$\text{H}^+ + \text{SeO}_4^{2-} \rightleftharpoons \text{HSeO}_4^-$	1.800 ±0.140	-10.274 ±0.799	23.800 ±5.000	114.286 ^(a) ±16.983
$\text{HN}_3(\text{aq})$	$\text{H}^+ + \text{N}_3^- \rightleftharpoons \text{HN}_3(\text{aq})$	4.700 ±0.080	-26.828 ±0.457	-15.000 ±10.000	39.671 ^(a) ±33.575
$\text{NH}_3(\text{aq})$	$\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3(\text{aq})$	-9.237 ±0.022	52.725 ±0.126	52.090 ±0.210	-2.130 ^(a) ±0.821

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Table 5.2: (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)
HNO ₂ (aq)	H ⁺ + NO ₂ ⁻ ⇌ 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⁻ ⇌ H ⁺ + PO ₄ ³⁻	-12.350	70.494	14.600	-187.470 ^(a)
		±0.030	±0.171	±3.800	±12.758
P ₂ O ₇ ⁴⁻	HP ₂ O ₇ ³⁻ ⇌ H ⁺ + P ₂ O ₇ ⁴⁻	-9.400	53.656		
		±0.150	±0.856		
H ₂ PO ₄ ⁻	H ⁺ + HPO ₄ ²⁻ ⇌ H ₂ PO ₄ ⁻	7.212	-41.166	-3.600	125.998 ^(a)
		±0.013	±0.074	±1.000	±3.363
H ₃ PO ₄ (aq)	H ⁺ + H ₂ PO ₄ ⁻ ⇌ H ₃ PO ₄ (aq)	2.140	-12.215	8.480	69.412 ^(a)
		±0.030	±0.171	±0.600	±2.093
HP ₂ O ₇ ³⁻	H ₂ P ₂ O ₇ ²⁻ ⇌ H ⁺ + HP ₂ O ₇ ³⁻	-6.650	37.958		
		±0.100	±0.571		
H ₂ P ₂ O ₇ ²⁻	H ₃ P ₂ O ₇ ⁻ ⇌ H ⁺ + H ₂ P ₂ O ₇ ²⁻	-2.250	12.843		
		±0.150	±0.856		
H ₃ P ₂ O ₇ ⁻	H ₄ P ₂ O ₇ (aq) ⇌ H ⁺ + H ₃ P ₂ O ₇ ⁻	-1.000	5.708		
		±0.500	±2.854		
H ₄ P ₂ O ₇ (aq)	2H ₃ PO ₄ (aq) ⇌ H ₂ O(l) + H ₄ P ₂ O ₇ (aq)	-2.790	15.925	22.200	21.045 ^(a)
		±0.170	±0.970	±1.000	±4.674
CO ₂ (aq)	H ⁺ + HCO ₃ ⁻ ⇌ CO ₂ (aq) + H ₂ O(l)	6.354	-36.269		
		±0.020	±0.114		
CO ₂ (g)	CO ₂ (aq) ⇌ CO ₂ (g)	1.472	-8.402		
		±0.020	±0.114		
HCO ₃ ⁻	CO ₃ ²⁻ + H ⁺ ⇌ HCO ₃ ⁻	10.329	-58.958		
		±0.020	±0.114		
SiO ₂ (OH) ₂ ²⁻	Si(OH) ₄ (aq) ⇌ 2H ⁺ + SiO ₂ (OH) ₂ ²⁻	-23.140	132.084	75.000	-191.461 ^(a)
		±0.090	±0.514	±15.000	±50.340
SiO(OH) ₃ ⁻	Si(OH) ₄ (aq) ⇌ H ⁺ + SiO(OH) ₃ ⁻	-9.810	55.996	25.600	-101.948 ^(a)
		±0.020	±0.114	±2.000	±6.719

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Table 5.2: (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(OH) ₄ (aq)	2H ₂ O(l) + SiO ₂ (quar) ⇌ Si(OH) ₄ (aq)	-4.000 ±0.100	22.832 ±0.571	25.400 ±3.000	8.613 ^(a) ±10.243
Si ₂ O ₃ (OH) ₄ ²⁻	2Si(OH) ₄ (aq) ⇌ 2H ⁺ + H ₂ O(l) + Si ₂ O ₃ (OH) ₄ ²⁻	-19.000 ±0.300	108.453 ±1.712		
Si ₂ O ₂ (OH) ₅ ⁻	2Si(OH) ₄ (aq) ⇌ H ⁺ + H ₂ O(l) + Si ₂ O ₂ (OH) ₅ ⁻	-8.100 ±0.300	46.235 ±1.712		
Si ₃ O ₆ (OH) ₃ ³⁻	3Si(OH) ₄ (aq) ⇌ 3H ⁺ + 3H ₂ O(l) + Si ₃ O ₆ (OH) ₃ ³⁻	-28.600 ±0.300	163.250 ±1.712		
Si ₃ O ₅ (OH) ₅ ³⁻	3Si(OH) ₄ (aq) ⇌ 3H ⁺ + 2H ₂ O(l) + Si ₃ O ₅ (OH) ₅ ³⁻	-27.500 ±0.300	156.971 ±1.712		
Si ₄ O ₈ (OH) ₄ ⁴⁻	4Si(OH) ₄ (aq) ⇌ 4H ⁺ + 4H ₂ O(l) + Si ₄ O ₈ (OH) ₄ ⁴⁻	-36.300 ±0.500	207.202 ±2.854		
Si ₄ O ₇ (OH) ₅ ³⁻	4Si(OH) ₄ (aq) ⇌ 3H ⁺ + 4H ₂ O(l) + Si ₄ O 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 $\Delta_r G_m^\circ$.

Part III

Discussion of neptunium data selection

Chapter 6

Elemental neptunium

6.1 Neptunium crystal and liquid

The isotope of neptunium most commonly encountered is ^{237}Np , and all the available thermodynamic data were measured on material all containing essentially this isotope.

6.1.1 Crystal structure and phase transitions

Neptunium has three allotropic modifications stable at atmospheric pressure, and the results of two separate data measurements suggest there may be a fourth (see below). The low-symmetry f-bonded α and β phases are more dense than the bcc γ phase, which is not stable above the $\beta + \gamma +$ liquid triple point at (998K, 3.2 GPa) [66STE]. The crystal structures, given in Table 6.1, are based on studies by Zachariasen [52ZAC] and Stephens [66STE]; the lattice parameters are those selected by Fahey ([86FAH] p. 454), from which the densities have been recalculated with the latest value for the Avogadro constant.

There is reasonable consistency in the measurements of the transition temperatures, *cf.* Table 6.2.

The values selected are those from [70WIT/VAU], in which a relatively massive sample was used, and whose results are near the middle of the experimental ranges. This choice also maintains good consistency with enthalpies of transition (see below). The dilatometric measurements by Cort [87COR] seem to give values which are appreciably too low, especially for higher temperature transitions, probably due to preferred orientation in the sample, as discussed by the author.

Both Lee *et al.* [59LEE/MAR] and Foltyn [90FOL] observed small peaks or discontinuities in the heating and cooling curves just below the $\beta \rightarrow \gamma$ transition, though not consistently. It is tempting to attribute this to the possible existence of another allotope of Np, as suggested by Lee *et al.* [59LEE/MAR] (*cf.* the δ' phase of Pu, formed with a very small enthalpy change from the fcc δ phase, and stable only from 736 to 756 K). Further investigation of this phenomenon is required.

6.1.2 Heat capacity and entropy

There is little difference in the results of the low-temperature measurements of Sandenaw [65SAN], using an impure sample, and those of Lee *et al.* [70LEE/MEN], using purer metal. Gordon *et al.* [76GOR/HAL] made further measurements, but only

Table 6.1: Allotropy of neptunium

Phase	Stability range/K	Structure type and space group	Lattice parameters 10^{10} m	Z	Density $\text{g}\cdot\text{cm}^{-3}$
α	below 553	orthorhombic Pnma	$a = 6.663$ $b = 4.723$ $c = 4.887$ at 293 K	8	20.48
β	553 to 849	tetragonal P4 ₂ 12	$a = 4.897$ $c = 3.388$ at 586 K	4	19.38
γ	849 to 912	bc cubic Im3m	$a=3.518$ at 873 K	2	18.08

Table 6.2: Transition temperatures for neptunium allotropes

Reference	$T(\alpha \rightarrow \beta)$ K	$T(\beta \rightarrow \gamma)$ K	$T(\gamma \rightarrow \text{liquid})$ K
[51WES/EYR]			(913 ± 1)
[52ZAC]	551	843	
[59LEE/MAR]	(553 ± 3)	(850 ± 3)	(910 ± 3)
[70WIT/VAU]	553	849	913
[90FOL]	555	856	917
Selected	(553 ± 3)	(849 ± 3)	(912 ± 3)

at very low temperatures (2.5 to 9.4 K). The selected values for α -Np are those from [70LEE/MEN]:

$$C_{p,m}^{\circ}(\text{Np}, \alpha, 298.15 \text{ K}) = (29.62 \pm 0.80) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and the derived entropy:

$$S_m^{\circ}(\text{Np}, \alpha, 298.15 \text{ K}) = (50.46 \pm 0.80) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

There have been only two rather limited investigations of the heat capacities of neptunium above room temperature. Eldred and Curtis [57ELD/CUR], in a preliminary study of neptunium metal, measured the heat capacity from 302 to 371 K and reported a constant value of $C_{p,m}^{\circ}(\text{Np}, \alpha) = 31.63 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Evans and Mardon [59EVA/MAR] made measurements from 333 to 480 K, reporting a value for the heat capacity of $31.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 333 K, increasing to $39.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 480 K. These data are approximately fitted by the equation:

Table 6.3: Enthalpies of transformation for neptunium allotropes

Reference	$\Delta_{\text{trs}}H(\alpha \rightarrow \beta)$ kJ·mol ⁻¹	$\Delta_{\text{trs}}H(\beta \rightarrow \gamma)$ kJ·mol ⁻¹	$\Delta_{\text{trs}}H(\beta \rightarrow 1)$ kJ·mol ⁻¹
[59EVA/MAR]	8.37		
[70WIT/VAU]	5.607	5.272	5.188
[90FOL]	4.73	2.99	3.19
Calculated from high pressure measurements	(5.04 ± 0.51)	(5.4 ± 0.8)	—
Selected	(5.607 ± 1.000)	(5.272 ± 1.000)	(5.188 ± 1.000)

$$C_{p,m}^{\circ}(\text{Np}, \alpha, T) = (-4.0543 + 8.2555 \times 10^{-2}T + 805714T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ (298.15 K to 553 K)}$$

which joins smoothly with the low-temperature data of Lee *et al.* [70LEE/MEN] at 298.15 K. Lacking any experimental data for the β and γ allotropes, we have estimated the heat capacity of tetragonal β -Np to be 39.33 J·K⁻¹·mol⁻¹, the average of the values for the tetragonal phases β -U and δ' -Pu and the heat capacity of bcc γ -Np to be 36.40 J·mol⁻¹K⁻¹, the average bcc γ -U and ε -Pu. The heat capacity of the liquid is also estimated from U(l) and Pu(l). The totality of the estimated heat capacities and enthalpies of transition were also selected to make $\Delta_{\text{vap}}S(1840 \text{ K})$ close to 99.5 J·K⁻¹·mol⁻¹, as measured by [75ACK/RAU] (see below). If the appreciably lower enthalpies of transition given by [90FOL] are used, the required heat capacities for β , γ and liquid Np all have to be near (but not beyond) their reasonable upper bounds.

The experimental data on the enthalpies of transition are summarised in Table 6.3.

Wittenberg *et al.* [70WIT/VAU] used differential thermal analysis of a 7.3 g sample of a metal containing less than 0.35 wt% impurities. They reported enthalpies of 5607 J·mol⁻¹ for the α to β transition and 5272 J·mol⁻¹ for the β to γ transition, and 5188 J·mol⁻¹ for the enthalpy of fusion. More recently Foltyn [90FOL] reported rather different values of 4700, 3000 and 3200 J·mol⁻¹, again using differential analysis, but of a much smaller (0.1 g), but purer (99.97 wt%) sample of Np. In view of the large differences in these enthalpies of transition, approximate values were calculated from the molar volumes of the phases, calculated from Zachariassen's data [52ZAC] and the variation of the transition temperatures with pressure, given by Stephens [66STE]. There is an appreciable uncertainty in the calculated value for the $\beta \rightarrow \gamma$ transition, since the thermal expansion of the phases is not well-defined at these temperatures. The molar volumes (cm³·mol⁻¹) used at the given transition temperatures were: α (553 K) 11.838; β (553 K) 12.165; β (849 K) 12.75 ± 0.03; γ (849 K) 13.09 ± 0.04. However, the calculated data indicate that the measurements of [70WIT/VAU] are to be preferred. The higher enthalpies of transition also lead to better consistency with the entropy of vaporisation, as discussed below.

Table 6.4: Neptunium allotropes: Heat capacity coefficients and transformation data

Phase	$C_{p,m}^{\circ}/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} =$ $(a + b (T/\text{K}) + c (T/\text{K})^{-2})$			T_{trs}/K	$\Delta_{\text{trs}}H^{\circ}/\text{J}\cdot\text{mol}^{-1}$
	a	b	c		
α	-4.0543	8.2555×10^{-2}	805714	553	5607
β	39.33	0	0	849	5272
γ	36.40	0	0	912	5188
liquid	45.396	0	0	—	—

The selected heat capacity and transition data are summarised in Table 6.4; these are in fact the same as those selected by [76OET/RAN].

6.2 Neptunium ideal monatomic gas

Only 13 energy levels up to 9000 cm^{-1} were known when Feber and Herrick [65FEB/HER] made the first statistical-mechanical calculations of the thermal functions of Np(g). In subsequent calculations, Oetting *et al.* [76OET/RAN] used 400 levels up to 40000 cm^{-1} provided by Fred [75FRE]. It is not clear how many levels Ward *et al.* [86WAR/KLE] used in their calculations, but presumably the 176 levels up to 19800 cm^{-1} given by Brewer [84BRE], based on a listing of 440 levels provided by Fred and Blaise [83FRE/BLA]. The levels listed by Brewer [84BRE], which contain some estimates, include all the levels up to 16000 cm^{-1} . Blaise and Wyart [92BLA/WYA] have recently published a comprehensive listing of the known energy levels of all the actinide gases, which contains 641 levels for Np(g). However these do not include the 30 relatively low-energy levels estimated by Brewer, so these have been added in the current calculation. The revised values of the thermal functions calculated from these 671 levels are therefore superior to the two earlier sets [76OET/RAN, 86WAR/KLE]. The Gibbs energy functions begin to differ from these by more than $0.05\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at about 1600 K.

The values at 298.15 K for ^{237}Np , molar mass $237.048\text{ g}\cdot\text{mol}^{-1}$, are of course essentially the same as the earlier values [76OET/RAN, 86WAR/KLE] after allowing for the different standard-state pressure:

$$\begin{aligned} C_{p,m}^{\circ}(\text{Np, g, 298.15 K}) &= (20.824 \pm 0.020)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ S_{\text{m}}^{\circ}(\text{Np, g, 298.15 K}) &= (197.719 \pm 0.005)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

The heat capacity equations used are

$$\begin{aligned} C_{p,m}^{\circ}(\text{Np, g, } T) &= (17.782 + 3.3525 \times 10^{-3}T + 6.68071 \times 10^{-6}T^2 \\ &\quad + 1.288 \times 10^5 T^{-2})\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \quad (298.15 \text{ to } 800\text{ K}) \end{aligned}$$

$$C_{p,m}^{\circ}(\text{Np, g, } T) = (14.132 + 1.55677 \times 10^{-2}T - 1.59546 \times 10^{-6}T^2 - 3.9887 \times 10^{-5}T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \text{ (800 to 2000 K)}$$

6.2.1 Enthalpy of formation

There have been two investigations of the vapour pressure of neptunium metal, by Eick and Mulford [64EIC/MUL] from 1700 to 1950 K, and Ackermann and Rauh [75ACK/RAU], from 1540 to 2140 K. As discussed by Oetting *et al.* [76OET/RAN] and Ward *et al.* [86WAR/KLE], the appreciably higher pressures measured by [64EIC/MUL] were undoubtedly due to the presence of NpO(g) from their (oxygen-contaminated) sample. With the thermal functions for Np(cr, l) and Np(g) derived from the thermodynamic data discussed above, the calculated third-law enthalpy of vaporisation at 298.15 K is 465.1 kJ·mol⁻¹. It will be recalled that the heat capacities of β , γ and liquid Np were chosen to give good agreement with the entropy of vaporisation at 1840 K, derived from the measurements of [75ACK/RAU]. This automatically gives good agreement between the second- and third-law enthalpies of sublimation.

The selected value for the enthalpy of formation of Np(g) is thus:

$$\Delta_f H_m^{\circ}(\text{Np, g, 298.15 K}) = (465.1 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$$

Chapter 7

Neptunium aqua ions

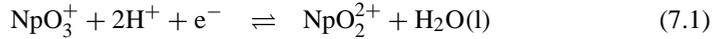
Neptunium exists in aqueous solution in the oxidation states +3, +4, +5, +6, and +7. During the past three decades, the thermodynamic properties of the neptunium aqua ions were compiled and reviewed by Newton [75NEW], Fuger and Oetting [76FUG/OET], Martinot and Fuger [85MAR/FUG], Fahey [86FAH], and Morss [86MOR]. The three latter reviews are based on the very thorough review by Fuger and Oetting. Therefore, the data of their review will serve as a basis for this NEA review.

The selected thermodynamic quantities for Np^{3+} , Np^{4+} , NpO_2^+ and NpO_2^{2+} are strongly connected, and there is a minimum amount of redundant information to provide confirmation for these values. The selection process used in the present review relies strongly on an enthalpy of formation value for Np^{4+} derived from measurements of the enthalpy of dissolution of neptunium metal and subsequent oxidation of the neptunium to the IV oxidation state. Values for the entropies are all linked to values for the solubility and enthalpy of formation of $\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$. Potential measurements of the formal potentials (E°), measurements of $(\partial E^\circ/\partial T)$ and calorimetric measurements are used to link and derive the other thermodynamic quantities. It is assumed (except for reactions involving the highly-charged $\text{Np}^{4+}(\text{aq})$ ion), that the value of the enthalpy of a reaction at $I = 0$ is equal to that in 1 M HClO_4 within the uncertainties of the measurements. This approximation leads to the differences between values of the formal potentials in 1 M $\text{HClO}_4(\text{aq})$ and the standard potentials being assigned primarily to entropy differences. The assumption is undoubtedly incorrect (and would actually be consistent with temperature-independent activity coefficients) but, used consistently, in the absence of experimental information, is probably subject to smaller errors than would be introduced by some of the other options.

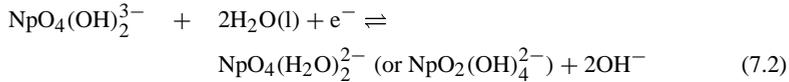
7.1 NpO_3^+ , $\text{NpO}_4(\text{OH})_2^{3-}$ and redox potentials in alkaline solution

Heptavalent neptunium is unstable in acidic solution, but can be formed by acidification of basic solutions of $\text{Np}(\text{VII})$. Reduction by water occurs rapidly in acid solutions – generally in a few seconds to minutes at room temperature. Formal potentials were determined by Musikas *et al.* [74MUS/COU] and by Sullivan and Zielen [69SUL/ZIE] as $E^\circ(7.1, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (2.04 \pm 0.03) \text{ V}$ and

$E^\circ(7.1, 1 \text{ M HNO}_3, 298.15 \text{ K}) > 2.00 \text{ V}$, respectively, for reaction



It has recently been proposed [91SHI/TAN] that the structure of the cationic Np(VII) species might be better written as $\text{Np}(\text{OH})_6^+$ rather than NpO_3^+ . Heptavalent neptunium can be generated in alkaline solutions, but is reduced by water to Np(VI) over a period of hours to weeks at room temperature. Several measurements exist of the formal Np(VII)/Np(VI) potential in basic solution. The alkaline chemistry of the transuranium elements was recently reviewed by Peretrukhin *et al.* [95PER/SHI]. They derive $E^\circ(7.2, 1 \text{ M NaOH}, 298.15 \text{ K}) = (0.59 \pm 0.01) \text{ V}$ for the reaction



From the reversibility of the electrochemical reduction reaction, the authors suggest that the structure of the hepta- and hexavalent ions must be similar and six coordinate. This would exclude the existence of NpO_5^{3-} which was postulated by several other authors that are referred to in the review of Peretrukhin *et al.* Table 7.1 gives the reported formal redox potentials for neptunium in 1 M NaOH [95PER/SHI].

Table 7.1: Formal potentials for neptunium in 1 M NaOH at 298.15 K reported by [95PER/SHI]

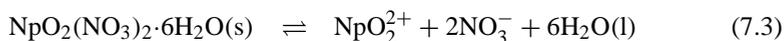
Formal potential (V. vs. SHE)			
VII/VI	VI/V	V/IV	IV/III
0.59	0.14	-0.95	-1.8

7.2 NpO_2^{2+}

The thermodynamic quantities for NpO_2^{2+} are derived from the value of the entropy based on the solubility and the enthalpy of dissolution of the salt $\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ in water, the enthalpy of formation of Np^{4+} and the enthalpy of oxidation of NpO_2^+ to NpO_2^{2+} as determined calorimetrically and from values of the standard potential based on electrochemical measurements. The temperature coefficients for the VI/V and V/IV potentials are used to calculate, sequentially, $S_m^\circ(\text{NpO}_2^+)$ and $S_m^\circ(\text{Np}^{4+})$, and from the latter $\Delta_f G_m^\circ(\text{Np}^{4+})$. The values of the V/IV potential are then used to determine $\Delta_f G_m^\circ(\text{NpO}_2^+)$ and hence $\Delta_f H_m^\circ(\text{NpO}_2^+)$. Finally, the values of the VI/V potential and the calorimetric enthalpy of oxidation of NpO_2^+ to NpO_2^{2+} are examined together to determine $\Delta_f G_m^\circ(\text{NpO}_2^{2+})$ and hence $\Delta_f H_m^\circ(\text{NpO}_2^{2+})$.

This is straight forward (although propagation of the uncertainties through the cycle becomes a problem), but most of the potentials were determined in a medium of approximately 1 M acid (usually HClO₄(aq)) as were the calorimetric results leading to several of the key enthalpy values. It is then necessary to adjust these values to infinite dilution. In the present review, in the absence of evidence to the contrary, the potentials (Gibbs energies) have been adjusted using the SIT equations (*cf.* Appendix B). The enthalpies of transfer from 1 M HClO₄ to zero ionic strength are assumed small, and the main changes in $\Delta_r G_m^\circ$ with the medium are taken into the value of $\Delta_r S_m^\circ$.

To calculate the standard entropy of the NpO₂²⁺ ion, this review follows the approach of Fuger and Oetting's review that is based on the solubility and the enthalpy of dissolution of the salt NpO₂(NO₃)₂·6H₂O(s) in water. Brand and Cobble [70BRA/COB] calculated for the dissolution reaction of



$\Delta_r G_m^\circ(7.3, \text{aq}, 298.15 \text{ K}) = -(12.30 \pm 1.09) \text{ kJ}\cdot\text{mol}^{-1}$, using a mean activity coefficient from the corresponding uranium system to correct to infinite dilution. A SIT correction by this review using single ion activity coefficients did not lead to a more accurate Gibbs energy of reaction (*cf.* discussion of [70BRA/COB] in Appendix A). The value given above is therefore accepted. Fuger and Oetting corrected Brand and Cobble's value of $\Delta_{\text{soln}}H$ for a hydrolysis contribution for dioxoneptunium(VI) using hydrolysis data from the analogous dioxouranium(VI) system (*cf.* Appendix A) and obtained the value that we recommend, $\Delta_r H_m^\circ(7.3, 298.15 \text{ K}) = -(18.83 \pm 1.67) \text{ kJ}\cdot\text{mol}^{-1}$. This review accepts Brand and Cobble's estimate for the standard entropy of the salt (converted directly from the original units of $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), $S_m^\circ(\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})) = (516.306 \pm 8.000) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. With $\Delta_r S_m^\circ(7.3, 298.15 \text{ K}) = (104.4 \pm 6.7) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and CODATA auxiliary values,

$$S_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(92.4 \pm 10.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

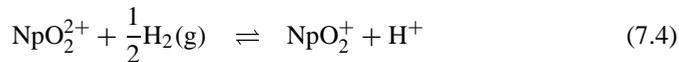
is determined.

There are four independent determinations of the NpO₂²⁺/NpO₂⁺ potential in perchloric acid solutions and one additional measurement of the temperature coefficient of this potential (Table 7.2). The formal potentials $E^{o'}$ in 1 M HClO₄ of Cohen and Hindman [52COH/HIN], Sullivan, Hindman and Zielen [61SUL/HIN], and Riglet, Robouch and Vitorge [89RIG/ROB] agree within their uncertainties, and the unweighted average value from these three measurements, $(1.137 \pm 0.001) \text{ V vs. SHE}$, is accepted in the present review, resulting in $\Delta_r G_m = -(109.70 \pm 0.10) \text{ kJ}\cdot\text{mol}^{-1}$ in 1 M HClO₄. The standard potential E° , was derived by Brand and Cobble [70BRA/COB] and by Riglet, Robouch and Vitorge [89RIG/ROB]. Riglet, Robouch and Vitorge applied the Specific Ion Interaction Theory (SIT) to data from voltametric measurements at 1, 2, and 3 M ionic strengths. The measurements, however, were carried out at the non-standard temperature of 293.15 K. The authors used a correction of -0.0003 V/K to adjust the value

to the standard temperature. This correction was derived from the isothermal temperature coefficient $(\partial E^\circ/\partial T) = -(0.00027 \pm 0.00005) \text{ V}\cdot\text{K}^{-1}$ determined from Cohen and Hindman's [52COH/HIN] emf measurements at only three different temperatures. The value is not in particularly good agreement with $(\partial E^\circ/\partial T) = 0.00023 \text{ V}\cdot\text{K}^{-1}$ as determined by Blanc and Madic [84BLA/MAD] (though $\partial E^\circ/\partial T$ should be approximately $0.0002 \text{ V}\cdot\text{K}^{-1}$ less positive than $\partial E^\circ/\partial T$). Their measurement of the thermal temperature coefficient of the $\text{NpO}_2^{2+}/\text{NpO}_2^+$ couple was corrected to isothermal conditions in the present review.

Although the value of Cohen and Hindman was derived using only three data points, the value of Blanc and Madic was derived using several approximations of deBethune *et al.* [59DEB/LIC]. The later value (for $I = 0$) is only roughly of the same order of magnitude as the (isothermal) value from the temperature dependence of the potential measurements (and has the opposite sign), and the theoretical relationship between the isothermal and thermal values of $\partial E^\circ/\partial T$ for a 1 M $\text{HClO}_4(\text{aq})$ medium is not obvious. Therefore, only the Cohen and Hindman value is used here, $(\partial E^\circ/\partial T)_{\text{isotherm}} = -(0.00027 \pm 0.00005) \text{ V}\cdot\text{K}^{-1}$. The standard potential derived by Brand and Cobble [70BRA/COB], $E^\circ = (1.236 \pm 0.010) \text{ V}$, was corrected to $E^\circ = (1.161 \pm 0.008) \text{ V}$ by Riglet, Vitorge and Grenthe [87RIG/VIT] using the SIT and a value of $\Delta\varepsilon = \varepsilon_{(\text{NpO}_2^{2+}, \text{ClO}_4^-)} - \varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$ derived from analogous $\text{UO}_2^{2+}/\text{UO}_2^+$ studies.

This review also recalculated these data using a slightly different value for the Debye-Hückel term and obtained $E^\circ = (1.158 \pm 0.008) \text{ V}$. Applying the selected isothermal temperature coefficient, $(\partial E^\circ/\partial T)_{\text{isotherm}} = -(0.00027 \pm 0.00005) \text{ V}\cdot\text{K}^{-1}$ to Riglet, Robouch and Vitorge's [89RIG/ROB] potential at 293.15 K gives $E^\circ = (1.161 \pm 0.011) \text{ V}$ at 298.15 K. SIT extrapolations of Sullivan, Hindman and Zielen's [61SUL/HIN] and Cohen and Hindman's [52COH/HIN] formal potentials, corrected in the present review using $\Delta\varepsilon = -(0.21 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ (*cf.* [89RIG/ROB]) and adjusted to 1 bar both give $E^\circ = (1.160 \pm 0.002) \text{ V}$. This is also the source of $\varepsilon_{(\text{NpO}_2^{2+}, \text{ClO}_4^-)}$ as listed in the uranium volume [92GRE/FUG]. Taking the average of these two values, as well as the one obtained by Riglet, Robouch and Vitorge and the value of Brand and Cobble that was recalculated by this review, the standard potential is obtained for the reaction



Because of the accuracy and precision of the measurements of Cohen and Hindman [52COH/HIN], and Sullivan, Hindman and Zielen [61SUL/HIN], this review assigns an uncertainty of 0.004 V to the standard potential and corrects to the standard pressure of 1 bar to obtain the following values accepted here

$$\begin{aligned} E^\circ(7.4, 298.15 \text{ K}) &= (1.159 \pm 0.004) \text{ V} \\ \log_{10} K^\circ(7.4, 298.15 \text{ K}) &= (19.59 \pm 0.07) \\ \Delta_r G_m^\circ(7.4, 298.15 \text{ K}) &= -(111.8 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Using the accepted Gibbs energy of reaction (for 1 M HClO_4) and $\Delta_r S_m(7.4, 1 \text{ M } \text{HClO}_4) = -(26.05 \pm 4.82) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ that is obtained from

Table 7.2: Experimental formal potentials in 1 M HClO₄, derived standard potentials and temperature coefficients for NpO₂²⁺ / NpO₂⁺ couple at 298.15 K. (reference state is 1 atm. for E^{o'}, 1 bar for E^o)

Method	Formal potential (V, vs. SHE)	Standard potential (V, vs. SHE)	dE ^{o'} /dT V·K ⁻¹	Reference
Redox couple: NpO ₂ ²⁺ /NpO ₂ ⁺ , according to: NpO ₂ ²⁺ + 1/2H ₂ (g) ⇌ NpO ₂ ⁺ + H ⁺				
pot	(1.1373 ± 0.0010) ^(a)		−(0.00027 ±0.00005)	[52COH/HIN]
	(1.1361 ± 0.0010) ^(b)			
	(1.1366 ± 0.0010) ^(c)	(1.1601 ± 0.0039) ^(d)		
pot	(1.13638 ± 0.00016)	(1.1598 ± 0.0037) ^(d)		[61SUL/HIN]
pot		(1.236 ± 0.010)		[70BRA/COB]
		(1.161 ± 0.008) ^(e)		
		(1.158 ± 0.008) ^(d)		
emf			0.00023 ⁽ⁱ⁾	[84BLA/MAD]
pol	(1.140 ± 0.009) ^(f)	(1.162 ± 0.011) ^(f)		[89RIG/ROB]
	(1.138 ± 0.009) ^(g)	(1.160 ± 0.011) ^(g)		
rev		(1.236 ± 0.010)		[76FUG/OET]
	(1.137 ± 0.001)	(1.159 ± 0.004) ^(h)	−(0.00027 ±0.00005)	this review

(a) Measured in 1.027 m (0.9725 M) HClO₄.

(b) Corrected by [61SUL/HIN] from 1 m to 1 M HClO₄; this, however, is incorrect, because the solution was 1.027 m and not 1 m.

(c) Corrected by this review from 1.027 m to 1 M HClO₄.

(d) Calculated by this review using SIT extrapolation.

(e) Recalculated by [87RIG/VIT] using SIT extrapolation.

(f) Value determined at 293.15 K.

(g) Corrected by this review to 298.15 K using the selected (dE/dT) value.

(h) At 1 bar

(i) $\partial E^o / \partial T$

$(\partial E^\circ/\partial T) = -(0.00027 \pm 0.00005) \text{ V}\cdot\text{K}^{-1}$, $\Delta_r H_m(7.4, 1 \text{ M HClO}_4) = -(117.47 \pm 1.44) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated. The enthalpy of transfer to infinite dilution is assumed to be zero, and the value of $\Delta_r H_m^\circ$ is the same as the value of $\Delta_r H_m(7.4, 1 \text{ M HClO}_4)$. This value, derived from electrochemical data, agrees with $\Delta_r H_m^\circ = -(117.4 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1}$ obtained by Brand and Cobble [70BRA/COB] from calorimetric measurements of the NpO_2^{2+} reduction to NpO_2^+ by hydrogen peroxide. These values were adjusted to infinite dilution. The weighted average of these two independent values is $\Delta_r H_m^\circ(7.4, 298.15 \text{ K}) = -(117.4 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1}$. Taking this, and using $\Delta_r G_m^\circ(7.4, 298.15 \text{ K}) = -(111.8 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ as accepted above, $\Delta_r S_m^\circ = -(18.9 \pm 2.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This value is required in the following section, and corresponds to $(\partial E^\circ/\partial T) = -(0.00019 \pm 0.00002) \text{ V}\cdot\text{K}^{-1}$ for the Np(VI)/Np(V) couple. From $\Delta_r H_m^\circ(7.4)$ and from $\Delta_f H_m^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K}) = -(978.2 \pm 4.6) \text{ kJ}\cdot\text{mol}^{-1}$ (cf. Section 7.3), we determine the selected value for the enthalpy of Reaction 7.5



to be

$$\Delta_f H_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(860.7 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1}$$

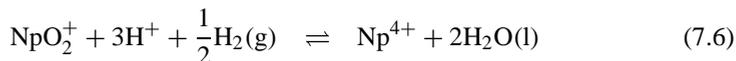
Similarly, using the selected value, $\Delta_f G_m^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K}) = -(907.8 \pm 5.6) \text{ kJ}\cdot\text{mol}^{-1}$ (cf. Section 7.3), we determine the selected value

$$\Delta_f G_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(795.9 \pm 5.6) \text{ kJ}\cdot\text{mol}^{-1}$$

7.3 NpO_2^+

The thermodynamic quantities for NpO_2^+ are derived from the value of $S_m^\circ(\text{NpO}_2^{2+})$, and from the values of the standard potential based on electrochemical potential measurements. The temperature coefficients for the VI/V and V/IV potentials are used to calculate sequentially $S_m^\circ(\text{NpO}_2^+)$ and $S_m^\circ(\text{Np}^{4+})$, and from the latter $\Delta_f G_m^\circ(\text{Np}^{4+})$. The value of the V/IV potential is then used to determine $\Delta_f G_m^\circ(\text{NpO}_2^+)$ and $\Delta_f H_m^\circ(\text{NpO}_2^+)$.

Cohen and Hindman [52COH/HIN2] determined the formal potential in 1 molal HClO_4 for the reaction



with junction-free emf measurements. They derived $E^\circ = (0.7391 \pm 0.0010) \text{ V}$, and $(\partial E^\circ/\partial T) = -(0.00269 \pm 0.00006) \text{ V}\cdot\text{K}^{-1}$. This review corrects the formal potential from 1 m to 1 M and 1 bar pressure and derives the NEA recommended values $E^\circ(7.6, 298.15 \text{ K}) = (0.7431 \pm 0.0010) \text{ V}$, $\Delta_r G_m^\circ(7.6, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(71.7 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_r S_m^\circ(7.6, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(259.5 \pm 5.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$,

and $\Delta_r H_m(7.6, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(149.1 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$. In order to correct the formal potential for Reaction 7.6 to standard conditions, this review applies a SIT correction using $\varepsilon_{(\text{Np}^{4+}, \text{ClO}_4^-)} = (0.84 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$, $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.25 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{H}^+, \text{ClO}_4^-)} = (0.14 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ and obtains¹

$$\begin{aligned} E^\circ(7.6, 298.15 \text{ K}) &= (0.604 \pm 0.007) \text{ V} \\ \log_{10} K^\circ(7.6, 298.15 \text{ K}) &= (10.21 \pm 0.12) \\ \Delta_r G_m^\circ(7.6, 298.15 \text{ K}) &= -(58.3 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

The difference $E^\circ - E^{\circ'} = -(0.139 \pm 0.007) \text{ V}$ between the standard and formal potentials is substantially different from an earlier estimate [76FUG/OET] of $-(0.069 \pm 0.060) \text{ V}$ for the corresponding plutonium equilibrium. Capdevila, Vitorge and Giffaut [92CAP/VIT] reported two values for the corresponding plutonium potential at 1 M for Reaction (7.6). Depending on the experimental approach, they derived $E^{\circ'} = (1.134 \pm 0.050) \text{ V}$ and $E^{\circ'} = (1.154 \pm 0.050) \text{ V}$. From the first set of data, they calculated $E^\circ = (0.991 \pm 0.060) \text{ V}$, applying the SIT. The difference, $E^\circ - E^{\circ'} = -(0.143 \pm 0.078) \text{ V}$, is obtained. A correction of the formal potential to standard state using the SIT treatment is preferred by this review over applying the difference between the two corresponding plutonium potentials (with its large uncertainty) to the neptunium formal potential of Reaction (7.6). To evaluate other thermodynamic data in 1 M HClO₄ for Np⁴⁺, Fuger and Oetting [76FUG/OET] applied a correction of $0.42 \text{ kJ}\cdot\text{mol}^{-1}$ to $\Delta_f H_m^\circ(\text{Np}^{4+}, \text{aq}, 298.15 \text{ K})$ to obtain a value for $\Delta_f H_m^\circ(\text{Np}^{4+}, 1 \text{ M HClO}_4, 298.15 \text{ K})$. This was done to account for the extent of the first hydrolysis reaction of Np⁴⁺ in 1 M HClO₄. This reasoning is accepted here. Because it applies to Np⁴⁺ and the correction to NpO₂⁺ is negligible, the correction can be applied directly to our accepted value for $\Delta_r H_m^\circ(7.6, 1 \text{ M HClO}_4)$ to determine $\Delta_r H_m^\circ(7.6)$.

Using this approximation $\Delta_r H_m^\circ(7.6) = -(149.5 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_r G_m^\circ(7.6) = -(58.3 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$ as accepted above, $\Delta_r S_m^\circ(7.6, 298.15 \text{ K}) = -(305.9 \pm 6.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This value is used in the following section.

$S_m^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K})$ is calculated from $\Delta_r S_m^\circ = -(18.9 \pm 2.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Reaction (7.4), using $S_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(92.4 \pm 10.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and CODATA auxiliary data to give

$$S_m^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K}) = -(45.9 \pm 10.7) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

which is significantly different from Fuger and Oetting's value $S_m^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K}) = -(20.9 \pm 8.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [76FUG/OET]. Such widely discrepant and

¹As this book was in the final stages of being prepared for printing, a minor error (much smaller than the assigned uncertainties) was discovered in our calculation of $\log_{10} K^\circ(7.6, 298.15 \text{ K})$. Correction of the error decreases the value of $\log_{10} K^\circ(7.6, 298.15 \text{ K})$ by 0.002. This error is propagated through the unrounded calculated values of $\Delta_r G_m^\circ(7.6)$ and $\Delta_r S_m^\circ(7.6)$, so that the values of $\Delta_f G_m^\circ(\text{Np}^{4+}, 298.15 \text{ K})$ and $\Delta_f G_m^\circ(\text{Np}^{3+}, 298.15 \text{ K})$ should be $0.010 \text{ kJ}\cdot\text{mol}^{-1}$ more positive than the values in Table 3.1 that have been used in calculations for this volume. Similarly, the values of $S_m^\circ(\text{Np}^{4+}, 298.15 \text{ K})$ and $S_m^\circ(\text{Np}^{3+}, 298.15 \text{ K})$ should be $0.034 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ more negative than the values in Table 3.1 that have been used in calculations for this volume.

non-systematic values for $S_m^\circ(\text{MO}_2^+(\text{aq}), \text{M} = \text{U}, \text{Np}, \text{Pu}, \text{Am})$ (respectively, -25, -46, 2 and -21 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, cf. Section 16.3 and References [92GRE/FUG, 95SIL/BID]) were not indicated in previous reviews [76FUG/OET, 86MOR] that relied more heavily on estimates. The differences in the entropy values for these key ions appear to be beyond those easily attributable to specific experimental uncertainties, and need to be confirmed or refuted by further experimental work.

Using $\Delta_f H_m^\circ(\text{Np}^{4+}, 298.15 \text{ K}) = -(556.0 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f G_m^\circ(\text{Np}^{4+}, 298.15 \text{ K}) = -(491.8 \pm 5.6) \text{ kJ}\cdot\text{mol}^{-1}$ (cf. Section 7.4) and CODATA auxiliary data, the following selected values are calculated:

$$\begin{aligned}\Delta_f H_m^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K}) &= -(978.2 \pm 4.6) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K}) &= -(907.8 \pm 5.6) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Values of ionic apparent molar heat capacities vary strongly with temperature, and to a somewhat lesser degree with ionic strength. The influence of heat capacity on the Gibbs energy of reaction is usually too small to determine $\Delta_r C_{p,m}$ or $\Delta_r C_{p,m}(T)$ from second and higher order derivatives of functions describing the temperature dependence of solubilities or potentials. Lemire and Campbell [93LEM/CAM, 96LEM/CAM] have reported apparent molar heat capacities of $\text{NpO}_2\text{ClO}_4(\text{aq})$ as a function of temperature (18 to 100°C) for a limited range of ionic strengths (0.05 to 0.22 m). The extrapolated values for the partial molar heat capacities can be expressed as:

$$\begin{aligned}C_{p,m,2}^\circ(\text{NpO}_2\text{ClO}_4, \text{aq}, T) &= (3.56770 \times 10^3 - 4.95931T \\ &\quad - 6.32344 \times 10^5 T^{-1}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\end{aligned}$$

The value of $C_{p,m,2}^\circ(\text{NpO}_2\text{ClO}_4, \text{aq})$ at 298.15 K is $-(32 \pm 25) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, where the uncertainty is assigned in the present review, and comparable uncertainties apply to values throughout the temperature range of the measurements. This value and the equation above are accepted in the present review. For the usual standard state ($C_{p,m,2}^\circ(\text{H}^+, \text{aq}, 298.15 \text{ K}) = 0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), using $C_{p,m,2}^\circ(\text{HClO}_4, \text{aq}, 298.15 \text{ K}) = -27.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [96LEM/CAM2] the value of the partial molar heat capacity, $C_{p,m,2}^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K}) = -(4 \pm 25) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, is calculated.

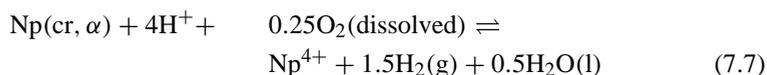
Lemire and Campbell [96LEM/CAM] have used their values for $C_{p,m,2}^\circ(\text{NpO}_2\text{ClO}_4, \text{aq}, T)$ with values of the partial molar heat capacities of other electrolytes [89HOV/NGU, 96LEM/CAM2] to estimate the variation of the potential of the Np(VI)/Np(V) couple as a function of temperature. The apparent molar heat capacity as a function of temperature of NpO_2^{2+} was assumed equal to that of UO_2^{2+} [89HOV/NGU, 96LEM/CAM]. The uncertainties in values of $\Delta_r C_{p,m}(7.4, T)$ estimated in that way are estimated here as $\pm 70 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

7.4 Np⁴⁺

The thermodynamic quantities for Np^{4+} are derived from the value of the entropy based on the solubility and the enthalpy of dissolution of $\text{NpO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}(\text{s})$ in water, the

enthalpy of formation of Np⁴⁺ and values of the standard potential based on electrochemical measurements. The value of $\Delta_f H_m^\circ(\text{Np}^{4+})$ is obtained from calorimetric measurements of the heat of solution of neptunium metal. The temperature coefficients for the VI/V and V/IV potentials are used to calculate, sequentially $S_m^\circ(\text{NpO}_2^+)$ and $S_m^\circ(\text{Np}^{4+})$, and from the latter, $\Delta_f G_m^\circ(\text{Np}^{4+})$.

This review accepts the enthalpy of formation derived by Fuger and Oetting [76FUG/OET] from three independent calorimetric measurements of the dissolution of neptunium metal in 1 M HCl/0.005 M Na₂SiF₆ in the presence of dissolved oxygen according to the reaction



The authors corrected for the complexing effect due to the presence of Na₂SiF₆ in HCl and obtained $\Delta_f H(\text{Np}^{4+}, 1 \text{ M HCl}) = -(551.87 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ by subtracting $0.5 \times \Delta_f H_m^\circ(\text{H}_2\text{O}, \text{aq}, 298.15 \text{ K})$ and adding $0.25 \times \Delta_{\text{soln}} H(\text{O}_2, \text{g})$ in 1 M HCl = $-(2.3 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}$ from the obtained $\Delta_{\text{soln}} H(\text{Np}, \alpha) = -(692.5 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$. Fuger and Oetting introduced a correction of $-4.18 \text{ kJ}\cdot\text{mol}^{-1}$ to extrapolate to zero acidity to obtain the selected value

$$\Delta_f H_m^\circ(\text{Np}^{4+}, \text{aq}, 298.15 \text{ K}) = -(556.0 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$$

To evaluate other thermodynamic data in 1 M HClO₄ for Np⁴⁺, $\Delta_f H_m(\text{Np}^{4+}, 1 \text{ M HClO}_4, 298.15 \text{ K})$ is derived according to the procedure selected by Fuger and Oetting. They applied a correction of $0.42 \text{ kJ}\cdot\text{mol}^{-1}$ to $\Delta_f H_m^\circ(\text{Np}^{4+}, \text{aq}, 298.15 \text{ K})$ in order to account for the first hydrolysis reaction of Np⁴⁺ in 1 M HClO₄, and obtained

$$\Delta_f H_m(\text{Np}^{4+}, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(555.6 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$$

which is the recommended value.

$S_m^\circ(\text{Np}^{4+}, \text{aq}, 298.15 \text{ K})$ is calculated from $\Delta_r S_m^\circ = -(305.9 \pm 6.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Reaction (7.6), using $S_m^\circ(\text{NpO}_2^+, \text{aq}, 298.15 \text{ K}) = -(45.9 \pm 10.7) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and CODATA auxiliary data to give

$$S_m^\circ(\text{Np}^{4+}, \text{aq}, 298.15 \text{ K}) = -(426.4 \pm 12.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

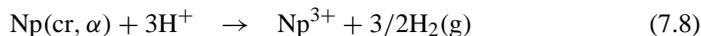
Based on this, CODATA values, and $S_m^\circ(\text{Np}(\text{cr})) = (50.46 \pm 0.80) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\Delta_f S_m^\circ(\text{Np}^{4+}) = -(215.5 \pm 12.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Then, using the Gibbs-Helmholtz relation and the selected value for $\Delta_f H_m^\circ$, the selected standard Gibbs energy of formation of Np⁴⁺ is calculated

$$\Delta_f G_m^\circ(\text{Np}^{4+}, \text{aq}, 298.15 \text{ K}) = -(491.8 \pm 5.6) \text{ kJ}\cdot\text{mol}^{-1}$$

7.5 Np³⁺

The enthalpy of formation for Np³⁺ is derived from calorimetric measurements of the solution enthalpy for the dissolution of neptunium metal in hydrochloric acid according

to the reaction

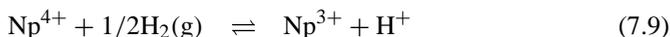


This review accepts

$$\Delta_f H_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K}) = -(527.2 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$$

derived by Fuger and Oetting [76FUG/OET] as the selected value.

The values for the standard Gibbs energy of formation and the standard entropy of Np^{3+} can be derived from potential measurements for the reaction



Four independent experimental determinations on the $\text{Np}^{4+}/\text{Np}^{3+}$ potential and one additional measurement of the temperature coefficient of this potential are available. Two of these were done in hydrochloric acid and three in perchloric acid solutions. Hindman *et al.* [49HIN/MAG2] and Hindman and Kritschinsky [50HIN/KRI] determined the formal potential in 1 M HCl to be $E^{o'} = (0.137 \pm 0.005) \text{ V}$ and $E^{o'} = (0.142 \pm 0.005) \text{ V}$. The formal potentials in 1 M HClO_4 were measured by Cohen and Hindman [52COH/HIN] and by Riglet, Robouch and Vitorge [89RIG/ROB]. Table 7.3 summarises the data in HClO_4 . Also included in the table are results of Blanc and Madic [84BLA/MAD] on the temperature coefficient of the potential and the extrapolated standard potential of Fuger and Oetting [76FUG/OET]. From the average

Table 7.3: Experimental formal potentials in 1 M HClO_4 , derived standard potentials and temperature coefficients for the neptunium(IV)/neptunium(III) couple at 298.15 K.

Method	Formal potential (V, <i>vs.</i> SHE)	Standard potential (V, <i>vs.</i> SHE)	$\partial E^{o'}/\partial T$ $\text{V}\cdot\text{K}^{-1}$	Reference
Redox couple: $\text{Np}^{4+}/\text{Np}^{3+}$, according to: $\text{Np}^{4+} + 1/2\text{H}_2(\text{g}) \rightleftharpoons \text{Np}^{3+} + \text{H}^+$				
pot	(0.1551 ± 0.0010)	(0.219 ± 0.010)	(0.00136 ± 0.00005)	[52COH/HIN]
pot	(0.154 ± 0.005)	(0.218 ± 0.010)	$(0.0016 \pm 0.0014)^{\text{(a)}}$	[89RIG/ROB]
emf			$(0.0019 \pm 0.0004)^{\text{(c)}}$	[84BLA/MAD]
rev		$(0.179 \pm 0.005)^{\text{(b)}}$		[76FUG/OET]
rev	(0.155 ± 0.001)	(0.219 ± 0.010)	(0.00136 ± 0.00005)	this review

(a) The calculation of the uncertainty was corrected in the present review.

(b) Value of [52COH/HIN] extrapolated to standard conditions, by [76FUG/OET], using analogy with the plutonium system.

(c) $\partial E^\circ/\partial T$

of the standard potentials of Cohen and Hindman [52COH/HIN] and Riglet, Robouch and Vitorge [89RIG/ROB], 0.2186, this review selects

$$E^\circ = (0.219 \pm 0.010) \text{ V}$$

for reaction (7.9). Hence,

$$\Delta_r G_m^\circ(7.9, 298.15 \text{ K}) = -(21.1 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$$

The weighted average value [52COH/HIN, 89RIG/ROB] for E° is

$$E^\circ = (0.155 \pm 0.001) \text{ V}$$

and hence,

$$\Delta_r G_m(7.9, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(15.0 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}$$

is also accepted.

The isothermal temperature coefficient determined from Cohen and Hindman [52COH/HIN], $(\partial E^\circ/\partial T)_{\text{isotherm}}$, is $(0.00136 \pm 0.00005) \text{ V}\cdot\text{K}^{-1}$. Due to its large uncertainty, the value of Riglet, Robouch and Vitorge was not considered, but it is in agreement with the selected value. Using this value, we derive

$$\Delta_r S_m(7.9, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (131.2 \pm 4.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Thus, $\Delta_r H_m(7.9, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (24.2 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}$. Using the enthalpy of formation for Np^{4+} in 1 M HClO_4 (*cf.* Section 7.4), $\Delta_f H_m(7.9, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(555.6 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$, this review determines from electrochemical data in 1 M HClO_4 $\Delta_f H_m(\text{Np}^{3+}, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(531.5 \pm 12.3) \text{ kJ}\cdot\text{mol}^{-1}$. If $\Delta_f H_m^\circ(\text{Np}^{3+}) \approx \Delta_f H_m(\text{Np}^{3+})$, then $\Delta_f H_m^\circ(\text{Np}^{3+}, 298.15 \text{ K}) = -(531.5 \pm 12.3) \text{ kJ}\cdot\text{mol}^{-1}$. This value is somewhat more negative than the value based on calorimetric data, $\Delta_f H_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K}) = -(527.2 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$, which is selected in the present review because of its smaller uncertainty. From the selected values for $\Delta_f H_m^\circ(\text{Np}^{4+}, \text{aq}, 298.15 \text{ K})$ and $\Delta_f H_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K})$, $\Delta_r H_m^\circ(7.9) = (28.8 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated. From this value and $\Delta_r G_m^\circ = -(21.1 \pm 1.0)$ for Reaction (7.9), $\Delta_r S_m^\circ = (167.5 \pm 16.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is obtained. Hence, with CODATA auxiliary data and the previously selected value for $S_m^\circ(\text{Np}^{4+})$,

$$S_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K}) = -(193.6 \pm 20.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

is calculated and selected.

The difference between the standard entropies for Np^{4+} and Np^{3+} is $-(233.3 \pm 16.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ which agrees well with the value of $-(230.0 \pm 9.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the corresponding plutonium species.

The standard Gibbs energy of formation

$$\Delta_f G_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K}) = -(512.9 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1}$$

was obtained using $\Delta_r G_m^\circ$ for Reaction (7.9), calculated from the standard potential, and the Gibbs energy of formation of Np^{4+} (*cf.* Section 7.4).

7.6 Summary

Table 7.4 summarizes the NEA selected thermodynamic constants for the neptunium aqua ions.

Table 7.4: NEA selected chemical thermodynamic values for neptunium aqua ions

	$\Delta_f H_m^\circ$ (kJ·mol ⁻¹)	$\Delta_f G_m^\circ$ (kJ·mol ⁻¹)	S_m° (J·K ⁻¹ ·mol ⁻¹)
NpO ₂ ²⁺	-(860.7 ± 4.7)	-(795.9 ± 5.6)	-(92.4 ± 10.5)
NpO ₂ ⁺	-(978.2 ± 4.6)	-(907.8 ± 5.6)	-(45.9 ± 10.7)
Np ⁴⁺	-(556.0 ± 4.2)	-(491.8 ± 5.6)	-(426.4 ± 12.4)
Np ³⁺	-(527.2 ± 2.1)	-(512.9 ± 5.7)	-(193.6 ± 20.3)

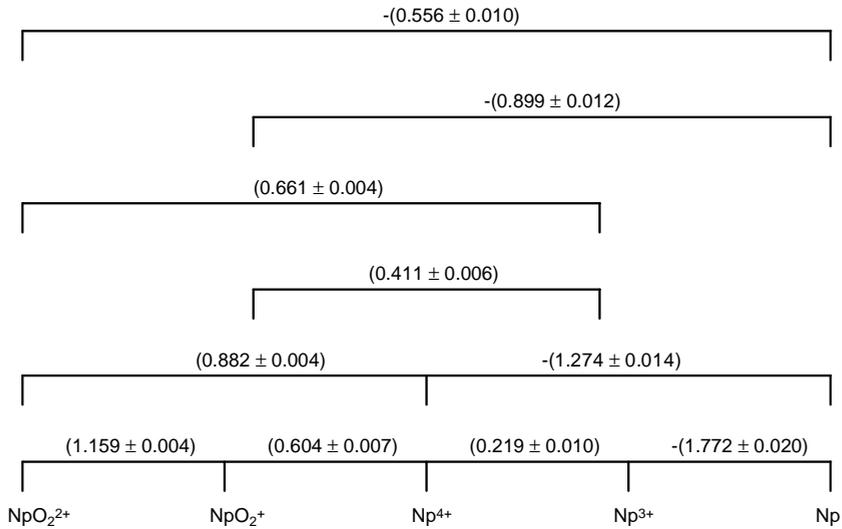
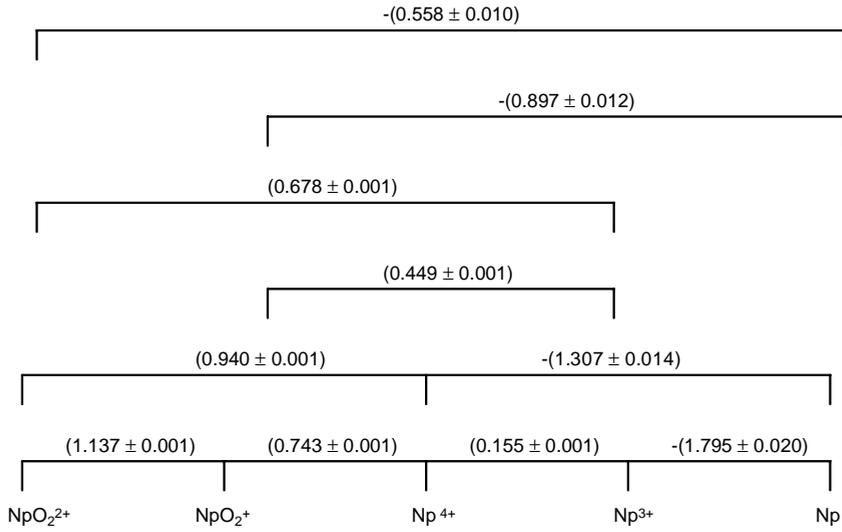
Figure 7.1: Standard potentials ($I = 0$, 25°C) for neptunium, in units of V vs. SHE.

Figure 7.2: Formal potentials (1 M HClO₄, 25°C) for neptunium, in units of V vs. SHE.



Chapter 8

Neptunium oxygen and hydrogen compounds and complexes

8.1 Aqueous neptunium hydroxide complexes

8.1.1 Neptunium(VII) hydroxide complexes

Only limited information on these species appears to be available. There is evidence for a cationic species of Np(VII) in acidic solutions [69SUL/ZIE, 72CHA/LEI, 91SHI/TAN], and an anionic species in strongly alkaline solutions [69COH/FRI, 70ZIE/COH, 75CHA/MAT], but no thermodynamic parameters have been estimated in this review (see also Section 6.1)

8.1.2 Neptunium(VI) hydroxide complexes

The hydrolysis data of NpO_2^{2+} reported in the literature are summarised in Table 8.1. Cassol *et al.* [72CAS/MAG2] obtained hydrolysis constants for NpO_2^{2+} in 1 M aqueous NaClO_4 at 25°C. The value for $\log_{10} {}^*\beta_1^\circ$ based on this work ($-(5.1 \pm 0.4)$) is in fair agreement with the value (-5.5) reported by Schmidt *et al.* [83SCH/GOR]. The self-consistent set of values of Cassol *et al.* [72CAS/MAG2] is accepted in the present review for reasons discussed in Appendix A. Hence, using the estimated values for the interaction coefficients,

$$\begin{aligned}\varepsilon_{(\text{NpO}_2\text{OH}^+, \text{ClO}_4^-)} &= -(0.06 \pm 0.40) \text{ kg}\cdot\text{mol}^{-1} \\ \varepsilon_{((\text{NpO}_2)_2(\text{OH})_2^{2+}, \text{ClO}_4^-)} &= -(0.57 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1} \\ \varepsilon_{((\text{NpO}_2)_3(\text{OH})_5^+, \text{ClO}_4^-)} &= -(0.45 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}\end{aligned}$$

the following formation constants are selected

$$\begin{aligned}\log_{10} {}^*\beta_1^\circ &= -(5.1 \pm 0.4) \\ \log_{10} {}^*\beta_{2,2}^\circ &= -(6.27 \pm 0.21) \\ \log_{10} {}^*\beta_{5,3}^\circ &= -(17.12 \pm 0.22)\end{aligned}$$

From these,

$$\begin{aligned}\Delta_f G_m^\circ (\text{NpO}_2\text{OH}^+, \text{aq}, 298.15 \text{ K}) &= -(1004.0 \pm 6.1) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ ((\text{NpO}_2)_2(\text{OH})_2^{2+}, \text{aq}, 298.15 \text{ K}) &= -(2030.4 \pm 11.3) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ ((\text{NpO}_2)_3(\text{OH})_5^+, \text{aq}, 298.15 \text{ K}) &= -(3475.8 \pm 16.9) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Several groups have reported values for the potential of the Np(VI)/Np(V) couple in highly concentrated hydroxide solutions [73SIM/MAT, 74PER/ALE, 77ERM/PER]. From these data and the value of $\Delta_f G_m^\circ(\text{NpO}_2(\text{OH})_2^-)$ (see Section 8.1.3), it should be feasible to estimate the value of $\Delta_f G_m^\circ$ for the Np(VI) solution species, provided reasonable assumptions are made about its stoichiometry. Gradual precipitation has been reported [74PER/ALE] in the concentrated NaOH(aq) solutions, and therefore only the value of the Np(VI)/Np(V) potential as obtained in LiOH(aq) solutions is accepted in the present review.

Table 8.1: Experimental equilibrium data for the neptunium(VI) hydroxide system, according to the equilibria $m\text{NpO}_2^{2+} + n\text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{NpO}_2)_m(\text{OH})_n^{2m-n} + n\text{H}^+$.

$n:m$	Method	Temp. (°C)	Medium	$\log_{10}^* \beta_{n,m}$	$\log_{10}^* \beta_{n,m}^\circ$	Reference
1:1	sol	20 ?	self, var.	-3.4		[71MOS3]
2:1				-8.8		
3:1				-18.5		
3:2				-8.6		
5:2				-22.7		
1:1	pot	25	1.0 M NaClO ₄	-5.17	-(5.16±0.28)	[72CAS/MAG2]
2:2				-6.68	-(6.27±0.21)	
5:3				-18.25	-(17.06±0.22)	
1:1	tc	23	self 0.0005 M	-5.45		[83SCH/GOR]

If the major Np(VI) species in the alkaline solutions are not polymeric, and if the Np(V) species in 2.5 M LiOH solution is assumed to be $\text{NpO}_2(\text{OH})_2^-$ (as opposed to some more extensively hydrolysed and/or polymeric species), the potential of the Np(V)/Np(VI) couple can be rationalised if the Np(VI) species is $\text{NpO}_2(\text{OH})_3^-$ or $\text{NpO}_2(\text{OH})_4^{2-}$ (see Appendix A discussion for [77ERM/PER]). Given the monomeric assumption, the possible hydrolysis constants are $^* \beta_3^\circ = 10^{-(20.7 \pm 1.7)}$ or $^* \beta_4^\circ = 10^{-(34.8 \pm 1.7)}$. There does not appear to be a substantive reason for choosing one species over the other. If anionic polymers exist (as they have been found in the uranium system), both values may be regarded as limiting.

$$\log_{10}^* \beta_3^\circ \leq -19$$

$$\log_{10}^* \beta_4^\circ \leq -33$$

$$\Delta_f G_m^\circ (\text{NpO}_2(\text{OH})_3^-, \text{aq}, 298.15 \text{ K}) \geq -1399 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ (\text{NpO}_2(\text{OH})_4^{2-}, \text{aq}, 298.15 \text{ K}) \geq -1556 \text{ kJ}\cdot\text{mol}^{-1}$$

The uncertainties are estimated in this review, and are based primarily on an estimated uncertainty of 0.1V in the values of E° and the uncertainty in $\Delta_f G_m^\circ$

($\text{NpO}_2(\text{OH})_2^-$, aq, 298.15 K) (see Section 8.1.3). The selected limiting value of $\log_{10}^*\beta_3^\circ$ is compatible with the value $\log_{10}^*\beta_3 = -(19.61 \pm 0.11)$ reported by Moriyama, Pratopo and Higashi [95MOR/PRA]. Their value, based on solubility measurements, is not accepted in the present work for reasons discussed in Appendix A.

There do not appear to be any reliable data to supply thermodynamic parameters for $\text{NpO}_2(\text{OH})_2(\text{aq})$ or for polymeric neutral or anionic Np(VI) hydrolysis species, although such species may well exist.

8.1.3 Neptunium(V) hydroxide complexes

Several groups have reported values for the formation constants for neptunium(V) hydroxo species (Table 8.2). There is no consensus as to the value for the formation constant of $\text{NpO}_2\text{OH}(\text{aq})$ [87RÖS/MIL], although the recent hydrolysis studies [85LIE/TRE, 87RÖS/MIL, 92ITA/NAK, 92NEC/KIM] lead to smaller values than found in earlier studies. The data of Kraus and Nelson [48KRA/NEL], Moskvina [71MOS3] and the potentiometric study of Sevost'yanova and Khalturin [76SEV/KHA] are difficult to analyse because the experimental conditions were not well controlled, and because precipitation of $\text{NpO}_2\text{OH}(\text{am})$ interfered with attempts to study the hydrolysis of the NpO_2^+ ion by titration of acidic solutions with base (see Appendix A). The studies of Bidoglio *et al.* [85BID/TAN] and Maya [83MAY] were primarily designed to evaluate carbonate complexation constants with NpO_2^+ , and the values for the hydrolysis constant, $^*\beta_1$, are not well defined by these studies.

The experiments of Schmidt *et al.* [80SCH/GOR] suggest an upper limit of -8.75 for $\log_{10}^*\beta_1$ (see Appendix A). Based on their spectrophotometric study, Sevost'yanova and Khalturin [76SEV/KHA] reported $\log_{10}^*\beta_1 = -8.9$ at low ionic strength. The value is also probably an upper limit, because no account was taken of carbonate complexation. Indeed, the spectral band at 990 nm assigned by these workers to $\text{NpO}_2\text{OH}(\text{aq})$ should actually be attributed to $\text{NpO}_2\text{CO}_3^-$ [81BIL, 90NIT/STA, 90RIG].

The data from the electromigration study of Rösch *et al.* [87RÖS/MIL] and the solubility studies of Lierse, Treiber and Kim [85LIE/TRE], Itagaki *et al.* [92ITA/NAK] and Neck, Kim and Kanellakopoulos [92NEC/KIM] suggest that both $\text{NpO}_2\text{OH}(\text{aq})$ and $\text{NpO}_2(\text{OH})_2^-$ be considered as hydrolysis species – the anionic hydrolysis species being predominant for $\text{pH} > 11$. This is in agreement with earlier qualitative studies [69COH/FRI, 76SEV/KHA] and with the work discussed by Tananaev [90TAN, 94TAN]. None of these studies is as clear-cut as might be wished. The solubility studies suffer from lack of characterisation of the solids. Such studies indicate only the relative stabilities of the solids and solution species. The solids are discussed in detail in Section 8.2.3.2; however, to help with the interpretation and comparison of the results of different studies, some discussion concerning the nature of the oxide and hydroxide solid phases is included in the present section. Solids of the type MNpO_3 [76COH, 76SEV/KHA] or $\text{M}_x\text{NpO}_2(\text{OH})_{1+x}$ [90TAN] have been proposed as the stable solids in basic solutions containing high concentrations of alkali metal cations, M^+ . Values of $^*\beta_1$ (8.1) from the solubility studies are generally much smaller than values suggested by other types of measurements. The data of Rösch *et al.* are

Table 8.2: Experimental equilibrium data for the neptunium(V) hydroxide system, according to the equilibria $m\text{NpO}_2^+ + n\text{H}_2\text{O}(l) \rightleftharpoons (\text{NpO}_2)_m(\text{OH})_n^{m-n} + n\text{H}^+$

$n:m$	Method	T (°C)	Medium	$\log_{10}^*\beta_{n,m}$	$\log_{10}^*\beta_{n,m}^\circ$	Reference
1:1	pot	RT	0.1 M Cl^-	-8.85		[48KRA/NEL]
1:1	sol	RT	self	-10.08		[71MOS3]
1:1	sp	20	0.001 M	-8.89	> -8.9	[76SEV/KHA]
1:1	pot	23	0.02 M NaNO_3	-8.91		
1:1	pot	23	0.02 M NaClO_4	-8.88		
1:1	tc	25	0.01 M $\text{C}_2\text{H}_5\text{OH}/$ 0.0005 M NaClO_4	-8.75		[80SCH/GOR]
1:1	sol	25	1.0 M NaClO_4	-9.12		[83MAY]
1:1	sol	25	1.0 M NaClO_4	-11.47		[85LIE/TRE]
2:1				-22.71		
1:1	sol	25	1.0 M NaClO_4	-11.69	-(11.81 ± 0.62)	[85LIE/TRE] [92NEC/KIM]
2:1				-23.15	-(23.54 ± 0.18)	
1:1	dis	25	0.2 M NaClO_4	-9.60		[85BID/TAN]
1:1	mig	25	0.1 M NaClO_4	-10.45	-(10.46 ± 0.25)	[87RÖS/MIL]
2:1				-21.95	-(22.17 ± 0.35)	
-1:1 ^(a)				4		
1:1	eph	RT	0.005 M var. med.	-8.2		[88NAG/TAN]
2:1				-18.7		
1:1			0.1 M var. med.	-7.8		
2:1				-17.7		
1:1	sol	25	0 M NaClO_4	-10.70	-(10.7 ± 0.7)	[92ITA/NAK]
2:1			extrap. ($I = 0.012$ to 0.8)	-22.42	-(22.4 ± 0.7)	
1:1	sol	25	0.1 M NaClO_4	-11.36	-(11.37 ± 0.16)	[92NEC/KIM]
2:1				-23.50	-(23.72 ± 0.12)	
1:1	sol	25	1.0 M NaClO_4	-11.13	-(11.25 ± 0.20)	[92NEC/KIM]
2:1				-23.19	-(23.58 ± 0.14)	
1:1	sol	25	3.0 M NaClO_4	-11.02	-(11.41 ± 0.33)	[92NEC/KIM]
2:1				-23.25	-(23.68 ± 0.26)	
1:1	sol	25	0.1/0.02 M NaClO_4	-8.5		[95PAN/CAM]
1:1	sol	23	5.0 M NaCl	3.66 ^(b)		[96RUN/NEU]
2:1				5.98 ^(b)		

^(a) Refers to: $\text{NpO}_2^+ + \text{H}_3\text{O}^+ = \text{NpO}_2^+(\text{H}_3\text{O}^+)$, this species is rejected, cf. [87RÖS/MIL] in Appendix A.

^(b) $\log_{10} \beta_{n,m}$, not $\log_{10}^* \beta_{n,m}$

quite scattered, and the decrease in mobility at low pH values raises questions about the sensitivity of the method (see Appendix A). Although the paper-electrophoresis study of Nagasaki *et al.* [88NAG/TAN] is in qualitative agreement with those of Rösch *et al.* and Lierse, Treiber and Kim, the reported value for the first hydroxide complexation constant, $\log_{10} K_1 \approx 6$, is greater than even the limiting values from other studies [48KRA/NEL, 80SCH/GOR]. The values from the study of Nagasaki *et al.* [88NAG/TAN] are rejected in the present review.

Recently Pan and Campbell [95PAN/CAM] carried out solubility measurements for $\text{Np}_2\text{O}_5(\text{cr})$. The total concentrations of neptunium species as a function of pH do not parallel those from solubility measurements [92ITA/NAK, 92NEC/KIM] over hydrated $\text{NpO}_2\text{OH}(\text{am})$ except for pH values below 8. The solid was carefully characterised before and after the experiments. The equilibration time for the $\text{Np}_2\text{O}_5(\text{cr})$ study [95PAN/CAM] was considerably longer than for the other studies. This raises the question as to whether equilibrium was established in those earlier studies (especially near pH 11), or whether the long equilibration times resulted in radiolytic oxidation. There is also a possibility that some carbonate was present in the solutions of Pan and Campbell (see Appendix A). Although the data are not reported in a form suitable for determining hydrolysis constants, the even longer-term study of Silber *et al.* [94SIL/NIT] shows trends similar to those reported by Pan and Campbell [95PAN/CAM] (the nature of the solid controlling the solubility in the experiments of Silber *et al.* [94SIL/NIT] is not clear).

The differences between the results of the long-term studies and the fairly extensive data from other studies of the solubility of $\text{NpO}_2\text{OH}(\text{am})$ cannot be resolved at this time. In the absence of other studies corroborating the hydrolysis behaviour suggested by Pan and Campbell, in the present review we have selected hydrolysis constants for NpO_2^+ based only on the studies of the solubility of $\text{NpO}_2\text{OH}(\text{am})$. Because it is an amorphous solid, $\text{NpO}_2\text{OH}(\text{am})$ is a very difficult solid to characterise. Also, the value estimated in this review for $\Delta_f G_m^\circ(\text{NpO}_2(\text{OH})_2(\text{cr}))$ is such, that under oxidising conditions, $\text{NpO}_2\text{OH}(\text{am})$ may not be the stable neptunium solid in contact with aqueous solutions (even though it may be in equilibrium with $\text{Np}(\text{V})$ solution species). This suggests that values for the hydrolysis constants of $\text{Np}(\text{V})$, as derived from solubility measurements over uncharacterised $\text{NpO}_2\text{OH}(\text{am})$, must be accepted only with considerable caution. Solubility measurements over mixed solid phases such as $\text{NpO}_2\text{OH}(\text{am})$ (or $\text{NaNpO}_2(\text{OH})_2(\text{s})$) and $\text{NaNpO}_2\text{CO}_3(\text{s})$ (or $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$) or such as $\text{Ca}(\text{OH})_2(\text{cr})$ and $\text{CaCO}_3(\text{cr})$ might prove useful. Carbonate complexation may well account for the high solubilities reported by Nakayama *et al.* [88NAK/ARI] for pH values above 11 (*cf.* Figure 8.3, Section 8.2.4.2). However, the study of Ewart *et al.* [86EWA/HOW] showed no indication of hydrolysis of $\text{Np}(\text{V})$ even in very basic solutions. This study was carried out in a water that had been equilibrated with aged concrete and had a carbonate concentration of 0.03 mM. Hence, it is somewhat puzzling that carbonate complexation did not cause a levelling out or increase in the concentration of neptunium for pH values above 11. One possible cause of the low values is that the bulk of neptunium may have been coprecipitated with calcium-containing solids in the more basic solutions. Also, when Lierse, Treiber and Kim [85LIE/TRE] measured solubilities in experiments using filters with markedly different pore sizes, they found

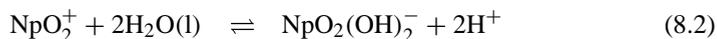
lower neptunium concentrations, in the pH range above 10, if the solutions were passed through a filter with a small pore size (~ 1 nm). It was suggested [85LIE/TRE] that sorption of neutral species on the filter might lead to incorrect (low) solubility values. This may have happened in the work of Ewart *et al.* It is also possible the water used by Ewart *et al.* contained reducing agents after equilibration with the concrete.

This said, the values summarised by Neck, Kim and Kanellakopoulos [92NEC/KIM] were refitted using our selected value of $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = 0.25 \text{ kg}\cdot\text{mol}^{-1}$. The resulting value for $\varepsilon_{(\text{Na}^+, \text{NpO}_2(\text{OH})_2^-)} = -(0.01 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$ is accepted. Because the values for β_1 and β_2 from each set of solubility experiments are undoubtedly correlated, no attempt was made to weight the results from the different studies [85LIE/TRE, 92ITA/NAK, 92NEC/KIM]. Instead the refitted values based on those tabulated by Neck, Kim and Kanellakopoulos [92NEC/KIM] were used (*cf.* Table 8.5). The uncertainties were based on the original experimental uncertainties and, for β_2 , increased to be consistent with the values from the work of Itagaki *et al.* [92ITA/NAK].

Thus, the formation constants ($I = 0$) have been estimated as

$$\log_{10}^* \beta_1^\circ(8.1) = -(11.3 \pm 0.7)$$

$$\log_{10}^* \beta_2^\circ(8.2) = -(23.6 \pm 0.5)$$



Thus,

$$\begin{aligned} \Delta_f G_m^\circ(\text{NpO}_2\text{OH}, \text{aq}, 298.15 \text{ K}) &= -(1080.4 \pm 6.9) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{NpO}_2(\text{OH})_2^-, \text{aq}, 298.15 \text{ K}) &= -(1247.3 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Although there is evidence for formation of additional anionic hydrolysis species in strongly basic solutions [90TAN, 94TAN], the available data are not adequate to be used to derive reliable values of the formation constants. Sets of Pitzer-equation ion-interaction parameters have recently been reported for NpO_2^+ and $\text{Np}(\text{V})$ hydrolysis species [95FAN/NEC, 95NEC/FAN, 95NOV/ROB, 96RUN/NEU], and may be particularly useful for modelling the behaviour of neptunium(V) in solutions containing NaCl at high molalities. However, no evaluation of the Pitzer-equation parameters has been carried out in the present review.

The $\text{NpO}_2^+ \cdot \text{H}_3\text{O}^+$ species proposed by Rösch *et al.* [87RÖS/MIL] is not accepted in the present review. If this species actually forms, it is not clear why it would not have been detected in previous potentiometric studies.

A value for the enthalpy of hydrolysis of NpO_2^+ was reported by Sullivan, Choppin and Rao [91SUL/CHO] but, as discussed in Appendix A, the measured heat is probably not the heat of this hydrolysis reaction. Recently, the entropy values of $\text{NpO}_2\text{OH}(\text{aq})$ and $\text{NpO}_2(\text{OH})_2^-$ have been estimated by Lemire [84LEM] and Lemire and Garisto [89LEM/GAR]. The value $S_m^\circ(\text{NpO}_2\text{OH}, \text{aq}, 298.15 \text{ K}) = (25 \pm 60) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

was based on use of Equation (18-13) of [76BAE/MES] to determine the entropy. Assuming identical parameters for UO_2^{2+} and NpO_2^+ , except for the charge difference, leads to $\Delta_r S(8.1) = -22 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and

$$S_m^\circ(\text{NpO}_2\text{OH, aq, 298.15 K}) = (25 \pm 60) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

This value is considerably smaller than S_m° for many other neutral aqueous species [52LAT]. The uncertainty is an estimate. The entropy of $\text{NpO}_2(\text{OH})_2^-$ was estimated by assuming the entropy of the reaction



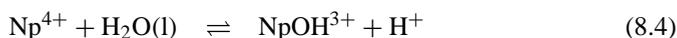
to be $(0 \pm 100) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and hence,

$$S_m^\circ(\text{NpO}_2(\text{OH})_2^-, \text{aq, 298.15 K}) = (40 \pm 100) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

In the absence of experimental data, these values are accepted in the present review.

8.1.4 Neptunium(IV) hydroxide complexes

The hydrolysis data of Np^{4+} reported in the literature are summarised in Table 8.3. Three quantitative studies of the first hydrolysis step for Np^{4+} have been reported.



Sullivan and Hindman [59SUL/HIN] reported ${}^*\beta_1(8.4) = (5.0 \pm 0.3) \times 10^{-3}$ in 2 M aqueous perchlorate solutions from spectrophotometric measurements. Paul [70PAU] also used spectrophotometry, and reported a value of “ β_{Hydr} ” = $(1.24 \pm 0.02) \times 10^{-2}$ ($I=1.0 \text{ M}$). This “ β_{Hydr} ” incorporates the hydrogen ion activity (as pH), whereas Sullivan and Hindman’s constant is purely a concentration quotient. These results appear to contrast with those of Duplessis and Guillaumont [77DUP/GUI] who reported ${}^*\beta_1 = 0.3(1 \text{ M LiClO}_4)$ from extraction experiments involving tracer quantities of ${}^{239}\text{Np}$. As noted by Duplessis and Guillaumont [77DUP/GUI], similar differences are found when the results of potentiometric and tracer studies of Pu(IV) hydrolysis are compared.

The results of the extraction study of Duplessis and Guillaumont [77DUP/GUI] are in qualitative agreement with an earlier extraction study by Sullivan and Hindman [54SUL/HIN]. Both groups found evidence for hydrolysis at acid concentrations below 0.5 M. The constants reported from the two spectrophotometric studies [59SUL/HIN, 70PAU] appear to be based on the assumption that hydrolysis is not significant at substantially lower (0.1 to 0.2 M) acid concentrations. Recalculation of the results of Paul [70PAU], as discussed in Appendix A, leads to ${}^*\beta_1 = 0.060$ for an aqueous 1 M NaClO_4 medium, considerably larger than Paul’s reported value, but still significantly smaller than the value of Duplessis and Guillaumont. The recalculation also suggests that effects of the hydrolysis on the molar absorptivity at 960.4 nm should be noticeable even for solutions with acid concentrations greater than 0.2 M.

There are insufficient details in the paper reporting the spectrophotometric study of Sullivan and Hindman [59SUL/HIN] to allow a reanalysis of their raw data, but

Table 8.3: Experimental equilibrium data for the neptunium(IV) hydroxide system, according to the equilibria $m\text{Np}^{4+} + n\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Np}_m(\text{OH})_n^{4m-n} + n\text{H}^+$.

$n:m$	Method	Temp. (°C)	Medium	$\log_{10}^*\beta_{n,m}$ ^(a)	$\log_{10}^*\beta_{n,m}^\circ$ ^(a)	Reference
1:1	sp	25	2.0 M Na/HClO ₄	-2.30	-(1.25±0.40)	[59SUL/HIN]
1:1	sp	25	1.0 M Na/HClO ₄	-1.90		[70PAU]
1:1	sp	25	1.0M Na/HClO ₄	-1.24	-(0.18±0.50)	recalc. from [70PAU] (Appendix A)
1:1	ext	25	1.0M Li/HClO ₄	-0.50	(0.56±0.50)	[77DUP/GUI]
2:1				-1.5		
2:1	tc	25	0.01 M C ₂ H ₅ OH/ 0.0005 NaClO ₄	-4.5		[80SCH/GOR]
1:1	sp	25	2.0M Na/ DClO ₄ /D ₂ O	-2.49		[59SUL/HIN]

^(a) The constants in column 5 are molar constants; those in column 6 are molal constants.

more measurements appear to have been made than in Paul's study. The reported [59SUL/HIN] ratio of the molar absorbance of NpOH^{3+} to that of Np^{4+} is 0.14, much smaller than the 0.48 found on reanalysis of Paul's data [70PAU] (Appendix A). However, the fitted values of the molar absorbance of NpOH^{3+} and the first hydrolysis constant are strongly correlated – the lower the fitted value for the molar absorbance of NpOH^{3+} , the lower the value for $^*\beta_1$. Therefore, it appears that absorbance data from the two spectrophotometric studies are consistent even though they lead to quite different values for $^*\beta_1$.

In the present review the selected value

$$\log_{10}^*\beta_1^\circ(8.4, 298.15 \text{ K}) = -(0.29 \pm 1.00)$$

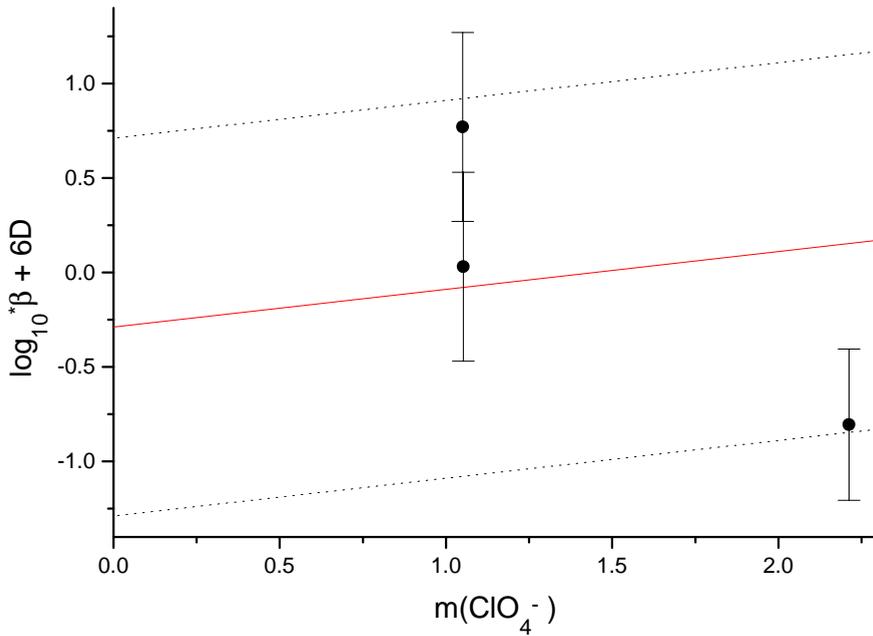
is the unweighted average of the results from the three studies [59SUL/HIN], [70PAU] and [77DUP/GUI], after conversion to molal constants, correction to $I = 0$ using the specific-ion interaction theory and, in the case of [70PAU], recalculation of the raw data. Hence,

$$\Delta_f G_m^\circ(\text{NpOH}^{3+}, \text{aq}, 298.15 \text{ K}) = -(727.3 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$$

On the basis of hydrolysis data for other metals with a 4+ charge [76BAE/MES, 83BRO/ELL], polymeric neptunium hydrolysis species would be expected to predominate for solutions having pH values above 1 to 2 at 25°C, if neptunium is present in greater than tracer quantities. Furthermore, Sullivan and Hindman [59SUL/HIN] reported evidence for polymerization of $\text{Np}(\text{IV})$ at a concentration of $2 \times 10^{-3} \text{ M}$ near $\text{pH} = 2$. For this reason, the value $\log_{10}^*K(8.5) = -4.5$ for the reaction



Figure 8.1: Comparison of experimental values [59SUL/HIN, 70PAU, 77DUP/GUI] of the first hydrolysis constant for Np^{4+} and the SIT plot (—) with uncertainties (···) using the selected value $\log_{10}^*\beta^\circ(8.4) = -(0.29 \pm 1.00)$ and the estimated value $\Delta\varepsilon = -0.20 \text{ kg}\cdot\text{mol}^{-1}$. The value shown based on [70PAU] has been recalculated in the present review.



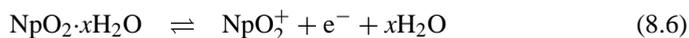
determined by Schmidt *et al.* [80SCH/GOR] with solutions 10^{-3} to 10^{-4} M in neptunium, must be considered suspect. Based on results of their extraction study, Duplessis and Guillaumont [77DUP/GUI] also reported a value ($\log_{10}K(8.5) = -1.5$) for the equilibrium constant for this reaction. For reasons discussed in Appendix A, neither this value nor that of Schmidt *et al.* [80SCH/GOR] is accepted in the present review. In acidic solutions, there is certainly evidence of species more extensively hydrolysed than NpOH^{3+} , but the structure and charge of these species have not been established.

There is no experimental evidence that $\text{Np}(\text{OH})_3^+$ is formed in the $\text{Np}(\text{IV})/\text{water}$ system, and this species is not credited in the present review. Rai and Ryan [85RAI/RYA] reported a limiting, pH-independent solubility of $\leq 10^{-8.3}$ M for “neptunium(IV) hydrous oxide” in neutral to very basic solutions at room temperature in the presence of reducing agents. Ewart *et al.* [85EWA/GOR] reported a limiting neptunium concentration of $10^{-8.1}$ M over “ $\text{Np}(\text{OH})_4$ ” under similar conditions, but over a more limited pH range. The use of ^{235}Np in carrier ^{237}Np by this group allowed considerably lower concentrations of neptunium to be detected than was possible in the work of Rai and Ryan. Also, Pratopo, Moriyama and Higashi [89PRA/MOR] reported pH-independent equilibrium neptunium concentrations of $10^{-8.5}$ M $\text{Np}(\text{IV})$ in aqueous Na_2SO_4 solutions for pH values between 8.5 and 12.5. The two studies that claimed not to be limited by their analytical methods suggest values that differ by only a factor of 2.5. In the present review we accept a value of $10^{-(8.3 \pm 0.3)}$ M, where the uncertainties have been increased slightly to allow for possible difficulties with sample handling and analytical methods. The selected value is also in good agreement with a value of $-(8.28 \pm 0.23)$ reported by Eriksen *et al.* [93ERI/NDA] from solubilities measured in 0.5 M $\text{NaClO}_4(\text{aq})$ over $\text{NpO}_2 \cdot x\text{H}_2\text{O}$ prepared by electroreduction of $\text{Np}(\text{V})$ on a platinum electrode.

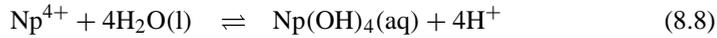
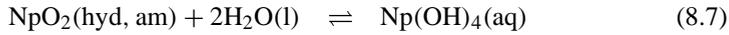
After most of this review was complete, Nakayama, Yamaguchi and Sekine [96NAK/YAM] published a paper that reported a gradual decrease in the solubility of $\text{Np}(\text{OH})_4$ in 0.1 M and 1 M NaClO_4 (from $10^{-(7.5 \pm 0.3)}$ to $\leq 10^{-9}$ M in some cases) for equilibration periods between 28 and 119 days, and some variation in the measured solubilities depending on the holding reductant. These results suggest the value selected in the present review might require revision at a future date.

The pH independence of the solubility suggests that the main solution species is uncharged, *i.e.*, $\text{Np}(\text{OH})_4(\text{aq})$ (or a polymer thereof). Thus, if the Gibbs energy of formation of the solid is known, a value can be calculated for $\Delta_f G_m^\circ(\text{Np}(\text{OH})_4, \text{aq}, 298.15 \text{ K})$.

In a paper by Rai *et al.* [87RAI/SWA] a value of $\log_{10}^*K_{s,0} = 1.5$ for $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ was reported, based on the concentration of Np^{4+} over $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in the presence of $\text{Cu}(\text{I})/\text{Cu}(\text{II})$ as a redox buffer. In the same paper a value of $\log_{10}^*K_{s,0} = 2.7$ was reported, based on the equilibrium concentration of NpO_2^+ over $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in the same solutions (higher equilibrium $\text{Np}(\text{V})$ concentrations were reported by Moriyama, Pratopo and Higashi [89MOR/PRA] from a similar, but less-well defined experiment at higher ionic strength with Na_2SO_4 as holding reductant).



As discussed in Appendix A and Section 8.2.5.2, after recalculation $\log_{10}^*K_{s,0}(8.13) = (1.53 \pm 1.0)$ is selected.



Using $\Delta_f G_m^\circ(\text{NpO}_2, \text{hyd, am}, 298.15 \text{ K}) = -(957.3 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$ and $\log_{10}K(8.7) = -(8.3 \pm 0.3)$, the value $\log_{10}K(8.8) = -(9.8 \pm 1.1)$ is calculated, and the value

$$\Delta_f G_m^\circ(\text{Np}(\text{OH})_4, \text{aq}, 298.15 \text{ K}) = -(1384.2 \pm 8.2) \text{ kJ}\cdot\text{mol}^{-1}$$

is selected. The reported uncertainties do not include those arising from the fact that the hydrated amorphous oxide is not thermodynamically stable, and may not be a unique compound reproducibly precipitated under different conditions. Colloids may form during the solubility experiments, and the work of Silber *et al.* [94SIL/NIT] suggests radiolytic effects may also be important in long term experiments involving the use of Np(IV) solids.

It is clear from the work of Rai and Ryan [85RAI/RYA], Ewart *et al.* [85EWA/GOR] and Pratopo, Moriyama and Higasi [89PRA/MOR] that $\text{Np}(\text{OH})_5^-$ is not an important hydrolysis species for neptunium(IV). The thermodynamic parameters previously suggested for $\text{Np}(\text{OH})_5^-$ in [82ALL] and [84LEM] are rejected in the present review, and no new values are proposed for this species.

8.1.5 Neptunium(III) hydroxide complexes

Np(III) is stable in 1 M HClO_4 , but it is rapidly oxidised by air to the Np(IV) state. Hydrolysis will shift the $[\text{Np}(\text{IV})]/[\text{Np}(\text{III})]$ ratio towards the (IV) state, and so will solvent extraction with an extractant like HTTA; under these conditions, Np(III) will be stable only in the presence of strong reductants like hydroxylamine. However, studies of the formation of hydrophilic Np(III) complexes have been carried out in an oxygen-free atmosphere without interference from hydrolysis, *e.g.* [49HIN/MAG, 49MAG/LAC]. The literature appears to contain only one experimental study of the equilibrium



Mefodeva *et al.* [74MEF/KRO] determined $\log_{10}^*\beta_1(8.9) = -(7.43 \pm 0.11)$ for 25°C and 0.3 M NaClO_4 from potentiometric measurements in the pH-range 6-8 in 0.1 M NaClO_4 at 20°C and comparison with the hydrolysis behaviour of Pr^{3+} and Nd^{3+} under the same conditions (as discussed in Appendix A). Table 8.4 compares the result with various estimates for the first hydrolysis constant of Np(III).

The results seem reliable, except that the uncertainty in $\log_{10}^*\beta_1(8.9, 298.15 \text{ K}, 0.3 \text{ M NaClO}_4)$ is probably overly optimistic, as can be inferred from the uncertainty in the reference Nd/Pr system [66FRO/KUM].

This value was extrapolated to $I = 0$, using $\Delta\varepsilon = (0.04 \pm 0.09) \text{ kg}\cdot\text{mol}^{-1}$ from the corresponding Am system [95SIL/BID] (with uncertainties expanded by 0.05), resulting in $\log_{10}^*\beta_1^\circ = -(6.8 \pm 0.3)$. The uncertainty is an estimate.

Table 8.4: Equilibrium data for the neptunium(III) hydroxide system (Reaction 8.9)

t (°C)	Method	Ionic strength (medium)	$\log_{10}^*\beta_1$	$\log_{10}^*\beta_1^\circ$	Reference
ca. 25	est.			-9.20	[54HIN]
25	pot	0.3 M NaClO ₄	-7.43	-(6.8 ± 0.3)	[74MEF/KRO]
25	est.			-7.40	[80ALL/KIP]
25	est.			-7.77	[87BRO/WAN]

Other predictions based on systematics are $\log_{10}^*\beta_1(I = 0) = -7.40$ [80ALL/KIP] and $= -7.77$ [87BRO/WAN]. We recommend

$$\log_{10}^*\beta_1^\circ(8.9, 298.15\text{K}) = -(6.8 \pm 0.3)$$

8.2 Crystalline and amorphous neptunium oxides and hydroxides

8.2.1 The neptunium-oxygen system phase diagram

There are two known oxides, NpO₂(cr) and a higher oxide variously described as Np₂O₅(cr) and Np₃O₈(cr); the hexagonal sesquioxide Np₂O₃(cr) may just be stable under some conditions. The phase diagram is still not completely established, although it is known that the dioxide, like UO₂(cr) and PuO₂(cr), has an appreciable hypostoichiometry down to about NpO_{1.8}(cr) [87RIC/SAR], but unlike UO₂(cr) does not show any appreciable hyperstoichiometry.

8.2.2 Neptunium(VII) hydrated oxides and hydroxides

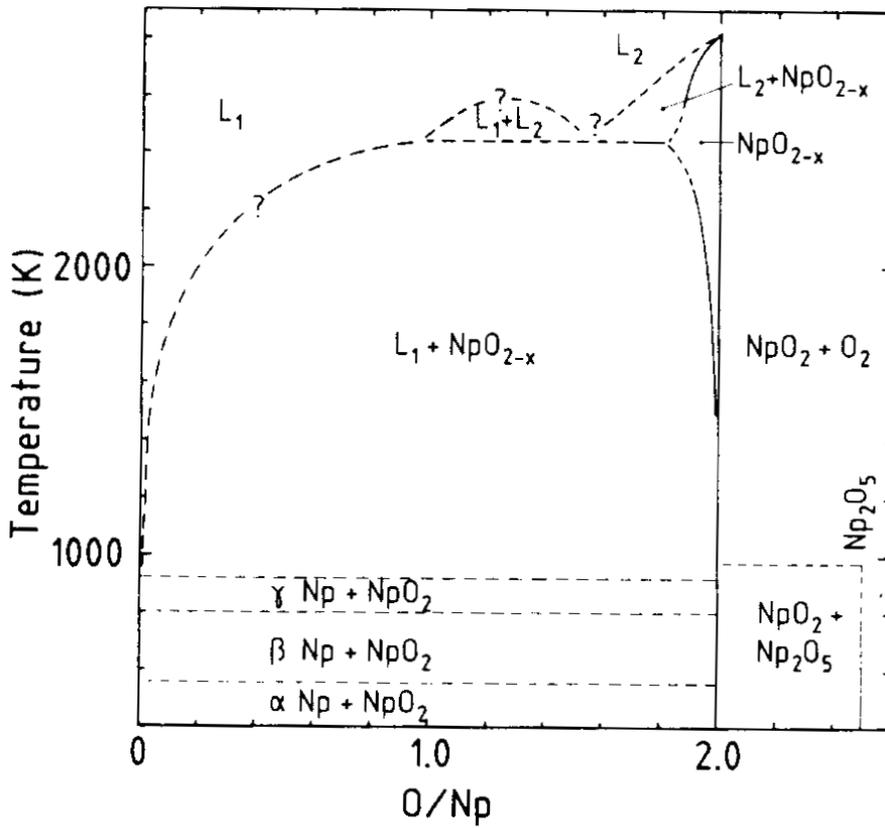
Several groups have prepared neptunium(VII) hydroxide or hydrated oxide solids by acidification of basic solutions containing neptunium(VII) [68KRO/MEF, 72CHA/LEI] or by passing ozone/oxygen mixtures through suspensions of NpO₂OH(am), or over dried NpO₂OH(am) [74CHA/MAT] or NpO₃·H₂O(am) [94NIK/BES]. In most cases the solids, which also contained neptunium(VI) hydroxides, were not purified, and the neptunium(VII) solids were not characterised. Nikonov *et al.* [94NIK/BES] report one such compound to be NpO₂OHNpO₄·4H₂O(am). These compounds gradually decompose to form less oxidised neptunium solids. No thermodynamic data for neptunium(VII) oxides and hydroxides are available.

8.2.3 Neptunium(VI) oxides and hydroxides

8.2.3.1 Anhydrous neptunium(VI) oxide

No successful attempts to prepare this compound have been reported. By analogy with the corresponding uranium compounds, Belyaev, Smirnov and Taranov [79BEL/SMI]

Figure 8.2: Phase relations for the neptunium-oxygen system (from [87RIC/SAR], with permission).



have used $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{cr}))$ to estimate the enthalpy of formation of the anhydrous oxide to be $-1058 \text{ kJ}\cdot\text{mol}^{-1}$, and they further estimated an oxygen pressure of 10^{14} Pa would be required to stabilise the solid. Similarly, using values from Grenthe *et al.* [92GRE/FUG] and $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{cr}))$ from the present review, $\Delta_f H_m^\circ(\text{NpO}_3(\text{cr})) = -(1068 \pm 7) \text{ kJ}\cdot\text{mol}^{-1}$, and if the difference in the entropies of $\text{NpO}_3(\text{cr})$ and $\text{NpO}_2(\text{OH})_2(\text{cr})$ is approximately the same as for the corresponding uranium compounds, $\Delta_f G_m^\circ(\text{NpO}_3(\text{cr})) = -(990 \pm 10) \text{ kJ}\cdot\text{mol}^{-1}$. By comparison with the Gibbs energies of formation for $\text{Np}_2\text{O}_5(\text{cr})$ and $\text{NpO}_2(\text{cr})$, it appears that synthesis of this anhydrous oxide from the lower oxides and oxygen gas is not feasible at practical pressures (see also [77MAL]) and no thermodynamic data are selected for $\text{NpO}_3(\text{cr})$ in the present review.

8.2.3.2 Dioxoneptunium(VI) hydrated oxides and hydroxides

The uranium(VI)-water system has been found to be quite complex [92GRE/FUG], and even with the sparse experimental data available it is evident that several different solids can be found in the corresponding neptunium(VI)-water system.

A hydrated neptunium(VI) oxide or hydroxide can be synthesised by passing ozone/oxygen mixtures through suspensions of $\text{NpO}_2\text{OH}(\text{am})$ at 90°C [64BAG/LAI, 75BEL/IL]. The solid produced by this method may also contain some $\text{Np}(\text{VII})$ [74CHA/MAT]. The resulting precipitate (which has an X-ray diffraction pattern similar to that of uranium trioxide dihydrate [64BAG/LAI]), when dried in air at 100 to 105°C , is converted to a solid that was reported [64BAG/LAI] to be isostructural with $\beta\text{-UO}_2(\text{OH})_2(\text{cr})$ (on the basis of the X-ray diffraction pattern). Infrared and proton magnetic resonance spectroscopic results [75BEL/IL] added evidence in favour of considering this compound to be a true hydroxide with no water of hydration. However, Kato *et al.* [96KAT/KIM] have recently reported preparation of a neptunium trioxide monohydrate by neutralisation of an acidic solution of $\text{Np}(\text{VI})$. Their solid has an X-ray diffraction pattern and an infrared spectrum that differ markedly from those of the solid of Bagnall and Laidler [64BAG/LAI] of the same stoichiometry and from those of other hydrated solids reported previously [64BAG/LAI, 75BEL/IL, 75CHA/MAT]. For the purposes of the present review, these two different solids with the same apparent stoichiometry are distinguished by referring to the dried solid of Bagnall and Laidler as “ $\text{NpO}_2(\text{OH})_2(\text{cr})$ ”, and to the solid of Kato *et al.* as “ $\text{NpO}_3\cdot\text{H}_2\text{O}(\text{cr})$ ”. Chaikhorskii, Matuzenko and Leikina [75CHA/MAT] also reported formation of an amorphous solid, $\text{NpO}_3\cdot 4\text{H}_2\text{O}(\text{am})$, on storage of the dihydrate over water in a sealed vessel for 12-15 days at “room temperature”. It appears the $\text{Np}(\text{VI})$ hydrated oxides and hydroxides may be a fairly complicated system, and more work remains to be done to clarify which compounds are stable.

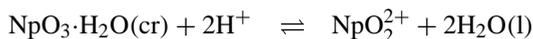
Moskvin [71MOS3] reported the solubility of “ $\text{NpO}_2(\text{OH})_2(\text{s})$ ” (at 20°C) as a function of pH ($I \ll 0.1\text{M}$, self medium with small amounts of an unidentified acid). This solid was apparently not well characterised, nor does it appear that the material was re-examined after equilibration with the aqueous solutions. However, it appears likely that under the stated experimental conditions the solid was primarily the hydrated hydrox-

ide $\text{NpO}_3 \cdot \text{H}_2\text{O}(\text{cr})$ [96KAT/KIM], the trioxide dihydrate $\text{NpO}_3 \cdot 2\text{H}_2\text{O}$ (perhaps better written as $\text{NpO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$) [64BAG/LAI, 75BEL/IL'] or, possibly $\text{NpO}_3 \cdot 4\text{H}_2\text{O}(\text{am})$ [75CHA/MAT]. Moskvin reported $\log_{10} K_{s,0} = -22.1$ for the solubility product of his solid. As discussed in Appendix A, these solubility results are consistent with a value of $10^{(5.5 \pm 1.5)}$ for the solubility product, *K_s , at 25°C (a somewhat lower value than is directly calculated from Moskvin's data). Also, based on the precipitation line shown in Figure 4 of Cassol *et al.* [72CAS/MAG] (for a freshly precipitated form of the solid in a 1 M perchlorate medium), a compatible limiting value, $^*K_s < 10^{6.7}$ is calculated.

Kato *et al.* [96KAT/KIM] have determined the solubility of their trioxide monohydrate at 25°C in acidic 0.1 M NaClO_4 solutions. The measured solubilities are lower than those measured by Moskvin [71MOS3] for what may (or may not) have been the same solid under apparently comparable conditions. Recalculations based on their data (Appendix A) result in a value of

$$\log_{10} {}^*K_{s,0}^\circ = (5.47 \pm 0.40)$$

for the reaction



This value is accepted in the present review. It is likely that one or more of the other solids reported in the Np oxide-hydroxide system [64BAG/LAI, 75BEL/IL'] are similar in stability to the compound of Kato *et al.* The value

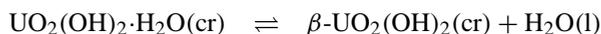
$$\Delta_f G_m^\circ(\text{NpO}_3 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(1239.0 \pm 6.1) \text{ kJ} \cdot \text{mol}^{-1}$$

is accepted in the present review. Though no calorimetric measurements have been carried out for $\text{NpO}_3 \cdot \text{H}_2\text{O}(\text{cr})$, two groups have reported calorimetric results leading to estimates of $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{cr}))$. The more straightforward experiments, by Fuger *et al.* [69FUG/BRO], obtained $\Delta_r H_m^\circ = -(53.1 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}$ for the dissolution of $\text{NpO}_2(\text{OH})_2(\text{cr})$ in 1 M aqueous hydrochloric acid and $\Delta_r H_m^\circ = -(53.8 \pm 1.2) \text{ kJ} \cdot \text{mol}^{-1}$ for the dissolution of $\text{NpO}_2(\text{OH})_2(\text{cr})$ in 1 M aqueous perchloric acid. Although $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, 1 \text{ M HCl})$ has not been measured, the value can be estimated from uranium data and $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, \text{aq})$ (see Appendix A), and a value of $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{cr})) = -(1377 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$ can be calculated. From the enthalpy of solution in perchloric acid and a value of $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, 1 \text{ M HClO}_4) = -(860.7 \pm 4.7)$ (Appendix A) a value of $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{cr})) = -(1379 \pm 5) \text{ kJ} \cdot \text{mol}^{-1}$ is calculated. Belyaev, Smirnov and Taranov [79BEL/SMI] have determined the heat of reaction of $\text{NpO}_2(\text{OH})_2(\text{cr})$ in 6 M HCl containing 0.04 M FeCl_2 and 0.004 M Na_2SiF_6 . The experimental enthalpy data are reanalyzed in the present review (*cf.* Appendix A) using the value $\Delta_f H_m^\circ(\text{Np}^{4+}, 6 \text{ M HCl}(\text{aq})) = (532.9 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$ [2000RAN/FUG] and literature enthalpy of dilution data for HCl [65PAR, 2000RAN/FUG]. The experimental enthalpy of reaction of the $\text{NpO}_2(\text{OH})_2(\text{cr})$ is assumed to include an exothermic contribution of $-(1.7 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ from the effect of the 0.004 M Na_2SiF_6 [76FUG/OET]. Thus, $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{cr})) = -(1363 \pm 13) \text{ kJ} \cdot \text{mol}^{-1}$

is calculated. Combining the results of Belyaev, Smirnov and Taranov with those of Fuger *et al.* gives

$$\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2, \text{cr}, 298.15 \text{ K}) = -(1377 \pm 5) \text{ kJ}\cdot\text{mol}^{-1}$$

where the uncertainty has been increased to allow for the fact that the two most precise measurements were done using the same calorimeter and samples from a single synthesis. As discussed above, heating the $\text{NpO}_3\cdot 2\text{H}_2\text{O}(\text{s})$ ($\text{NpO}_2(\text{OH})_2\cdot\text{H}_2\text{O}(\text{s})$) in air at 100 to 105°C results in conversion to the anhydrous hydroxide, as does heating in contact with liquid water (saturated with an ozone/oxygen mixture) at 90°C. For the corresponding uranium compounds the differences in the $\Delta_f G_m^\circ$ for



and



at 298.15 K are estimated to be 0.7 kJ·mol⁻¹ and -0.4 kJ·mol⁻¹, respectively. Thus, regardless of the actual structures of the solids, the value of $\Delta_f G_m^\circ(\text{NpO}_2(\text{OH})_2, \text{cr}, 298.15 \text{ K})$ can be estimated as identical to that selected for $\text{NpO}_3\cdot\text{H}_2\text{O}(\text{cr})$ within an uncertainty of $\pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$. Thus,

$$\Delta_f G_m^\circ(\text{NpO}_2(\text{OH})_2, \text{cr}, 298.15 \text{ K}) = -(1239.0 \pm 6.4) \text{ kJ}\cdot\text{mol}^{-1}$$

is selected. Combining this with the value derived above for $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2, \text{cr}, 298.15 \text{ K})$ gives $\Delta_f S_m^\circ(\text{NpO}_2(\text{OH})_2, \text{cr}, 298.15 \text{ K}) = -(463 \pm 27) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Using $S_m^\circ(\text{Np}, \alpha, 298.15 \text{ K}) = (50.46 \pm 0.80) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, selected in this review, and CODATA [89COX/WAG] values for $S_m^\circ(\text{H}_2(\text{g}))$ and $S_m^\circ(\text{O}_2(\text{g}))$ leads to

$$S_m^\circ(\text{NpO}_2(\text{OH})_2, \text{cr}, 298.15 \text{ K}) = 129 \pm 27 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

By analogy with the value $S_m^\circ(\text{UO}_2(\text{OH})_2, \beta, 298.15 \text{ K}) = 138 \pm 4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ selected by Grenthe *et al.* [92GRE/FUG], a value for $S_m^\circ(\text{NpO}_2(\text{OH})_2, \text{cr}, 298.15 \text{ K})$ closer to 140 J·K⁻¹·mol⁻¹ might have been expected. This suggests a somewhat lower equilibrium solubility for the solid, or a less negative enthalpy of formation. More experimental work on this solid would be useful.

The heat capacity of $\text{NpO}_2(\text{OH})_2(\text{cr})$ was estimated as 112 J·K⁻¹·mol⁻¹ by Lemire [84LEM] based on a Kopp's law calculation as outlined by Sturtevant [59STU]. As noted in [84LEM], this value is markedly smaller than a value previously estimated for $\beta\text{-UO}_2(\text{OH})_2(\text{cr})$, (141 ± 15) kJ·mol⁻¹ [72NIK/SER, 80LEM/TRE]. However, in general, experimental heat capacity values for actinide solids tend to be somewhat greater than the Kopp's law estimates, and in the present review

$$C_{p,m}^\circ(\text{NpO}_2(\text{OH})_2, \text{cr}, 298.15 \text{ K}) = (120 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

is accepted, based on the heat capacity of the hypothetical compound $\text{NpO}_3(\text{cr})$ being similar to that for $\gamma\text{-UO}_3(\text{cr}, \text{gamma})$ [92GRE/FUG] and an estimate of 40 J·K⁻¹·mol⁻¹ for the extra bound H₂O [93TAY/LEM].

8.2.4 Neptunium(V) oxides and hydroxides

8.2.4.1 Dineptunium pentoxide

A neptunium oxide with the composition $\text{NpO}_{2.5}(\text{cr})$ (*i.e.* $\text{Np}_2\text{O}_5(\text{cr})$) can be synthesized by calcination of $\text{NpO}_3 \cdot \text{H}_2\text{O}(\text{cr})$ [64BAG/LAI] or $\text{NpO}_2\text{OH}(\text{am})$ [73SUD/SOL, 79BEL/DOB] or by molten salt techniques [63COH, 64COH/WAL]. The X-ray diffraction pattern of the powder indicates a monoclinic structure for the solid ($a = 418.8$ pm, $b = 659.2$ pm, $c = 409.0$ pm, $\beta = 90.16^\circ$ [76FAH/TUR]). The composition range has been shown to be quite limited [76FAH/TUR], and earlier reports of compositions nearer $\text{NpO}_{2.6}(\text{cr})$, such as $\text{Np}_3\text{O}_8(\text{cr})$ [63ROB/WAL], were apparently in error [76FAH/TUR, 87RIC/SAR]. Richter and Sari [87RIC/SAR] found $\text{Np}_2\text{O}_5(\text{cr})$ decomposes to NpO_2 and $\text{O}_2(\text{g})$ in oxygen atmospheres at temperatures between 700 and 970 K, and were unable to prepare $\text{Np}_2\text{O}_5(\text{cr})$ from NpO_2 and $\text{O}_2(\text{g}, 0.3$ MPa) from 570 to 1670 K.

Recently a solid with a powder X-ray diffraction pattern similar to $\text{Np}_2\text{O}_5(\text{cr})$ was reported to precipitate from near-neutral aqueous solutions of neptunium(V) at 90°C [91NIT]. Merli and Fuger [94MER/FUG] reported that if $\text{Np}_2\text{O}_5(\text{cr})$ is maintained in water at 573 K (8.59 MPa) for seven days, the crystallinity of the phase is greatly improved. Furthermore, Pan and Campbell [95PAN/CAM], who measured the solubility of $\text{Np}_2\text{O}_5(\text{cr})$ in neutral and basic aqueous solutions at 25°C , reported gradual ripening of crystalline $\text{Np}_2\text{O}_5(\text{cr})$ in contact with their aqueous solutions over a period of months. This observation suggests $\text{Np}_2\text{O}_5(\text{cr})$, in contact with $\text{H}_2\text{O}(\text{l})$, has a stability equal to or greater than $\text{NpO}_2\text{OH}(\text{am})$ even at 25°C , and not only at higher temperatures.

There have been two experimental studies of the enthalpy of formation of $\text{Np}_2\text{O}_5(\text{cr})$. Merli and Fuger [94MER/FUG] measured the enthalpy of solution of the solid in 6 M $\text{HCl}(\text{aq})$ (see Appendix A). Belyaev, Smirnov and Taranov [79BEL/SMI] determined the heat of reaction of “ $\text{Np}_2\text{O}_5(\text{s})$ ” in aqueous HCl (6 M) containing 0.04 M FeCl_2 and 0.004 M Na_2SiF_6 . Using $\Delta_f H_m^\circ(\text{Np}^{4+}, 6 \text{ M HCl}(\text{aq})) = -(532.9 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$ [73FUG/BRO, 2000RAN/FUG] with the experimental enthalpy data in the paper of Belyaev, Smirnov and Taranov [79BEL/SMI], the recently assessed values for the enthalpies of formation for the iron chloride solids [95PAR/KHO], the literature enthalpy of dilution data for HCl [65PAR, 2000RAN/FUG], and by assuming the experimental enthalpy of reaction of the $\text{Np}_2\text{O}_5(\text{cr})$ includes an exothermic contribution of $-(1.7 \pm 0.8) \text{ kJ}\cdot(\text{mol Np})^{-1}$ from the effect of the 0.004 M Na_2SiF_6 [76FUG/OET]), $\Delta_f H_m^\circ(\text{Np}_2\text{O}_5(\text{cr})) = -(2142 \pm 13) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated. This value is only in marginal agreement with the value $\Delta_f H_m^\circ(\text{Np}_2\text{O}_5(\text{cr})) = -(2162.7 \pm 9.5) \text{ kJ}\cdot\text{mol}^{-1}$ determined by the direct dissolution of $\text{Np}_2\text{O}_5(\text{cr})$ in HCl [94MER/FUG].

However, the sample of “ Np_2O_5 ” used by Belyaev, Smirnov and Taranov [79BEL/SMI] was reported to be 85.11 wt% neptunium. This actually corresponds to $\text{NpO}_{2.59}$. If their analysis was in error, the enthalpy of reaction value of Belyaev, Smirnov and Taranov cannot explain the apparent stability of $\text{Np}_2\text{O}_5(\text{cr})$ with respect to $\text{NpO}_2\text{OH}(\text{am})$. If the stoichiometry is assumed to be $\text{NpO}_{2.59}$, $\Delta_f H_m^\circ(\text{NpO}_{2.59}(\text{cr})) = -(1086 \pm 13) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated. Then, using reasonable entropy values for

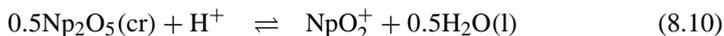
the solids, it is further calculated that accepting this enthalpy value means $\text{NpO}_{2.59}(\text{cr})$ would exclude $\text{NpO}_2\text{OH}(\text{am})$ (or $\text{Np}_2\text{O}_5(\text{cr})$ based on the value from Fuger and Merli [94MER/FUG]) from the neptunium-oxygen-water phase diagram – at least near room temperature. Considering the large uncertainties in the enthalpy values, the difficulty in carrying out the analyses [76FAH/TUR] and the lack of agreement between $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{cr}))$ as similarly determined by Belyaev, Smirnov and Taranov [79BEL/SMI] and the value determined from the simpler experiment by Fuger and Brown [69FUG/BRO], only the value from Merli and Fuger [94MER/FUG] (for a compound assumed to be stoichiometric $\text{Np}_2\text{O}_5(\text{cr})$) is used in the present review, and is selected.

$$\Delta_f H_m^\circ(\text{Np}_2\text{O}_5, \text{cr}, 298.15\text{K}) = -(2162.7 \pm 9.5) \text{ kJ}\cdot\text{mol}^{-1}$$

This is done with the recognition that the stable compound may have a stoichiometry that differs slightly from $\text{NpO}_{2.50}$. The selected value of $\Delta_f H_m^\circ(\text{Np}_2\text{O}_5, \text{cr}, 298.15 \text{ K})$ is compatible, within the uncertainty limits, with marginal stability with respect to decomposition to NpO_2 . Also, this value is reasonable compared to the estimated values for $\Delta_f H_m^\circ(\text{NpO}_3, \text{cr}, 298.15 \text{ K})$, -1068 (this review) or $-(1070 \pm 6) \text{ kJ}\cdot\text{mol}^{-1}$ ([82MOR/FUG] based on UO_3 and experimental data on the homologous U - Np species), if one takes uncertainty limits into account and assumes that the entropy change for



is only due to the formation of $\text{O}_2(\text{g})$. Pan and Campbell [95PAN/CAM] have measured the solubility of $\text{Np}_2\text{O}_5(\text{cr})$ in aqueous solutions as a function of pH. Their measurements for pH values below 8 can be used to obtain a value of $\log_{10} {}^*K_{s,0} = (3.90 \pm 0.02)$ for the reaction



and $\Delta_f G_m^\circ(\text{Np}_2\text{O}_5, \text{cr}, 298.15 \text{ K}) = -(2008 \pm 11) \text{ kJ}\cdot\text{mol}^{-1}$. From this and the selected value for $\Delta_f H_m^\circ$, $S_m^\circ(\text{Np}_2\text{O}_5, \text{cr}, 298.15 \text{ K}) = (95 \pm 46) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is calculated. This value is not in agreement with values of $S_m^\circ(\text{Np}_2\text{O}_5, \text{cr}, 298.15 \text{ K})$ previously estimated by Merli and Fuger [94MER/FUG] ($(186 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and Lemire [84LEM] ($(163 \pm 23) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and the value is almost certainly too small for well-crystallised bulk $\text{Np}_2\text{O}_5(\text{cr})$. Indeed, it is much less than twice the experimentally determined value for crystalline $\text{NpO}_2(\text{cr})$ (Section 8.2.5.1), and less than twice $S_m^\circ(\text{UO}_{2.25}(\text{cr})) = (83.53 \pm 0.17) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $S_m^\circ(\text{UO}_{2.6667}(\text{cr})) = (94.18 \pm 0.17) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [92GRE/FUG]. The difference may simply indicate that the surface of the $\text{Np}_2\text{O}_5(\text{cr})$ samples used in the solubility experiments had large numbers of active sites. It may also indicate the selected entropy for $\text{NpO}_2^+(\text{aq})$ in the present review is too negative. In the present review the value

$$S_m^\circ(\text{Np}_2\text{O}_5, \text{cr}, 298.15 \text{ K}) = (174 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

is accepted as a value for “ideal”, crystalline $\text{NpO}_{2.5}(\text{cr})$, and hence,

$$\Delta_f G_m^\circ(\text{Np}_2\text{O}_5, \text{cr}, 298.15 \text{ K}) = -(2031.6 \pm 11.2) \text{ kJ}\cdot\text{mol}^{-1}$$

Belyaev *et al.* [79BEL/DOB] have measured the heat capacity of $\text{Np}_2\text{O}_5(\text{cr})$ from 350 to 750 K by drop calorimetry. This work appears to be more precise than the work on $\text{NpO}_2(\text{cr})$ from the same research group [74ARK/GUT]. On conversion to a molar basis, the equation in [79BEL/DOB] becomes

$$C_{p,m}^\circ(\text{Np}_2\text{O}_5(\text{cr})) = (99.2 + 98.6 \times 10^{-3}T) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and this equation has been accepted in the present review for the temperature range 298.15 K to 750 K, and from this the accepted value

$$C_{p,m}^\circ(\text{Np}_2\text{O}_5, \text{cr}, 298.15\text{K}) = (128.6 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

is calculated. The uncertainty is estimated in the present review.

8.2.4.2 Dioxoneptunium(V) hydroxide

Experimental values for the solubility of $\text{NpO}_2\text{OH}(\text{am})$ as a function of pH, as reported in various publications, are shown in Figure 8.3. Most reported solubility determinations for $\text{NpO}_2\text{OH}(\text{am})$ [48KRA/NEL, 71MOS3, 76SEV/KHA, 85LIE/TRE, 86EWA/HOW, 92NEC/KIM, 96ROB/SIL] are in reasonable agreement for pH values less than or equal to 10. Above that pH even trace quantities of dissolved $\text{CO}_2(\text{g})$ will react to form carbonato complexes and increase the solubility of the solid, and, in the absence of CO_2 , hydrolysis reactions may be important (*cf.* Section 8.1.3). Hence, at high pH the solubility results would be expected to show more scatter, and this is indeed what has been found [86EWA/HOW, 85LIE/TRE, 91YAM/PRA].

Neck, Kim and Kanellakopulos [92NEC/KIM] have shown that ageing a dioxoneptunium(V) hydroxide precipitate in contact with sodium perchlorate solutions having an ionic strength greater than 0.1 m leads to a solid that is several $\text{kJ}\cdot\text{mol}^{-1}$ more stable than freshly precipitated $\text{NpO}_2\text{OH}(\text{am})$. Thus, the low solubility values obtained by Musikas [78MUS] may have been caused by the effect on the solid of the very high ionic strength ($I \approx 9$) medium used for his experiments. The solubilities reported by Yamaguchi *et al.* [91YAM/PRA] are badly scattered even for experiments in which the pH value was < 11 , and are generally low (see Appendix A) compared to most of the reported values. The results obtained by Itagaki *et al.* [92ITA/NAK] for solubilities in solutions of low ionic strength with pH values less than 9 show no dependence on pH. As discussed in Appendix A, this may be the result of formation of a colloidal or metastable solid.

For many of the measurements, exact temperatures were not reported (*e.g.* [48KRA/NEL, 91YAM/PRA]), nor were details provided concerning the calibration of the glass electrodes (including junction potentials). In most cases, the experimental solubilities were reported only in graphical form. Thus, additional uncertainties are introduced in recovering the values from the original reports and journal articles. Furthermore, in most cases, the nature of the solid in equilibrium with the aqueous phase was not established. Most of the equilibration times ranged from a few hours to two weeks, although the experiments of Roberts *et al.* [96ROB/SIL] lasted for 37 days, and some of those of Nakayama *et al.* [88NAK/ARI] for two months.

In view of the scatter in the solubilities, ill-defined ageing effects on the solid and the discrepancies in the reported hydrolysis constants for neptunium(V) that preclude selection of solubility products and hydrolysis constants from independent experimental data, it is difficult to select an accurate value for the solubility product for $\text{NpO}_2\text{OH}(\text{am})$



An upper bound of approximately $\log_{10}^*K_{s,0}^\circ(8.11) = 5.4$ seems to be set by the values obtained from recalculation of the data of Lierse, Treiber and Kim [85LIE/TRE, 92NEC/KIM] ($\log_{10}^*K_{s,0}^\circ = 5.35 \pm 0.1$), Kraus and Nelson [48KRA/NEL] ($\log_{10}^*K_{s,0}^\circ = 4.8 \pm 0.2$), Moskvín [71MOS3] ($\log_{10}^*K_{s,0}^\circ = 4.9 \pm 0.1$ based on the four low pH values only), Neck, Kim and Kanellakopoulos [92NEC/KIM] ($\log_{10}^*K_{s,0}^\circ = 5.3 \pm 0.1$) and Itagaki *et al.* [92ITA/NAK] ($\log_{10}^*K_{s,0}^\circ = 5.0 \pm 0.2$) for the amorphous solid equilibrated in low ionic strength solutions (except for values from Kim's group [85LIE/TRE, 92NEC/KIM], only solubilities obtained for solutions with pH values ≤ 9 were considered). In the present review, it is accepted that the nature of the precipitated solid changes with time and with the medium with which it is brought to equilibrium. For "freshly precipitated" (green) material in a low ionic strength medium,

$$\log_{10}^*K_{s,0}^\circ(8.11) = (5.3 \pm 0.2)$$

is selected based on refitting the molal solubility products reported by Neck, Kim and Kanellakopoulos [92NEC/KIM] using the values of the interaction coefficients, ε , from Appendix B of this review and hence,

$$\Delta_f G_m^\circ(\text{NpO}_2\text{OH}(\text{am}, \text{"fresh"})) = -(1114.7 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1}$$

The "aged" (white) solid may be a slightly more ripened form of the hydroxide, or it may be a material with a surface layer of Np_2O_5 , or even incorporating alkali metal ions. Neck, Kim and Kanellakopoulos [92NEC/KIM] reported $\log_{10}^*K_{s,0}^\circ = 4.6$ for this solid — somewhat greater than suggested by several other studies, but also slightly greater than the value proposed above (Section 8.2.4.1) for $\text{Np}_2\text{O}_5(\text{cr})$. The results of Roberts *et al.* [96ROB/SIL] and Runde, Neu and Clark [96RUN/NEU] suggest a similar difference in apparent solubility products for the two NpO_2OH solids in 5.6 *m* (5.0 M) NaCl. Apparently both solids are more soluble in NaCl solutions than in NaClO_4 solutions of comparable ionic strength [95NEC/FAN, 96ROB/SIL]. The solids in these studies using $\text{NpO}_2\text{OH}(\text{am})$ have not been (nor could have been easily) characterised, but the solid in the study of Pan and Campbell [95PAN/CAM] was characterised as crystalline Np_2O_5 , and did not appear to be transformed to an amorphous solid even after several months. Therefore, the value

$$\log_{10}^*K_{s,0}^\circ(8.11) = (4.7 \pm 0.5)$$

is accepted for the "aged" solid, and the uncertainty has been assigned in this review to reflect the uncertainty in the nature of the compound. Hence,

$$\Delta_f G_m^\circ(\text{NpO}_2\text{OH}(\text{am}, \text{"aged"})) = -(1118.1 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1}$$

The enthalpy of solution of amorphous $\text{NpO}_2\text{OH}(\text{am})$ has been recently measured by two different groups [94MER/FUG, 94CAM/LEM]. As discussed above, it is not clear how the nature of this compound changes with time in contact with aqueous solution, and isolating and/or drying the material could result in a compound that might not be readily identified with either the “fresh” or “aged” precipitates discussed above. Both groups prepared material that, in contact with its mother liquor during the synthesis, was the green “freshly precipitated” solid. The solid isolated by Merli and Fuger [94MER/FUG] had 2.2-2.5 moles of associated water per mole of neptunium. The solids of Campbell and Lemire [94CAM/LEM], stored over a desiccant, had a $\text{H}_2\text{O}:\text{Np}$ ratio of 1.28-1.52.

The molar enthalpies of solution, calculated here based on the reported analyses (see Appendix A) are $-(38.5 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ [94MER/FUG] in 1 M HCl and $-(43.7 \pm 4.4) \text{ kJ}\cdot\text{mol}^{-1}$ in 1 m HClO_4 [94CAM/LEM]. If the enthalpy effect corresponding to the transfer of the NpO_2^+ ion from 1 $\text{mol}\cdot\text{dm}^{-3}$ HCl or 1.0 $\text{mol}\cdot\text{kg}^{-1}$ HClO_4 to infinite dilution is assumed to be negligible, these values are in marginal agreement within the uncertainties of the measurements. The unweighted average of the results from the two sets of measurements, $\Delta_f H_m^\circ(8.11) = -(41.1 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$, is used to calculate

$$\Delta_f H_m^\circ(\text{NpO}_2\text{OH}(\text{am})) = -(1222.9 \pm 5.5) \text{ kJ}\cdot\text{mol}^{-1}$$

assuming the compound is not a true hydrate, and that the enthalpy of the associated water in the solid does not differ significantly from that of liquid water.

Within the uncertainty this selected value of $\Delta_f H_m^\circ$ is assumed to apply to both the “freshly precipitated” and “aged” forms of the solid, and by using the values selected above for $\Delta_f G_m^\circ$ of the “aged” and “freshly precipitated” forms of $\text{NpO}_2\text{OH}(\text{am})$, the accepted values

$$S_m^\circ(\text{NpO}_2\text{OH}, \text{am} \text{ (“fresh”)}, 298.15 \text{ K}) = (60 \pm 27) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^\circ(\text{NpO}_2\text{OH}, \text{am} \text{ (“aged”)}, 298.15 \text{ K}) = (72 \pm 28) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

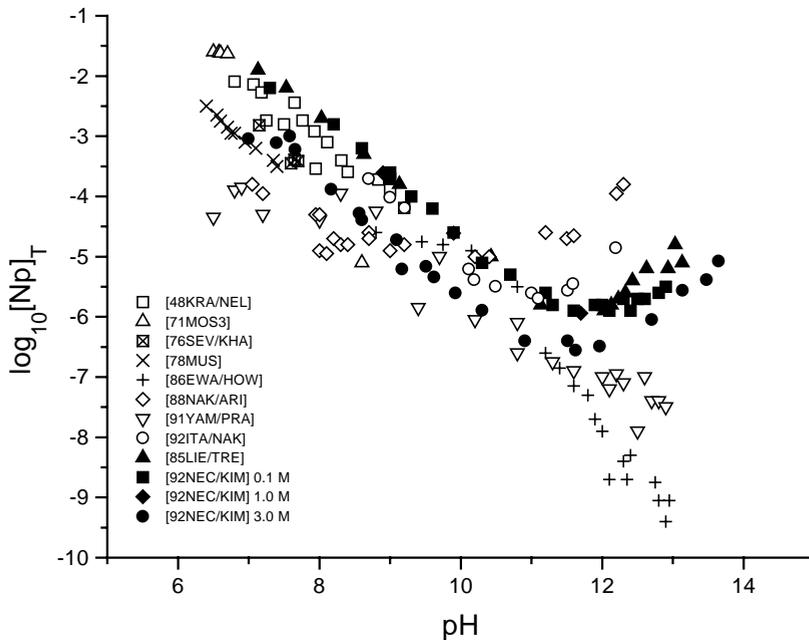
are calculated. These entropy values are low compared to Latimer’s rule [52LAT, 92GRE/FUG] estimates of 101 to 111 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and may indicate the selected entropy for $\text{NpO}_2^+(\text{aq})$ in the present review is too negative. The heat capacity of $\text{NpO}_2\text{OH}(\text{am})$ was estimated as 86 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ by Lemire [84LEM] based on a Kopp’s-law calculation as outlined by Sturtevant [59STU]. In the absence of any experimental value, this is accepted in the present review with an estimated uncertainty of 20 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

$$C_{p,m}^\circ(\text{NpO}_2\text{OH}, \text{am}, 298.15 \text{ K}) = (86 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Table 8.5: Summary of selected formation constants for the neptunium(V)-water system at 25°C and $I = 0$.

Species		\log_{10}^*K	$\Delta\varepsilon$
$\text{NpO}_2\text{OH}(\text{am}, \text{“fresh”})$	$\log_{10}^*K_{s,0}$ (8.11)	(5.3 ± 0.2)	(0.29 ± 0.08)
$\text{NpO}_2\text{OH}(\text{am}, \text{“aged”})$	$\log_{10}^*K_{s,0}$ (8.11)	(4.7 ± 0.5)	(0.29 ± 0.08)
$\text{NpO}_{2.50}(\text{cr})$	$\log_{10}^*K_{s,0}$ (8.10)	(1.8 ± 0.8)	(0.29 ± 0.08)
$\text{NpO}_2\text{OH}(\text{aq})$	$\log_{10}^*\beta_1^\circ$ (8.1)	$-(11.3 \pm 0.7)$	$-(0.29 \pm 0.08)$
$\text{NpO}_2(\text{OH})_2^-$	$\log_{10}^*\beta_2^\circ$ (8.2)	$-(23.6 \pm 0.5)$	$-(0.34 \pm 0.13)$

Figure 8.3: Experimental determinations of the solubility of $\text{NpO}_2\text{OH}(\text{am})$. The data are taken from [48KRA/NEL] (\square), [71MOS3] (\triangle), [76SEV/KHA] (\boxtimes), [78MUS] (\times), [86EWA/HOW] ($+$), [88NAK/ARI] (\diamond), [91YAM/PRA] (∇), [85LIE/TRE] (\blacktriangle), [92NEC/KIM] 0.1 M NaClO_4 (\blacksquare), 1.0 M NaClO_4 (fresh solid) (\blacklozenge), 3.0 M NaClO_4 (aged solid) (\bullet)



8.2.5 Neptunium(IV) oxides and hydroxides

8.2.5.1 Neptunium dioxide

8.2.5.1.1 Crystal structure

$\text{NpO}_2(\text{cr})$ has the fluorite fcc structure (space group $\text{Fm}\bar{3}\text{m}$) with $a = 5.434 \times 10^{-10}$ m; the X-ray density is $11.14 \text{ g}\cdot\text{cm}^{-3}$. An orthorhombic phase is formed in a gradual transition at 33 to 37 GPa at room temperature [86BEN/DAB].

8.2.5.1.2 Thermodynamic values

The enthalpy of formation of $\text{NpO}_2(\text{cr})$

$$\Delta_f H_m^\circ(\text{NpO}_2, \text{cr}, 298.15 \text{ K}) = -(1074.0 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$$

was taken from the work of Huber and Holley [68HUB/HOL], who determined the heat of combustion of $\alpha\text{-Np}(\text{cr})$. Combining this value with the entropy

$$S_m^\circ(\text{NpO}_2, \text{cr}, 298.15 \text{ K}) = (80.3 \pm 0.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from the work of Westrum *et al.* [53WES/HAT] leads to

$$\Delta_f G_m^\circ(\text{NpO}_2, \text{cr}, 298.15 \text{ K}) = -(1021.731 \pm 2.514) \text{ kJ}\cdot\text{mol}^{-1}$$

Two sets of experimental heat capacity data are available for $\text{NpO}_2(\text{cr})$. Westrum *et al.* [53WES/HAT] have reported $C_{p,m}$ measurements for temperatures from 10 to 312.68 K. There is an anti-ferromagnetic transition at 25 K. Archipov *et al.* [74ARK/GUT] made drop-calorimetry measurements from 350 to 1100 K. Extrapolations of the two sets of measurements appear to differ by 10 to 15 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in the range 300 to 400 K. The uncertainties are considerably larger in the results from the drop-calorimetry study (see Appendix A). Therefore, in this review, the low-temperature heat capacity results from 228.55 to 312.69 K from Westrum *et al.* [53WES/HAT] have been fitted to

$$C_{p,m}^\circ(\text{NpO}_2, \text{cr}, T) = (67.511 + 26.599 \times 10^{-3}T - 8.190 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

From this, the selected value at 298.15 K

$$C_{p,m}^\circ(\text{NpO}_2, \text{cr}, 298.15 \text{ K}) = (66.2 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

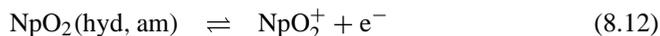
is obtained. A fit of the drop-calorimetry results [74ARK/GUT] with the constraint that the value for $C_{p,m}^\circ(\text{NpO}_2, \text{cr})$ at 298.15 K is $66.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ does not result in $C_{p,m}^\circ$ values above 300 K that differ markedly from those calculated using the $C_{p,m}^\circ(T)$ equation above (*i.e.* the equation based only on the low-temperature measurements). Furthermore, the values for $C_{p,m}^\circ(T)$ from the equation differ by less than 6% from the corresponding values selected for $\text{UO}_2(\text{cr})$ [92GRE/FUG] and $\text{PuO}_2(\text{cr})$ (Section

17.2.1.2) for temperatures from 298.15 to 1200 K. Thus, the equation for $C_{p,m}^{\circ}(T)$ is selected for the temperature range 220 K to 800 K.

The same difficulties that were described in the uranium volume [92GRE/FUG] with respect to the relative stabilities of “hydrous UO_2 ”, crystalline UO_2 and the neutral aqueous U(IV) solution species, and to possible changes in the surface properties of solids with changes in pH, apply equally well to the corresponding neptunium species. It is therefore not surprising that few attempts have been made to measure even the dissolution rate of $\text{NpO}_2(\text{cr})$, and true solubility measurements in acidic media do not appear to have been reported [88HIR/LIE].

8.2.5.2 “Hydrous” or “amorphous” neptunium(IV) oxide

In a paper by Rai *et al.* [87RAI/SWA] a value of $\log_{10}^*K_{s,0} = 1.5$ for $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ was reported, based on the concentration of Np^{4+} over $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in the presence of Cu(I)/Cu(II) as a redox buffer. In the same paper a value of $\log_{10}^*K_{s,0} = 2.7$ was reported based on the equilibrium concentration of NpO_2^+ over $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in the same solutions (Reaction 8.12).



As discussed in Appendix A, recalculation of these results, also considering values for the Np(V/IV) reduction potential, first hydrolysis constant and chloride complexation constants as selected in the present review, leads to the value

$$\log_{10}^*K_{s,0}(8.13) = (1.53 \pm 1.0)$$



Thus,

$$\Delta_f G_m^{\circ}(\text{NpO}_2(\text{hyd, am}, 298.15\text{K})) = -(957.3 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$$

(or equivalently, $\Delta_f G_m^{\circ}(\text{Np}(\text{OH})_4, \text{am}, 298.15\text{K}) = -(1432 \pm 8) \text{ kJ}\cdot\text{mol}^{-1}$). The reported uncertainties do not include those arising from the fact that the hydrated amorphous oxide is not thermodynamically stable, and may not be a unique compound reproducibly precipitated under different conditions. The selected value is also consistent with $\log_{10}^*K_{s,0} = 0.8$ reported by Moskvina [71MOS3], based on solubility measurements on an uncharacterised sample of the solid hydroxide in perchloric acid solutions containing 0.1 to 0.2 M hydrazine at 20°C. The “best” value found for $^*K_{s,0}^{\circ}$ is greater (by about an order of magnitude) than the value suggested for the corresponding uranium compound [92GRE/FUG], and the value suggested for the corresponding plutonium solid (*cf.* Section 17.2.2.3) is even smaller ($\log_{10}^*K_{s,0}^{\circ} = -(2 \pm 1)$). These differences are probably more a reflection of uncertainties related to the ill-defined nature of the solids than an indication of large difference in behaviour between the three actinide systems.

8.2.6 Neptunium(III) oxide

According to Ackermann *et al.* [66ACK/FAI], traces of a possible rare-earth type-A hexagonal phase formed on cooling hypostoichiometric NpO_{2-x} . Lattice parameters $a = 4.234 \times 10^{-10}$ m, $c = 6.10 \times 10^{-10}$ m were reported by Ackermann and Chandrasekharaiyah [75ACK/CHA]. However, Ritcher and Sari [87RIC/SAR] could not confirm this phase. The intermediate formation of Np_2O_3 was reported to have been observed by photoelectron spectroscopy [88ITU], in situ, during the slow oxidation of clean metal surfaces. Morss [86MOR] estimated that, at 298 K under standard conditions, $\Delta_r G_m$ for the disproportionation of Np_2O_3 into metal and dioxide is approximately $-85 \text{ kJ} \cdot (\text{mol of } \text{Np}_2\text{O}_3)^{-1}$. In the present review no chemical thermodynamic quantities are selected for $\text{Np}_2\text{O}_3(\text{s})$.

8.2.7 Neptunium(III) hydroxide

No systematic study of ${}^*K_{s,0}$ for the actinide(III) hydroxides as a function of temperature or ionic strength has been made. No usable experimental values for $\text{Np}(\text{OH})_3(\text{s})$ appear to have been reported. In the NEA/TDB americium volume [95SIL/BID], the values of $\log_{10} {}^*K_{s,0}^\circ$ for $\text{Am}(\text{OH})_3(\text{s}) = (17.0 \pm 0.6)$ (amorphous) and (15.2 ± 0.6) (crystalline) have been chosen. It seems reasonable to assume that the solubility product decreases slightly in the order $\text{U(III)} > \text{Np(III)} > \text{Pu(III)} > \text{Am(III)} > \text{Cm(III)}$, probably by less than a factor of two for each element. No further evaluation is made here.

Chapter 9

Neptunium group 17 (halogen) compounds and complexes

9.1 Neptunium halide compounds

9.1.1 Introduction

The experimental thermodynamic data for the neptunium halides are far from complete, consisting essentially of some measurements of enthalpies of solution and some vapour pressure determinations. The only experimental data for low temperature heat capacities, and thus standard entropies, are those for $\text{NpF}_6(\text{cr})$. This means that many, indeed most, of the data given in this section are interpolated (or extrapolated) from those of the corresponding thorium, uranium and plutonium compounds. In practice, this means that the trivalent compounds are related more to the U and Pu systems, the quadrivalent compounds to Th and U systems (where the data are often fairly well defined). The comparisons for the few compounds of higher valency rely heavily on the data for the corresponding uranium compounds, since there are often no Pu analogues.

9.1.2 Neptunium fluoride compounds

9.1.2.1 $\text{NpF}(\text{g})$ and $\text{NpF}_2(\text{g})$

These species were observed in the mass-spectrometric study of NpF_4 by Kleinschmidt *et al.* [92KLE/LAU] but no thermodynamic data (other than appearance potentials) were reported. However their stabilities can be estimated fairly reliably from the data for the corresponding Th, U and Pu compounds.

9.1.2.1.a Enthalpies of formation

The enthalpy of formation of $\text{ThF}(\text{g})$, $\text{UF}(\text{g})$ and $\text{PuF}(\text{g})$ are close to a linear function of atomic number, suggesting that the enthalpy of formation of $\text{NpF}(\text{g})$ is close to the mean of those for $\text{UF}(\text{g})$ ($-(52 \pm 30) \text{ kJ}\cdot\text{mol}^{-1}$ [92GRE/FUG]) and $\text{PuF}(\text{g})$ ($-(112.6 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$, see Section 18.1.2.1). The selected value is

$$\Delta_f H_m^\circ(\text{NpF}, \text{g}, 298.15 \text{ K}) = -(82 \pm 30) \text{ kJ}\cdot\text{mol}^{-1}$$

The situation for $\text{NpF}_2(\text{g})$ is less clear-cut, since the enthalpies of formation of $\text{ThF}_2(\text{g})$ [85HIL/GUR] and $\text{PuF}_2(\text{g})$ (see Section 18.1.2.1) are very similar, while

that of $\text{UF}_2(\text{g})$ is about $80 \text{ kJ}\cdot\text{mol}^{-1}$ more positive. Nevertheless we estimate the enthalpy of formation of $\text{NpF}_2(\text{g})$ to be close to the mean of those for $\text{UF}_2(\text{g})$ ($-(530 \pm 30) \text{ kJ}\cdot\text{mol}^{-1}$ [92GRE/FUG]) and $\text{PuF}_2(\text{g})$ ($-(614.3 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1}$, Section 18.1.2.1), the selected value being

$$\Delta_f H_m^\circ(\text{NpF}_2, \text{g}, 298.15 \text{ K}) = -(570 \pm 50) \text{ kJ}\cdot\text{mol}^{-1}$$

9.1.2.1.b Standard entropy and heat capacity

The thermal functions of $\text{NpF}(\text{g})$ and $\text{NpF}_2(\text{g})$ were calculated assuming the molecular parameters discussed in Rand and Fuger [2000RAN/FUG]. These are essentially those estimated by Glushko *et al.* [82GLU/GUR] for the gaseous species UF^- and UF_2^- , which are isoelectronic with the corresponding neutral neptunium fluoride species. These assumptions give

$$\begin{aligned} S_m^\circ(\text{NpF}, \text{g}, 298.15 \text{ K}) &= (251 \pm 5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{NpF}, \text{g}, 298.15 \text{ K}) &= (33.8 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ \\ S_m^\circ(\text{NpF}_2, \text{g}, 298.15 \text{ K}) &= (304 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{NpF}_2, \text{g}, 298.15 \text{ K}) &= (55.9 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

Full tables of the estimated thermal functions of these species up to 2000 K are given by Rand and Fuger [2000RAN/FUG].

9.1.2.2 $\text{NpF}_3(\text{cr})$

9.1.2.2.a Enthalpy of formation

The enthalpy of formation of $\text{NpF}_3(\text{cr})$ is estimated from the correlation between the difference of the enthalpies of formation of the actinide trihalides and the aqueous M^{3+} ions and the radius of the M^{3+} ions, as discussed in detail by Fuger *et al.* [83FUG/PAR].

The data in the first two lines of Table 9.1 when combined with the ionic radius of Np^{3+} give the tabulated value for $\Delta_f H_m^\circ(\text{NpF}_3, \text{cr}, 298.15 \text{ K}) - \Delta_f H_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K})$. The ionic radii in Table 9.1 have been taken from [76SHA] which with the selected $\Delta_f H_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K}) = -(527.2 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$ selected by this review (identical to [76FUG/OET]) gives finally

$$\Delta_f H_m^\circ(\text{NpF}_3, \text{cr}, 298.15 \text{ K}) = -(1529.0 \pm 8.3) \text{ kJ}\cdot\text{mol}^{-1}$$

9.1.2.2.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of $\text{NpF}_3(\text{cr})$, and the standard entropy is derived from two related estimates from the entropies of

Table 9.1: Extrapolation of $\Delta_f H_m^\circ(\text{MF}_3, \text{cr}) - \Delta_f H_m^\circ(\text{M}^{3+}, \text{aq})$ vs. ionic radii of M^{3+} for a coordination number of VI.

Element	Ionic radius ($\times 10^{10}$ m)	$\Delta_f H_m^\circ(\text{MF}_3, \text{cr}) - \Delta_f H_m^\circ(\text{M}^{3+}, \text{aq})$	Reference
U	1.025	$-(1012.3 \pm 6.0)$ kJ·mol ⁻¹	[92GRE/FUG]
Pu	1.00	$-(994.9 \pm 2.1)$ kJ·mol ⁻¹	This review
Np	1.01	$-(1001.8 \pm 8.0)$ kJ·mol ⁻¹	Interpolated

UF₃(cr) and PuF₃(cr): the spin-only method and the simple average of the entropies [2000RAN/FUG]. From the two estimates of 125.0 and 124.8 J·K⁻¹·mol⁻¹, the selected value is

$$S_m^\circ(\text{NpF}_3, \text{cr}, 298.15 \text{ K}) = (124.9 \pm 2.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.2.2.c High temperature heat capacity

There are no measurements of the heat capacity and values have been estimated to be close to the mean of UF₃(cr) [92GRE/FUG] and PuF₃(cr) (Section 18.1.2.2);

$$C_{p,m}^\circ(\text{NpF}_3, \text{cr}, T) = (105.2 + 0.812 \times 10^{-3}T - 10.0 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 K to 1735 K.

$$C_{p,m}^\circ(\text{NpF}_3, \text{cr}, 298.15 \text{ K}) = (94.2 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.2.2.d Fusion data

The fusion data and heat capacity of the liquid are all taken to be close to the mean of the values for UF₃(cr) and PuF₃(cr), giving:

$$\begin{aligned} T_{\text{fus}} &= (1735 \pm 30) \text{ K} \\ \Delta_{\text{fus}} H_m^\circ(\text{NpF}_3, \text{cr}, 1735 \text{ K}) &= (36.1 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{NpF}_3, \text{l}) &= (132 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

9.1.2.3 NpF₃(g)

9.1.2.3.a Enthalpy of formation

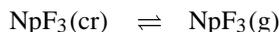
There are no vapour pressure measurements for NpF₃(g), and the enthalpy of formation has been estimated by assuming that the vapour pressure is intermediate between those of UF₃(cr) [92GRE/FUG] and PuF₃(cr) [2000RAN/FUG] which in the region where they have been measured differ by a factor of between 2 and 3. However, it

should be noted that although the vapour pressures of UF₆, NpF₆ and PuF₆ in the liquid state follow this expected behaviour, the vapour pressure of NpF₆(cr) is slightly higher than those of UF₆(cr) and PuF₆(cr) (which are almost identical) [59WEI/WEA], so the uncertainty in the enthalpy of formation has been increased.

The selected value is

$$\Delta_f H_m^\circ(\text{NpF}_3, \text{g}, 298.15 \text{ K}) = -(1112 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$$

When combined with the entropy values estimated below, the calculated sublimation pressure for the reaction



is closely represented by the expression:

$$\log_{10}(p/\text{bar}) = -20574T^{-1} + 8.977$$

from 1000 to 1600 K.

9.1.2.3.b Standard entropy and heat capacity

The thermal functions of NpF₃(g) were calculated assuming the molecular parameters given by Rand and Fuger [2000RAN/FUG], using the rigid-rotator, harmonic oscillator approximation. The molecule is assumed to be pyramidal, with C_{3v} symmetry.

These assumptions give

$$\begin{aligned} S_m^\circ(\text{NpF}_3, \text{g}, 298.15 \text{ K}) &= (330.5 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{NpF}_3, \text{g}, 298.15 \text{ K}) &= (72.2 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

9.1.2.4 NpF₄(cr)

9.1.2.4.a Enthalpy of formation

The enthalpy of formation of NpF₄(cr) is estimated from the correlation between the difference of the enthalpies of formation of the actinide tetrahalides and the aqueous M⁴⁺ ions and the radius of the M⁴⁺ ions [76SHA], as discussed in detail by Fuger *et al.* [83FUG/PAR, 2000RAN/FUG]. This analysis when combined with $\Delta_f H_m^\circ(\text{Np}^{4+}, \text{aq}, 298.15 \text{ K}) = -(556.0 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$, selected in this review, gives

$$\Delta_f H_m^\circ(\text{NpF}_4, \text{cr}, 298.15 \text{ K}) = -(1874 \pm 16) \text{ kJ}\cdot\text{mol}^{-1}$$

which is the selected value.

9.1.2.4.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of NpF₄(cr), and the standard entropy is derived from two independent estimates: the spin-only method

and Latimer estimate [2000RAN/FUG]. From these two estimates of 153.8 and $153.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, the selected value is

$$S_{\text{m}}^{\circ}(\text{NpF}_4, \text{cr}, 298.15 \text{ K}) = (153.5 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.2.4.c High temperature heat capacity

This is assumed to be close to the mean of $\text{UF}_4(\text{cr})$ [92GRE/FUG] and the estimated value for $\text{PuF}_4(\text{cr})$, (see Section 18.1.2.4).

$$C_{p,\text{m}}^{\circ}(\text{NpF}_4, \text{cr}, T) = (122.635 + 9.684 \times 10^{-3}T - 8.36465 \times 10^{-5}T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 K to 1305 K.

9.1.2.4.d Fusion data

The fusion data and heat capacity of the liquid are all taken to be close to the values for $\text{UF}_4(\text{cr})$, giving:

$$\begin{aligned} T_{\text{fus}} &= (1305 \pm 30) \text{ K} \\ \Delta_{\text{fus}}H_{\text{m}}^{\circ}(\text{NpF}_4, \text{cr}, 1305 \text{ K}) &= (47 \pm 5) \text{ kJ}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{NpF}_4, \text{l}) &= (165 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

9.1.2.5 $\text{NpF}_4(\text{g})$

9.1.2.5.a Enthalpy of formation

The vapour pressure of $\text{NpF}_4(\text{cr})$ has been measured by Chudinov and Choporov [70CHU/CHO] from 902 to 1092 K, and by Kleinschmidt *et al.* [92KLE/LAU] from 818 to 979 K, both using the Knudsen effusion method. Chudinov and Choporov determined the amount of effused material directly by radiometric analysis, but Kleinschmidt *et al.* had to calculate the vapour pressures indirectly from the measured ion currents, assuming the cross-sections of NpF_3 and NpF_4 were the same as those of the uranium analogues. The pressures from the first study are lower by about a factor of four.

We have analysed these data by second- and third-law analyses, using the thermal functions for NpF_4 discussed below, to give the results shown in Table 9.2.

Table 9.2: Enthalpies of sublimation of $\text{NpF}_4(\text{cr})$. Values are in $\text{kJ}\cdot\text{mol}^{-1}$

Reference	$\Delta_{\text{sub}}H(\text{NpF}_4, 298.15 \text{ K})$	
	Second-law	Third-law
[70CHU/CHO]	(315.3 ± 3.6)	(313.3 ± 0.7)
[92KLE/LAU]	(286.8 ± 15.6)	(303.6 ± 4.4)

The excellent agreement between the second- and third-law analyses for the data by Chudinov and Choporov gives confidence to this study, which in addition measured the absolute values of the pressures, as distinct from the relative measurements by Kleinschmidt *et al.* It may be noted that were the $\text{NpF}_4(\text{g})$ molecule taken to have lower symmetry than tetrahedral (see below), the entropies and Gibbs energy functions, $-[G_m^\circ - H_m^\circ(298.15 \text{ K})]/T$, would be increased, thus worsening the second- and third-law disagreement from the study by Kleinschmidt *et al.* However, in view of their appreciably lower second-law enthalpy of sublimation (which should be independent of cross-sections), and the uncertainties in the electronic contributions to the calculated thermal properties of the vapour, the uncertainty in the selected value for the enthalpy of sublimation

$$\Delta_{\text{sub}}H(\text{NpF}_4, 298.15 \text{ K}) = (313.0 \pm 15.0) \text{ kJ}\cdot\text{mol}^{-1}$$

has been increased substantially.

This is identical to the assessed values for the enthalpy of sublimation of $\text{UF}_4(\text{cr})$ ($313 \text{ kJ}\cdot\text{mol}^{-1}$, [92GRE/FUG]), although this value should probably be reduced by $2\text{--}3 \text{ kJ}\cdot\text{mol}^{-1}$ to correct for revised thermal functions for the gaseous actinide tetrafluorides (*cf.* the discussion in the next section). The derived enthalpy of formation of $\text{NpF}_4(\text{g})$ is thus

$$\Delta_f H_m^\circ(\text{NpF}_4, \text{g}, 298.15 \text{ K}) = -(1561 \pm 22) \text{ kJ}\cdot\text{mol}^{-1}$$

This value (and the enthalpy of sublimation) are slightly different from those suggested by [2000RAN/FUG], since a small previously undetected error in a regression equation in [70CHU/CHO] has been corrected.

9.1.2.5.b Standard entropy and heat capacity

Konings *et al.* [96KON/BOO] have recently studied the infrared spectrum of $\text{UF}_4(\text{g})$ between 1300 and 1370 K. Based on this, and a re-analysis of the previously determined gas electron diffraction data, they have demonstrated that the $\text{UF}_4(\text{g})$ molecule almost certainly has tetrahedral symmetry and that the entropy of sublimation calculated from the vapour pressure measurements (see [92GRE/FUG]) is in substantial agreement with this model when the newly determined smaller stretching vibration frequency is used to calculate the thermal functions of $\text{UF}_4(\text{g})$. These molecular parameters for $\text{UF}_4(\text{g})$ have thus been adopted for the $\text{NpF}_4(\text{g})$ molecule, except for a small decrease in the M-F distance from $2.059 \times 10^{-10} \text{ m}$ for $\text{UF}_4(\text{g})$ to $2.05 \times 10^{-10} \text{ m}$ for $\text{NpF}_4(\text{g})$. The ground-state energy level was assumed to have a statistical weight of 6, and the higher electronic levels were taken to be the same as those suggested for the gaseous species UF_4^- by Glushko *et al.* [82GLU/GUR]. The calculated values for the entropy and heat capacity of $\text{NpF}_4(\text{g})$ at 298.15 K are

$$\begin{aligned} S_m^\circ(\text{NpF}_4, \text{g}, 298.15 \text{ K}) &= (369.8 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{NpF}_4, \text{g}, 298.15 \text{ K}) &= (95.3 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

and these are the selected values. The input data used and a complete table of thermal functions up to 2000 K are given by Rand and Fuger [2000RAN/FUG]. The input data are very similar to those suggested by Konings and Hildenbrand [98KON/HIL], which appeared after the current assessment was completed.

9.1.2.6 Intermediate fluorides and NpF₅(cr)

No solid fluorides between NpF₄(cr) and NpF₅(cr), analogous to the well-established uranium compounds U₄F₁₇(cr), U₂F₉(cr) have been found, (*cf.* plutonium fluorides). However NpF₅(cr) has been prepared by both reduction of NpF₆ [70COH/FRI, 80BAL/YEH, 82BRO/WHI, 93MAL/WIL] and oxidation of NpF₄ [75DRO/SER, 78DRO/SER]. Cohen *et al.* [70COH/FRI] and Brown *et al.* [82BRO/WHI] used iodine dissolved in IF₅ to reduce NpF₆, while Baluka *et al.* [80BAL/YEH] used PF₃ as a reductant; Drobyshevskii *et al.* [75DRO/SER, 78DRO/SER] reacted NpF₄ and KrF₂. Malm *et al.* [93MAL/WIL] have studied the reduction of NpF₆ in some detail; their preferred method of preparation was to react an anhydrous HF(aq) solution containing NpF₆⁻ ions with BF₃ and LiF. A range of colours is reported for NpF₅(cr), from creamy-white through bluish-white to yellow-brown. The latter material was shown to contain at least 98% Np(V) from its Mössbauer spectrum. NpF₅(cr) is isomorphous with the high temperature tetragonal form of UF₅(cr) (stable above *ca.* 398 K), space group I4/m with cell parameters $a = 6.5358 \times 10^{-10}$ m and $c = 4.4562 \times 10^{-10}$ m [93MAL/WIL]. This structure was retained at 133 K [82BRO/WHI], suggesting that NpF₅(cr) may not undergo the transformation to the different low-temperature tetragonal structure, space group I42d, that occurs in UF₅(cr).

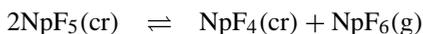
No thermodynamic data have been reported for NpF₅(cr), but approximate values have been derived from the observation by Malm *et al.* [93MAL/WIL] that disproportionation to NpF₆(g) and NpF₄ is not appreciable below 591 K, a much higher temperature than for UF₅(cr) which begins to lose UF₆(g) at 423 K.

The standard entropy and heat capacity have been assumed to be close to those for the isostructural UF₅(cr, α) [92GRE/FUG]:

$$S_{\text{m}}^{\circ}(\text{NpF}_5, \text{cr}, 298.15 \text{ K}) = (200 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,\text{m}}^{\circ}(\text{NpF}_5, \text{cr}, T) = (126 + 3 \times 10^{-2}T - 1.9 \times 10^5 \times T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ (298.15 \text{ to } 600 \text{ K})$$

If the pressure of NpF₆(g) in the reaction



is assumed to be 0.1 bar at 591 K, the derived value of $\Delta_{\text{f}}H_{\text{m}}^{\circ}$ (NpF₅, cr, 298.15 K) is $-(1941 \pm 5) \text{ kJ}\cdot\text{mol}^{-1}$, where the given uncertainty excludes those of NpF₄(cr) and NpF₆(g). The latter are independent, and the selected value for the enthalpy of formation of NpF₅(cr) is:

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{NpF}_5, \text{cr}, 298.15 \text{ K}) = -(1941 \pm 25) \text{ kJ}\cdot\text{mol}^{-1}$$

With these values the pressures of $\text{NpF}_6(\text{g})$ in the above decomposition reaction are *ca.* 3×10^{-5} bar at 400 K and 5×10^{-3} bar at 500 K, in accord with the observation of Malm *et al.* [93MAL/WIL].

9.1.2.7 $\text{NpF}_6(\text{cr})$

Osborne *et al.* [70OSB/WEI] have given an almost complete, consistent description of the relative properties of $\text{NpF}_6(\text{cr}, \text{l}, \text{g})$ based on their measurements of the low temperature heat capacity (7 to 350 K) and the vapour pressure measurements by Weinstock *et al.* [59WEI/WEA] from 273.15 to 350 K. Since there has been no other thermodynamic work on this compound, we have accepted the values of Osborne *et al.* [70OSB/WEI] with only essentially trivial updating, but have also ventured to estimate the enthalpies of formation of the crystal and gas.

9.1.2.7.a Enthalpy of formation

The enthalpy of sublimation of $\text{NpF}_6(\text{cr})$ is well defined below, but the individual enthalpies of formation of the solid and gas are not known accurately. Approximate values have been estimated by interpolating the difference $\Delta_f H_m^\circ(\text{MF}_6, \text{cr}) - \Delta_f H_m^\circ(\text{MO}_2^{2+}, \text{aq})$ for $\text{M} = \text{U}, \text{Np}, \text{Pu}$, using the ionic radii of the $\text{M}(\text{VI})$ ions (for co-ordination number VI) [76SHA] as the interpolator. Since these values are 0.73×10^{-10} m, 0.72×10^{-10} m and 0.71×10^{-10} m for U, Np and Pu, the value of the enthalpy difference, $\Delta_f H_m^\circ(\text{NpF}_6, \text{cr}) - \Delta_f H_m^\circ(\text{NpO}_2^{2+}, \text{aq})$, for Np becomes the mean of the corresponding values for U and Pu, namely $-(1109.0 \pm 15.0)$ $\text{kJ}\cdot\text{mol}^{-1}$, where the uncertainty is estimated here. With $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(860.7 \pm 4.7)$ $\text{kJ}\cdot\text{mol}^{-1}$ selected by this review, this gives finally $\Delta_f H_m^\circ(\text{NpF}_6, \text{cr}, 298.15 \text{ K}) = -(1969.7 \pm 15.7)$ $\text{kJ}\cdot\text{mol}^{-1}$. The selected value is the rounded value, with a somewhat increased uncertainty

$$\Delta_f H_m^\circ(\text{NpF}_6, \text{cr}, 298.15 \text{ K}) = -(1970 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$$

9.1.2.7.b Standard entropy and heat capacity

The low temperature heat capacity of $\text{NpF}_6(\text{cr})$ has been measured by Osborne *et al.* [70OSB/WEI] from 7 to 350 K. No anomalies were observed in the heat capacity curve over this temperature range. Because $\text{NpF}_6(\text{cr})$ has one non-bonding electron, there will be a twofold degeneracy in the ground-state, and it is anticipated that at some temperature below the current range of measurements, there will be a co-operative phenomenon to remove this degeneracy. Thus a term of $R \ln 2$ has been added to the entropy obtained by extrapolation of the observed heat capacity curve from 7 to 0 K. The validity of this addition is confirmed by the excellent agreement for the entropy of the gas as calculated from the calorimetric data and from statistical mechanics, as described in the following section (discussion on $\text{NpF}_6(\text{g})$). The derived standard entropy

and heat capacity of the solid at 298.15 K are:

$$\begin{aligned} S_{\text{m}}^{\circ}(\text{NpF}_6, \text{cr}, 298.15 \text{ K}) &= (229.09 \pm 0.50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{NpF}_6, \text{cr}, 298.15 \text{ K}) &= (167.44 \pm 0.40) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

The variation of the heat capacities of $\text{NpF}_6(\text{cr}$ and l) have been taken from the same study [70OSB/WEI] :

$$C_{p,\text{m}}^{\circ}(\text{NpF}_6, \text{cr}, T) = (62.333 + 352.547 \times 10^{-3}T) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 to 327.91 K, and

$$C_{p,\text{m}}^{\circ}(\text{NpF}_6, \text{l}, T) = (150.344 + 110.076 \times 10^{-3}T) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 327.91 to 350 K.

9.1.2.7.c Fusion data

The measured melting point, $(327.91 \pm 0.02) \text{ K}$ and the enthalpy of fusion from the calorimetric study [70OSB/WEI] agree excellently with those calculated from the vapour pressure curves for the solid and liquid [59WEI/WEA]. The selected values are

$$\begin{aligned} T_{\text{fus}} &= (327.91 \pm 0.02) \text{ K} \\ \Delta_{\text{fus}}H_{\text{m}}^{\circ}(\text{NpF}_6, \text{cr}, 327.91 \text{ K}) &= (17.524 \pm 0.017) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

9.1.2.8 $\text{NpF}_6(\text{g})$

9.1.2.8.a Enthalpy of formation

This has been calculated from the estimate for $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{NpF}_6, \text{cr}, 298.15 \text{ K})$ selected by this review, and the enthalpy of sublimation calculated from the vapour pressure measurements of Weinstock *et al.* [59WEI/WEA] for the crystal and liquid from 273.15 to 350.0 K. Their data have been treated by a third-law analysis to give the enthalpy of sublimation

$$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(\text{NpF}_6, 298.15 \text{ K}) = (48.34 \pm 0.07) \text{ kJ}\cdot\text{mol}^{-1}$$

As indicated by the excellent agreement in the calculated and experimental entropies of sublimation implied by the discussion in the next section, there is only a very small drift in the calculated third-law enthalpies from these vapour pressure data.

The derived enthalpy of formation of the vapour is

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{NpF}_6, \text{g}, 298.15 \text{ K}) = -(1921.66 \pm 20.00) \text{ kJ}\cdot\text{mol}^{-1}$$

where the additional significant figures are retained to reproduce the correct vapour pressure from thermodynamic calculations.

9.1.2.8.b Standard entropy and heat capacity

The thermal functions of $\text{NpF}_6(\text{g})$ were calculated using the rigid-rotator, harmonic oscillator approximation. The molecule is taken to be octahedral with O_h symmetry, with a Np-F interatomic distance of 1.981×10^{-10} m, taken from the electron diffraction measurements of [68KIM/SCH]. The frequencies were taken from the assessment by Osborne *et al.* [70OSB/WEI], whose values are based mainly on the review by Weinstock and Goodman [65WEI/GOO], plus the later experimental value of Frlec and Claasen [67FRL/CLA]. The molecular parameters are given in full in the report by Rand and Fuger [2000RAN/FUG].

Thus,

$$\begin{aligned} S_m^\circ(\text{NpF}_6, \text{g}, 298.15 \text{ K}) &= (376.643 \pm 0.500) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{NpF}_6, \text{g}, 298.15 \text{ K}) &= (129.072 \pm 1.000) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

Osborne *et al.* [70OSB/WEI] have made a rigorous calculation of the entropy of the ideal $\text{NpF}_6(\text{g})$ at 340 K by adding the entropy of vaporisation from the vapour pressure measurements of Weinstock *et al.* [59WEI/WEA] to that of the liquid from purely calorimetric measurements. Their value of $(393.78 \pm 1.59) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which includes a correction of $(0.75 \pm 0.25) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for non-ideality of the vapour, agrees excellently with that for the ideal gas calculated from the molecular parameters given in the report by Rand and Fuger [2000RAN/FUG], $(393.94 \pm 0.50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, where the uncertainty is that suggested by Osborne *et al.* [70OSB/WEI].

The heat capacities of the vapour have been fitted to the expression

$$\begin{aligned} C_{p,m}^\circ(\text{NpF}_6, \text{g}, T) &= (143.242 + 2.44158 \times 10^{-2} T \\ &\quad - 1.13115 \times 10^{-5} T^2 - 1.8174 \times 10^6 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

from 298.15K to 1000 K.

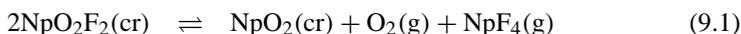
9.1.2.9 $\text{NpF}_7(\text{g})$

Fried and Schreiner [69FRI/SCH] were unable to detect any higher fluoride than $\text{NpF}_6(\text{g})$ when the latter was reacted with $\text{F}_2(\text{g})$ under pressure and with $\text{KrF}_2(\text{g})$, so $\text{NpF}_7(\text{g})$ is probably not a stable molecule.

9.1.2.10 $\text{NpO}_2\text{F}_2(\text{cr})$

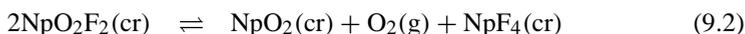
Kleinschmidt *et al.* [92KLE/LAU2] have measured the pressures of $\text{NpF}_4(\text{g})$ arising from the decomposition of $\text{NpO}_2\text{F}_2(\text{cr})$ by mass-spectrometric Knudsen effusion. The results of two runs differed by about a factor of 3, probably due to a change in instrument sensitivity. The only Np-containing ions observed were NpF_n^+ , $n = 1$ to 4, suggesting the decomposition of $\text{NpO}_2\text{F}_2(\text{cr})$ gives predominantly $\text{NpF}_4(\text{g})$ and is thus simpler than that of $\text{UO}_2\text{F}_2(\text{cr})$, which gives $\text{UF}_4(\text{g})$, $\text{UF}_5(\text{g})$ and $\text{UOF}_4(\text{g})$ in the gas phase. The product after loss of most of the $\text{NpF}_4(\text{g})$ showed the X-ray diffraction

pattern corresponding to $\text{NpO}_2(\text{cr})$, although the weight loss was less than half of that corresponding to the reaction



This was attributed to the presence of considerable $\text{NpO}_2(\text{cr})$ in the original sample, which was prepared by the controlled hydrolysis of $\text{NpF}_6(\text{cr})$ by small amounts of water in anhydrous HF. The results of this study have been interpreted in terms of the reaction (9.1), which was probably the principal process occurring in the decomposition. The pressure of $\text{O}_2(\text{g})$ could not be measured under the conditions of the experiment, and was assumed to be the same as that of $\text{NpF}_4(\text{g})$, in accord with reaction (9.1). This would not, of course, be true if other modes of decomposition (*e.g.*, to Np_2O_5) were also occurring.

Since these experiments by Kleinschmidt *et al.* [92KLE/LAU2] were carried out in the same apparatus, and in the same period as the study of the sublimation of $\text{NpF}_4(\text{cr})$ [92KLE/LAU], we have preferred to combine the two studies to calculate the properties of $\text{NpO}_2\text{F}_2(\text{cr})$. When the mean $\text{NpF}_4(\text{g})$ pressures over $\text{NpO}_2\text{F}_2(\text{cr})$ in the two runs is combined with the similar pressures over pure $\text{NpF}_4(\text{cr})$, the Gibbs energy of the similar reaction involving $\text{NpF}_4(\text{cr})$



is calculated to be

$$\Delta_r G_m(9.2) = (272642 - 146.109 T) \text{ J}\cdot\text{mol}^{-1}$$

from 829 to 996 K.

When the derived values of the enthalpy and entropy of this reaction at the mean temperature of 912 K are reduced to 298.15 K using the thermal functions of $\text{NpO}_2(\text{cr})$, $\text{NpO}_2\text{F}_2(\text{cr})$ and $\text{NpF}_4(\text{cr})$ assessed in this review, the corresponding values are $\Delta_r H(9.2, 298.15 \text{ K}) = (273.4 \pm 15.0) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S(9.2, 298.15 \text{ K}) = (146.4 \pm 15.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, where the uncertainties have been increased to allow for uncertainties in the oxygen pressure. These values in turn give for the enthalpy of formation $\Delta_f H_m^\circ(\text{NpO}_2\text{F}_2, \text{cr}, 298.15 \text{ K}) = -(1610.7 \pm 21.2) \text{ kJ}\cdot\text{mol}^{-1}$, where the uncertainty includes those of $\text{NpF}_4(\text{cr})$ and $\text{NpO}_2(\text{cr})$.

However, this value would make the difference $\Delta_f H_m^\circ(\text{UO}_2\text{F}_2, \text{cr}, 298.15 \text{ K}) - \Delta_f H_m^\circ(\text{NpO}_2\text{F}_2, \text{cr}, 298.15 \text{ K})$ only $-42.8 \text{ kJ}\cdot\text{mol}^{-1}$, whereas the corresponding difference for the aqueous MO_2^{2+} ions is $-158.3 \text{ kJ}\cdot\text{mol}^{-1}$. Thus with the above enthalpy of formation of $\text{NpO}_2\text{F}_2(\text{cr})$, its solubility in water would be extremely small (less than 10^{-9} M at $\text{pH}=5$). Since by comparison with $\text{UO}_2\text{F}_2(\text{cr})$, which is very soluble, this is thought to be very improbable, it seems that some substantial experimental error, possibly premature decomposition of their NpO_2F_2 , occurred in the experiments of Kleinschmidt *et al.* [92KLE/LAU2]. This topic is discussed more fully in the review by Rand and Fuger [2000RAN/FUG], but at the moment no value can be recommended for the enthalpy of formation of $\text{NpO}_2\text{F}_2(\text{cr})$.

9.1.2.10.a Standard entropy and heat capacity

A value of the standard entropy can be derived from the second-law analysis of the data of Kleinschmidt *et al.* [92KLE/LAU2] discussed above. The value of $(146.4 \pm 15.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $\Delta_r S(298.15 \text{ K})$ for reaction (9.1) gives the value $S_m^\circ(\text{NpO}_2\text{F}_2, \text{cr}, 298.15 \text{ K}) = (146.4 \pm 15.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which is consistent with the corresponding value for $\text{UO}_2\text{F}_2(\text{cr})$ [92GRE/FUG] namely $(135 \pm 3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. However, in view of the discrepancy noted above for the enthalpy of formation, no value for the entropy has been selected.

The heat capacities which have been used in the above analysis were estimated to be the same as those of $\text{UO}_2\text{F}_2(\text{cr})$ given by Glushko *et al.* [82GLU/GUR].

$$\begin{aligned} C_{p,m}^\circ(\text{NpO}_2\text{F}_2, \text{cr}, T) &= (106.238 + 2.8326 \times 10^{-2} T \\ &\quad - 1.0208 \times 10^{-6} T^2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ &\quad (T = 298.15 - 1000 \text{ K}) \end{aligned}$$

The heat capacity equation for $\text{UO}_2\text{F}_2(\text{cr})$ given by Grenthe *et al.* [92GRE/FUG] is valid only up to 400 K; therefore it cannot be used to estimate that for $\text{NpO}_2\text{F}_2(\text{cr})$.

9.1.2.11 $\text{Na}_3\text{NpF}_8(\text{cr})$

Trevorrow *et al.* [68TRE/GER] have shown that neptunium hexafluoride reacts reversibly with $\text{NaF}(\text{cr})$ at 523 to 673 K to form the ternary fluoride containing $\text{Np}(\text{V})$,



and have measured the equilibrium constant to be

$$\log_{10}(K_p/\text{bar}^{-0.5}) = (3147T^{-1} - 2.787)$$

from 523 to 673 K, giving

$$\Delta_r G_m(9.3) = (-60249 + 53.354 T) \text{ J}\cdot\text{mol}^{-1}$$

With the data for $\text{NaF}(\text{cr})$ from [82GLU/GUR] and the heat capacities estimated below, the derived values for reaction (9.3) are $\Delta_r H(298.15 \text{ K}) = -(62.7 \pm 6.9) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S(298.15 \text{ K}) = -(59.4 \pm 11.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, giving finally

$$\begin{aligned} \Delta_f H_m^\circ(\text{Na}_3\text{NpF}_8, \text{cr}, 298.15 \text{ K}) &= -(3714 \pm 21) \text{ kJ}\cdot\text{mol}^{-1} \\ S_m^\circ(\text{Na}_3\text{NpF}_8, \text{cr}, 298.15 \text{ K}) &= (369 \pm 12) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

These correspond to an enthalpy change of $-43.2 \text{ kJ}\cdot\text{mol}^{-1}$ and to an entropy change of $+15.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the formation reaction from $\text{NaF}(\text{cr})$ and $\text{NpF}_5(\text{cr})$. Reaction (9.3) is, of course, different from the corresponding reaction for $\text{UF}_6(\text{g})$, in which $\text{Na}_2\text{UF}_8(\text{cr})$, containing $\text{U}(\text{VI})$, is formed.

The heat capacities of $\text{Na}_3\text{NpF}_8(\text{cr})$ which have been used in the above analysis were estimated to be close to the sum of $C_{p,m}^\circ(3\text{NaF}(\text{cr}) + \text{NpF}_5(\text{cr}))$:

$$C_{p,m}^\circ(\text{Na}_3\text{NpF}_8, \text{cr}, T) = (270 + 5.66 \times 10^{-2}T - 1.3 \times 10^6 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ (298.15 \text{ to } 800 \text{ K})$$

9.1.3 Neptunium chloride compounds

9.1.3.1 $\text{NpCl}_3(\text{cr})$

9.1.3.1.a Enthalpy of formation

The enthalpy of formation of $\text{NpCl}_3(\text{cr})$ has not been measured, and is estimated by two methods [2000RAN/FUG]. The first is from the correlation between the difference of the enthalpies of formation of the actinide trihalides and the aqueous M^{3+} ions and the ionic radius of M^{3+} , as discussed in detail by Fuger *et al.* [83FUG/PAR]. The second estimate is by interpolation of the differences of the enthalpies of formation $\Delta_f H_m^\circ(\text{MCl}_3, \text{cr}, 298.15 \text{ K}) - \Delta_f H_m^\circ(\text{MBr}_3, \text{cr}, 298.15 \text{ K})$, for $\text{M} = \text{U}$ [92GRE/FUG] and Pu , (this review).

The selected value is the mean:

$$\Delta_f H_m^\circ(\text{NpCl}_3, \text{cr}, 298.15 \text{ K}) = -(896.8 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$$

9.1.3.1.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of $\text{NpCl}_3(\text{cr})$, and the standard entropy is derived from three reasonably consistent estimates. Details of these estimates (162.9, 160.0, 158.4 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) are given in [2000RAN/FUG]; the selected value is

$$S_m^\circ(\text{NpCl}_3, \text{cr}, 298.15 \text{ K}) = (160.4 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.3.1.c High temperature heat capacity

Lacking experimental data, the heat capacity of $\text{NpCl}_3(\text{cr})$ is assumed to be similar to $\text{UCl}_3(\text{cr})$ ¹. The suggested values for $\text{NpCl}_3(\text{cr})$ are:

$$C_{p,m}^\circ(\text{NpCl}_3, \text{cr}, T) = (89.6 + 27.5 \times 10^{-3}T + 3.6 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

¹It should be noted that the coefficient of T in the equation for $C_{p,m}^\circ(\text{UCl}_3)$ given by Grenthe *et al.* [92GRE/FUG] is incorrect. Even when this value is corrected to reproduce $C_{p,m}^\circ(298.15 \text{ K})$, there is a shallow minimum in $C_{p,m}^\circ$ around 315 K [95GRE/PUI], which is probably an artefact of the fitting procedure.

from 298.15 to 1075 K, and hence

$$C_{p,m}^{\circ}(\text{NpCl}_3, \text{cr}, 298.15 \text{ K}) = (101.85 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.3.1.d Fusion data

The fusion data and heat capacity of the liquid are all taken to be close to the mean of the values for $\text{UCl}_3(\text{cr})$ (1115 K [96KOV/BOO]) and $\text{PuCl}_3(\text{cr})$ (1041 K, this review), giving:

$$\begin{aligned} T_{\text{fus}} &= (1075 \pm 30) \text{ K} \\ \Delta_{\text{fus}}H_{\text{m}}^{\circ}(\text{NpCl}_3, \text{cr}, 1735 \text{ K}) &= (50 \pm 8) \text{ kJ}\cdot\text{mol}^{-1} \\ C_{p,m}^{\circ}(\text{NpCl}_3, \text{l}) &= (137 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

9.1.3.2 $\text{NpCl}_3(\text{g})$

9.1.3.2.a Enthalpy of formation

There are no vapour pressure measurements for $\text{NpCl}_3(\text{g})$, and the enthalpy of formation has been estimated by assuming that the vapour pressure is intermediate between those of $\text{UCl}_3(\text{g})$, calculated from the values given by Grenthe *et al.* [92GRE/FUG], and $\text{PuCl}_3(\text{g})$, selected by this review, which in the region where the latter have been measured differ by a factor of 2-3. As noted in Section 9.1.2.3 on $\text{NpF}_3(\text{g})$, it has been necessary to assign a relative high uncertainty to this enthalpy of formation.

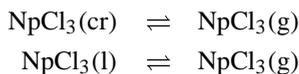
The selected value corresponds to

$$\Delta_{\text{sub}}H(298.15 \text{ K}) = (307.8 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$$

and hence the selected value is

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{NpCl}_3, \text{g}, 298.15 \text{ K}) = -(589.0 \pm 10.4) \text{ kJ}\cdot\text{mol}^{-1}$$

When combined with the entropy values estimated below, the calculated vapour pressures for the sublimation and vaporisation reactions



are closely represented by the respective expressions:

$$\begin{aligned} \log_{10}(p/\text{bar}) &= -15177T^{-1} + 9.057 \quad (\text{from } 900 \text{ to } 1075 \text{ K}) \\ \log_{10}(p/\text{bar}) &= -12259T^{-1} + 6.346 \quad (\text{from } 1075 \text{ to } 1300 \text{ K}) \end{aligned}$$

9.1.3.2.b Standard entropy and heat capacity

The thermal functions of $\text{NpCl}_3(\text{g})$ were calculated using the rigid-rotator, harmonic oscillator approximation. The molecular parameters are given in full in the report by Rand and Fuger [2000RAN/FUG]. The selected molecular parameters give

$$\begin{aligned} S_{\text{m}}^{\circ}(\text{NpCl}_3, \text{g}, 298.15 \text{ K}) &= (362.8 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{NpCl}_3, \text{g}, 298.15 \text{ K}) &= (78.5 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

9.1.3.3 $\text{NpCl}_4(\text{cr})$

9.1.3.3.a Enthalpy of formation

Fuger *et al.* [69FUG/BRO] measured the enthalpy of solution of $\text{NpCl}_4(\text{cr})$ in 1 M HCl to be $-(225.39 \pm 0.54) \text{ kJ}\cdot\text{mol}^{-1}$. With the partial molar enthalpy of formation of Cl^- in this solution, $-(164.37 \pm 0.10) \text{ kJ}\cdot\text{mol}^{-1}$ [2000RAN/FUG], and $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Np}^{4+}, 1 \text{ M HCl}, 298.15 \text{ K}) = -(551.9 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$, [2000RAN/FUG], the enthalpy of formation of $\text{NpCl}_4(\text{cr})$ becomes:

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{NpCl}_4, \text{cr}, 298.15 \text{ K}) = -(984.0 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

which is the selected value.

9.1.3.3.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of $\text{NpCl}_4(\text{cr})$, and the standard entropy is derived from three reasonably consistent estimates. Details of these estimates (209.6, 199.5, 197.4 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) are given in [2000RAN/FUG]; the selected value is biased towards the lower value [2000RAN/FUG]

$$S_{\text{m}}^{\circ}(\text{NpCl}_4, \text{cr}, 298.15 \text{ K}) = (200 \pm 8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.3.3.c High temperature heat capacity

This is assumed to be similar to that of $\text{UCl}_4(\text{cr})$, which have been refitted from the data of Ferguson and Prather (given in full by Katz and Rabinowitch [51KAT/RAB]), Ginnings and Corruccini [47GIN/COR] and Popov *et al.* [59POP/GAL]. The selected values for $\text{NpCl}_4(\text{cr})$ are represented by the equation

$$C_{p,\text{m}}^{\circ}(\text{NpCl}_4, \text{cr}, T) = (112.5 + 3.6 \times 10^{-2} T - 1.1 \times 10^5 \times T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 to 811 K, and hence

$$C_{p,\text{m}}^{\circ}(\text{NpCl}_4, \text{cr}, 298.15 \text{ K}) = (122.0 \pm 6.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.3.3.d Fusion data

The melting point and enthalpy of fusion are calculated from the vapour pressure studies discussed in the next section.

$$\begin{aligned} T_{\text{fus}} &= (811 \pm 15) \text{ K} \\ \Delta_{\text{fus}}H_{\text{m}}^{\circ}(\text{NpCl}_4, \text{cr}, 811 \text{ K}) &= (59.6 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

The liquid heat capacity is estimated to be similar to that of $\text{UCl}_4(\text{l})$ [59POP/GAL],

$$C_{p,\text{m}}^{\circ}(\text{NpCl}_4, \text{l}) = (108.0 + 60.0 \times 10^{-3}T) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 811 to 1000 K.

9.1.3.4 $\text{NpCl}_4(\text{g})$

9.1.3.4.a Enthalpy of formation

Gruen *et al.* [76GRU/MCB] have analysed the data on the vapour pressure of $\text{NpCl}_4(\text{cr}, \text{l})$ reported by Choporov and Chudinov [68CHO/CHU] (Knudsen effusion, from 552 to 696 K), Malm [57MAL] (Bourdon gauge, from 709 to 874 K) and themselves (spectroscopic analysis, from 741 to 905 K). The three sets of measurements are very consistent, and we have accepted the equations given by Gruen *et al.* for the vapour pressure of the solid,

$$\log_{10}(p/\text{bar}) = -9932T^{-1} + 10.661$$

from 552 to 810 K, and the liquid

$$\log_{10}(p/\text{bar}) = -6471T^{-1} + 6.351$$

from 812 to 905 K.

The first equation has been combined with the estimated thermal functions of the solid (Section 9.1.3.3) and the vapour (see below) to calculate the third-law enthalpy of sublimation at 298.15 K

$$\Delta_{\text{sub}}H_{\text{m}}(\text{NpCl}_4, 298.15 \text{ K}) = (197.0 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$$

where the uncertainty is estimated here to allow for some uncertainty in the thermal functions. The experimental entropy of sublimation at the mid temperature, 912 K, ($204.1 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) agrees well with that calculated from the estimated molecular parameters ($201.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The above enthalpy of sublimation is the selected value and gives finally

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{NpCl}_4, \text{g}, 298.15 \text{ K}) = -(787.0 \pm 4.6) \text{ kJ}\cdot\text{mol}^{-1}$$

The consistency of the vapour pressure measurements around the melting point by Malm [57MAL] and Gruen *et al.* [76GRU/MCB] is not high enough to define the melting point with great precision, and we have accepted the value of $T_{\text{fus}} = (811 \pm$

15) K suggested by Gruen *et al.* from a statistical analysis of all the vapour pressure data. This is the same as that measured directly on a 20 μg sample by Fried and Davidson [52FRI/DAV], but appreciably higher than the direct measurement (790.7 ± 2.5) K by Choporov and Chudinov [68CHO/CHU]. The vapour pressure data for the liquid then define quite well the enthalpy of fusion

$$\Delta_{\text{fus}}H_{\text{m}}(\text{NpCl}_4, \text{cr}, 811 \text{ K}) = (59.6 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$$

A plot of the experimental and calculated vapour pressures is given in the report by Rand and Fuger [2000RAN/FUG].

9.1.3.4.b Standard entropy and heat capacity

The thermal functions of $\text{NpCl}_4(\text{g})$ have been estimated from statistical mechanical calculations using the rigid-rotator, harmonic oscillator approximation. Following the work of Haaland *et al.* [95HAA/MAR] on the electron diffraction and infrared spectroscopy of $\text{UCl}_4(\text{g})$, the molecule was assumed to be an undistorted tetrahedron, with an Np-Cl distance of 2.50×10^{-10} m, *cf.* $r(\text{U-Cl}) = 2.503 \times 10^{-10}$ m in $\text{UCl}_4(\text{g})$ [95HAA/MAR]. The vibration frequencies were taken to be the same as those determined for $\text{UCl}_4(\text{g})$ by these authors [95HAA/MAR], and the electronic states were taken to be the same as those estimated for the isoelectronic gaseous molecule UCl_4^- by Hildenbrand *et al.* [85HIL/GUR], but with higher statistical weights in view of the higher symmetry used. The full data used are given in the report by Rand and Fuger [2000RAN/FUG]. They are very similar to those suggested by Konings and Hildenbrand [98KON/HIL], which appeared after the current assessment was completed. As noted above the entropy of sublimation calculated with these assumptions is in good agreement with the experimental value. Clearly other combinations of molecular parameters could provide as good agreement, but the current set has the merit of being consistent with the broad corpus of other data adopted for the gaseous actinide halide species.

The selected data give

$$\begin{aligned} S_{\text{m}}^{\circ}(\text{NpCl}_4, \text{g}, 298.15 \text{ K}) &= (423.0 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{NpCl}_4, \text{g}, 298.15 \text{ K}) &= (105.0 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

9.1.3.5 $\text{NpCl}_5(\text{g})$

Gruen *et al.* [76GRU/MCB] observed no new features in the spectrum of $\text{NpCl}_4(\text{g})$ in the presence of $\text{Cl}_2(\text{g})$ from 573 to 1273 K, compared to $\text{NpCl}_4(\text{g})$ alone. A closed cell was used, so p_{Cl_2} increased with temperature (from *ca.* 1.4 bar at 573 K to *ca.* 3.1 bar at 1273 K). This suggests that $\text{NpCl}_5(\text{g})$ is not formed in appreciable amounts under these conditions.

9.1.3.6 NpOCl₂(cr)

9.1.3.6.a Enthalpy of formation

Fuger *et al.* [69FUG/BRO] have studied the dissolution of NpOCl₂(cr) in 1 M HCl. Their enthalpy of dissolution $-(140.75 \pm 0.50)$ kJ·mol⁻¹ gives with auxiliary data from [2000RAN/FUG]

$$\Delta_f H_m^\circ(\text{NpOCl}_2, \text{cr}, 298.15 \text{ K}) = -(1025.7 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

However, with this value and the selected thermal functions of NpCl₄(cr) and NpOCl₂(cr), the Gibbs energy of the decomposition reaction



is slightly negative at all temperatures up to 775 K (*ca.* $-(3.3 \pm 3.1)$ kJ·mol⁻¹ at 298.15 K), making NpOCl₂(cr) unstable with respect to this decomposition. We therefore prefer to make the enthalpy of formation of NpOCl₂(cr) slightly more negative than the above value. As noted by Fuger *et al.* [83FUG/PAR], the extrapolation of the difference, $\Delta_f H_m^\circ(\text{MOCl}_2, \text{cr}, 298.15 \text{ K}) - \Delta_f H_m^\circ(\text{M}^{4+}, \text{aq}, 298.15 \text{ K})$, vs. ionic radii of M⁴⁺, taken from [76SHA], suggests a value of $-(1037.6 \pm 12.0)$ kJ·mol⁻¹ for the enthalpy of formation of NpOCl₂(cr). The selected value is

$$\Delta_f H_m^\circ(\text{NpOCl}_2, \text{cr}, 298.15 \text{ K}) = -(1030.0 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$$

which includes both the experimental and extrapolated values within the uncertainty, and keeps NpOCl₂(cr) stable with respect to decomposition to NpO₂(cr) and NpCl₄(cr) at all temperatures up to the melting point of NpCl₄(cr). Above this temperature, the vapour pressure of NpCl₄(g) above NpOCl₂(cr) becomes appreciable (as it does above NpCl₄(l)).

9.1.3.6.b Standard entropy and heat capacity

The standard entropy is derived from two consistent estimates: the Latimer method and the spin-only contribution [2000RAN/FUG]. From these two estimates of 144.0 and 140.7 J·K⁻¹·mol⁻¹, the selected value is

$$S_m^\circ(\text{NpOCl}_2, \text{cr}, 298.15 \text{ K}) = (143.5 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

since a value weighted toward the higher estimate is in better accord with the experimental enthalpy of formation, as discussed in the preceding section.

9.1.3.6.c High temperature heat capacity

These have been estimated to be similar to those for UOCl₂(cr) [92GRE/FUG]

$$C_{p,m}^\circ(\text{NpOCl}_2, \text{cr}, T) = (98.8 + 22.0 \times 10^{-3}T - 9.2 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 to 1000 K, and hence

$$C_{p,m}^\circ(\text{NpOCl}_2, \text{cr}, 298.15 \text{ K}) = (95.0 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.3.7 Cs₂NpCl₆(cr)

9.1.3.7.a Enthalpy of formation

Fuger *et al.* [83FUG/PAR] have analysed the results of the calorimetric study by Fuger and Brown [71FUG/BRO] who reported the enthalpy of the dissolution of this complex salt in 1 M HCl to be $-(84.35 \pm 0.29)$ kJ·mol⁻¹. We have reworked this analysis, with the following different enthalpy values: $\Delta_f H_m^\circ(\text{CsCl, cr, 298.15 K}) = -(442.31 \pm 0.16)$ kJ·mol⁻¹ [82GLU/GUR], compatible with [89COX/WAG]; $\Delta_f H_m^\circ(\text{NpCl}_4, \text{ cr, 298.15 K}) = -(984.0 \pm 1.8)$ kJ·mol⁻¹ (this review), $\Delta_{\text{sln}} H_m(\text{CsCl, 1 M HCl}) = +(16.69 \pm 0.08)$ kJ·mol⁻¹ (see Section 9.1.3.9) and $\Delta_{\text{sln}} H_m(\text{NpCl}_4, \text{ 1 M HCl}) = -(225.39 \pm 0.34)$ kJ·mol⁻¹ (this review). The calculated value, from 1 M HCl medium, for the enthalpy of formation of the complex salt becomes $\Delta_f H_m^\circ(\text{Cs}_2\text{NpCl}_6, \text{ cr, 298.15 K}) = -(1976.3 \pm 1.9)$ kJ·mol⁻¹.

Fuger and Brown also made measurements of the enthalpy of dissolution of the salt in 6 M HCl, as $-(31.30 \pm 0.42)$ kJ·mol⁻¹. Using $\Delta_{\text{sln}} H_m(\text{CsCl, 6 M HCl}) = +(11.88 \pm 0.13)$ kJ·mol⁻¹, $\Delta_f H_m(\text{HCl, 6 M HCl, partial}) = -(153.40 \pm 0.11)$ kJ·mol⁻¹, and the enthalpy of formation of Np⁴⁺ in 6 M HCl, as $-(532.9 \pm 2.1)$ kJ·mol⁻¹ [2000RAN/FUG] extrapolated from the variation of the enthalpies of solution of other actinide quadrivalent ions between 1 M and 6 M HCl. We obtain from this medium $\Delta_f H_m^\circ(\text{Cs}_2\text{NpCl}_6, \text{ cr, 298.15 K}) = -(1976.1 \pm 2.2)$ kJ·mol⁻¹.

The mean of the two results is $-(1976.2 \pm 1.9)$ kJ·mol⁻¹, which is the selected value

$$\Delta_f H_m^\circ(\text{Cs}_2\text{NpCl}_6, \text{ cr, 298.15 K}) = -(1976.2 \pm 1.9) \text{ kJ}\cdot\text{mol}^{-1}$$

This corresponds to an enthalpy of formation of -107.6 kJ·mol⁻¹ from the binary halides, showing the appreciable stabilisation given to the actinide tetrahalides by complexing with CsCl, - *cf.* in particular, the stability of Cs₂PuCl₆(cr), as against the instability of PuCl₄(cr) - see Section 18.1.3.9.a.

9.1.3.7.b Standard entropy

The standard entropy has been taken to be the mean of two reasonably consistent estimates. Details of these estimates (405.3 and 418.0 J·K⁻¹·mol⁻¹) are given in [2000RAN/FUG]; the selected value is

$$S_m^\circ(\text{Cs}_2\text{NpCl}_6, \text{ cr, 298.15 K}) = (410 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

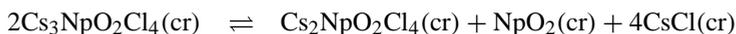
9.1.3.8 Cs₃NpO₂Cl₄(cr) and Cs₂NpO₂Cl₄(cr)

The enthalpies of formation of these compounds (which contain Np(V) and Np(VI), respectively), were reported by Fuger [79FUG] from unpublished enthalpies of solution measurements in 1 M HCl by Bastin and Fuger, $\Delta_{\text{sln}} H_m(\text{Cs}_3\text{NpO}_2\text{Cl}_4, \text{ cr, 298.15 K}) = (29.06 \pm 0.52)$ kJ·mol⁻¹ and by Tikhon and Fuger $\Delta_{\text{sln}} H_m(\text{Cs}_2\text{NpO}_2\text{Cl}_4, \text{ cr, 298.15 K}) = (17.41 \pm 0.26)$ kJ·mol⁻¹.

The analysis leading to the enthalpies of formation for the compounds by Fuger and Parker [83FUG/PAR] have been recalculated with the slightly different auxiliary values given in the previous section (this review), with $\Delta_f H_m^\circ(\text{Cl}^-, 1 \text{ M HCl, partial}) = -(164.37 \pm 0.10) \text{ kJ}\cdot\text{mol}^{-1}$, with $\Delta_f H_m^\circ(\text{NpO}_2^+, 1 \text{ M HCl, 298.15 K})$ assumed to be identical with $\Delta_f H_m^\circ(\text{NpO}_2^+, \text{aq, or } 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(978.2 \pm 4.6) \text{ kJ}\cdot\text{mol}^{-1}$ (this review), $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, 1 \text{ M HCl, 298.15 K}) = -(858.3 \pm 5.3) \text{ kJ}\cdot\text{mol}^{-1}$ derived from $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, \text{aq, 298.15 K}) = -(860.7 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1}$ also accepted in this review. This derivation was made by assuming [83FUG/PAR] that the enthalpy of transfer of $\text{NpO}_2^{2+}(\text{aq})$ to 1 M HCl is the same as for the UO_2^{2+} ion, $(2.4 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$, and by increasing the uncertainty limits accordingly. The resulting values are:

$$\begin{aligned}\Delta_f H_m^\circ(\text{Cs}_3\text{NpO}_2\text{Cl}_4, \text{cr, 298.15 K}) &= -(2449.1 \pm 4.8) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f H_m^\circ(\text{Cs}_2\text{NpO}_2\text{Cl}_4, \text{cr, 298.15 K}) &= -(2056.1 \pm 5.4) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

which are the selected values. It may be noted that the enthalpy of the reaction



from the selected results is calculated to be $-(1.1 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$. Thus the Np(V) compound on the left of this equation will still be stable to disproportionation at 298.15 K and above, if the entropy of this reaction is slightly negative.

9.1.3.9 $\text{Cs}_2\text{NaNpCl}_6(\text{cr})$

Schoebrechts *et al.* [89SCH/GEN] measured the enthalpy of dissolution of this compound and of $\text{NpCl}_3(\text{cr})$, in 1 M $\text{HClO}_4 - 0.5 \text{ M Fe}(\text{ClO}_4)_3$ solutions as $+(12.02 \pm 0.12) \text{ kJ}\cdot\text{mol}^{-1}$ and $-(50.35 \pm 0.18) \text{ kJ}\cdot\text{mol}^{-1}$, respectively, and have reported the enthalpy of formation of $\text{Cs}_2\text{NaNpCl}_6(\text{cr})$. In their thermodynamic cycle, they accepted, from a critical examination of the literature data, $\Delta_{\text{sln}} H_m^\circ(\text{NaCl, 1 M HCl or HClO}_4, 298.15 \text{ K}) = +(4.46 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_{\text{sln}} H_m^\circ(\text{CsCl, 1 M HCl or HClO}_4, 298.15 \text{ K}) = +(16.69 \pm 0.08) \text{ kJ}\cdot\text{mol}^{-1}$. Using the above values and with $\Delta_f H_m^\circ(\text{CsCl, cr, 298.15 K}) = -(442.31 \pm 0.16) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\circ(\text{NaCl, cr, 298.15 K}) = -(411.26 \pm 0.11) \text{ kJ}\cdot\text{mol}^{-1}$ [82GLU/GUR] compatible with [89COX/WAG] and $\Delta_f H_m^\circ(\text{NpCl}_3, \text{cr, 298.15 K}) = -(896.8 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$ we recalculate

$$\Delta_f H_m^\circ(\text{Cs}_2\text{NaNpCl}_6, \text{cr, 298.15 K}) = -(2217.2 \pm 3.1) \text{ kJ}\cdot\text{mol}^{-1}$$

which is the adopted value. This corresponds to an enthalpy of formation of $-24.5 \text{ kJ}\cdot\text{mol}^{-1}$ from the constituent binary chlorides.

9.1.4 Neptunium bromide compounds

9.1.4.1 NpBr₃(cr)

NpBr₃(cr) exists in two crystal modifications, the hexagonal structure isomorphous with UBr₃(cr) (space group P6₃/m) and the orthorhombic form (TbCl₃-type, space group Cmc₂m) in which PuBr₃(cr) crystallises.

9.1.4.1.a Enthalpy of formation

Hurtgen [78HUR] has measured the enthalpy of solution of the hexagonal form of NpBr₃(cr) to be $-(161.4 \pm 2.0)$ kJ·mol⁻¹ in oxygen-free 10⁻³ M HCl and $-(158.8 \pm 0.9)$ kJ·mol⁻¹ in oxygen-free 0.1 M HCl. The partial molar enthalpy of formation of HBr in HCl solutions is assumed to be the same as in HBr solutions of the same molality, which have been recalculated from the enthalpy of dilution data given by Parker [65PAR], and are $-(121.33 \pm 0.15)$ and $-(120.71 \pm 0.15)$ [2000RAN/FUG]. These and the currently assessed value for $\Delta_f H_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K}) = -(527.2 \pm 2.1)$ kJ·mol⁻¹ assumed to be the same as in 10⁻³ and 0.1 M HCl give the values of $-(729.8 \pm 2.9)$ kJ·mol⁻¹ and $-(730.5 \pm 2.9)$ kJ·mol⁻¹ for $\Delta_f H_m^\circ(\text{NpBr}_3, \text{cr, hex}, 298.15 \text{ K})$ from these solutions. The selected value is the weighted mean

$$\Delta_f H_m^\circ(\text{NpBr}_3, \text{cr, hex}, 298.15 \text{ K}) = -(730.2 \pm 2.9) \text{ kJ}\cdot\text{mol}^{-1}$$

The use of the infinite dilution value for $\Delta_f H_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K})$ in 0.001 and 0.1 M HCl solutions in these calculations has been justified by Fuger *et al.* [83FUG/PAR] on the grounds that the enthalpies of formation of all the actinide trivalent ions vary by less than 0.5 kJ·mol⁻¹ between 0.1 M HCl solutions and the infinitely dilute solution. We accept this reasoning, but have increased the uncertainty on the value derived from the measurement in 0.1 M HCl.

9.1.4.1.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of NpBr₃(cr), and the standard entropy is derived from three reasonably consistent estimates by [2000RAN/FUG]. From these three estimates of 206.1, 194.9, 195.6 J·K⁻¹·mol⁻¹, the selected value is biased towards the lower estimates [2000RAN/FUG]

$$S_m^\circ(\text{NpBr}_3, \text{cr, hex}, 298.15 \text{ K}) = (196 \pm 8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.4.1.c High temperature heat capacity

Lacking experimental data, the heat capacity of NpBr₃(cr) is assumed to be similar to UBr₃(cr) and those estimated for PuBr₃(cr) by this review. The values suggested for NpBr₃(cr) are:

$$C_{p,m}^\circ(\text{NpBr}_3, \text{cr, hex}, T) = (101.23 + 20.68 \times 10^{-3}T - 3.2 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 to 975 K, and hence

$$C_{p,m}^{\circ}(\text{NpBr}_3, \text{cr, hex, 298.15 K}) = (103.8 \pm 6.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.4.1.d Fusion data

The fusion data are taken to be close to the mean values for $\text{UBr}_3(\text{cr})$ [63RAN/KUB] and $\text{PuBr}_3(\text{cr})$ (this review, Section 18.1.4.2.a), giving:

$$\begin{aligned} T_{\text{fus}} &= (975 \pm 30) \text{ K} \\ \Delta_{\text{fus}}H_{\text{m}}^{\circ}(\text{NpBr}_3, \text{cr, ortho, 975 K}) &= (48 \pm 8) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

The heat capacity of the liquid has been estimated to be similar to those of the liquid lanthanide tribromides, which lie between 145 and 155 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

$$C_{p,m}^{\circ}(\text{NpBr}_3, \text{l}) = (150 \pm 8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.4.2 $\text{NpBr}_3(\text{g})$

There are no experimental thermodynamic data involving $\text{NpBr}_3(\text{g})$ and since the vapour pressures of $\text{UBr}_3(\text{cr})$ and $\text{PuBr}_3(\text{cr})$ at 1000 K calculated from the assessed data ([92GRE/FUG] for UBr_3 , this review, Section 18.1.4.2 for PuBr_3) differ by a factor of more than 100, and also both have large uncertainties, we have not attempted to estimate any data for this species.

9.1.4.3 $\text{NpBr}_4(\text{cr})$

9.1.4.3.a Enthalpy of formation

Fuger and Brown [73FUG/BRO] measured the enthalpy of solution of $\text{NpBr}_4(\text{cr})$ to be $-(258.78 \pm 0.50) \text{ kJ}\cdot\text{mol}^{-1}$ in 1 M HCl and $-(199.20 \pm 0.42) \text{ kJ}\cdot\text{mol}^{-1}$ in 6 M HCl. With the partial molar enthalpy of formation of Br^- in these solutions, assumed to be the same as those in HBr solutions of the same molality, $-(119.40 \pm 0.15)$ and $-(109.55 \pm 0.20)$, and $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Np}^{4+})$ in these solutions $-(551.9 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ and $-(532.9 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$ [2000RAN/FUG], the calculated values for the enthalpy of formation of $\text{NpBr}_4(\text{cr})$ become $-(770.7 \pm 1.9) \text{ kJ}\cdot\text{mol}^{-1}$ (from 1 M HCl) and $-(771.9 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$ (from 6 M HCl). The selected value is the weighted mean:

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{NpBr}_4, \text{cr, 298.15 K}) = -(771.2 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

9.1.4.3.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of $\text{NpBr}_4(\text{cr})$, and the standard entropy is derived from two reasonably consistent estimates by [2000RAN/FUG]. The selected value is thus the rounded mean of the two estimates:

$$S_{\text{m}}^{\circ}(\text{NpBr}_4, \text{cr, 298.15 K}) = (243 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.4.3.c High temperature heat capacity

This is assumed to be similar to $\text{UBr}_4(\text{cr})$, [92GRE/FUG] the selected values being represented by the expression:

$$C_{p,m}^{\circ}(\text{NpBr}_4, \text{cr}, T) = (119.0 + 30.0 \times 10^{-3}T) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 K to 800 K, and hence

$$C_{p,m}^{\circ}(\text{NpBr}_4, \text{cr}, 298.15 \text{ K}) = (128.0 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.4.3.d Fusion data

The melting point and enthalpy of fusion and liquid heat capacity are estimated to be similar to those of $\text{UBr}_4(\text{cr})$, for which $T_{\text{fus}} = (792 \pm 15) \text{ K}$ and $\Delta_{\text{fus}}H = (48.5 \pm 6.7) \text{ kJ}\cdot\text{mol}^{-1}$ [83FUG/PAR].

$$\begin{aligned} T_{\text{fus}} &= (800 \pm 20) \text{ K} \\ \Delta_{\text{fus}}H(\text{NpBr}_4, \text{cr}, 800 \text{ K}) &= (50 \pm 8) \text{ kJ}\cdot\text{mol}^{-1} \\ C_{p,m}(\text{NpBr}_4, \text{l}) &= (170 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

from 800 to 1000 K.

9.1.4.4 $\text{NpBr}_4(\text{g})$

There are no studies of the vaporisation of $\text{NpBr}_4(\text{g})$ to indicate whether gaseous neptunium tetrabromide is stable with respect to decomposition to $\text{NpBr}_3(\text{g})$ and bromine, and no thermodynamic data are given for this species.

9.1.4.5 $\text{NpOBr}_2(\text{cr})$ **9.1.4.5.a Enthalpy of formation**

Following Fuger *et al.* [83FUG/PAR], the enthalpy of formation has been estimated by two not entirely independent methods from the trends in the actinide series, $-(948 \pm 13) \text{ kJ}\cdot\text{mol}^{-1}$ and $-(951 \pm 11) \text{ kJ}\cdot\text{mol}^{-1}$ [2000RAN/FUG]. The selected value is the close to the mean

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{NpOBr}_2, \text{cr}, 298.15 \text{ K}) = -(950 \pm 11) \text{ kJ}\cdot\text{mol}^{-1}$$

9.1.4.5.b Standard entropy and heat capacity

The standard entropy is derived from two consistent estimates, 161.5 and 160.0 J·K⁻¹·mol⁻¹ [2000RAN/FUG]. The selected value is

$$S_{\text{m}}^{\circ}(\text{NpOBr}_2, \text{cr}, 298.15 \text{ K}) = (160.8 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.4.5.c High temperature heat capacity

These have been estimated to be similar to those for UOBr₂(cr) [92GRE/FUG]

$$C_{p,\text{m}}^{\circ}(\text{NpOBr}_2, \text{cr}, T) = (111.0 + 13.7 \times 10^{-3}T - 1.5 \times 10^6 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 to 800 K, and hence

$$C_{p,\text{m}}^{\circ}(\text{NpOBr}_2, \text{cr}, 298.15 \text{ K}) = (98.2 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.4.6 Cs₂NpBr₆(cr)

9.1.4.6.a Enthalpy of formation

Fuger *et al.* [83FUG/PAR] have analysed the results of the calorimetric study by Magette and Fuger [77MAG/FUG] of the dissolution of this complex salt in 1 M HCl. The heat of solution is $-(107.3 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$. These authors also obtained $\Delta_{\text{sol}}H_{\text{m}}(\text{CsBr}, 1 \text{ M HCl}) = (25.54 \pm 0.14) \text{ kJ}\cdot\text{mol}^{-1}$. We have reworked this analysis, with the following different enthalpy values: $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{CsBr}, \text{cr}, 298.15 \text{ K}) = -(405.60 \pm 0.25) \text{ kJ}\cdot\text{mol}^{-1}$ [82GLU/GUR] compatible with [89COX/WAG], and $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Np}^{4+}, 1 \text{ M HCl}, 298.15 \text{ K}) = -(551.9 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$.

The final calculated value for the enthalpy of formation of the complex salt becomes

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Cs}_2\text{NpBr}_6, \text{cr}, 298.15 \text{ K}) = -(1682.3 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$$

This corresponds to an enthalpy of formation of $-99.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ from the constituent bromides.

9.1.4.6.b Standard entropy

The standard entropy has been estimated to be $(469 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ by assuming $\Delta_{\text{r}}S_{\text{m}}^{\circ} = 0$ for the reaction from the constituent bromides. The Latimer estimate is not used for NpBr₄(cr) or the complex salt since the Latimer prediction for UBr₄(cr) ($267.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) seems excessively high (*cf.* the value of $238.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ estimated by Fuger *et al.* [83FUG/PAR] and accepted by Grenthe *et al.* [92GRE/FUG]).

The selected value is

$$S_{\text{m}}^{\circ}(\text{Cs}_2\text{NpBr}_6, \text{cr}, 298.15 \text{ K}) = (469 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.5 Neptunium iodide compounds

The only known simple compounds of neptunium (and plutonium) containing iodine are the tri-iodide and the trivalent oxyiodide MOI(cr). There are no thermodynamic data for the oxyiodide.

9.1.5.1 NpI₃(cr)

9.1.5.1.a Enthalpy of formation

Hurtgen [78HUR] has measured the enthalpy of a solution of NpI₃(cr) in 0.001 M HCl and 0.1 M HCl to be $-(184.7 \pm 0.4)$ and $-(183.6 \pm 0.7)$ kJ·mol⁻¹ respectively. The partial molar enthalpy of formation of HI in oxygen-free HCl solutions is assumed to be the same as in HI solutions of the same molality, which have been recalculated from the enthalpy of dilution data given by Parker [65PAR], and are $-(56.710 \pm 0.050)$ and $-(56.20 \pm 0.05)$ [2000RAN/FUG]. These and the currently assessed value for $\Delta_f H_m^\circ(\text{Np}^{3+}, \text{aq}, 298.15 \text{ K}) = -(527.2 \pm 2.1)$ kJ·mol⁻¹ give values of $-(512.6 \pm 2.2)$ kJ·mol⁻¹ and $-(512.2 \pm 2.2)$ kJ·mol⁻¹ for $\Delta_f H_m^\circ(\text{NpI}_3, \text{cr}, 298.15 \text{ K})$ from these solutions. The selected value is the mean

$$\Delta_f H_m^\circ(\text{NpI}_3, \text{cr}, 298.15 \text{ K}) = -(512.4 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$$

9.1.5.1.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of NpI₃(cr), and the standard entropy is derived from two reasonably consistent estimates, 224.8 and 224.2 J·K⁻¹·mol⁻¹ [2000RAN/FUG]. The selected value is the rounded mean

$$S_m^\circ(\text{NpI}_3, \text{cr}, 298.15 \text{ K}) = (225 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.5.1.c High temperature heat capacity

This has been estimated to be consistent with current estimates for NpCl₃(cr) and NpBr₃(cr) and uranium trihalides ([92GRE/FUG], with some corrections)

$$C_{p,m}^\circ(\text{NpI}_3, \text{cr}, T) = (104.0 + 20.0 \times 10^{-3} T) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15K to 975 K, and hence

$$C_{p,m}^\circ(\text{NpI}_3, \text{cr}, 298.15 \text{ K}) = (110.0 \pm 8.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

9.1.5.1.d Fusion data

The melting point, enthalpy of fusion and heat capacity of the liquid are estimated from the values for the lanthanide tri-iodides (Dworkin and Bredig [63DWO/BRE, 71DWO/BRE]):

$$\begin{aligned} T_{\text{fus}} &= (975 \pm 50) \text{ K} \\ \Delta_{\text{fus}}H_{\text{m}}^{\circ}(\text{NpI}_3, \text{cr}) &= (50 \pm 5) \text{ kJ}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{NpI}_3, \text{l}) &= (150 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

9.1.5.2 NpI₃(g)

No thermodynamic data are available for this species, and since the data for UI₃(g) [92GRE/FUG] are rather uncertain, and those for PuI₃(g) are estimated in this review (Section 18.1.5.2) by comparison with the lanthanide iodides, there is no firm basis for the derivation of reliable estimates of the data for NpI₃(g).

9.1.5.3 NpOI(cr)

Brown and Edwards obtained this oxyiodide as an impurity in the preparation of NpI₃, [72BRO/EDW]; it can be prepared more readily by the reaction of Sb₂O₃ on NpI₃, Brown *et al.* [77BRO/HUR]. No thermodynamic data have been reported for this phase, and it is not considered further in this review.

9.2 Aqueous neptunium group 17 (halogen) complexes

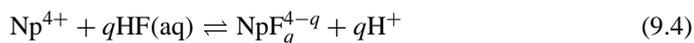
9.2.1 Aqueous neptunium fluoride complexes

9.2.1.1 Aqueous Np(III) fluorides

No fluoride complexes of Np³⁺ have been identified.

9.2.1.2 Aqueous Np(IV) fluorides

Experimental equilibrium data have been published for the following reactions



All experiments were carried out in strongly acidic solutions, and the relevant equilibrium is thus Reaction (9.4), although data bases usually contain reactions of type (9.5). The data reported in [90SAW/CHA2] are converted to refer to Reaction (9.4) by taking the authors' protonation constant of F⁻, *cf.* Appendix A. All reported constants are listed in Table 9.3. The constants obtained in HNO₃ solutions

[69KRY/KOM3] are corrected for the formation of NpNO_3^{3+} (see Appendix A) and used in the evaluation procedure of $\log_{10} {}^*\beta_1^\circ$. The values reported for $\log_{10} {}^*\beta_1$ at 20°C [66AHR/BRA] and 23°C [90SAW/CHA2] are corrected to 25°C by using the enthalpy value selected below.

The values for $\log_{10} {}^*\beta_1$ are in good agreement with the exception of the most recent determination of this constant by Sawant, Chaudhuri and Patil [90SAW/CHA2], who used a fluoride ion selective electrode. The constants reported in that study for U(IV) and Pu(IV) are also inconsistent with those of other determinations. Further irregularities, *cf.* Appendix A, have led us to exclude the constants reported in [90SAW/CHA2] from the selection procedure. Having done this, a simultaneous determination of $\log_{10} {}^*\beta_1^\circ$ and $\Delta\varepsilon$ by weighted linear regression appears feasible, *cf.* Figure 9.1, where the 25°C data from [66AHR/BRA, 69KRY/KOM, 69KRY/KOM3, 75PAT/RAM, 76BAG/RAM, 76CHO/UNR] are used. The resulting value is $\log_{10} {}^*\beta_1^\circ(9.4, q = 1, 298.15 \text{ K}) = (5.78 \pm 0.14)$. The slope of the straight line in Figure 9.1 corresponds to $\Delta\varepsilon(9.4, q = 1) = -(0.12 \pm 0.04)\text{kg}\cdot\text{mol}^{-1}$, which compares well with $\Delta\varepsilon = -0.14\text{kg}\cdot\text{mol}^{-1}$ estimated for the corresponding U(IV)-HF reaction [92GRE/FUG]. We convert this constant to conform to Equation (9.5) using our selected protonation constant of fluoride [92GRE/FUG]. The resulting selected value is

$$\log_{10} \beta_1^\circ(9.5, q = 1, 298.15 \text{ K}) = 8.96 \pm 0.14.$$

It should be noted that Krupka *et al.* [85KRU/RAI] observed no measurable increase of Np(IV) solubility in the presence of up to 100 ppm fluoride. However, this observation is not necessarily in contradiction with our selected value, *cf.* Appendix A.

For the formation of the 1:2 complex, NpF_2^{2+} , Ahrland and Brandt [66AHR/BRA] published two values measured independently with a cation exchange method and with a redox electrode, respectively. The values are in very good agreement, as is the value published by Patil and Ramakrishna [75PAT/RAM] who used a solvent extraction technique. Again, the value published by Sawant, Chaudhuri and Patil [90SAW/CHA2] differs considerably from the other values and is omitted in the selection procedure. The values of $\log_{10} {}^*\beta_2^\circ$ listed in Table 9.3 are obtained by extrapolating the reported constants to $I = 0$ by using $\Delta\varepsilon(9.4, q = 2) = -(0.18 \pm 0.15)\text{kg}\cdot\text{mol}^{-1}$ from the corresponding U(IV) fluoride system [92GRE/FUG], where the uncertainty has been increased by 0.05. The weighted average of the three values is $\log_{10} {}^*\beta_2^\circ(9.4, q = 2) = (9.34 \pm 0.29)$. We convert this value to conform to Equation (9.5) using our selected protonation constant of fluoride [92GRE/FUG]. The resulting selected value is

$$\log_{10} \beta_2^\circ(9.5, q = 2, 298.15 \text{ K}) = 15.7 \pm 0.3$$

Data for the 1:3 and 1:4 complexes were published by Ahrland and Brandt [66AHR/BRA], and by Sawant, Chaudhuri and Patil [90SAW/CHA2]. The values differ considerably, even after correction to $I = 0$ using the $\Delta\varepsilon$ values from the corresponding U(IV) fluoride system [92GRE/FUG], *cf.* Table 9.3. If we use $\varepsilon(\text{NpF}_3^+, \text{ClO}_4^-) \approx \varepsilon(\text{M}^+, \text{ClO}_4^-) \approx 0.3\text{kg}\cdot\text{mol}^{-1}$ (*cf.* Appendix B) instead of

Table 9.3: Experimental equilibrium data for the neptunium(IV) fluoride system.

Method	Ionic medium	t (°C)	$\log_{10} {}^*\beta_q^{(a)}$	$\log_{10} {}^*\beta_q^\circ^{(a)}$	Reference
$\text{Np}^{4+} + \text{HF}(\text{aq}) \rightleftharpoons \text{NpF}^{3+} + \text{H}^+$					
cix	4 M HClO ₄	20	(4.82 ± 0.02)		[66AHR/BRA]
	4 M HClO ₄	25	(4.79 ± 0.10) ^(b,c)		
cix	2 M HClO ₄	25	(4.70 ± 0.30) ^(b)		[69KRY/KOM]
	1 M HClO ₄	25	(4.56 ± 0.30) ^(b)		
cix	2 M HNO ₃	25	(4.75 ± 0.30) ^(b,d)		[69KRY/KOM3]
	1 M HNO ₃	25	(4.74 ± 0.30) ^(b,d)		
dis-HD	2 M HClO ₄	25	(4.62 ± 0.20) ^(b)		[75PAT/RAM]
dis-HTTA	2 M HClO ₄	25	(4.60 ± 0.20) ^(b)		
dis-HTTA	2 M HClO ₄	25	(4.70 ± 0.15) ^(b)		[76BAG/RAM]
dis	1 M HClO ₄	10	4.71		[76CHO/UNR]
	1 M HClO ₄	25	(4.60 ± 0.20) ^(b)		
	1 M HClO ₄	40	4.52		
ise-F ⁻	1 M (H,Na)ClO ₄	23	5.21 ^(c,e)		[90SAW/CHA2]
$\text{Np}^{4+} + 2\text{HF}(\text{aq}) \rightleftharpoons \text{NpF}_2^{2+} + 2\text{H}^+$					
cix	4 M HClO ₄	20	(7.57 ± 0.15) ^(b)	(9.30 ± 0.75)	[66AHR/BRA]
red	4 M HClO ₄	20	(7.51 ± 0.15) ^(b,f)	(9.24 ± 0.75)	
dis-HTTA	2 M HClO ₄	25	(7.49 ± 0.40) ^(b)	(9.44 ± 0.52)	[75PAT/RAM]
dis-HTTA	2 M HClO ₄	25	(7.38 ± 0.30) ^(b)	(9.32 ± 0.45)	[76BAG/RAM]
ise-F ⁻	1 M (H,Na)ClO ₄	23	8.62 ^(e)	10.49	[90SAW/CHA2]
$\text{Np}^{4+} + 3\text{HF}(\text{aq}) \rightleftharpoons \text{NpF}_3^+ + 3\text{H}^+$					
red	4 M HClO ₄	20	9.85 ^(f)	11.8	[66AHR/BRA]
ise-F ⁻	1 M HClO ₄	23	11.20 ^(e)	13.4	[90SAW/CHA2]
$\text{Np}^{4+} + 4\text{HF}(\text{aq}) \rightleftharpoons \text{NpF}_4(\text{aq}) + 4\text{H}^+$					
red	4 M HClO ₄	20	~ 11.15 ^(f)	13.3	[66AHR/BRA]
ise-F ⁻	1 M HClO ₄	23	14.15 ^(e)	16.4	[90SAW/CHA2]

(a) Refers to the reactions indicated, the ionic strength and temperature given in the table. $\log_{10} {}^*\beta_q^\circ$ is in molal units, at $I = 0$ and 298.15 K.

(b) Uncertainty estimated in this review (cf. Appendix A).

(c) Corrected to 25°C using the reaction enthalpy selected in this review.

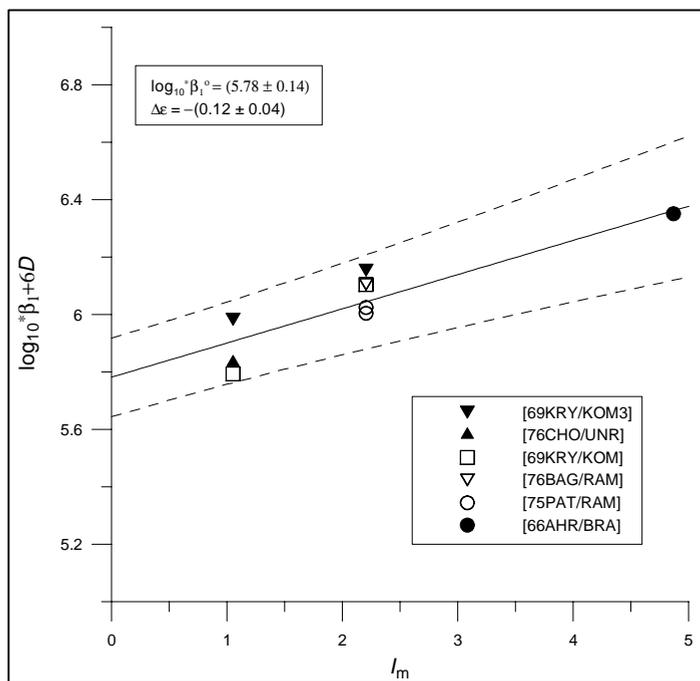
(d) Corrected for the formation of NpNO_3^{3+} (cf. Appendix A).

(e) The published values refer to Reactions (9.5) and have been converted to conform to the reactions of this table (cf. Appendix A).

(f) Reported as stepwise constants: $\log_{10} {}^*K_2 = (2.69 \pm 0.10)$, $\log_{10} {}^*K_3 = (2.34 \pm 0.15)$, and $\log_{10} {}^*K_4 \approx 1.3$. They are converted to overall formation constants by using $\log_{10} {}^*K_1 = 4.82$ from the ion exchange experiments [66AHR/BRA] (see Appendix A).

Figure 9.1: Extrapolation to $I = 0$ of experimental data for the formation of NpF^{3+} using the specific ion interaction equation. The data refer to HClO_4 media and are taken from [66AHR/BRA], [69KRY/KOM], [69KRY/KOM3], [75PAT/RAM], [76BAG/RAM] and [76CHO/UNR]. The solid line represents the prediction of $(\log_{10}^* \beta_1^\circ + 6D)$ using our selected data, and the dotted lines are the limits of the uncertainty range obtained by propagating the resulting uncertainties at $I = 0$ back to $I = 5 \text{ mol}\cdot\text{kg}^{-1}$.

Equilibrium: $\text{Np}^{4+} + \text{HF}(\text{aq}) \rightleftharpoons \text{NpF}^{3+} + \text{H}^+$



$\varepsilon_{(\text{NpF}_3^+, \text{ClO}_4^-)} \approx \varepsilon_{(\text{UF}_3^+, \text{ClO}_4^-)} = 0.1 \text{ kg}\cdot\text{mol}^{-1}$ [92GRE/FUG], the resulting $\log_{10} \beta_3^\circ$ values are in better agreement. However, on the present basis we do not consider it possible to make any selection for the formation constants of NpF_3^+ and $\text{NpF}_4(\text{aq})$.

The Gibbs energies of formation of NpF^{3+} and NpF_2^{2+} are calculated using the selected values for Np^{4+} and F^- .

$$\begin{aligned}\Delta_f G_m^\circ(\text{NpF}^{3+}, \text{aq}, 298.15 \text{ K}) &= -(824.4 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{NpF}_2^{2+}, \text{aq}, 298.15 \text{ K}) &= -(1144.4 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

From the equilibrium constants of Choppin and Unrein [76CHO/UNR] at 10, 25 and 40°C it is possible to extract an enthalpy of reaction: $\Delta_r H_m(9.4, q = 1) = -(10.7 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$, *cf.* Appendix A. Assuming its dependence on the ionic strength to be negligible, and combining it with the enthalpy of protonation of the fluoride ion [92GRE/FUG], we obtain

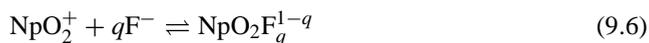
$$\Delta_r H_m^\circ(9.5, q = 1, 298.15 \text{ K}) = (1.5 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$$

From this value we derive the enthalpy of formation and the entropy of NpF^{3+} :

$$\begin{aligned}\Delta_f H_m^\circ(\text{NpF}^{3+}, \text{aq}, 298.15 \text{ K}) &= -(889.9 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1} \\ S_m^\circ(\text{NpF}^{3+}, \text{aq}, 298.15 \text{ K}) &= -(264 \pm 14) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

9.2.1.3 Aqueous Np(V) fluorides

Fluoride complexation has been studied in near-neutral solutions by several authors using spectrophotometric [78RAO/PAT], solvent extraction [79RAO/GUD, 84CHO/RAO, 85INO/TOC2] and potentiometric [85SAW/RIZ] techniques, *cf.* Table 9.4.



Some authors (*e.g.* [70AL-/WAI]) reported that they could not observe the formation of any Np(V) fluoride complex. However, those investigations were carried out at high acidity, where the proton is too powerful a competitor for the fluoride ion. Np(V) fluoride complexation studies thus need to be carried out at moderate acidity to be successful. The solvent extraction study of Rao *et al.* [79RAO/GUD] is the most reliable one, because the oxidation state of Np(V) was checked spectroscopically both at the beginning and at the end of the experiment. This was not done in the studies of Choppin and Rao [84CHO/RAO] and of Inoue and Tochiyama [85INO/TOC2], but this does not mean that the results must be in error. Sawant *et al.* [85SAW/RIZ] used a fluoride ion selective electrode and carefully tried to eliminate interfering side effects by running a blank titration, *cf.* Appendix A. However, under their experimental conditions (low fluoride concentration and comparatively low pH), only very low average complexation degrees could be reached, and their data are associated with a high uncertainty. The spectrophotometric determination of Rao and Patil [78RAO/PAT] lacks

Table 9.4: Experimental equilibrium data for the neptunium(V) fluoride system.

Method	Ionic medium	t (°C)	$\log_{10} \beta_q^{(a)}$	$\log_{10} \beta_q^{\circ(a)}$	Reference
$\text{NpO}_2^+ + \text{F}^- \rightleftharpoons \text{NpO}_2\text{F}(\text{aq})$					
sp	2 M NaClO ₄	25	$(1.35 \pm 0.30)^{(b)}$	(1.18 ± 0.37)	[78RAO/PAT]
dis	2 M NaClO ₄	25	$(0.99 \pm 0.10)^{(b)}$	(0.82 ± 0.24)	[79RAO/GUD]
dis	1 M NaClO ₄	23	$(1.26 \pm 0.30)^{(b)}$	(1.37 ± 0.32)	[84CHO/RAO]
dis	1 M NaClO ₄	25	$(1.39 \pm 0.30)^{(b)}$	(1.50 ± 0.32)	[85INO/TOC2]
ise-F ⁻	0.1 M NaClO ₄	21	$(1.51 \pm 0.50)^{(b)}$	(1.70 ± 0.50)	[85SAW/RIZ]
	1 M NaClO ₄	21	$(1.15 \pm 0.80)^{(b)}$	(1.26 ± 0.81)	
$\text{NpO}_2^+ + 2\text{F}^- \rightleftharpoons \text{NpO}_2\text{F}_2^-$					
dis	1 M Na(ClO ₄ , F)	25	$(2.07 \pm 0.50)^{(b)}$		[85INO/TOC2]

^(a) Refers to the reactions indicated, the ionic strength and temperature given in the table. $\log_{10} \beta_q^{\circ}$ is in molal units, at $I = 0$ and 298.15 K.

^(b) Uncertainty estimated in the present review (*cf.* Appendix A).

documentation of experimental measurements, but the reported formation constant lies well in the range of other values.

For the extrapolation to $I = 0$ we use $\Delta\varepsilon(9.6) = -(0.27 \pm 0.10)\text{kg}\cdot\text{mol}^{-1}$ from the interaction coefficients of $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.25 \pm 0.05)\text{kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{F}^-, \text{Na}^+)} = (0.02 \pm 0.02)\text{kg}\cdot\text{mol}^{-1}$, and by increasing the uncertainty in $\Delta\varepsilon$ by 0.05. Table 9.4 shows that there is considerable variation in the resulting $\log_{10} \beta_q^{\circ}$ values. Although the study of Rao *et al.* [79RAO/GUD] appears very reliable, its resulting value at $I = 0$ is incompatible with the result of [85INO/TOC2] and the 0.1 M result of [85SAW/RIZ]. The IAEA review [92FUG/KHO] selected the results of [85SAW/RIZ] and recommended $\log_{10} \beta_1^{\circ}(9.6, q = 1, 298.15 \text{ K}) = (1.9 \pm 0.2)$. The weighted average of the six values listed in Table 9.4 is $\log_{10} \beta_1^{\circ}(9.6, q = 1, 298.15 \text{ K}) = (1.20 \pm 0.14)$, and the unweighted average is (1.3 ± 0.9) , where the uncertainty covers the entire range of expectation of all values. Though the constants in Table 9.4 are not entirely consistent, the disagreement is not serious, and we prefer to select the rounded weighted average with an increased uncertainty:

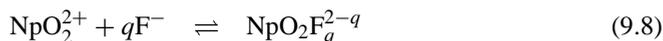
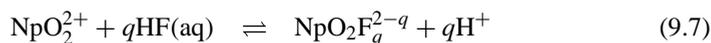
$$\log_{10} \beta_1^{\circ}(9.6, q = 1, 298.15 \text{ K}) = 1.2 \pm 0.3$$

Only one study reported a value for the 1:2 complex, NpO_2F_2^- [85INO/TOC2] at fluoride concentrations up to 0.25 M. However, we cannot accept this single reported $\log_{10} \beta_2$ value, as it is correlated with the authors' value for $\log_{10} \beta_1$ [85INO/TOC2]. Our selected average value for $\log_{10} \beta_1$ is somewhat different, and the value of $\log_{10} \beta_2$ value from [85INO/TOC2] would not be consistent with the selected value of $\log_{10} \beta_1$. The Gibbs energy of formation is calculated using the selected $\Delta_f G_m^{\circ}$ values for NpO_2^+ and F^- .

$$\Delta_f G_m^{\circ}(\text{NpO}_2\text{F}, \text{aq}, 298.15 \text{ K}) = -(1196.1 \pm 5.9) \text{ kJ}\cdot\text{mol}^{-1}$$

9.2.1.4 Aqueous Np(VI) fluorides

The investigation of fluoride complexation of neptunium(VI) is complicated by the fact that NpO_2^{2+} has oxidising properties, and that reduction to Np(IV) is favoured in acidic medium and in the presence of fluoride ion. The constants reported in the literature refer to either of the following reaction types,



depending whether the fluoride ion was protonated or deprotonated under the experimental conditions. The constants are listed in Table 9.5. For $q = 1$, agreement is reasonable, except for the study published by Krylov, Komarov and Pushlenkov [68KRY/KOM], in which a reduction of Np(VI) is likely to have occurred, *cf.* Appendix A. The most reliable study is that of Ahrland and Brandt [68AHR/BRA], and the reported constants are given a high weight in our selection procedure. A simultaneous evaluation of $\Delta\varepsilon$ and $\log_{10} {}^*\beta_1$ is not considered to give representative results in the present case, and we prefer to use $\Delta\varepsilon(9.7, q = 1) = -(0.03 \pm 0.09)\text{kg}\cdot\text{mol}^{-1}$ as evaluated from the corresponding U(VI) system [92GRE/FUG], after increasing the uncertainty in $\Delta\varepsilon$ by 0.05. The constants determined by Al-Niaimi, Wain and McKay [70AL-/WAI] are linearly correlated with the ionic strength of the medium, *cf.* Figure 9.2, showing that our $\Delta\varepsilon$ value is reasonable. We assign a high uncertainty to the constant reported by Patil and Ramakrishna [76PAT/RAM], because they did not consider the formation of the 1:2 complex in their evaluation, which must have formed to some extent in their experiments, *cf.* Appendix A. The data of Sontag and Musikas [68SON/MUS] are compatible with those of other studies, but they are given a low weight in our evaluation procedure (by assigning a high uncertainty), because insufficient experimental details are given in the paper. The constants reported in acidic media [68AHR/BRA, 68SON/MUS, 70AL-/WAI, 76PAT/RAM, 84KAS/JOS] are corrected to $I = 0$ and converted to correspond to Reaction 9.8 using our selected value for the protonation of fluoride ion. The weighted average of these values is $\log_{10} \beta_q^\circ(9.8, q = 1) = (4.51 \pm 0.09)$. The uncertainties of the five values of [70AL-/WAI] were doubled (to ± 0.40 each) in the calculation of the weighted average, in order to avoid an undue emphasis of this study with respect to the others.

Fluoride-ion selective electrode studies [84CHO/RAO, 85SAW/CHA] provide a second set of data for $q = 1$ according to Reaction (9.8). Here the values at $I = 0$ are calculated by using $\Delta\varepsilon(9.8, q = 1) = -(0.19 \pm 0.11)\text{kg}\cdot\text{mol}^{-1}$ as in the corresponding uranium system [92GRE/FUG], but by increasing the uncertainty by 0.05. The weighted average of the values at $I = 0$ is $\log_{10} \beta_q^\circ(9.8, q = 1) = (4.66 \pm 0.10)$. The constant resulting from the studies in NaClO_4 media is slightly higher than that from the studies in HClO_4 solutions. A similar trend is observed in the constants of the U(VI) fluoride system [92GRE/FUG]. Although the present evaluation seems to confirm a medium effect, the difference is not significant (*i.e.*, it is within the uncertainty ranges of the two values). Therefore, we can select the weighted average of all values

Table 9.5: Experimental equilibrium data for the neptunium(VI) fluoride system.

Method	Ionic medium	<i>t</i> (°C)	log ₁₀ *β _q ^(a)	log ₁₀ β _q ^(b)	log ₁₀ β _q ^(c)	Reference
NpO ₂ ²⁺ + HF(aq) ⇌ NpO ₂ F ⁺ + H ⁺ (a)						
NpO ₂ ²⁺ + F ⁻ ⇌ NpO ₂ F ⁺ (b)						
dis	1 M HClO ₄	21	(0.93 ± 0.11)		(4.49 ± 0.15)	[68AHR/BRA]
cix	1.04 M HClO ₄	25	2.20			[68KRY/KOM]
	2.1 M HClO ₄	25	2.11			
pot	2.1 M (Na,H)ClO ₄	25	(0.96 ± 0.40) ^(d)		(4.54 ± 0.45)	[68SON/MUS]
emf	0.1 M HClO ₄	25	(1.20 ± 0.20) ^(d)		(4.60 ± 0.20)	[70AL-/WAI]
	0.2 M HClO ₄	25	(1.16 ± 0.20) ^(d)		(4.61 ± 0.20)	
	0.3 M HClO ₄	25	(1.14 ± 0.20) ^(d)		(4.62 ± 0.20)	
	0.4 M HClO ₄	25	(1.16 ± 0.20) ^(d)		(4.62 ± 0.20)	
	0.5 M HClO ₄	25	(1.11 ± 0.20) ^(d)		(4.63 ± 0.21)	
dis	2 M HClO ₄	25	(1.12 ± 0.50) ^(d)		(4.70 ± 0.54)	[76PAT/RAM]
ise-F ⁻	1 M NaClO ₄	23		(4.27 ± 0.15) ^(d)	(4.87 ± 0.19)	[84CHO/RAO]
cou	0.5 M HClO ₄	23	(0.97 ± 0.21) ^(d)		(4.49 ± 0.21)	[84KAS/JOS]
	1 M (H,Na)ClO ₄	23	(0.82 ± 0.22) ^(d)		(4.38 ± 0.22)	
ise-F ⁻	0.1 M NaClO ₄	21		(4.18 ± 0.15) ^(d)	(4.60 ± 0.15)	[85SAW/CHA]
	1 M NaClO ₄	21		(3.94 ± 0.15) ^(d)	(4.54 ± 0.19)	
NpO ₂ ²⁺ + 2HF(aq) ⇌ NpO ₂ F ₂ (aq) + 2H ⁺ (a)						
NpO ₂ ²⁺ + 2F ⁻ ⇌ NpO ₂ F ₂ (aq) (b)						
dis	1 M HClO ₄	21	(1.11 ± 0.10)		(7.69 ± 0.15)	[68AHR/BRA]
pot	2.1 M (Na,H)ClO ₄	25	(1.23 ± 0.40) ^(d)		(7.64 ± 0.46)	[68SON/MUS]
emf	0.1 M HClO ₄	25	(1.17 ± 0.40) ^(d)		(7.73 ± 0.40)	[70AL-/WAI]
	0.2 M HClO ₄	25	(1.19 ± 0.40) ^(d)		(7.19 ± 0.40)	
	0.3 M HClO ₄	25	(1.20 ± 0.40) ^(d)		(7.81 ± 0.40)	
	0.4 M HClO ₄	25	(1.20 ± 0.40) ^(d)		(7.82 ± 0.40)	
	0.5 M HClO ₄	25	(1.14 ± 0.40) ^(d)		(7.76 ± 0.40)	
cou	0.5 M HClO ₄	23	(0.95 ± 0.40) ^(d)		(7.57 ± 0.40)	[84KAS/JOS]
	1 M (H,Na)ClO ₄	23	(1.02 ± 0.40) ^(d)		(7.60 ± 0.41)	
ise-F ⁻	0.1 M NaClO ₄	21		(6.96 ± 0.15) ^(d)	(7.56 ± 0.15)	[85SAW/CHA]
	1 M NaClO ₄	21		(6.82 ± 0.15) ^(d)	(7.49 ± 0.18)	
NpO ₂ ²⁺ + 3HF(aq) ⇌ NpO ₂ F ₃ ⁻ + 3H ⁺ (a)						
NpO ₂ ²⁺ + 3F ⁻ ⇌ NpO ₂ F ₃ ⁻ (b)						
pot	2.1 M (Na,H)ClO ₄	25	0.23			[68SON/MUS]
ise-F ⁻	0.1 M NaClO ₄	21		9.64		[85SAW/CHA]
	1 M NaClO ₄	21		8.49		

(a) log₁₀ *β_q refers to Reaction (9.7) and results from measurements in acidic solutions.

(b) log₁₀ β_q refers to Reaction (9.8) and results from measurements in mildly acidic or neutral solutions.

(c) log₁₀ β_q^o refers to Reaction (9.8). The experimental data have been corrected to *I* = 0 in the present review and, when necessary, converted to refer to Reaction (9.8) by using the selected protonation constant of fluoride ion.

(d) Uncertainty estimated in this review.

(using ± 0.40 as the uncertainty of the [70AL-/WAI] values as explained above):

$$\log_{10} \beta_1^\circ(9.8, q = 1, 298.15 \text{ K}) = 4.57 \pm 0.07$$

Figure 9.2 shows a recalculation of this constant (as “ $\log_{10} \beta_1^\circ + 2D$ ”, where D is the Debye-Hückel term, *cf.* Appendix B) back to $I = 3$ m for the HClO₄ media. This shows that the selected constant and $\Delta\varepsilon$ reproduce the experimental values reasonably well. We assume that the slight deviation of some experimental temperatures from 25°C (see Table 9.5) does not significantly influence the equilibrium.

The 1:2 complex was included in several publications, although it formed only to relatively small extents in most studies in HClO₄ media, *cf.* Appendix A. One exception is the study of Ahrland and Brandt [68AHR/BRA] who used HF(aq) concentrations up to 4.5 M. The other constants from studies in HClO₄ media are given comparatively large uncertainties for this reason. The constants are corrected to $I = 0$ by using $\Delta\varepsilon(9.8, q = 2) = -(0.18 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ in HClO₄ media and $\Delta\varepsilon(9.8, q = 2) = -(0.50 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ in NaClO₄ media, taken from the corresponding U(VI) equilibria [92GRE/FUG]. The resulting values of $\log_{10} \beta_2^\circ$ are in good agreement, *cf.* Table 9.5. The weighted average of the values from HClO₄ studies is $\log_{10} \beta_2^\circ = (7.68 \pm 0.12)$, and of the values from NaClO₄ it is $\log_{10} \beta_2^\circ = (7.53 \pm 0.12)$. The weighted average of all values is selected:

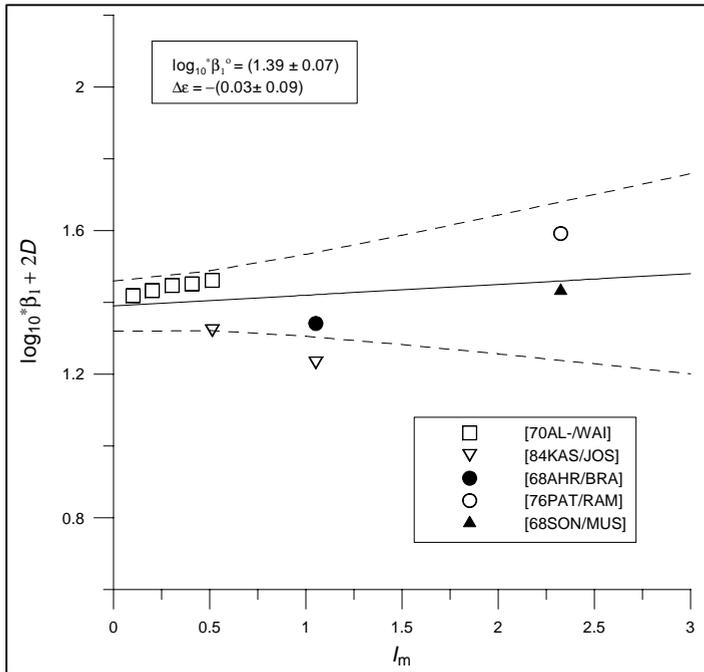
$$\log_{10} \beta_2^\circ(9.8, q = 2, 298.15 \text{ K}) = 7.60 \pm 0.08$$

Some authors [68SON/MUS, 85SAW/CHA] have reported formation constants for the 1:3 complex, NpO₂F₃⁻. The result of Sontag and Musikas [68SON/MUS] in HClO₄ medium cannot be judged, because the concentration range of HF(aq) used was not reported. However, Ahrland and Brandt [68AHR/BRA] convincingly demonstrated that no formation of NpO₂F₃⁻ is observed in 1 M HClO₄ up to a HF(aq) concentration of 4.51 M. According to the constant reported by Sawant *et al.* [85SAW/CHA], the 1:3 complex formed to some extent (about 15%) in the study of [68AHR/BRA2], but this may not be significant enough to be visible in the evaluation. The complex NpO₂F₃⁻ is therefore likely to form in less acidic solutions (pH > 3). Unfortunately, the constants reported by Sawant *et al.* [85SAW/CHA] for $I = 0.1$ M and $I = 1$ M are not compatible with the specific ion interaction coefficients in Appendix B. For the corresponding U(VI) system, we have $\Delta\varepsilon(9.8, q = 3) = -0.52 \text{ kg}\cdot\text{mol}^{-1}$ [92GRE/FUG], and by using this value to correct the data of [85SAW/CHA] to $I = 0$, we obtain $\log_{10} \beta_3^\circ(9.8, q = 3) = 10.2$ and 9.1 for the experiments carried out at $I = 0.1$ M and $I = 1$ M, respectively. In order to obtain consistent $\log_{10} \beta_3^\circ$ values from the two determinations, we would have to change the sign of $\Delta\varepsilon$, and this would be incompatible with the commonly observed ionic strength dependence of comparable equilibria. Additional experimental investigations will be necessary to obtain a consistent picture on the formation of NpO₂F₃⁻.

The Gibbs energy of formation values are derived from the above selected constants using the selected $\Delta_f G_m^\circ$ values for NpO₂²⁺ and F⁻.

$$\begin{aligned} \Delta_f G_m^\circ(\text{NpO}_2\text{F}^+, \text{aq}, 298.15 \text{ K}) &= -(1103.5 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{NpO}_2\text{F}_2, \text{aq}, 298.15 \text{ K}) &= -(1402.4 \pm 5.8) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Figure 9.2: Comparison of selected and experimental data for the formation of NpO_2F^+ in HClO_4 media from [68AHR/BRA], [68SON/MUS], [70AL-/WAI], [76PAT/RAM] and [84KAS/JOS]. The solid line represents the prediction of $(\log_{10}^* \beta_1^\circ + 2D)$ using our selected data, and the dotted lines are the limits of the uncertainty range obtained by propagating the resulting uncertainties at $I = 0$ back to $I = 3 \text{ m}$.



9.2.2 Aqueous neptunium chloride complexes

9.2.2.1 Aqueous Np(III) chlorides

The only quantitative information on chloride complexation of Np^{3+} according to the equilibria



has been published by Shiloh and Marcus [64SHI/MAR]. They observed changes in the visible absorption spectrum and concluded that NpCl_2^{2+} and NpCl_2^{+} were formed at LiCl concentrations between 5 and 12.7 M. Under these conditions they determined $\log_{10} \beta_1(9.9, q = 1) = -(2.4 \pm 0.1)$ and $\log_{10} \beta_2(9.9, q = 2) = -(5.0 \pm 0.1)$. The high and varying ionic strengths used do not allow the selection of any value for $I = 0$.

9.2.2.2 Aqueous Np(IV) chlorides

The experimental equilibrium data available for the reactions



are listed in Table 9.6. For reasons mentioned in Appendix A, we do not consider the data in [58STR/PEE] and [62SYK/TAY], as well as [73BAR/MUR] (very high and variable ionic strength) and [76SOU/SHA] (variable ionic strength). If we use the data of Shilin and Nazarov [66SHI/NAZ] (assuming, due to the lack of enthalpy data, that the temperature correction to 25°C is negligible), Danesi *et al.* [71DAN/CHI], and Patil and Ramakrishna [75PAT/RAM] (as re-evaluated by Giffaut [94GIF]) in a linear regression analysis, we obtain, for the first formation constant at $I = 0$, $\log_{10} \beta_1^{\circ} = (1.55 \pm 0.17)$ and $\Delta \varepsilon = -(0.10 \pm 0.08)\text{kg}\cdot\text{mol}^{-1}$. This $\Delta \varepsilon$ value is about the same as obtained for the corresponding Pu(IV) system, *cf.* Figure 18.1: $\Delta \varepsilon(9.10, q = 1) = -(0.09 \pm 0.07)\text{kg}\cdot\text{mol}^{-1}$, but it differs from the value of the corresponding U(IV) system, $\Delta \varepsilon = -(0.29 \pm 0.13)\text{kg}\cdot\text{mol}^{-1}$ [92GRE/FUG]. Considering that the parameter $Ba_j = 1.5$ in the specific ion interaction equation was optimised for ionic strengths below 3.5 m, *cf.* Appendix B, and that values measured at higher ionic strengths should thus be given a lower weight or not be included at all if possible, we redo the extrapolation to $I = 0$ by omitting the value of Danesi *et al.* [71DAN/CHI], and we obtain $\log_{10} \beta_1^{\circ} = (1.42 \pm 0.23)$ and $\Delta \varepsilon = -(0.19 \pm 0.14)\text{kg}\cdot\text{mol}^{-1}$. The $\Delta \varepsilon$ value is now between that of the corresponding Pu(IV) and U(IV) systems. We prefer to select an intermediate value and to assign it an uncertainty that covers the range of expectancy of the two results, which has the effect of lowering the weight of the value at $I = 4$ M [71DAN/CHI] without disregarding it completely.

$$\log_{10} \beta_1^{\circ}(9.10, q = 1, 298.15 \text{ K}) = 1.5 \pm 0.3$$

For $\Delta \varepsilon$ we select $-(0.15 \pm 0.18)\text{kg}\cdot\text{mol}^{-1}$ following the same procedure. Figure 9.3 shows the expected range of the value of $\log_{10} \beta_1$ (+8D) based on the selected

value of $\log_{10}\beta_1^\circ$ when recalculated to ionic strengths up to $I = 5$ m by using the selected $\Delta\varepsilon$ value. The IAEA review [92FUG/KHO] selected $\log_{10}\beta_1^\circ = (1.8 \pm 0.5)$, which is compatible with the present selection. Giffaut [94GIF] recommended $\log_{10}\beta_1^\circ = (1.45 \pm 0.25)$ based on the same literature values.

Table 9.6: Experimental equilibrium data for the neptunium(IV) chloride system.

Method	Ionic medium	t (°C)	$\log_{10}\beta_q^{(a)}$	$\log_{10}\beta_q^{\circ(a)}$	Reference
$\text{Np}^{4+} + \text{Cl}^- \rightleftharpoons \text{NpCl}^{3+}$					
red	1 M H(Cl,ClO ₄)	25	-0.3		[58STR/PEE]
sp	2 M Na(Cl,ClO ₄)	25	-0.28		[62SYK/TAY]
dis	0.5 M H(Cl,ClO ₄)	20	$(0.15 \pm 0.20)^{(b)}$		[66SHI/NAZ]
	1 M H(Cl,ClO ₄)	20	$-(0.04 \pm 0.20)^{(b)}$		
	2 M H(Cl,ClO ₄)	20	$(0.04 \pm 0.20)^{(b)}$		
dis	4 M (H,Na)(Cl,ClO ₄)	25	$-(0.11 \pm 0.30)^{(b)}$		[71DAN/CHI]
sp	9 M H(Cl,ClO ₄)	RT	2.12		[73BAR/MUR]
dis	2 M H(Cl,ClO ₄)	25	$-(0.05 \pm 0.05)$		[75PAT/RAM]
dis	2 M H(Cl,ClO ₄)	25	$(0.00 \pm 0.20)^{(b,c)}$		[75PAT/RAM] [94GIF]
cix	0.2 - 1 M HCl	25	0.34		[76SOU/SHA]
$\text{Np}^{4+} + 2\text{Cl}^- \rightleftharpoons \text{NpCl}_2^{2+}$					
dis	1 M H(Cl,ClO ₄)	20	$-(0.25 \pm 0.30)^{(b)}$	(1.9 ± 0.3)	[66SHI/NAZ]
	2 M H(Cl,ClO ₄)	20	$-(0.15 \pm 0.30)^{(b)}$	(1.5 ± 0.4)	
dis	4 M (H,Na)(Cl,ClO ₄)	25	$-(0.10 \pm 0.50)^{(b)}$	(0.0 ± 0.8)	[71DAN/CHI]
sp	9 M H(Cl,ClO ₄)	RT	3.04		[73BAR/MUR]
dis	2 M H(Cl,ClO ₄)	25	$-(0.15 \pm 0.06)$		[75PAT/RAM]
dis	2 M H(Cl,ClO ₄)	25	$-(0.22 \pm 0.40)^{(b,c)}$	(1.4 ± 0.4)	[75PAT/RAM] [94GIF]
$\text{Np}^{4+} + 3\text{Cl}^- \rightleftharpoons \text{NpCl}_3^+$					
dis	1 M H(Cl,ClO ₄)	20	-0.48		[66SHI/NAZ]

(a) Refers to the reactions indicated, the ionic strength and temperature given in the table. $\log_{10}\beta_q^\circ$ is in molal units, at $I = 0$ and 298.15 K.

(b) Uncertainty estimated in this review (cf. Appendix A).

(c) Result of a re-evaluation by Giffaut [94GIF] (cf. Appendix A [75PAT/RAM]).

The Gibbs energy of formation is calculated using the selected values for Np^{4+} and Cl^- .

$$\Delta_f G_m^\circ(\text{NpCl}^{3+}, \text{aq}, 298.15 \text{ K}) = -(631.6 \pm 5.8) \text{ kJ}\cdot\text{mol}^{-1}$$

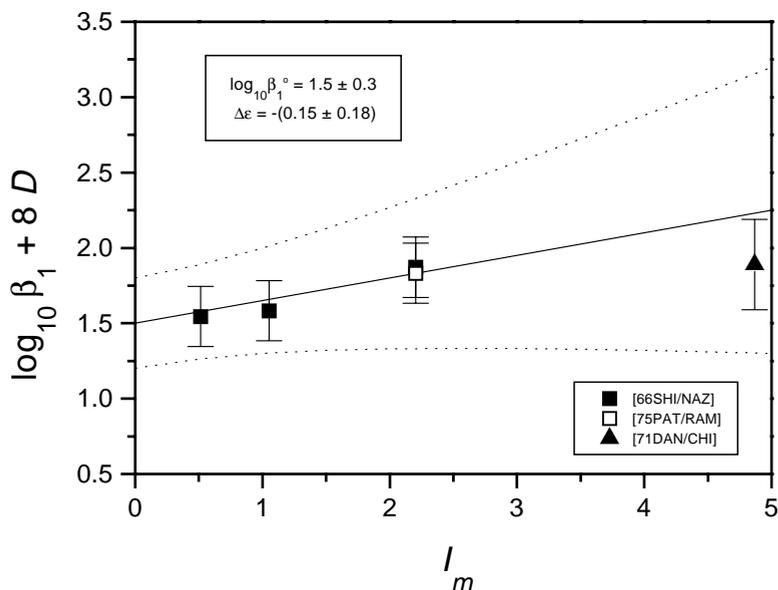
The 1:2 complex, NpCl_2^{2+} , if it exists, is very weak. Some values have been reported, cf. Table 9.6. If we tentatively use $\Delta\varepsilon(9.10, q = 2) = -(0.70 \pm 0.12)\text{kg}\cdot\text{mol}^{-1}$ as

estimated from the value of the formation of UF_2^{2+} , cf. [92GRE/FUG], Appendix B, the resulting $\log_{10} \beta_2^\circ$ values, see Table 9.6, are not consistent. Giffaut [94GIF] gives $\log_{10} \beta_2^\circ(9.10, q = 2) = (2.4 \pm 0.3)$, evaluated from the same literature data using an estimated $\Delta\varepsilon = -(0.63 \pm 0.23)\text{kg}\cdot\text{mol}^{-1}$. In order to obtain agreement between the four extrapolated values, a slope of about $\Delta\varepsilon(9.10, q = 2) = -0.2\text{kg}\cdot\text{mol}^{-1}$ would be necessary. This is far from being consistent with the $\Delta\varepsilon$ values of similar equilibria. The reported constants might well be artefacts due to medium changes, and we cannot select any thermodynamic data for the formation of NpCl_2^{2+} .

The 1:3 complex is very weak, see Appendix A [66SHI/NAZ, 71DAN/CHI]. If this complex exists, it will only form at very high chloride concentrations.

Figure 9.3: Comparison of selected and experimental data for the formation of NpCl^{3+} in mixed perchlorate/chloride media from [66SHI/NAZ] [71DAN/CHI] and [75PAT/RAM]. The solid line represents the prediction of $(\log_{10} \beta_1 + 8D)$, and the dotted lines are the limits of the uncertainty range obtained by propagating the resulting uncertainties at $I = 0$ back to $I = 5$ m.

Equilibrium: $\text{Np}^{4+} + \text{Cl}^- \rightleftharpoons \text{NpCl}^{3+}$

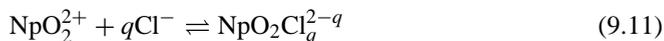


9.2.2.3 Aqueous Np(V) chlorides

Some authors have published formation constants for $\text{NpO}_2\text{Cl}(\text{aq})$ and $\text{NpO}_2\text{Cl}_2^-$ at ionic strengths from 2 to 5 M (*cf.* Table 9.7). The stability of these complexes is obviously very low. The cation exchange study of Gainar and Sykes [64GAI/SYK] can be interpreted equally well by formation of $\text{NpO}_2\text{Cl}(\text{aq})$ or activity factor effects, *cf.* the discussion in Appendix A about the nitrate experiments described in the same paper [64GAI/SYK]. It should be mentioned that Danesi *et al.* [71DAN/CHI] reported formation constants for these two complexes, which they withdrew later [74DAN/CHI] after re-evaluations based on an improved value for the liquid junction potential of their electrode system, *cf.* Appendix A. Vodovatov *et al.* [76VOD/KOL] could not observe any chloride complexes of Np(V) by the proton relaxation method. Rao *et al.* [79RAO/GUD] discussed the studies reported in the literature and concluded that high chloride concentrations are necessary ($> 3 \text{ M HCl}$) to distinguish the complexation effects from the experimental errors. The same group [81PAT/RAM] used a very high ionic strength of $I = 8.5 \text{ M}$ (NaClO_4) and chloride concentrations up to 0.75 M and interpreted their extraction data in terms of the formation of $\text{NpO}_2\text{Cl}(\text{aq})$. Neck, Kim and Kanellakopoulos [94NEC/KIM] reported formation constants for the 1:1 and the 1:2 complexes, but the ionic strength is high ($I = 5 \text{ M}$) and in the absence of precise estimates of the interaction coefficients, the error in the extrapolation to $I = 0$ will be dominated by the error of our estimates of the ionic interactions. Giffaut [94GIF] observed no significant changes in the visible absorption spectrum of NpO_2^+ in 1 M HClO_4 and 4 M NaCl . Hence, it would be highly speculative to make a selection on the basis of the existing data.

9.2.2.4 Aqueous Np(VI) chlorides

The influence of chloride concentration on the isotopic exchange rate between Np(V) and Np(VI) has been studied by Cohen, Sullivan and Hindman [55COH/SUL] at 0, 5 and 10°C in 3 M perchloric acid solution. At chloride concentrations above 1.5 M the fitting of the experimental data was improved by taking into account the formation of a 1:2 complex, $\text{NpO}_2\text{Cl}_2(\text{aq})$, although this is more likely to be a medium effect.



Other values for $q = 1$ and 2 were reported from potentiometric measurements [70AL-/WAI2, 74DAN/CHI] and from solvent extraction experiments [71DAN/CHI] (*cf.* Table 9.8). In the careful experiment of Al-Niaimi, Wain and McKay [70AL-/WAI2], the potential changes caused by the limited formation of NpO_2Cl^+ were very small, resulting in a low precision, although the experimental method seems reliable. Due to insufficient information, the results of the study of Sykes and Taylor [62SYK/TAY] are not used in selecting a recommended value. We use the constants reported in [55COH/SUL] (extrapolated to 25°C), and in [70AL-/WAI2, 71DAN/CHI, 74DAN/CHI, 78BED/FID] for our selection, but a statistical treatment seems difficult. We therefore adopt the $\Delta\varepsilon$ value of the corresponding Pu(VI) system and increase its uncertainty by 0.05:

Table 9.7: Experimental equilibrium data for the neptunium(V) chloride system.

Method	Ionic medium	t (°C)	$\log_{10} \beta_q^{(a)}$	Reference
$\text{NpO}_2^+ + \text{Cl}^- \rightleftharpoons \text{NpO}_2\text{Cl}(\text{aq})$				
cix	2 M H(Cl,ClO ₄)	25	$-(0.29 \pm 0.05)$	[64GAI/SYK]
emf	4 M (Na,H)(Cl,ClO ₄)	25	$-(2.5 \pm 0.4)^{(b)}$	[71DAN/CHI]
emf	4 M (Na,H)(Cl,ClO ₄)	25	“no complexation”	[74DAN/CHI]
prx	?	RT?	< -0.7	[76VOD/KOL]
dis	2 M Na(Cl,ClO ₄)	25	$-(0.42 \pm 0.04)$	[79RAO/GUD]
dis	8.5 M Na(Cl,ClO ₄)	25	0.48	[81PAT/RAM]
sp	4 M NaCl	25	“no complexation”	[94GIF]
dis	5 M Na(Cl,ClO ₄)	25	$-(0.05 \pm 0.02)$	[94NEC/KIM]
$\text{NpO}_2^+ + 2\text{Cl}^- \rightleftharpoons \text{NpO}_2\text{Cl}_2^-$				
emf	4 M H(Cl,ClO ₄)	25	$-(1.55 \pm 0.05)^{(b)}$	[71DAN/CHI]
emf	4 M H(Cl,ClO ₄)	25	“no complexation”	[74DAN/CHI]
dis	5 M Na(Cl,ClO ₄)	25	$-(0.71 \pm 0.04)$	[94NEC/KIM]

(a) Refers to the reactions indicated, as well as to the ionic strength and temperature given in the table.

(b) These values were withdrawn later by the same authors [74DAN/CHI].

$\Delta\varepsilon(9.11, q = 1) = -(0.08 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}$. The constants are converted to molal units and then corrected to $I = 0$, cf. Table 9.8. The resulting values at $I = 0$ are compatible. Their large uncertainties originate from the error propagation in the extrapolation procedure. We select the weighted average of these values:

$$\log_{10} \beta_1^\circ(9.11, q = 1, 298.15 \text{ K}) = 0.40 \pm 0.17.$$

As a comparison, the IAEA review [92FUG/KHO] selected $\log_{10} \beta_1^\circ = (0.4 \pm 0.1)$, which agrees with the present selection.

Two publications [55COH/SUL, 78BED/FID] reported constants for the formation of the 1:2 complex. Both these studies seem to be reliable, cf. Appendix A. If we adopt the $\Delta\varepsilon$ value accepted from Giffaut’s [94GIF] evaluation for the corresponding Pu(VI) system, $\Delta\varepsilon(9.11, q = 1) = -(0.43 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}$, we obtain $\log_{10} \beta_2^\circ = -0.7$ and -0.2 , respectively, cf. Table 9.8. These small values are likely due to inter-ionic interactions, rather than to the formation of $\text{NpO}_2\text{Cl}_2(\text{aq})$.

The Gibbs energy of formation value is derived from the above selected constant using the selected $\Delta_f G_m^\circ$ values for NpO_2^{2+} and Cl^- .

$$\Delta_f G_m^\circ(\text{NpO}_2\text{Cl}^+, \text{aq}, 298.15 \text{ K}) = -(929.4 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1}$$

Table 9.8: Experimental equilibrium data for the neptunium(VI) chloride system.

Method	Ionic medium	t (°C)	$\log_{10} \beta_q^{(a)}$	$\log_{10} \beta_q^{\circ(a)}$	Reference
$\text{NpO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{NpO}_2\text{Cl}^+$					
kin	3 M H(Cl,ClO ₄)	0.0	0.21 ^(c)		[55COH/SUL]
	3 M H(Cl,ClO ₄)	0.0	0.10 ^(d)		
	3 M H(Cl,ClO ₄)	4.78	0.06 ^(c)		
	3 M H(Cl,ClO ₄)	4.78	0.00 ^(d)		
	3 M H(Cl,ClO ₄)	9.84	-0.06 ^(c)		
	3 M H(Cl,ClO ₄)	9.84	-0.09 ^(d)		
	3 M H(Cl,ClO ₄)	25	-(0.37±0.20) ^(b,d,e) (0.29±0.49)		
sp	2M Na(Cl,ClO ₄)	25	-0.21		[62SYK/TAY]
emf	0.3 M H(Cl,ClO ₄)	25	-(0.32±0.40) ^(b)	(0.26±0.40)	[70AL-/WAI2]
	0.4 M H(Cl,ClO ₄)	25	-(0.36±0.40) ^(b)	(0.26±0.40)	
	0.5 M H(Cl,ClO ₄)	25	-(0.35±0.40) ^(b)	(0.31±0.41)	
dis	4 M (H,Na)(Cl,ClO ₄)	25	-(0.16±0.20) ^(b)	(0.41±0.66)	[71DAN/CHI]
emf	4 M (H,Na)(Cl,ClO ₄)	25	-(0.05±0.20) ^(b)	(0.52±0.66)	[74DAN/CHI]
dis	2 M H(Cl,ClO ₄)	25	-(0.04±0.20) ^(b)	(0.68±0.35)	[78BED/FID]
$\text{NpO}_2^{2+} + 2\text{Cl}^- \rightleftharpoons \text{NpO}_2\text{Cl}_2(\text{aq})$					
kin	3 M H(Cl,ClO ₄)	0.0	-0.80		[55COH/SUL]
	3 M H(Cl,ClO ₄)	4.78	-0.74		
	3 M H(Cl,ClO ₄)	9.84	-0.70		
	3 M H(Cl,ClO ₄)	25	-(0.56±0.40) ^(b,e)	-(0.7±0.8)	
dis	2 M H(Cl,ClO ₄)	25	-(0.57±0.40) ^(b)	-(0.2±0.6)	[78BED/FID]

(a) Refers to the reactions indicated, the ionic medium and temperature given in the table. $\log_{10} \beta_q^\circ$ is in molal units, at $I = 0$ and 298.15 K.

(b) Uncertainty estimated in this review.

(c) Refers to the model containing only a 1:1 complex.

(d) Refers to the model containing a both 1:1 and a 1:2 complex.

(e) Extrapolated to 25°C in this review (*cf.* Appendix A).

9.2.3 Aqueous neptunium bromide complexes

9.2.3.1 Aqueous Np(III) bromides

Quantitative information on bromide complexation of Np^{3+} has only been published by Shiloh and Marcus [64SHI/MAR] in concentrated LiBr solutions of varying ionic strength up to near 12 M. The authors gave formation constants for NpBr^{2+} ($\log_{10} \beta_1 = -(3.39 \pm 0.06)$) and NpBr_2^+ ($\log_{10} \beta_2 = -(6.48 \pm 0.05)$). These very negative values for the formation constants correspond to the complexation of only about 1% of Np(III) at the highest bromide concentration used in the experiment, which was probably barely detectable. Also, the ionic strength effects are expected to be considerable under these conditions. An extrapolation to $I = 0$ is not possible due to the lack of

good estimates of ionic interactions, and no standard formation value can be selected here.

9.2.3.2 Aqueous Np(IV) bromides

The only experimental equilibrium data available on the reactions



are from Raghavan, Ramakrishna and Patil [75RAG/RAM] at $I = 2 \text{ M}$ (HBr, HClO₄) and 25°C. The reported constants are lower than those of the analogous uranium and plutonium complexes: $\log_{10} \beta_1(9.12, q = 1) = -(0.21 \pm 0.01)$ and $\log_{10} \beta_2(9.12, q = 2) = -(0.57 \pm 0.03)$. The cause for the deviation could be experimental limitations, *cf.* comments in Appendix A. For the corresponding bromide complexes of Pu(IV) (Section 18.2.3.2) and U(IV) [92GRE/FUG], as well as for the Np(IV) complexes NpCl³⁺ and NpI³⁺, $\log K_1^\circ$ values between 1.25 and 1.8 are obtained, and the complexation constant of NpBr³⁺ is also expected to lie in the same range. However, on the weak basis of the available experimental information, it is not possible to select any constant for the Np(IV) bromide complexes.

9.2.3.3 Aqueous Np(V) and Np(VI) bromides

No aqueous species of the form NpO₂Br_q^{1-q} or NpO₂Br_q^{2-q}, respectively, have been identified.

9.2.4 Aqueous neptunium iodine complexes

9.2.4.1 Aqueous neptunium iodides

9.2.4.1.a Aqueous Np(III) iodides

No aqueous species of the form NpI_q^{3-q} have been identified.

9.2.4.1.b Aqueous Np(IV) iodides

Quantitative information on iodide complexation of Np⁴⁺ has been published by Kusumakumari *et al.* [79KUS/GAN] and Patil, Ramakrishna and Gudi [81PAT/RAM] on the equilibrium



The results are summarised in Table 9.9. The values originate all from Patil's group and are from solvent extraction studies (see Appendix A). It should be mentioned that the review paper [78PAT/RAM], which is cited in the IAEA review [92FUG/KHO], reports two new values referring to unpublished work of Rao, Bagawde, Ramakrishna and Patil, and these values were published later in [79KUS/GAN]. Some of the papers contain little experimental details, but we can

assume that the experimental procedures are the same in all studies. We estimate the corresponding values at $I = 0$ by converting the constants to molal units and by adopting the ion interaction coefficient of the corresponding Np(IV) chloride system with an increased uncertainty, $\Delta\varepsilon(9.13) = -(0.15 \pm 0.25)\text{kg}\cdot\text{mol}^{-1}$. The resulting uncertainties in $\log_{10} \beta_1^\circ$, *cf.* Table 9.9, are composed of the uncertainty assigned to the values at $I = 2$ M, *cf.* Appendix A, and the propagation of the uncertainty in the ion interaction coefficient. The values at $I = 0$ are consistent, and the weighted average is selected here²:

$$\log_{10} \beta_1^\circ(9.13, 298.15 \text{ K}) = (1.5 \pm 0.4)$$

The Gibbs energy of formation is calculated using the selected values for Np^{4+} and I^- .

$$\Delta_f G_m^\circ(\text{NpI}^{3+}, \text{aq}, 298.15 \text{ K}) = -(552.1 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1}$$

Table 9.9: Experimental equilibrium data for the neptunium(IV) iodide system.

Method	Ionic medium	t (°C)	$\log_{10} \beta_1^{(a)}$	$\log_{10} \beta_1^{\circ(a)}$	Reference
$\text{Np}^{4+} + \text{I}^- \rightleftharpoons \text{NpI}^{3+}$					
dis	2 M H(I,ClO ₄)	25	(0.02±0.30) ^(b)	(1.52 ± 0.63)	[78PAT/RAM]
dis (HTTA)	2 M H(I,ClO ₄)	25	-(0.10±0.30) ^(b)	(1.40 ± 0.63)	[79KUS/GAN]
dis (HD)	2 M H(I,ClO ₄)	25	(0.11±0.30) ^(b)	(1.61 ± 0.63)	
dis	2 M H(I,ClO ₄)	25	(0.04±0.30) ^(b)	(1.54 ± 0.63)	[81PAT/RAM]

(a) Refers to the reactions indicated, the ionic strength and temperature given in the table. $\log_{10} \beta_1^\circ$ is in molal units, at $I = 0$ and 298.15 K.

(b) The uncertainties are estimated in this review (*cf.* Appendix A).

9.2.4.1.c Aqueous Np(V) and Np(VI) iodides

No aqueous species of the form $\text{NpO}_2\text{I}_q^{1-q}$ or $\text{NpO}_2\text{I}_q^{2-q}$, respectively, are known to be stable.

9.2.4.2 Aqueous neptunium iodates

9.2.4.2.a Aqueous Np(III) iodates

No aqueous iodate complexes of Np^{3+} have been identified.

²The halide complexation constants of U(IV) [92GRE/FUG] suggest a trend of decreasing stability in the order $\text{Cl}^- > \text{Br}^- > \text{I}^-$. Although this trend is not exactly observed with NpI^{3+} and NpCl^{3+} , it should be considered that the uncertainties are high and that weak complexation and medium effects may be difficult to separate.

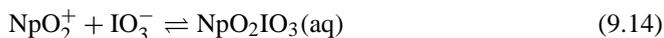
9.2.4.2.b Aqueous Np(IV) iodates

The formation of iodate complexes of Np^{4+} has been suggested by Patil, Ramakrishna and Ramaniah [78PAT/RAM] in their review of aqueous coordination complexes of neptunium. They refer to absorption spectra of Np(IV) in 1 M HClO_4 and 2 M HIO_3 , respectively, reported in an unpublished work of Rao, Bagawde, Ramakrishna and Patil, *cf.* [78PAT/RAM]. Based on these spectra, it was concluded that the spectral changes suggest formation of strong iodate complexes of Np(IV) [78PAT/RAM]. The description of the interactions between Np(IV) and IO_3^- as thermodynamically stable complexes is not feasible. These types of complexes can exist as precursor complexes in subsequent redox reactions.

It should be mentioned that the constants quoted for the formation of $\text{Np}(\text{IO}_3)_6^{2-}$ and $\text{Np}(\text{IO}_3)_8^{4-}$ in a table of the IAEA review [92FUG/KHO], *p.*92 are misplaced and in fact refer to $\text{Th}(\text{IO}_3)_6^{2-}$ and $\text{Th}(\text{IO}_3)_8^{4-}$ [61STO/FRY], as correctly noted in the text [92FUG/KHO], *p.* 93. The origin of the constants $\log_{10} \beta_1(\text{NpIO}_3^{3+}) = 2.4$ and $\log_{10} \beta_1(\text{Np}(\text{OH})\text{IO}_3^{2+}) = 0.3$ at $I = 1$ M (HClO_4) quoted in the IAEA review (*p.* 92) as originating from Patil, Ramakrishna and Ramaniah [78PAT/RAM], is unclear to us, since these authors reported only qualitative information on the formation of Np(IV) iodate complexes.

9.2.4.2.c Aqueous Np(V) iodates

Blokhin *et al.* [72BLO/BUK] observed a displacement of the UV absorption band of NpO_2^+ when adding KIO_3 to the solution, but he found that the changes in the spectrum were too small to allow a quantitative calculation of the formation constant. Later, Patil's group published a solvent extraction study [79RAO/GUD], and they used spectrophotometry as a check of the correct oxidation state of Np. At the same time, they used spectrophotometry measurements to derive the formation constant of a 1:1 complex [78RAO/PAT], $\text{NpO}_2\text{IO}_3(\text{aq})$, and they obtained very comparable results, *cf.* Table 9.10, according to the equilibrium



We accept the results of the two studies with increased uncertainties (see Appendix A), and we correct the constants to $I = 0$ by adopting the specific ion interaction coefficients published in the uranium book [92GRE/FUG] of this series: $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.25 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$ and $\varepsilon_{(\text{IO}_3^-, \text{Na}^+)} = -(0.06 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$. For Equilibrium (9.14) the ion interaction coefficient is thus $\Delta\varepsilon(9.14) = -(0.19 \pm 0.10) \text{ kg} \cdot \text{mol}^{-1}$, where we have increased the uncertainty due to the analogy made. The resulting values at $I = 0$ are consistent (see Table 9.10 – note that the values are identical to those at $I = 2$ M, because, coincidentally, the specific ion interaction term exactly compensates for the Debye-Hückel term under these conditions), and their average is selected here.

$$\log_{10} \beta_1^\circ(9.14, 298.15 \text{ K}) = 0.5 \pm 0.3$$

The Gibbs energy is calculated by using the selected $\Delta_f G_m^\circ$ values for NpO_2^+ and IO_3^- .

$$\Delta_f G_m^\circ(\text{NpO}_2\text{IO}_3, \text{aq}, 298.15 \text{ K}) = -(1037.0 \pm 5.9) \text{ kJ}\cdot\text{mol}^{-1}$$

Table 9.10: Experimental equilibrium data for the Np(V) and Np(VI) iodate systems.

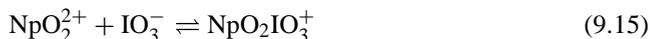
Method	Ionic medium	t (°C)	$\log_{10} \beta_1^{(a)}$	$\log_{10} \beta_1^{\circ(a)}$	Reference
$\text{NpO}_2^+ + \text{IO}_3^- \rightleftharpoons \text{NpO}_2\text{IO}_3(\text{aq})$					
sp	2 M $\text{H}(\text{IO}_3, \text{ClO}_4)$	25	$(0.58 \pm 0.30)^{(b)}$	(0.58 ± 0.37)	[78RAO/PAT]
dis	2 M $\text{H}(\text{IO}_3, \text{ClO}_4)$	25	$(0.32 \pm 0.30)^{(b)}$	(0.32 ± 0.37)	[79RAO/GUD]
$\text{NpO}_2^{2+} + \text{IO}_3^- \rightleftharpoons \text{NpO}_2\text{IO}_3^+$					
sp	0.3 M $(\text{HClO}_4, \text{NaIO}_3)$	25	(0.61 ± 0.02)	$(1.2 \pm 0.3)^{(b)}$	[72BLO/BUK]

(a) Refers to the reactions indicated, the ionic strength and temperature given in the table. $\log_{10} \beta_1^\circ$ is in molal units, at $I = 0$ and 298.15 K.

(b) The uncertainties are estimated in this review (*cf.* Appendix A).

9.2.4.2.d Aqueous Np(VI) iodates

Blokhin *et al.* [72BLO/BUK] published a spectrophotometric study on the iodate complex formation of Np(V) and Np(VI). In contrast to Np(V), they found a very marked change in the absorption spectrum of NpO_2^{2+} with increasing concentration of KIO_3 . They derived a formation constant for the 1:1 complex according to the equilibrium



and observed higher species when the iodate concentration exceeded 0.15 M. Their measurements seem reliable (see Appendix A), and we correct their value, $\log_{10} \beta_1(9.15, I = 0.3 \text{ M}, 298.15 \text{ K}) = 0.61$, to $I = 0$ by using $\Delta\varepsilon(9.15) = -(0.07 \pm 0.10)\text{kg}\cdot\text{mol}^{-1}$, calculated from the ε values of the corresponding uranium(VI) system [92GRE/FUG], by increasing the uncertainty in $\Delta\varepsilon$ by 0.05. The resulting value is assigned an uncertainty of ± 0.3 (*cf.* Appendix A):

$$\log_{10} \beta_1^\circ(9.15, 298.15 \text{ K}) = 1.2 \pm 0.3$$

It should be mentioned that this constant is lower than that for the corresponding uranium(VI) system ($\log_{10} \beta_1^\circ = 2.0$). This is one of the reasons why the IAEA review [92FUG/KHO] did not select any value for the formation of $\text{NpO}_2\text{IO}_3^+$. However, we believe that this reason is not sufficient by itself to discard our selection.

The Gibbs energy of formation is calculated using the selected values for NpO_2^{2+} and IO_3^- .

$$\Delta_f G_m^\circ(\text{NpO}_2\text{IO}_3^+, \text{aq}, 298.15 \text{ K}) = -(929.1 \pm 5.9) \text{ kJ}\cdot\text{mol}^{-1}$$

Chapter 10

Neptunium group 16 compounds and complexes

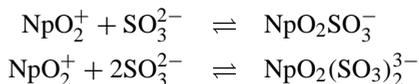
10.1 Neptunium sulphur compounds and complexes

10.1.1 Neptunium sulphites

10.1.1.1 Aqueous neptunium sulphites

10.1.1.1.a Np(V) sulphites

There are four reports of SO_3^{2-} complexes of NpO_2^+ [65MOS/MEF, 72BLO/BUK2, 78MOS/POZ, 79MOS/POZ]. Corresponding equilibrium constants are reported in Table 10.1. Moskvin *et al.* [65MOS/MEF] gave no original data that can be evaluated, and the work presented in [78MOS/POZ] and [79MOS/POZ] represents duplicate reports of the same data. All four reports conclude that two dioxoneptunium(V) sulphite complexes are formed:



Blokhin *et al.* [72BLO/BUK2] suggest, on the basis of solubility experiments at high SO_3^{2-} concentrations, that higher coordinated complexes may form. Although there is reasonable agreement between the reported results, there is insufficient data to permit the reported values to be extrapolated to the infinite dilution standard state.

10.1.1.2 Solid neptunium sulphites

Blokhin *et al.* [72BLO/BUK2] precipitated stable solids of the forms of: $\text{NaNpO}_2\text{SO}_3 \cdot \text{H}_2\text{O}(\text{s})$, $\text{NaNpO}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$, $\text{NH}_4\text{NpO}_2\text{SO}_3(\text{s})$ and $\text{KNpO}_2\text{SO}_3(\text{s})$. The composition of these solids was verified by chemical analysis. The Na-dihydrate salt dehydrates when heated to the monohydrate state. Thermogravimetric data are given in this reference. There are no thermodynamic data available for these solids.

Table 10.1: Experimental equilibrium data for the neptunium(V) sulphite system.

Method	I (m)	t (°C)	$\log_{10} \beta$	Reference
$\text{NpO}_2^+ + \text{SO}_3^{2-} \rightleftharpoons \text{NpO}_2\text{SO}_3^-$				
sol	(?)	(?)	2.15	[65MOS/MEF]
	1.03 Na(SO ₃ ²⁻ , NO ₂ ⁻)	25	(2.6±0.6)	[72BLO/BUK2]
	1.04 (Na ⁺ , NH ₄ ⁺), (SO ₃ ²⁻ , Cl ⁻)	(20 ±2)	(1.50±0.1)	[78MOS/POZ] [79MOS/POZ]
$\text{NpO}_2^+ + 2\text{SO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{SO}_3)_2^{3-}$				
sol	(?)	(?)	3.00	[65MOS/MEF]
	1.03 Na(SO ₃ ²⁻ , NO ₂ ⁻)	25	(3.6±2.4)	[72BLO/BUK2]
	1.04 (Na ⁺ , NH ₄ ⁺), (SO ₃ ²⁻ , Cl ⁻)	(20 ±2)	(3.01±0.08)	[78MOS/POZ] [79MOS/POZ]

10.1.2 Neptunium sulphates

10.1.2.1 Aqueous neptunium sulphates

10.1.2.1.a Np(VII) sulphates

No experimental evidence for the existence of Np(VII) sulphate complexes was found.

10.1.2.1.b Np(VI) sulphates

Six experimental studies of the aqueous Np(VI) sulphate system [62SYK/TAY, 68AHR/BRA2, 70AL-/WAI, 76PAT/RAM, 84KAS/JOS, 86ULL/SCH] have been reported. The results of these experiments and recalculations performed by the reviewers are given in Table 10.2.

Table 10.2: Experimentally determined formation constants in the Np(VI) sulphate system^(a).

Method	I	t (°C)	$\log_{10} \beta_q^{(b)}$	Reference
$\text{NpO}_2^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{NpO}_2\text{SO}_4(\text{aq})$				
sp	2 M NaClO ₄	25	1.64	[62SYK/TAY]
cal	0 ^(c)	25	(3.27±0.05)	[86ULL/SCH]
Recommended value	0	25	(3.28 ±0.06)	This review

(Continued on next page)

Table 10.2: (continued)

Method	<i>I</i>	<i>t</i> (°C)	log ₁₀ β _q ^(b)	Reference
$\text{NpO}_2^{2+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{NpO}_2(\text{SO}_4)_2^{2-}$				
cal	0 ^(c)	25	(4.65±0.05)	[86ULL/SCH]
Recommended value	0	25	(4.70 ±0.10)	This review
$\text{NpO}_2^{2+} + \text{HSO}_4^- \rightleftharpoons \text{NpO}_2\text{SO}_4(\text{aq}) + \text{H}^+$				
dis	1 M (H,Na)ClO ₄	21	(0.79±0.13)	[68AHR/BRA2]
recalc	1.05 m	21	(0.75±0.12)	
recalc	1.05	25	(0.76 ±0.12)	
pot	0.1 M HClO ₄	25	(0.88±0.01)	[70AL-/WAI]
recalc	0.1 m		(0.87±0.01)	
pot	0.2 M HClO ₄	25	(0.81±0.01)	[70AL-/WAI]
recalc	0.2 m		(0.81±0.01)	
pot	0.3 M HClO ₄	25	(0.78±0.01)	[70AL-/WAI]
recalc	0.31 m		(0.77±0.01)	
pot	0.4 M HClO ₄	25	(0.76±0.02)	[70AL-/WAI]
recalc	0.41 m		(0.75±0.01)	
pot	0.5 M HClO ₄	25	(0.75±0.01)	[70AL-/WAI]
recalc	0.52 m		(0.75±0.01)	
dis	2 M HClO ₄	25	1.07	[76PAT/RAM]
recalc	2.2 m		(1.00±0.05)	
cou	0.5 M HClO ₄	23	0.75	[84KAS/JOS]
recalc	0.52 m	23	(0.79±0.02)	
recalc	0.52 m	25	(0.80±0.03)	
recalc	0	25	(1.29±0.07)	[86ULL/SCH]
Recommended value	0	25	(1.30±0.04)	This review
$\text{NpO}_2^{2+} + 2\text{HSO}_4^- \rightleftharpoons \text{NpO}_2(\text{SO}_4)_2^{2-} + 2\text{H}^+$				
dis	1 M (H,Na)ClO ₄	21	(0.55±0.31)	[68AHR/BRA2]
recalc	1.05 m	21	(0.78±0.14)	
recalc	1.05 m	25	(0.82±0.15)	
pot	0.5 M HClO ₄	25	0.20	[70AL-/WAI]
dis	2 M HClO ₄	25	0.60	[76PAT/RAM]
recalc	2.2 m		(0.87±0.19)	
recalc	0	25	(0.69±0.09)	[86ULL/SCH]
Recommended value	0	25	(0.74±0.07)	This review

^(a) Recalculations based on a consistent non-linear least squares approach.

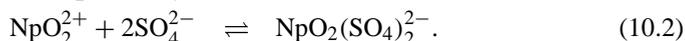
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(footnotes continued)

^(b)Here “ β ” refers to either β or ${}^*\beta$ as appropriate for the reaction as written and q is the number of ligands in the complex $\text{NpO}_2(\text{SO}_4)_q^{2-2q}$.

^(c)Measurements made at $I = 0.09 - 0.45$ m (H,Na)ClO₄ and extrapolated to $I = 0$.

Using the results of calorimetric experiments performed on solutions containing only dilute acid ($\text{pH} \geq 3$), Ullman and Schreiner [86ULL/SCH] calculated both the equilibrium constants and the enthalpies for the formation of $\text{NpO}_2\text{SO}_4(\text{aq})$ and $\text{NpO}_2(\text{SO}_4)_2^{2-}$:



Other researchers performed their experiments in acid medium and determined the equilibrium constants of the analogous reactions:



For the purposes of this review all useful association quotients measured at temperatures other than 25°C were converted to standard conditions using the auxiliary data for the SO_4^{2-} protonation reaction and the enthalpies determined by Ullman and Schreiner [86ULL/SCH]:

$$\Delta_r H_m^\circ(10.1, 298.15 \text{ K}) = (16.7 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m^\circ(10.2, 298.15 \text{ K}) = (26.0 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

The recommended value of $\log_{10} {}^*\beta_1^\circ(10.3)$ was determined from the SIT extrapolation to the standard state using the recalculated (Table 10.2) results of [70AL-/WAI, 76PAT/RAM, 84KAS/JOS]. This extrapolation yields $\log_{10} {}^*\beta^\circ(10.3) = (1.30 \pm 0.05)$ and $\Delta\varepsilon(10.3) = -(0.29 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$. The result of [86ULL/SCH] ($\log_{10} \beta_1^\circ(10.1) = (3.27 \pm 0.05)$) is used together with the auxiliary data for the protonation constant of SO_4^{2-} to determine an independent value for $\log_{10} {}^*\beta_1^\circ(10.3) = (1.29 \pm 0.07)$. The recommended values are taken as the weighted mean of these two estimates:

$$\log_{10} {}^*\beta_1^\circ(10.3, 298.15 \text{ K}) = (1.30 \pm 0.04)$$

$$\log_{10} \beta_1^\circ(10.1, 298.15 \text{ K}) = (3.28 \pm 0.06)$$

The ion interaction procedure used by [86ULL/SCH] to extrapolate to the standard state yields an equivalent interaction coefficient in the SIT model of $\Delta\varepsilon(10.1) = -(0.28 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$.

The recalculated equilibrium constants of [68AHR/BRA2] and [76PAT/RAM] are averaged to standard conditions to give $\log_{10} {}^*\beta_2^\circ(10.4) = (0.84 \pm 0.12)$ ($\Delta\varepsilon$ is indistinguishable from 0: $\Delta\varepsilon = -(0.04 \pm 0.21) \text{ kg}\cdot\text{mol}^{-1}$). The independent estimate of [86ULL/SCH], calculated as above, yields $\log_{10} {}^*\beta_2^\circ(10.4) = (0.69 \pm 0.09)$. The results

of [70AL-/WAI] are not used as no quantitative estimate of uncertainty could be made and the estimate of error made by the reviewers appeared to be much larger than those determined in other experiments. The weighted means of these two estimates yield the recommended values:

$$\log_{10}^* \beta_2^\circ(10.4, 298.15 \text{ K}) = (0.74 \pm 0.07)$$

$$\log_{10} \beta_2^\circ(10.2, 298.15 \text{ K}) = (4.70 \pm 0.10)$$

All other thermodynamic parameters can be calculated from those given above.

10.1.2.1.c Np(V) sulphates

Five experimental studies describing the Np(V) sulphate complexes [79MOS/POZ, 79RAO/GUD, 81PAT/RAM, 83HAL/OLI, 85INO/TOC2] have been reported (Table 10.3). In all cases only one complex was observed:



Table 10.3: Experimentally determined formation constants in the Np(V) sulphate system.

Method	<i>I</i>	<i>t</i> (°C)	$\log_{10} \beta_1$	Reference
$\text{NpO}_2^+ + \text{SO}_4^{2-} \rightleftharpoons \text{NpO}_2\text{SO}_4^-$				
coprecipitation	1.5 M NH ₄ Cl	(20 ± 2)	(1.04 ± 0.4)	[79MOS/POZ]
dis	2 M NaClO ₄	25	(0.44 ± 0.09)	[79RAO/GUD]
recalc	2.2 m		(0.45 ± 0.01)	
dis	8.5 M	25(?)	0.45	[81PAT/RAM]
dis	0.52 m NaClO ₄	5	−(0.43 ± 0.35)	[83HAL/OLI]
dis	1.05 m NaClO ₄	5	−(0.18 ± 0.09)	[83HAL/OLI]
dis	2.2 m NaClO ₄	5	−(0.04 ± 0.11)	[83HAL/OLI]
dis	0.52 m NaClO ₄	25	−(0.10 ± 0.08)	[83HAL/OLI]
dis	1.05 m NaClO ₄	25	(0.06 ± 0.04)	[83HAL/OLI]
dis	2.2 m NaClO ₄	25	(0.19 ± 0.04)	[83HAL/OLI]
dis	0.52 m NaClO ₄	45	(0.25 ± 0.03)	[83HAL/OLI]
dis	1.05 m NaClO ₄	45	(0.34 ± 0.03)	[83HAL/OLI]
dis	2.2 m NaClO ₄	45	(0.40 ± 0.05)	[83HAL/OLI]
dis	1 M NaClO ₄	25	(0.76 ± 0.04)	[85INO/TOC2]
Selected value	0 m	25	(0.44 ± 0.27)	This review

On the basis of the most reliable data at 25°C [79RAO/GUD] and [83HAL/OLI] the recommended value for the equilibrium constants for this reaction at standard state is determined using the SIT model:

$$\log_{10} \beta^\circ(10.5, 298.15 \text{ K}) = (0.44 \pm 0.27)$$

and $\Delta\varepsilon(10.5) = -(0.37 \pm 0.18)\text{kJ}\cdot\text{mol}^{-1}$. The enthalpy of Reaction (10.5) can be calculated from the three independent series of experiments performed at three ionic strengths by [83HAL/OLI]. The three estimates yield values of $\Delta_r H_m^\circ(10.5) = (28.8 \pm 1.6)\text{kJ}\cdot\text{mol}^{-1}$ at 0.52 m, $(22.0 \pm 1.8)\text{kJ}\cdot\text{mol}^{-1}$ at 1.05 m and $(18.7 \pm 0.2)\text{kJ}\cdot\text{mol}^{-1}$ at 2.2 m. The mean of these estimates yields the best value. The error was expanded to encompass the entire range of the three independent estimates.

$$\Delta_r H_m^\circ(10.5, 298.15\text{ K}) = (23.2 \pm 7.2)\text{kJ}\cdot\text{mol}^{-1}$$

The remaining thermodynamic parameters may be calculated from the selected values.

10.1.2.1.d Np(IV) sulphates

There are seven reliable studies of the complexing Np(IV) sulphate system [54SUL/HIN, 62SYK/TAY, 63MUS, 66AHR/BRA, 73PAT/RAM, 73PAT/RAM2, 76BAG/RAM]. In all but one case [62SYK/TAY], sufficient data have been given by the authors to permit the redetermination of formation constants and uncertainties. The remaining six studies (Table 10.4) are used to determine the best values for thermodynamic parameters in this system.

Table 10.4: Experimentally determined formation constants in the Np(IV) sulphate system^(a).

Method	<i>I</i>	<i>t</i> (°C)	$\log_{10} \beta_q^{(c)}$	Reference
$\text{Np}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{NpSO}_4^{2+}$				
sp	2 M NaClO ₄	25	3.51 ^(d)	[62SYK/TAY]
$\text{Np}^{4+} + \text{HSO}_4^- \rightleftharpoons \text{NpSO}_4^{2+} + \text{H}^+$				
dis	2.2 m HClO ₄	(10.2 ± 0.2)	(2.47 ± 0.09)	[54SUL/HIN]
recalc			(2.38 ± 0.06)	
dis	2.2 m HClO ₄	(25.2 ± 0.2)	(2.43 ± 0.09)	[54SUL/HIN]
recalc			(2.53 ± 0.07)	
dis	2.2 m HClO ₄	(35.3 ± 0.2)	(2.40 ± 0.09)	[54SUL/HIN]
recalc			(2.58 ± 0.05)	
sp	2 M NaClO ₄	25	(2.43 ± 0.05) ^(b)	[62SYK/TAY]
pol	3.5 m NaClO ₄	(25 ± 0.2)	(2.49 ± 0.03)	[63MUS]
recalc			(2.44 ± 0.03)	
ix	4.6 m HClO ₄	20	(2.70 ± 0.04)	[66AHR/BRA]
recalc			(2.65 ± 0.05)	
recalc		25	(2.66 ± 0.06)	
dis	2.2 m HClO ₄	25	2.51	[73PAT/RAM2]

(Continued on next page)

Table 10.4: (continued)

Method	<i>I</i>	<i>t</i> (°C)	$\log_{10}^* \beta_q^{(c)}$	Reference
recalc			(2.49±0.03)	
dis	2.2 m HClO ₄	10	2.45	[73PAT/RAM]
recalc			(2.44±0.05)	
dis	2.2 m HClO ₄	40	2.55	[73PAT/RAM]
recalc			(2.51±0.05)	
dis	2.2 m HClO ₄	10	2.44	[73PAT/RAM]
recalc			(2.42±0.02)	
dis	2.2 m HClO ₄	25	2.49	[73PAT/RAM]
recalc			(2.48±0.03)	
dis	2.2 m HClO ₄	40	2.53	[73PAT/RAM]
recalc			(2.56±0.08)	
dis	2.2 m HClO ₄	25	2.53 ^(e)	[76BAG/RAM]
recalc (benzene)			(2.52±0.20)	
recalc (<i>n</i> -heptane)			(2.35±0.21)	
Best value	0 m	25	(4.87±0.15)	This review
$\text{Np}^{4+} + 2\text{HSO}_4^- \rightleftharpoons \text{Np}(\text{SO}_4)_2(\text{aq}) + 2\text{H}^+$				
dis	2.2 m HClO ₄	(10.2 ± 0.2)	(3.38±0.19)	[54SUL/HIN]
recalc			(3.84±0.04)	
dis	2.2 m HClO ₄	(25.2 ± 0.2)	(3.47±0.19)	[54SUL/HIN]
recalc			(4.06±0.08)	
dis	2.2 m HClO ₄	(35.3 ± 0.2)	(3.53±0.19)	[54SUL/HIN]
recalc			(3.85±0.05)	
pol	3 M NaClO ₄	(25 ± 0.2)	3.64	[63MUS]
pol	3.5 m NaClO ₄	(25 ± 0.2)	(3.57±0.09)	[63MUS]
recalc			(3.92±0.11)	
ix	4.6 m HClO ₄	20	(4.26±0.05)	[66AHR/BRA]
recalc			(4.38±0.02)	
recalc		25	(4.41±0.03)	
dis	2.2 m HClO ₄	25	4.00	[73PAT/RAM2]
recalc			(4.03±0.02)	
dis	2.2 m HClO ₄	10	4.02	[73PAT/RAM]
recalc			(3.95±0.04)	
dis	2.2 m HClO ₄	40	4.04	[73PAT/RAM]
recalc			(4.15±0.03)	
dis	2.2 m HClO ₄	10	3.92	[73PAT/RAM]
recalc			(3.95±0.01)	

(Continued on next page)

Table 10.4: (continued)

Method	<i>I</i>	<i>t</i> (°C)	$\log_{10}^* \beta_q^{(c)}$	Reference
dis	2.2 m HClO ₄	25	4.06	[73PAT/RAM]
recalc			(4.06±0.02)	
dis	2.2 m HClO ₄	40	4.14	[73PAT/RAM]
recalc			(4.13±0.05)	
dis	2.2 m HClO ₄	25	4.04 ^(e)	[76BAG/RAM]
recalc (benzene)			(4.04±0.19)	
recalc (<i>n</i> -heptane)			(3.87±0.20)	
Best value	0 m	25	(7.09±0.25)	This review

(a) Recalculations based on a consistent non-linear least squares approach.

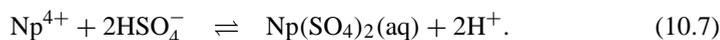
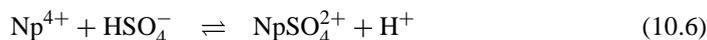
(b) Recalculated by [62SYK/TAY] from their reported experimental value for the reaction $\text{Np}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{NpSO}_4^{2+}$.

(c) *q* is the number of ligands in the complex $\text{Np}(\text{SO}_4)_q^{4-2q}$.

(d) This value is $\log_{10} \beta_1$, not $\log_{10}^* \beta_1$.

(e) Average value from studies of TTA in benzene and in *n*-heptane.

Because of concern about interferences due to hydrolysis, all the Np(IV) experiments were performed in strong acid medium. The results are therefore interpreted to describe the following reactions:



The results of [54SUL/HIN, 63MUS, 66AHR/BRA, 73PAT/RAM, 73PAT/RAM2, 76BAG/RAM], as recalculated by the reviewers (Table 10.4), are used to determine $\log_{10}^* \beta_1^\circ$ (10.6). The results of [66AHR/BRA] were corrected from 20 to 25°C using $\Delta_r H_m^\circ$ (10.6) determined below. Using the SIT model for extrapolation to the standard state, the recommended value was found to be:

$$\log_{10}^* \beta_1^\circ(10.6, 298.15 \text{ K}) = (4.87 \pm 0.15)$$

and $\Delta \varepsilon(10.6) = -(0.19 \pm 0.06) \text{ kg} \cdot \text{mol}^{-1}$, a value that overlaps with that reported for the analogous U(IV) reaction by [92GRE/FUG]. Assuming that $\varepsilon_{(\text{H}^+, \text{HSO}_4^-)} = -(0.01 \pm 0.07) \text{ kg} \cdot \text{mol}^{-1}$ (estimated from $\varepsilon_{(\text{Na}^+, \text{HSO}_4^-)}$), but with an expanded uncertainty), this yields an estimated value of

$$\varepsilon_{(\text{NpSO}_4^{2+}, \text{ClO}_4^-)} = (0.48 \pm 0.11) \text{ kg} \cdot \text{mol}^{-1}$$

which is selected by this review. This value differs somewhat from the estimate of $\varepsilon_{(\text{USO}_4^{2+}, \text{ClO}_4^-)} = (0.3 \pm 0.1) \text{ kg} \cdot \text{mol}^{-1}$ reported by [92GRE/FUG], but is within the range of interaction parameters between ClO_4^- and other divalent complexes, including for example FeSCN^{2+} [95SIL/BID].

The results of [54SUL/HIN, 63MUS, 66AHR/BRA, 73PAT/RAM, 73PAT/RAM2, 76BAG/RAM], as recalculated, were used to determine the association quotient of Reaction (10.7) at the standard state. The results of [66AHR/BRA] were corrected from 20 to 25°C, as above. Using the SIT model for extrapolation, the best value was found to be:

$$\log_{10}^* \beta_2^{\circ}(10.7, 298.15 \text{ K}) = (7.09 \pm 0.25)$$

and $\Delta \varepsilon$ (10.7) = $-(0.29 \pm 0.11) \text{ kg} \cdot \text{mol}^{-1}$, a value that overlaps with the one for the analogous reaction for the formation of $\text{U}(\text{SO}_4)_2(\text{aq})$ ($\Delta \varepsilon = -(0.46 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}$, [92GRE/FUG]).

$\Delta_r H_m^{\circ}(10.6)$ can be determined independently from the experiments of [54SUL/HIN, 73PAT/RAM, 73PAT/RAM2] in HDNNS (= dinonylnaphthalene-sulphonic acid)/benzene, and [73PAT/RAM] in TTA(= thenoyltrifluoroacetone)/benzene. These yield estimates of $\Delta_r H_m^{\circ}(10.6)$ of (13.6 ± 4.0) , (3.98 ± 1.6) and $(4.56 \pm 2.4) \text{ kJ} \cdot \text{mol}^{-1}$, respectively. As these estimates do not overlap and there is no basis on which to reject any of the estimates, the unweighted mean is chosen as the best value:

$$\Delta_r H_m^{\circ}(10.6, 298.15 \text{ K}) = (7.4 \pm 8.8) \text{ kJ} \cdot \text{mol}^{-1}$$

$\Delta_r H_m^{\circ}(10.7)$ is calculated from the two independent experiments of [73PAT/RAM, 73PAT/RAM2] in HDNNS/benzene, and [73PAT/RAM] in TTA/benzene. These yield estimates of (11.3 ± 3.2) and $(10.2 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$, respectively. The weighted mean yields the best value:

$$\Delta_r H_m^{\circ}(10.7, 298.15 \text{ K}) = (10.5 \pm 3.6) \text{ kJ} \cdot \text{mol}^{-1}$$

The remaining thermodynamic parameters may be calculated from the above estimates.

10.1.2.1.e Np(III) sulphates

No experimental evidence for the stability of Np(III)-sulphate complexes was found.

10.1.2.2 Solid neptunium sulphates

Although no thermodynamic information is available for solid Np sulphates, there exists a number of studies characterising such solids using X-ray diffraction, inferred spectroscopy, thermogravimetry and bulk analysis. Principal among these are [72MEF/KRO, 72MEF/KRO2, 78SAI/UEN, 82ALC/ROB, 82WES/MUL, 83HEL, 86WEI/HEL, 89BUD/FED]. Summaries of the compounds found and methods used for characterisation are given in Appendix A. The results of these studies may be useful to future researchers concerned about the stability of Np sulphate solid phases.

Chapter 11

Neptunium group 15 compounds and complexes

11.1 Neptunium nitrogen compounds and complexes

11.1.1 Neptunium nitrides and other pnictides

The only neptunium pnictides which have been characterised are the mono pnictides. These compounds possess the face-centred cubic rock salt structure (space group Fm3m). Studies on these compounds have been essentially concerned with the nature of the chemical bonding [87BEN, 90DAB/BEN, 94AMA/BRA, 95ARA/OHM]. Studies on the neptunium-nitrogen system include some other properties. The lattice parameters of the face-centred cubic neptunium pnictides are given in Table 11.1.

Table 11.1: Lattice parameters of the face-centred cubic neptunium pnictides

Compound	Lattice Parameter $a_0 \times 10^{10} \text{m}$	Reference
NpN	4.8987	[66OLS/MUL] [94ARA/OKA]
NpP	5.6148	[95ARA/OHM]
NpAs	5.8389	[95ARA/OHM]
NpSb	6.2485	[95ARA/OHM]
NpBi	6.3732	[87BEN]
The standard deviation is probably $0.0001 \times 10^{-10} \text{ m}$.		

NpSb transforms to the cubic CsCl structure at pressures above 12 Gpa [90DAB/BEN] or to a tetragonal phase above 10 GPa with space group P4/mmm, a distorted CsCl structure [94AMA/BRA].

11.1.1.1 NpN(cr)

11.1.1.1.a Heat Capacity and entropy

The heat capacity and entropy for NpN (cr) at 298.15 K have been estimated from the data for UN (cr) and PuN(cr)

$$\begin{aligned} C_{p,m}^{\circ}(\text{NpN, cr}) &= (48.7 \pm 0.9) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ S_{\text{m}}^{\circ}(\text{NpN, cr, 298.15 K}) &= (63.9 \pm 1.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

An estimated heat capacity for NpN (cr) was used in the evaluation of thermal conductivity from some measurements on the thermal diffusivity of this compound in the temperature range 740-1600 K [94ARA/OKA]. This estimate of heat capacity has been rejected because it is not consistent with analogous data for UN(cr) and PuN(cr). An estimate of the variation of specific heat in the temperature range 298.15 - 2000 K has been made using the estimated value for $C_{p,m}^{\circ}$ (NpN, cr, 298.15K) and the data for the variation of the specific heats of UN (cr) [72OET/LEI] and PuN(cr) [78OET].

$$C_{p,m}^{\circ}(\text{NpN, cr}) = 47.67 + 1.3174 \times 10^{-2}T - 2.5762 \times 10^5 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

11.1.1.1.b Enthalpy of formation

An estimate is given based on the quantities for UN(cr) [92GRE/FUG] and PuN(cr):

$$\Delta_f H_{\text{m}}^{\circ}(\text{NpN, cr, 298.15K}) = -(294.6 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$$

If the data for the Gibbs energy of formation are used to calculate the enthalpy of formation, then there is a discrepancy of some 20 kJ·mol⁻¹ between the second and the third law values. The average of these two values is very close to the estimated value. Because of this discrepancy, the assessed value is preferred as the value and the selected uncertainty is consistent with those for uranium and plutonium mononitrides.

11.1.1.1.c The Gibbs energy of formation

This quantity was assessed with the above data for the entropy and enthalpy of formation of NpN (cr) and the entropies of α -Np [76OET/RAN] and N₂ (gas) [89COX/WAG, 85CHA/DAV].

$$\Delta_f G_{\text{m}}^{\circ}(\text{NpN, cr, 298.15 K}) = -(270.0 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$$

The vaporisation behaviour of NpN(cr) from a Knudsen cell has been investigated by mass spectrometry [97NAK/ARA]. The magnitude of the vapour pressure of Np(g) indicated that decomposition to Np(l) was occurring in the temperature range of the experiments (1690-2030 K). The samples of NpN(cr) were prepared by the carbothermic reduction of NpO₂(cr) in nitrogen and contained low levels of oxygen and carbon impurities. The Gibbs energy of formation of NpN(cr) was calculated from

the measurements of Np(g) pressure [97NAK/ARA], and data obtained for N₂(g) pressures over the two phase field Np(l) + NpN(cr) in the temperature range 2480-3100 K [66OLS/MUL], extrapolated to the appropriate lower temperatures. The Gibbs energy of formation of Np(g) was taken from this assessment (Section 6.2). The Gibbs energy of formation of NpN(cr), calculated from the above experimental results, lies between those for PuN(cr) and UN(cr) [80POT/SPE],

$$\Delta_f G_m^\circ(\text{NpN, cr}) = -(295900 - 89.88T) \text{ J} \cdot \text{mol}^{-1} \text{ (1690 - 2030 K)}$$

The values for the Gibbs energy of formation obtained from this equation are some 3-7 % lower over the given temperature range than the values calculated from the assessed data presented here.

11.1.1.1.d The melting point of NpN(cr)

Nitrogen pressures for the phase field Np(l) + NpN(cr) have been measured in the temperature range 2480-3100 K

$$\log_{10}(p_{\text{N}_2(\text{g})}/\text{bar}) = 8.199 - 29.54 \times 10^3 T^{-1} + 7.87 \times 10^{-18} T^5$$

From these data an estimate was made of the congruent melting point at 9.87 bar N₂(g) of 3103 ± 30 K [66OLS/MUL].

11.1.2 Neptunium azide complexes

Formation constants (Table 11.2) for azido complexes of dioxoneptunium(V), NpO₂(N₃)_n¹⁻ⁿ (n = 1-5) at 25°C, I = 5 (mol · dm⁻³) have been reported [77CUI/MUS, 78MUS/MAR2], based on a spectroscopic study (970 to 1020 nm) at pH values between 6.2 and 9.4. Although the measurements were done at constant ionic strength, the nature of the ionic medium was very different for different solutions, and the apparent values for the complexation constants undoubtedly were affected. The results of this work cannot be used to derive serviceable values for I = 0, and the existence of the very weak higher complexes (especially n = 4,5) should be regarded as uncertain unless confirmed by other experiments.

Table 11.2: Reported formation constants for azido complexes of dioxoneptunium(V) [78MUS/MAR2]

NpO ₂ (N ₃) _n ¹⁻ⁿ		
n	log ₁₀ K _n	log ₁₀ β _n
1	1.08	1.08
2	0.77	1.85
3	0.38	2.23
4	-0.13	2.10
5	-0.70	1.40

11.1.3 Neptunium nitrites

The only data on neptunium nitrite complexes available to this review concern Np(V) complexes and originate from the same research group. The data are presented in Table 11.3 and refer to the reaction:



Rao *et al.* [79RAO/GUD] studied this system using solvent extraction with NaD-NNS at a total ionic strength of 2 M and obtained $\log_{10} \beta(11.1, I = 2 \text{ M}, 298.15 \text{ K}) = -(0.05 \pm 0.05)$. The complex is weak, and substantial changes were therefore necessary in the ionic medium in order to obtain measurable effects. As shown in Appendix A, the changes made in the ionic medium can also explain satisfactorily the measured effects.

Table 11.3: Experimental equilibrium data for the neptunium(V) nitrite system.

Method	Ionic medium	t (°C)	$\log_{10} \beta$	Reference
$\text{NpO}_2^+ + \text{NO}_2^- \rightleftharpoons \text{NpO}_2\text{NO}_2(\text{aq})$				
dis, DNNS	2 M NaClO ₄	25	$-(0.05 \pm 0.05)$	[79RAO/GUD]
sp	2 M NaClO ₄	~ 23	0.14	[78RAO/PAT]

Rao and Patil [78RAO/PAT] studied the same system at the same ionic strength, but using spectrophotometry, in order to confirm the solvent extraction results. They obtained a slightly higher value of the constant, $\log_{10} \beta(11.1, I = 2 \text{ M}, 296.15 \text{ K}) = 0.14$, by measuring molar absorptivities at various ligand concentrations. No experimental data are reported in this study, hence no recalculation or error estimation was possible. In view of the paucity of the available data, no selection is made in this review for Np(V) nitrite complexes.

11.1.4 Neptunium nitrates

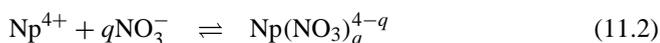
11.1.4.1 Aqueous neptunium nitrates

11.1.4.1.a Aqueous Np(III) nitrates

No Np³⁺ nitrate complexes have been identified.

11.1.4.1.b Aqueous Np(IV) nitrates

Complex formation in Np(IV) nitrate systems has been studied by several investigators and complexes formed according to the equilibria:



were proposed. The experimental equilibrium data have been summarised in Table 11.4. The distribution studies reported by Lahr and Knoch [70LAH/KNO]

and Moskvin [71MOS] lack experimental details and have possible experimental shortcomings, *cf.* Appendix A.

The same types of problems are found for the studies of Stomat, Peekema and Scott [58STR/PEE], Sykes and Taylor [62SYK/TAY] and Kusumakumari *et al.* [79KUS/GAN] (*cf.* Appendix A). Except for the value obtained using high ionic strength ($I = 9$ M) solutions by Barbanel and Muravieva [72BAR/MUR], the data from the other studies have been used to estimate a value for the formation constant for NpNO_3^{3+} .

All inner sphere complexes beyond the first are extremely weak at even moderate nitrate concentrations, and calculations have shown (Appendix A) that effects of higher complexes can often be accounted for by considering activity coefficient changes in sequential substitution for large amounts of the medium ions (*e.g.*, perchlorate) by nitrate ions, and assuming only the formation of the first complex up to 2 M nitrate [98SPA/PUI]. Such assumptions do not greatly influence the selection of a value for the first complexation constant as shown in Figure 11.1. The value of the constant reported by Danesi *et al.* [71DAN/CHI] was obtained in an electrolyte mixture consisting of 3 M $\text{NaClO}_4 + 1$ M HClO_4 , and the filled symbol in Figure 11.1 represents the value recalculated in 4 M HClO_4 in order to plot it together with the other values.

Table 11.4: Experimental equilibrium data for the Np(IV) nitrate system.

Method	Ionic medium	t (°C)	$\log_{10} \beta_q(I)^{(a)}$	$\log_{10} \beta_q(I)^{(c)}$	Reference
$\text{Np}^{4+} + \text{NO}_3^- \rightleftharpoons \text{NpNO}_3^{3+}$					
pot	1.0 M HNO_3	25	0.38		[58STR/PEE]
kin	2.0 M HNO_3	25	0.11		[62SYK/TAY]
dis, TTA	0.5 M HClO_4	20	0.45 (0.62±0.20) ^(b)	(0.48±0.10)	[66SHI/NAZ]
dis, TTA	1 M HClO_4	20	0.34 (0.23±0.20) ^(b)	(0.34±0.10)	
dis, TTA	1.5 M HClO_4	20	0.36 (0.41±0.20) ^(b)	(0.28±0.10)	
dis, TTA	2 M HClO_4	20	0.30 (0.11±0.20) ^(b)	(0.20±0.10)	
sp, kin	2 M HClO_4	25	0.34 (0.34±0.20) ^(b)	(0.42±0.15)	[66RYK/YAK]
dis, TOA	8 M HClO_4	20	-1.52		[70LAH/KNO]
dis, TBP	2 M HClO_4	25	0.83		[71MOS]
dis, TBP	4 M HClO_4	25		0.72	
dis, TTA	4 M (Na,H) ClO_4	25	-0.15 ± 0.12 -(0.15±0.12) ^(b)	-(0.12±0.10)	[71DAN/CHI]
sp	9 M HClO_4	25	0.9	(1.2 ± 0.1)	[72BAR/MUR]
dis, DNNS	2 M HClO_4	25	0.20 ^(d)		[72PAT]
sp	7 M HClO_4	25	0.9 ^(d)		[73ESC]
dis, HTTA	6 M (Na,H) ClO_4	25	0.53		[79KUS/GAN]

(Continued on next page)

Table 11.4: (continued)

Method	Ionic medium	t (°C)	$\log_{10} \beta_q(I)^{(a)}$	$\log_{10} \beta_q(I)^{(c)}$	Reference
$\text{Np}^{4+} + 2\text{NO}_3^- \rightleftharpoons \text{Np}(\text{NO}_3)_2^{2+}$					
dis, TTA	1 M HClO ₄	20	0.08		[66SHI/NAZ]
sp, kin	2 M HClO ₄	25	0.18		[66RYK/YAK]
dis, TOA	8 M HClO ₄	20	-0.17		[70LAH/KNO]
dis, TBP	2 M HClO ₄	25	1.08		[71MOS]
dis, TBP	4 M HClO ₄	25	1.31		
dis, TTA	4 M (Na,H)ClO ₄	25	$-(0.74 \pm 0.15)$		[71DAN/CHI]
dis, TTA	9 M HClO ₄	25	2.06		[72BAR/MUR]
dis, DNNS	2 M HClO ₄	25	0.65 ^(d)		[72PAT]
sp	7 M HClO ₄	20	1.93 ^(d)		[73ESC]
dis, HTTA	6 M (Na,H)ClO ₄	25	0.68		[79KUS/GAN]
$\text{Np}^{4+} + 3\text{NO}_3^- \rightleftharpoons \text{Np}(\text{NO}_3)_3^{+}$					
dis, TTA	1 M HClO ₄	20	-0.26		[66SHI/NAZ]
dis, TOA	8 M HClO ₄	20	-0.82		[70LAH/KNO]
dis, TBP	4 M HClO ₄	25	1.55		[71MOS]
dis, TBP	2 M HClO ₄	25	1.23		
$\text{Np}^{4+} + 4\text{NO}_3^- \rightleftharpoons \text{Np}(\text{NO}_3)_4(\text{aq})$					
dis, TOA	8 M HClO ₄	20	-0.89		[70LAH/KNO]
dis, TBP	2 M HClO ₄	25	1.56		[71MOS]
dis, TBP	4 M HClO ₄	25	1.16		

(a) Refers to the value reported for the reactions indicated for the ionic medium and at the temperature given in the table.

(b) Calculated using the method of the authors and estimating uncertainties.

(c) Calculated in this review by assuming only the first complex forms for nitrate concentrations ≤ 2 M and accounting for activity factor changes while substituting perchlorate ions with nitrate.

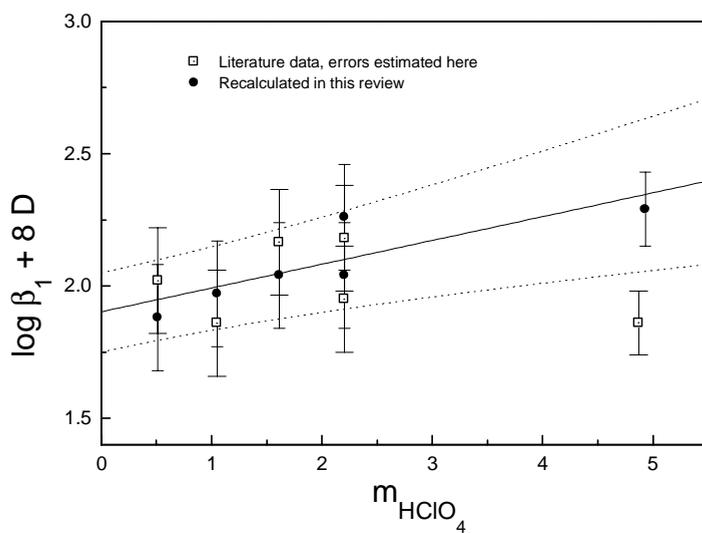
(d) [72PAT, 73ESC] are two doctoral theses cited in a review paper by Patil *et al.* [78PAT/RAM] and they have not been available to the reviewers.

Hence, the following formation constant results from the extrapolation

$$\log_{10} \beta_1^\circ(11.2, q = 1, 298.15 \text{ K}) = 1.90 \pm 0.15$$

and has been selected in this review. This value, as well as the value of $\Delta \varepsilon = -(0.09 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$ obtained simultaneously, compare reasonably well with the corresponding values of (1.47 ± 0.13) and $-(0.21 \pm 0.05)$ reported for the uranium complex [92GRE/FUG] and with the corresponding plutonium values, (1.95 ± 0.15) and $-(0.19 \pm 0.05)$.

Figure 11.1: Extrapolation to infinite dilution of the literature experimental data (open squares) and data recalculated in the present review at trace nitrate concentrations (filled circles) for the formation of NpNO_3^{3+} by using the specific interaction equations (*cf.* Appendix B).



There is evidence that anionic complexes form at very high nitrate concentrations in acidic solutions, and these complexes can be taken up on anion exchange resins [86FAH]; however, no data suitable for determining thermodynamic constants for these complexes are available.

11.1.4.1.c Aqueous Np(V) nitrates

Cation exchange and distribution studies have been used to obtain quantitative data on the stability of dioxoneptunium(V) nitrate complexes according to the reaction



Spectrophotometric studies fail to detect changes in the spectra of the NpO_2^+ ion in aqueous solutions even at relatively high nitrate concentrations. Also, in some potentiometric studies of the Np(V)/Np(VI) couple, the changes observed with the increase of nitrate concentration can at least tentatively be described in terms of the formation of Np(VI) nitrate complexes, neglecting Np(V) complexation. The reasons for rejecting the results from the study of Lahr and Knoch [70LAH/KNO] are discussed in Appendix A.

For all the other data reported in Table 11.5 recalculation of the tabulated or scanned primary data, by accounting for the changes of activity coefficients to allow for the substitution of large fraction of the perchlorate ions with nitrate ions, demonstrates that the observed experimental effects can be explained solely as changes of activity coefficients (see Appendix A entries for [64GAI/SYK, 71DAN/CHI, 79RAO/GUD, 81PAT/RAM]). This together with spectrophotometric evidence on the lack of

Table 11.5: Experimental equilibrium data for the Np(V) nitrate system.

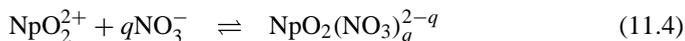
Method	Ionic medium	t (°C)	$\log_{10} \beta(I)^{(a)}$	Reference
$\text{NpO}_2^+ + \text{NO}_3^- \rightleftharpoons \text{NpO}_2\text{NO}_3(\text{aq})$				
cix	2 M HClO ₄	20	$-(0.25 \pm 0.05)$	[64GAI/SYK]
dis, TOA	8 M HClO ₄	20	-0.28	[70LAH/KNO]
pot	2 M HClO ₄	20	$-(1.60 \pm 0.02)$	[71DAN/CHI]
dis, DNNS	2 M NaClO ₄	20	$-(0.55 \pm 0.09)$	[79RAO/GUD]
dis, DNNS	8.5 M NaClO ₄	20	-0.52	[81PAT/RAM]
$\text{NpO}_2^+ + 2\text{NO}_3^- \rightleftharpoons \text{NpO}_2(\text{NO}_3)_2^-$				
pot	2 M HClO ₄	20	$-(1.37 \pm 0.01)$	[71DAN/CHI]

^(a) Refers to the value reported for the reactions indicated, for the ionic medium and at the temperature given in the table.

changes in the spectra at nitrate concentrations up to 4 M confirms the absence of inner sphere dioxoneptunium(V) nitrate complexes.

11.1.4.1.d Aqueous Np(VI) nitrates

The experimental equilibrium data available in the literature for the reactions



are collected in Table 11.6. There is no direct experimental (*e.g.*, spectroscopic) evidence for inner sphere Np(VI) nitrate complexation reported in the available literature. As discussed in Appendix A, the papers of Rykov and Yakovlev [66RYK/YAK], Lahr and Knoch [70LAH/KNO] and of Vasiliev, Andeichuk and Rykov [75VAS/AND] are subject to various shortcomings that preclude use of values from these sources. The

Table 11.6: Experimental equilibrium data for the Np(VI) nitrate system.

Method	Ionic medium	<i>t</i> (°C)	log ₁₀ β(<i>I</i>) ^(a)	Reference
$\text{NpO}_2^{2+} + \text{NO}_3^- \rightleftharpoons \text{NpO}_2\text{NO}_3^+$				
sp, kin	2 M HClO ₄	25	-0.4	[66RYK/YAK]
dis, TOA	8 M HClO ₄	20	-0.24	[70LAH/KNO]
dis, TTA	4 M (Na,H)ClO ₄	25	-(0.68 ± 0.06) -(0.68 ± 0.20) ^(b)	[71DAN/CHI]
pot	4 M (Na,H)ClO ₄	25	-(1.05 ± 0.14)	
pot	0.4 M HClO ₄	25	-(0.98 ± 0.02) -(0.98 ± 0.50) ^(b)	[70AL-/WAI2]
pot	0.5 M HClO ₄	25	-(0.96 ± 0.02) -(0.96 ± 0.50) ^(b)	
pot	0.6 M HClO ₄	25	-(0.89 ± 0.02) -(0.89 ± 0.50) ^(b)	
pot	0.8 M HClO ₄	25	-(0.94 ± 0.02) -(0.94 ± 0.50) ^(b)	
$\text{NpO}_2^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{NpO}_2(\text{NO}_3)_2(\text{aq})$				
pot	4 M (Na,H)ClO ₄	25	-(1.23 ± 0.14)	[71DAN/CHI]
sp	0.1 - 23 M HNO ₃	?	(4.74 ± 0.04) ^(c) < -2.06 ^(d)	[75VAS/AND]

(a) Refers to the value reported for the reactions indicated, for the ionic medium and at the temperature given in the table.

(b) Uncertainties estimated in this review.

(c) Refers to the constant for the reaction which includes water molecules, that is: $\text{NpO}_2(\text{H}_2\text{O})_6^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{NpO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_{6-x} + x\text{H}_2\text{O}$. The value for the constant corresponding to Equation (11.4), $q = 2$, has been calculated in this review.

(d) Upper limit value of the constant estimated in this review by assuming only the first complex to form for nitrate ≤ 2 M and accounting for activity factor changes while substituting perchlorate ions with nitrate.

various experimentally measured quantities may be expressed by accounting for both

activity coefficient changes and complex formation, which in the case of distribution studies have the following form:

$$\frac{D_0}{D} = \frac{\gamma_{\text{NpO}_2^+, \text{ClO}_4^-} \cdot \gamma_{\text{H}^+, \text{mix}}^2}{\gamma_{\text{NpO}_2^+, \text{mix}} \cdot \gamma_{\text{H}^+, \text{ClO}_4^-}^2} \cdot (1 + \beta_1 \cdot [\text{NO}_3^-] \cdot \gamma_{\text{cp}x1, \text{mix}}^{-1} + \beta_2 \cdot [\text{NO}_3^-]^2 \cdot \gamma_{\text{cp}x2, \text{mix}}^{-1} + \dots) \quad (11.5)$$

Since all experiments have been performed at constant molar ionic strength, the logarithm of the activity factor of an ion may be expressed as a linear function of nitrate concentration. By taking the logarithm of Equation (11.5), the only way that the logarithm of the left hand side can be expressed as a linear function of nitrate concentration is if the expression inside parentheses is equal to one, *i.e.*, the constants tend to zero. Similar expressions have been used in Appendix A in the case of potentiometric measurements (*e.g.*, [70AL-/WAI2, 71DAN/CHI]). In most of the papers negligibly small constants will provide an adequate fit to the experimental data. At this time it is not possible to select any constants for this system.

It is concluded that the dioxoneptunium(VI) nitrate complexes are weak, as is also the case for the other actinides [92GRE/FUG] (see also Section 20.1.3.1). This makes it difficult to distinguish between complex formation and changes in the activity coefficients of the species studied, caused by the large changes in the composition of the ionic medium when substituting an inert anion (often perchlorate) by the ligand ion (nitrate). If a β_1 value for formation of $\text{NpO}_2\text{NO}_3^+$ is required, the use of the first association constant recommended for the analogous uranium system [92GRE/FUG] will probably not cause too large an error.

11.1.4.2 Solid neptunium nitrates

11.1.4.2.a Np(IV)

The synthesis of $\text{Np}(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}(\text{s})$ was described by Laidler [66LAI]. No chemical thermodynamic data were reported.

11.1.4.2.b Np(V)

The synthesis of $\text{NpO}_2\text{NO}_3 \cdot \text{H}_2\text{O}(\text{s})$ and of $\text{NpO}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}(\text{s})$ were described by Laidler [66LAI]. There is some question as to whether the second of these compounds was properly characterised and if the neptunium is actually Np(V). The $\text{NpO}_2\text{NO}_3 \cdot \text{H}_2\text{O}(\text{s})$ of Laidler was prepared by drying a more hydrated salt under vacuum, and Grigor'ev *et al* [94GRI/CHA] have reported a crystal structure for $\text{NpO}_2\text{NO}_3 \cdot 2.5\text{H}_2\text{O}(\text{s})$. No chemical thermodynamic data have been reported.

11.1.4.2.c Np(VI)

The synthesis of $\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ was described by Laidler [66LAI]. Brand and Cobble [70BRA/COB] carried out a limited set of measurements of the solubility of this salt in water (reporting a saturation molality at $(25 \pm 0.2)^\circ\text{C}$ of (2.95 ± 0.26)). From this, and activities from the corresponding uranium system

[51ROB/LIM], $\Delta_r G_m$ for the dissolution of $\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ was calculated to be $-(12.3 \pm 1.1) \text{ kJ} \cdot \text{mol}^{-1}$. This value is used in determining the values of $S_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K})$ and $\Delta_f G_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K})$ in Section 7.2.

The enthalpy of solution in water of the nitrate salt was also measured by Brand and Cobble [70BRA/COB]. The result, $(21.59 \pm 0.54) \text{ kJ} \cdot \text{mol}^{-1}$, was corrected for hydrolysis to $(18.83 \pm 1.67) \text{ kJ} \cdot \text{mol}^{-1}$ by Fuger and Oetting [76FUG/OET]. The correction was calculated using hydrolysis constants for UO_2^{2+} that are somewhat greater than those selected in the present review (*cf.* Section 7.2) for NpO_2^{2+} , and used enthalpies for the hydrolysis reactions of uranium in the absence of data for Np(VI). However, the differences are probably within the uncertainty assigned by Fuger and Oetting [76FUG/OET], and their recalculation is accepted in the present review. The entropy for the solid was estimated as $(516.3 \pm 4.6) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ by Brand and Cobble [70BRA/COB] using the known entropy of the corresponding uranium salt and adding a contribution of $(10.5 \pm 4.6) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for the magnetic contribution of the unpaired electron in NpO_2^{2+} . Again, this value is also accepted here, (converted directly from the original units of $\text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), but with a slightly increased uncertainty to reflect the use of the uranium data,

$$S_m^\circ(\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}) = (516.306 \pm 8.000) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Using this, the selected value for $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(860.7 \pm 4.7) \text{ kJ} \cdot \text{mol}^{-1}$ from Section 7.2, and the CODATA value for $\Delta_f H_m^\circ(\text{NO}_3^-, \text{aq}, 298.15 \text{ K})$,

$$\Delta_f H_m^\circ(\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}) = -(3008.241 \pm 5.022) \text{ kJ} \cdot \text{mol}^{-1}$$

Then,

$$\Delta_f G_m^\circ(\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}) = -(2428.069 \pm 5.565) \text{ kJ} \cdot \text{mol}^{-1}$$

11.2 Neptunium phosphorus compounds and complexes

11.2.1 Aqueous Np(III) phosphates

There are no experimental data for the Np(III) phosphate system. Moskvin [69MOS], estimated constants for complexes of the general composition $\text{Np}(\text{H}_2\text{PO}_4)_n^{3-n}$, where $n = 1 - 3$, based on his study of Pu(III), Am(III) and Cm(III) phosphate systems [71MOS4]. The experimentally determined constants for complexes of the type $\text{Pu}(\text{H}_2\text{PO}_4)_n^{3-n}$ are rejected by this review (see Appendix A entries for [71MOS4] and [69MOS]); the same holds for values estimated for the $\text{Np}(\text{H}_2\text{PO}_4)_n^{3-n}$ complexes.

11.2.2 Aqueous Np(IV) phosphates

To our knowledge, there are no published experimental data for the Np(IV) phosphate system. Moskvin [67MOS/ESS] estimated constants for complexes of the general composition $\text{Np}(\text{HPO}_4)_n^{4-2n}$, where $n = 1 - 4$, from the values for the corresponding Pu(IV) phosphate system as reported by Denotkina and Moskvin [60DEN/MOS2], as well as from values for the thorium(IV) and the uranium(IV) systems [67MOS/ESS].

Since the experimentally determined constants for complexes of the type $\text{Pu}(\text{HPO}_4)_n^{4-2n}$ are not accepted by this review (see the discussion of [60DEN/MOS2] and [60DEN/MOS] in Appendix A), the same holds for the values for the $\text{Np}(\text{HPO}_4)_n^{4-2n}$ complexes.

11.2.3 Aqueous Np(V) phosphates

There have been several studies of the aqueous Np(V) phosphate system using spectrophotometric, ion exchange or co-precipitation methods (Table 11.7), and the results are in reasonable agreement. In all cases, the data were recalculated using the phosphoric acid dissociation constants calculated at the corresponding ionic medium and temperature with the SIT equations and interaction coefficients (Appendix B), together with the enthalpies of reaction selected in this review. Rees and Daniel [84REE/DAN] have carried out a careful study of the Np(V) phosphate system at constant pH and three different temperatures, 10, 25 and 35°C. No analysis of the proton content of the ligand can be made at constant pH, but they refer in their analysis to the speciation results of Moskvin and Peretrukhin [64MOS/PER].

The value of the equilibrium constant for the reaction



as recalculated in this review (Appendix A), is $\log_{10} \beta_1$ (11.6, 0.1 M NaClO₄, 298 K) = (2.42 ± 0.42). This is in good agreement with the values recalculated from the data of Moskvin and Peretrukhin [64MOS/PER], $\log_{10} \beta_1$ (11.6, 0.2 M NH₄ClO₄, 293 K) = (2.46 ± 0.15), and Morgenstern and Kim [96MOR/KIM], $\log_{10} \beta_1$ (11.6, 0.1 M NaClO₄, 298 K) = (2.52 ± 0.02). The weighted average of these three values after extrapolation to $I = 0$ has been selected:

$$\log_{10} \beta^\circ(11.6, 298.15 \text{ K}) = (2.95 \pm 0.10)$$

The value of the complexation constant reported by Moskvin and Pozniakov [79MOS/POZ] for the above reaction was not included in the selection because of possible experimental problems in the part of that study dealing with complexation of Np(V) (see Appendix A).

There are conflicting hypotheses as to the stoichiometry of other Np(V)-phosphate complexes at high pH. Therefore, none of these constants corresponding to the formation of the species $\text{NpO}_2\text{H}_2\text{PO}_4(\text{aq})$, [64MOS/PER, 85INO/TOC2], the species $\text{NpO}_2\text{PO}_4^{2-}$ [79MOS/POZ, 96MOR/KIM] and the species $\text{NpO}_2(\text{H}_2\text{PO}_4)_2^-$ and $\text{NpO}_2(\text{HPO}_4)_2^{3-}$ [85INO/TOC2] are selected, *cf.* Appendix A. If the formation

Table 11.7: Stability constants for Np(V) phosphate complexes.

Method Reaction	Ionic medium	<i>t</i> (°C)	$\log_{10} \beta_q$	Reference
$\text{NpO}_2^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{NpO}_2\text{H}_2\text{PO}_4(\text{aq})$				
cix	0.2 M NH_4ClO_4	20	0.8	[64MOS/PER]
dis	1.0 M NaClO_4	25	(1.04±0.18)	[85INO/TOC2]
$\text{NpO}_2^+ + 2\text{H}_2\text{PO}_4^- \rightleftharpoons \text{NpO}_2(\text{H}_2\text{PO}_4)_2^-$				
dis	1.0 M NaClO_4	25	(1.87±0.29)	[85INO/TOC2]
$\text{NpO}_2^+ + \text{HPO}_4^{2-} \rightleftharpoons \text{NpO}_2\text{HPO}_4^-$				
cix	0.2 M NH_4ClO_4	20	(2.85±0.15)	[64MOS/PER]
cppt	1 M NH_4Cl	20	(2.9±0.1)	[79MOS/POZ]
cix	0.1 M NaClO_4	10	(3.11±0.19)	[84REE/DAN]
cix	0.1 M NaClO_4	25	(2.36±0.42)	
cix	0.1 M NaClO_4	35	(2.06±0.39)	
dis	1.0 M NaClO_4	25	(2.11±0.09)	[85INO/TOC2]
sp	0.1 M NaClO_4	25	(2.54±0.02)	[96MOR/KIM]
	$I \rightarrow 0$	25	(2.95±0.10)	This review
$\text{NpO}_2^+ + 2\text{HPO}_4^{2-} \rightleftharpoons \text{NpO}_2(\text{HPO}_4)_2^{3-}$				
dis	1.0 M NaClO_4	25	(3.43±0.16)	[85INO/TOC2]
$\text{NpO}_2^+ + \text{PO}_4^{3-} \rightleftharpoons \text{NpO}_2\text{PO}_4^{2-}$				
cppt	1 M NH_4ClO_4	20	(5.78±0.25)	[79MOS/POZ]
sp.	0.1 M NaClO_4	25	(6.33±0.08)	[96MOR/KIM]

constant for $\text{NpO}_2\text{PO}_4^{2-}$ of Morgenstern and Kim [96MOR/KIM] were correct, then $\text{NpO}_2\text{PO}_4^{2-}$ could be an important species at high pH in moderately concentrated phosphate solutions. Thus, attempts to confirm the stoichiometry and stability of this species would be useful.

Rees and Daniel [84REE/DAN] have carried out measurements of the constant β_1 (11.6, 0.1 M NaClO_4) at 10, 25 and 35°C. Because of possible shortcomings in their experiments (see Appendix A), the data at 35°C were not considered usable. A weighted linear regression of the type “ $\ln \beta_1$ versus $1/T$ (K^{-1})” for the measurements at 10 and 25°C results in $\Delta_r H_m$ (11.6, 0.1 M NaClO_4 , 298 K) = $-(52 \pm 50)$ $\text{kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S_m$ (11.6, 0.1 M NaClO_4 , 298 K) = $-(127 \pm 167)$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Because of the high uncertainties, these values are not extrapolated to $I = 0$, nor selected in the present review.

11.2.4 Aqueous Np(VI) phosphates

For the Np(VI) phosphate system there is only one study - the solvent extraction work by Mathur and Choppin [94MAT/CHO]. Another study was claimed by Moskvin in a compilation paper [69MOS], but has not been available to this review, apparently because it was never published.

Mathur and Choppin in [94MAT/CHO] explain their solvent extraction data by proposing the formation of three complexes $\text{NpO}_2\text{H}_2\text{PO}_4^+$, $\text{NpO}_2\text{HPO}_4(\text{aq})$ and $\text{NpO}_2(\text{HPO}_4)_2^{2-}$. This is the only study available on this system, apparently with some uncertainties as to the stoichiometry of the species (*cf.* Appendix A) and there is not enough information to permit recalculation. Hence, the values reported for the equilibrium constants of the reactions:



have been selected with substantially increased uncertainty limits:

$$\log_{10} \beta(11.7, 1 \text{ M } \text{NaClO}_4, 298.15 \text{ K}) = (2.52 \pm 0.50)$$

$$\log_{10} \beta(11.8, 1 \text{ M } \text{NaClO}_4, 298.15 \text{ K}) = (4.54 \pm 0.70)$$

$$\log_{10} \beta(11.9, 1 \text{ M } \text{NaClO}_4, 298.15 \text{ K}) = (7.5 \pm 1.0)$$

From these, using approximations discussed in the entry for [94MAT/CHO] in Appendix A, the following selected values were calculated.

$$\log_{10} \beta^\circ(11.7, 298.15 \text{ K}) = (3.32 \pm 0.50)$$

$$\log_{10} \beta^\circ(11.8, 298.15 \text{ K}) = (6.2 \pm 0.70)$$

$$\log_{10} \beta^\circ(11.9, 298.15 \text{ K}) = (9.5 \pm 1.0)$$

Chapter 12

Neptunium group 14 compounds and complexes

12.1 Neptunium carbon compounds and complexes

12.1.1 Neptunium carbides

The thermodynamical properties of neptunium carbides were reviewed in the early 1980s by Holley, Rand and Storms [84HOL/RAN], and little significant information has been published since then. Thermodynamic quantities for these compounds are included here for information, but no additional assessment has been carried out. Compounds in the Np-C system include a sub-stoichiometric monocarbide NpC_x ($x = 0.82 - 0.94$), a sesquicarbide and, at temperatures approaching 3000 K, a dicarbide. In the present review we accept the (calorie unit) values as assessed by Holley, Rand and Storms, except for the entropy of the monocarbide, where a non zero value for $S_m^\circ(0 \text{ K})$ has been taken.

12.1.1.1 Neptunium monocarbide

Reliable thermodynamic data exist only for one composition of the monocarbide phase, $\text{NpC}_{(0.91 \pm 0.02)}(\text{cr})$. Sandenaw, Gibney and Holley [73SAN/GIB] made heat capacity measurements from 15 to 373 K and Huber and Holley [72HUB/HOL] measured the enthalpy of combustion by oxygen bomb calorimetry using samples of the same (rather impure) material. The monocarbide showed a lambda peak at $(228.4 \pm 0.2) \text{ K}$ due to ferromagnetic ordering; the heat capacity values were rather irreproducible from 240 to 310 K, and possible reasons for this were discussed by Sandenaw *et al.* Integration of the heat capacity values gave for $\text{NpC}_{0.91}(\text{cr})$:

$$S_m^\circ(298.15 \text{ K}) - S_m^\circ(0 \text{ K}) = (69.66 \pm 2.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

where the uncertainty has been estimated in this review; it allows for the fact that the material contained 2.3% of impurities, and the irreproducibility of the data around 300 K.

If the vacancies in this phase are assumed not to have ordered at the lowest temperature of measurement, $S_m^\circ(0 \text{ K}) = -R(0.91 \ln(0.91) + 0.09 \ln(0.09)) = 2.52 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, giving finally

$$S_m^\circ(\text{NpC}_{0.91}, \text{cr}, 298.15 \text{ K}) = (72.2 \pm 2.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

which is the selected value. Owing to the irreproducibility of the results around 300 K, the selected value of the heat capacity has been given a larger uncertainty than normal:

$$C_{p,m}^{\circ}(\text{NpC}_{0.91}, \text{cr}, 298.15 \text{ K}) = (50.0 \pm 1.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Values of $C_{p,m}^{\circ}(T)$ for the temperature interval from 298.15 to 1000 K have been estimated from those for $\text{PuC}_{0.84}$:

$$C_{p,m}^{\circ}(\text{NpC}_{0.91}, \text{cr}, T) = 61.250 - 3.52747 \cdot 10^{-2}T + 3.62834 \cdot 10^{-5}T^2 \\ - 3.4842 \cdot 10^{-5}T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

From their combustion measurements, Huber and Holley [72HUB/HOL] derived

$$\Delta_f H_m^{\circ}(\text{NpC}_{0.91}, \text{cr}, 298.15 \text{ K}) = -(71.1 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$$

which is the selected value. However, the uncertainty has been increased in the present review; this allows for the large uncertainty in the Np-metal content of the solid (the α -Np(cr) content was estimated as (3 ± 2) mass per cent in the original publication).

The calculated Gibbs energy of formation thus becomes

$$\Delta_f G_m^{\circ}(\text{NpC}_{0.91}, \text{cr}, 298.15 \text{ K}) = -(76.0 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$$

12.1.1.2 Neptunium sesquicarbide

Holley, Rand and Storms [84HOL/RAN] estimated the entropy of formation of $\text{Np}_2\text{C}_3(\text{cr})$ at 298.15 K to be $(16.8 \pm 8.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ to make the Gibbs energy of formation to be similar to that of $\text{U}_2\text{C}_3(\text{cr})$. We have accepted this value and thus select

$$S_m^{\circ}(\text{Np}_2\text{C}_3, \text{cr}, 298.15 \text{ K}) = (135 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

These authors took the enthalpy of formation of the sesquicarbide to be

$$\Delta_f H_m^{\circ}(\text{Np}_2\text{C}_3, \text{cr}, 298.15 \text{ K}) = -(187.4 \pm 19.2) \text{ kJ}\cdot\text{mol}^{-1}$$

based on unpublished measurements of the enthalpy of combustion by Holley. This is also the selected value.

The calculated Gibbs energy of formation thus becomes

$$\Delta_f G_m^{\circ}(\text{Np}_2\text{C}_3, \text{cr}, 298.15 \text{ K}) = -(192.4 \pm 19.4) \text{ kJ}\cdot\text{mol}^{-1}$$

The heat capacity at 298.15 K has been estimated from those of $\text{U}_2\text{C}_3(\text{cr})$ and $\text{Pu}_2\text{C}_3(\text{cr})$:

$$C_{p,m}^{\circ}(\text{Np}_2\text{C}_3, \text{cr}, 298.15 \text{ K}) = (110 \pm 8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

12.1.1.3 Neptunium dicarbide

There is insufficient information on the stability of this compound to make meaningful estimates of its thermodynamic properties.

12.1.2 Neptunium carbonates

12.1.2.1 The aqueous neptunium carbonates

Studies of the carbonate complexes are not straightforward since the carbonate ion, CO_3^{2-} , is a basic anion. Therefore hydrolysis, including formation of mixed CO_3^{2-} – OH^- complexes, may occur together with carbonate complexation. In acidic media, the carbonate ion is converted to carbon dioxide gas, $\text{CO}_2(\text{g})$. Therefore, when alkali metal or ammonium carbonate aqueous solutions (M_2CO_3) are in contact with the air, $\log_{10} p_{\text{CO}_2}$ can increase from -7 or -6 to -3.5 (*i.e.*, the pH of the solution is not buffered). This can introduce a shift of more than six orders of magnitude in the calculated formation constant for the Np(IV) carbonate complex as deduced from redox measurements of the Np(V)/Np(IV) couple. One way to avoid this problem is to work in closed cells containing carbonate-bicarbonate buffers. To control (and study) the effects of lower concentrations of carbonate ions, solutions buffered by bicarbonate and carbon dioxide are also extensively used. Carbon dioxide gas is continually bubbled through the open system (this type of buffering cannot be done in a closed system), and the major anion of the carbonate system is then the bicarbonate anion, HCO_3^- . The carbonate aqueous system is a two-component system, and it can be formally described using only two species (if OH^- and $\text{CO}_2(\text{g})$ are used to describe the system, HCO_3^- and CO_3^{2-} are often written as OHCO_2^- and $(\text{OH})_2\text{CO}_2^{2-}$, respectively). Consequently, when experiments are carried out in equilibrium with air, the effects of CO_3^{2-} are equivalent to those of 2OH^- , and no unique interpretation can be proposed from such experimental work (typically such methodology cannot distinguish between reaction of NpO_2^+ to form $\text{NpO}_2\text{CO}_3^-$ or to form $\text{NpO}_2(\text{OH})_2^-$). This problem was discussed in detail in the earlier review of the uranium-carbonate system [92GRE/FUG] (pages 308 and 312). The same observations apply when the neptunium-carbonate aqueous system is studied, and the same methodology is used in the present review for treating measurements reported in the literature.

Some published measurements were performed in concentrated aqueous M_2CO_3 or MHCO_3 media ($\text{M} = \text{Na}, \text{K}$ or NH_4) without addition of an inert salt. The ionic strength was then dependent on the concentration of the complexing species (typically CO_3^{2-}). The junction potentials also varied during these pH or potential measurements. It is difficult to develop a quantitative interpretation from such work, or to deduce accurate thermodynamic values from it. Nevertheless, these measurements are considered in the present review, as there are too few other experimental results.

Parallel species (having the same stoichiometry) with similar formation constant (or solubility product) values are expected within the actinide series: U(V), Np(V), Pu(V) and Am(V) (but not Pa(V)). Neptunium is the most stable actinide element in the +5 oxidation state. Hence there are more published works on complexes of Np(V) than on the complexes of the other elements of this actinide(V) series, and the stoichiometries of these actinide(V) species were usually determined from experimental information concerning Np(V). The analysis of the Pu(V) system for which there is less data was guided by analogy to the Np(V) system as was previously the case for U(V) species [92GRE/FUG]. Conversely, Np(IV) and Np(VI) species are expected to be the same

as those reasonably well-documented for uranium [92GRE/FUG]. There is usually not enough published information to determine the stoichiometry and propose thermodynamic data for all these expected Np(IV) and Np(VI) species. Therefore, this review has extensively used analogy with the uranium system (for specific interaction coefficients of anions with charge -1 to -3 , and for stoichiometry) and prefers proposing values with large uncertainties or even maximum formation constant values, rather than proposing no value at all. Values could be proposed for Np(III) species in the same way, by analogy with values for Am(III) species [95SIL/BID]; but usually Np(III) reduces water under conditions where Np(III) carbonate complexes are expected to form.

12.1.2.1.1 Np(VII) carbonate complexes

Evidence of the formation of a neptunium(VII) carbonate complex was proposed [76SHI/STE].

12.1.2.1.2 Np(VI) carbonate complexes

There are several publications on the neptunium(VI) carbonate system. The available information is summarized in Table 12.1, where the results of reinterpretation of data as carried out in the present review and some experimental information are also provided. Details of the selection or reinterpretation of published works are given in the Appendix A. There is satisfactory experimental information available for only two Np(VI) complexes in aqueous carbonate/bicarbonate media:

- Simakin's experimental study of the Np(VI)/Np(V) redox equilibrium in Na_2CO_3 and K_2CO_3 aqueous media [77SIM] was used to propose the stoichiometry and the formation constant of the limiting complex, $\text{NpO}_2(\text{CO}_3)_3^{4-}$. This work was later confirmed by Riglet [90RIG] and by Offerlé, Capdevila and Vitorge [95OFF/CAP].
- Grenthe, Riglet and Vitorge [86GRE/RIG] and Riglet [90RIG] showed that, as for uranium, the limiting complex can polymerize to form the trinuclear species $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$.

cal	0.3-1.6 M Na ₂ SO ₄ + Na ₂ CO ₃	25	$\Delta_r H_m = -(33.4^{(i)} \pm 12.2^{(j)}) \text{ kJ}\cdot\text{mol}^{-1}$	[85SCH/FRI]
cal	0.98-1.135 M Na ₂ SO ₄ + 0.123-0.363 M Na ₂ CO ₃	25	$\Delta_r H_m = -(41.9 \pm 3.2^{(i)}) \text{ kJ}\cdot\text{mol}^{-1}$	[88ULL/SCH]
red	1 M NaClO ₄	25	21.6 $\geq (19.2 \pm 4.4)^{(a)}$	[84MAY]
red, rev	1 M NaClO ₄ ,	25	$(20.6 \pm 1.5)^{(a)}$	[84MAY]
pot	1 M NaClO ₄	25	(21.15 ± 0.12)	[84MAY]
red, sol	3 M (Na, ClO ₄)	25	$(21.8 \pm 0.3)^{(a)}$	[90RIG]
$\text{NpO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_2^{2-} + \text{CO}_3^{2-}$				
red	1 M NaClO ₄	25	-4.51 $\leq -(5.7 \pm 2.0)^{(a)}$	[84MAY]
pot	1 M NaClO ₄	25	$-(4.64 \pm 0.18)$ $\leq -4.74^{(a)}$	[84MAY]
sol, rev	3 M NaClO ₄	22	$-(6.3 \pm 0.7)$	[98VIT/CAP]
$\text{NpO}_2^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_2^{2-}$				
red	1 M NaClO ₄	25	(13.5 ± 4.8) $\leq (14.9 \pm 2.1)^{(a)}$	[84MAY]
pot	1 M NaClO ₄	25	(16.51 ± 0.14)	[84MAY]

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sol	3 M NaClO ₄	22	(15.72±0.51) (15.77±0.52) ^{(a) (b)}	[98VIT/CAP]
$\text{NpO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)(\text{aq}) + 2\text{CO}_3^{2-}$				
red	1 M NaClO ₄	25	$\leq -(11.1 \pm 2.0)^{(a)}$	[84MAY]
sol, rev	3 M NaClO ₄	22	$-(13.55 \pm 0.7)$	[98VIT/CAP]
$\text{NpO}_2^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)(\text{aq})$				
red	1 M NaClO ₄	25	$\leq (9.5 \pm 2.1)^{(a)}$	[84MAY]
red	1 M NaClO ₄	25	(7.9 ± 1.0)	[84MAY]
sol	3 M NaClO ₄	22	$(8.5 \pm 1.0), (8.72 \pm 0.52)^{(a) (b)}$	[98VIT/CAP]
$3\text{NpO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons (\text{NpO}_2)_3(\text{CO}_3)_6^{6-} + 3\text{CO}_3^{2-}$				
pot	1 M NaClO ₄	25	$-(9.2 \pm 2.9)^{(d)}$ $-(8.81 \pm 1.08)^{(a) (b)}$	[84MAY]
sp	3 M NaClO ₄	22	$-(10.0 \pm 0.1)$ $-(10.06 \pm 0.57)^{(a) (b)}$	[86GRE/RIG] [90RIG]
$2\text{NpO}_2(\text{CO}_3)_3^{4-} + 7\text{H}^+ \rightleftharpoons (\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^- + 5\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$				
pot	1 M NaClO ₄	25	(41.76 ± 0.94) $(41.75 \pm 1.46)^{(a)}$	[84MAY]

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vlt	0	25	(0.340±0.002) ^(k)	[95OFF/CAP]	
red	0.13 M Na ₂ CO ₃	?	(0.437±0.010)	[77SIM]	0.421
red	0.20 M Na ₂ CO ₃	?	(0.447±0.010)		0.440
vlt	0.22 M Na ₂ CO ₃	25	(0.434±0.004) ^(l)	[95OFF/CAP]	0.428
red	0.31 M Na ₂ CO ₃	?	(0.459±0.010)	[77SIM]	0.456
red	0.51 M Na ₂ CO ₃	?	(0.466±0.010)		0.466
vlt	0.55 M Na ₂ CO ₃	25	(0.467±0.003) ^(l)	[95OFF/CAP]	0.466
red	0.74 M Na ₂ CO ₃	?	(0.475±0.043)	[77SIM]	0.475
red	1 M Na ₂ CO ₃ , 1 M NaHCO ₃	?	0.465	[81WES/SUL]	
red	1 M Na ₂ CO ₃	25	(0.46±0.01) ^{(a)(b)}	[77SIM]	
cou	1 M Na ₂ CO ₃	23	0.49	[93LI/KAT]	
vlt	1 M Na ₂ CO ₃	25	(0.500±0.003) ^(l)	[95OFF/CAP]	0.500
red	1.02 M Na ₂ CO ₃	?	(0.492±0.010)	[77SIM]	0.492
vlt	1.25 M Na ₂ CO ₃	25	(0.500±0.009) ^(l)	[95OFF/CAP]	0.500
vlt	1.5 M Na ₂ CO ₃	25	(0.498±0.006) ^(l)		0.498
red	1.53 M Na ₂ CO ₃	?	(0.499±0.010)	[77SIM]	0.499
vlt	2 M Na ₂ CO ₃	?	0.474	[84VAR/HOB]	
vlt	2 M Na ₂ CO ₃	25	(0.507±0.010) ^(l)	[95OFF/CAP]	0.507
red	2.09 M Na ₂ CO ₃	?	(0.511±0.010)	[77SIM]	0.511
red	1 M NaClO ₄ , 0.2 M NaHCO ₃	25	(0.426±0.087) ^(a)	[84MAY]	
vlt	3 M NaClO ₄	22	(0.496±0.005)	[90RIG]	0.495
red	0.19 M K ₂ CO ₃	?	(0.446±0.010) ^(b)	[77SIM]	

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red	0.51 M K ₂ CO ₃	?		(0.451±0.010) ^{(a)(b)}	[77SIM]
red	0.78 M K ₂ CO ₃	?		(0.452±0.010)	
red	0.8 M K ₂ CO ₃	20		(0.44±0.01)	[74SIM/VOL] ^(f)
red	1.01 M K ₂ CO ₃	?		(0.464±0.010) ^{(a)(b)}	[77SIM]
red	1.53 M K ₂ CO ₃	?		(0.473±0.010)	
red	1.99 M K ₂ CO ₃	?		(0.473±0.010)	
red	2.54 M K ₂ CO ₃	?		(0.472±0.010)	
red	3 M K ₂ CO ₃	20		(0.44±0.01)	[74SIM/VOL] ^(f)
$\text{NpO}_2(\text{CO}_3)_3^{5-} + \text{NpO}_2^{2+} \rightleftharpoons \text{NpO}_2^+ + \text{NpO}_2(\text{CO}_3)_3^{4-}$					
cou	1 M Na ₂ CO ₃	23	11.5		[93LI/KAT]
red	1 M NaClO ₄	25	(12.06±0.75) ^(a)		[84MAY]
vlt	3 M NaClO ₄	22	(11.13±0.2) ^(a)		[90RIG]
red	0.4-6 M K ⁺ , 1 M ClO ₄ ⁻	20	(11.2±0.9) ^(a)		[74SIM/VOL]
red	0.4-2 M Na ₂ CO ₃ or K ₂ CO ₃	20	(12.0±1.2) ^(a)		[74SIM/VOL]
$\text{NpO}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{NpO}_2^{2+} + \text{CO}_3^{2-}$					
sol	3 M NaClO ₄	22	-(13.8±0.38)		[98VIT/CAP]
			-(13.99±0.33) ^{(a)(b)}		
sol	0.1 M NaClO ₄	25	-(14.62±0.12)		[96KAT/KIM]
			-(14.18±0.56) ^(a)		

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sol	$K^+, CO_3^{2-},$ $NpO_2(CO_3)_3^{4-}$ ^(h)	20	$-(2.31 \pm 0.40)^{(b)}$	[66GOR/KLI] ^{(a)(e)}
sol	0.2 M K_2CO_3	20	$-(2.81 \pm 0.40)^{(b)}$	
sol	1 M K_2CO_3	20	$-(0.85 \pm 0.40)^{(b)}$	
sol	5.573 M K_2CO_3	20	(0.11 ± 0.40)	
$(NH_4)_4NpO_2(CO_3)_3(s) \rightleftharpoons NpO_2(CO_3)_3^{4-} + 4NH_4^+$				
sol	0 M $(NH_4)_2CO_3$?	$-(3.42 \pm 0.40)^{(b)}$	[71MOS2] ^{(a)(g)}
sol	0.1 M $(NH_4)_2CO_3$?	$-(3.48 \pm 0.40)^{(b)}$	
sol	0.5 M $(NH_4)_2CO_3$?	$-(2.33 \pm 0.40)^{(b)}$	
sol	0.75 M $(NH_4)_2CO_3$?	$-(1.82 \pm 0.40)^{(b)}$	
sol	0.75 M $(NH_4)_2CO_3$?	$-(1.91 \pm 0.40)$	
sol	1 M $(NH_4)_2CO_3$?	$-(1.43 \pm 0.40)^{(b)}$	
sol	1 M $(NH_4)_2CO_3$?	$-(1.45 \pm 0.40)$	
sol	1.25 M $(NH_4)_2CO_3$?	$-(1.19 \pm 0.40)^{(b)}$	
sol	1.25 M $(NH_4)_2CO_3$?	$-(1.25 \pm 0.40)$	
sol	1.5 M $(NH_4)_2CO_3$?	$-(0.89 \pm 0.40)^{(b)}$	
sol	1.8 M $(NH_4)_2CO_3$?	$-(0.66 \pm 0.40)^{(b)}$	
sol	2.20 M $(NH_4)_2CO_3$?	$-(0.47 \pm 0.40)^{(b)}$	

(a) This constant is calculated in the present review (Appendix A) from data given by the author.

(b) These data were used to obtain the standard values selected in the present review.

(c) Corrected by this review for the dissociation of $NpO_2(CO_3)_3^{5-}$ into $NpO_2(CO_3)_2^{3-}$

(d) This value was calculated by the author; who finally decided there was no firm evidence for this particular species.

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- was unique. The interpretation (proposed by the author(s)) contradicts experimental observations published elsewhere. The equilibrium constant tabulated here was calculated in the present review (Appendix A).
- (h) The chemical composition of the aqueous solution, was only due to the dissolution of the solid compound under study (without addition of any other chemical reagent).
- (i) Value corrected in this review (see Appendix A)
- (j) Uncertainty corrected in this review (see Appendix A)
- (k) E° , $\Delta_r H_m^\circ = -(89 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_r S_m^\circ = -(188 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\Delta_r C_p^\circ = -(759 \pm 141) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at 25°C , were obtained from a second order polynomial regression on $E^\circ(5 \text{ to } 55^\circ\text{C})$ [98CAP/VIT], where $E^\circ(T)$ was calculated from a SIT linear regression on $E'^\circ(T)$ in 0.22, 0.55, 1, 1.25 and 2 M Na_2CO_3 media. From the slope of the SIT linear regression, $\Delta\varepsilon = (0.13 \pm 0.03) - (5.3 \pm 1.0)(t - 25) + (0.11 \pm 0.26)(t - 25)^2/2$.
- (l) From a second order polynomial regression (0° to 55°C), using the experimental $E'^\circ(T)$ data: $\Delta_r H_m^\circ = -(88.7 \pm 0.9)$, $-(94.2 \pm 1.2)$, $-(99.1 \pm 0.9)$, $-(108 \pm 3)$, $-(108 \pm 1)$, $-(119 \pm 2) \text{ kJ}\cdot\text{mol}^{-1}$; $\Delta_r S_m^\circ = -(157 \pm 3)$, $-(165 \pm 4)$, $-(170 \pm 3)$, $-(203 \pm 9)$, $-(199 \pm 3)$, $(234 \pm 8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$; $\Delta_r C_p^\circ = -(304 \pm 86)$, $-(352 \pm 112)$, $-(282 \pm 87)$, (475 ± 329) , (64 ± 124) , $(891 \pm 262) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for 0.22, 0.55, 1, 1.25, 1.5 and 2 M Na_2CO_3 , respectively [98CAP/VIT]. Only the $E'^\circ(25^\circ\text{C})$ values are tabulated here.

This is a sparse set when compared with the species and thermodynamic data proposed [92GRE/FUG] for uranium(VI) carbonate and mixed hydroxide-carbonate complexes: $\text{UO}_2\text{CO}_3(\text{aq})$, $\text{UO}_2(\text{CO}_3)_2^{2-}$, $\text{UO}_2(\text{CO}_3)_3^{4-}$, $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$, $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$, $(\text{UO}_2)_3\text{O}(\text{OH})_2\text{HCO}_3^+$ and solids $(\text{UO}_2\text{CO}_3(\text{s}))$, $\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$. Using the complexes $\text{NpO}_2(\text{CO}_3)_3^{4-}$ and $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$ as a starting point, several other published studies were interpreted or reinterpreted in the present review:

- Solubility products for $\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$ and $(\text{NH}_4)_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$ were estimated from the work of Gorbenko-Germanov and Klimov [66GOR/KLI] and from solubility measurements of Moskvina (despite the completely erroneous interpretation of the experimental results in the original paper [71MOS2], see Appendix A).
- Although there are really insufficient solubility data available, the work of Vitorge and Capdevila [98VIT/CAP] was used to estimate the solubility product of $\text{NpO}_2\text{CO}_3(\text{s})$ and the formation constants of the lower mononuclear complexes, $\text{NpO}_2(\text{CO}_3)_2^{2-}$ and $\text{NpO}_2\text{CO}_3(\text{aq})$.
- As for uranium [92GRE/FUG], Maya [84MAY] showed evidence of formation of at least one polynuclear mixed Np(VI) hydroxide-carbonate complex. Unfortunately, in this potentiometric study, the total concentration of Np(VI) was kept practically constant. Thus, the data are insufficient to unambiguously define the stoichiometry of any polynuclear complexes (see the discussion of [84MAY] in Appendix A). Maya proposed the formation of $(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$ which seems quite reasonable when compared with species found in the uranium system; but, for the reasons explained below and in Appendix A, no accurate quantitative interpretation could be extracted from this work.

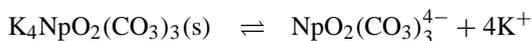
Other published work [74SIM/VOL, 81WES/SUL, 93LI/KAT] contain data that, after reinterpretation (Appendix A), are consistent with the species and values for formation constants of the carbonate complexes selected in the present review. However, it was not possible to use the results of these studies to deduce quantitative information related to the minor species in the $\text{Np}(\text{VI})\text{-CO}_3^{2-}$ system.

The Np(VI) and U(VI) carbonate complexes are formed under similar conditions. At high ionic strength (3 M NaClO_4) a regular progression was observed in the U, Np, Pu series for the formation and stepwise complexation constants, and for the $\text{MO}_2\text{CO}_3(\text{s})$ solubility products (M=U, Np, Pu) [98VIT/CAP]. The limiting and the trinuclear Np(VI) complexes are a little less stable than the corresponding uranium ones, while the solubility products are probably of the same order of magnitude for uranium and neptunium. Consequently solubility in carbonate-bicarbonate (3 M NaClO_4) media is lower for Np(VI) than for U(VI). In such solutions, the trinuclear Np(VI) complex can occur at 25° only in supersaturated solutions. However, for kinetic reasons (the solid $\text{NpO}_2\text{CO}_3(\text{s})$ is much slower to precipitate from carbonate solutions than $\text{UO}_2\text{CO}_3(\text{s})$ and $\text{PuO}_2\text{CO}_3(\text{s})$ under similar conditions), the trinuclear species was probably present in several reported studies, and it is actually the easiest trinuclear species to study in the U, Np, Pu series.

Aside from these studies from which equilibrium constants and then $\Delta_r G_m^\circ$ were extracted, other thermodynamic parameters are proposed based on the study of the variation of redox potential with temperature by Offerlé, Capdevila and Vitorge [95OFF/CAP], and from the calorimetric measurements of Ullman and Schreiner [88ULL/SCH].

12.1.2.1.2.a The Np(VI) carbonate limiting complex

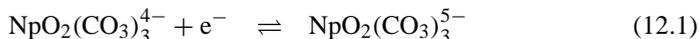
The starting point of this review, was the determination of the stoichiometry and stability of the Np(VI) carbonate limiting complex. One of the first studies of Np(VI) in carbonate media, was the preparation and characterization of the solid $K_4NpO_2(CO_3)_3(s)$ [66GOR/KLI]. Its solubility was interpreted by this review by analogy with the uranium system (see Section 12.1.2.2.1 and the discussion of [66GOR/KLI] in Appendix A) in terms of the equilibrium



The stoichiometry of the limiting complex, $NpO_2(CO_3)_3^{4-}$, was proposed only later by Simakin [77SIM]. Careful measurements showed that the potential of the Np(VI)/Np(V) redox couple is constant in concentrated sodium and potassium carbonate media of various concentrations, it was then concluded that the limiting carbonate complexes of Np(VI) and Np(V) have the same stoichiometry. In the same work, $NpO_2(CO_3)_3^{5-}$ was proposed as the Np(V) limiting complex from slope analysis of Np(V) solubility controlled by the equilibrium (see Section 12.1.2.2.2)



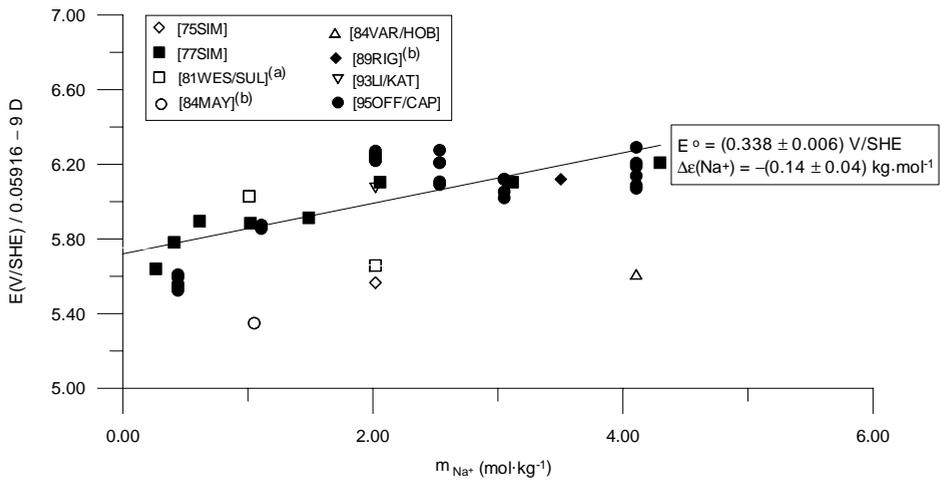
This two-step demonstration implicitly assumed (at each step) that no polynuclear soluble complex could be formed. Fortunately, this is the case in these particular conditions as demonstrated later by Riglet for Np(V) [90RIG] and Grenthe, Riglet and Vitorge [86GRE/RIG] and Riglet [90RIG] for Np(VI) using spectrophotometric measurements in both cases. Due to the lack of other reliable data, this review only used potential measurements of the redox equilibrium



Formal potentials versus the standard hydrogen reference electrode were determined from the information in a paper by Simakin [77SIM]. This was done by digitizing the points shown in Simakin's Figure 1, and despite some ambiguities in the meaning of the reported junction potential measurements.

The results of two different studies have been published by Vitorge and co-workers. The first was reported only in Section IV.4.4.2.3 of Riglet's thesis [90RIG]. The experimental methodology used was satisfactory, and the procedure was checked by determining values for the corresponding uranium system. The results for the uranium system were consistent with those determined by others [92GRE/FUG]. In the second study, Offerlé, Capdevila and Vitorge [95OFF/CAP] report both the experimental details and the original data. The treatment of the data was checked in the present review,

Figure 12.1: Extrapolation to $I = 0$ of the formal potential for the $\text{NpO}_2(\text{CO}_3)_3^{4-} + e^- \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-}$ redox equilibrium, using the SIT with data (filled symbols) from measurements in aqueous Na_2CO_3 or $(\text{Na}_2\text{CO}_3 + \text{NaHCO}_3)$ (a), or NaClO_4 (b), as accepted in the present review after correction for the dissociation of the Np(V) limiting complex.



and a standard potential value was obtained that was consistent with the value in the original report (despite small errors later pointed out by two of the authors, Capdevila and Vitorge [98VIT/CAP]).

Small corrections were made for the dissociation of the Np(V) limiting complex (see discussion of [77SIM] and [95OFF/CAP] in Appendix A for further details on the calculations performed in this review). A statistical analysis was also performed independently on the results from the two publications [77SIM, 95OFF/CAP] that reported sufficient data. The estimated uncertainties are consistent with those suggested by the original authors. The values from all three studies were extrapolated to zero ionic strength using the SIT, and the results of these determinations appear to be in very good agreement (Figure 12.1 and [98VIT/CAP]).

The reduction potentials were converted to potentials relative to the standard hydrogen electrode (H₂(g) at unit fugacity, 0.1 MPa) using the conventions adopted by this review. The value selected from linear regression by this review is

$$E^\circ(\text{12.1}, 298.15 \text{ K}) = (0.338 \pm 0.006) \text{ V}$$

then

$$\Delta_r G_m^\circ(\text{12.1}, 298.15 \text{ K}) = -(32.65 \pm 0.54) \text{ kJ}\cdot\text{mol}^{-1}$$

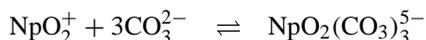
Linear regression (Figure 12.1) also gives

$$\Delta\varepsilon(\text{12.1}, 298.15 \text{ K}) = -(0.14 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$$

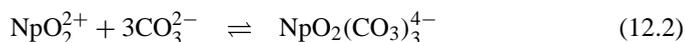
Other measurements (*cf.* Table 12.1) of the potential of the same redox equilibrium have been reported in the literature; but the publications do not include enough experimental information about reference electrode calibration, so the uncertainty for possible junction potential contributions must be systematically increased. Junction potential problems are quite apparent in the earlier work of Simakin *et al.* [74SIM/VOL] and Simakin [75SIM], and were also probably present in the studies of Maya [84MAY] and Varlashkin *et al.* [84VAR/HOB]. The results of measurements of Wester and Sullivan [81WES/SUL], and Li, Kato and Yoshida [93LI/KAT] were rejected for similar reasons (Appendix A) although the resulting values for the potentials are in fair agreement with those selected above [77SIM, 90RIG, 95OFF/CAP]. From $\Delta\varepsilon(\text{12.1}, 298.15 \text{ K}) = -(0.14 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{Na}^+) = -(0.53 \pm 0.19) \text{ kg}\cdot\text{mol}^{-1}$ (see Section 12.1.2.1.3)

$$\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+) = -(0.40 \pm 0.19) \text{ kg}\cdot\text{mol}^{-1}$$

This $E^\circ(\text{12.1}, 298.15 \text{ K})$ value was combined with the standard potential for the $\text{NpO}_2^{2+}/\text{NpO}_2^+$ redox couple, $E^\circ(\text{7.4})$, and the formation constant $\log_{10} \beta_3^\circ(\text{12.18}, 298.15 \text{ K})$ selected in this review (*cf.* Sections 7.2 and 12.1.2.1.3, respectively) for the reaction



to calculate $\log_{10} \beta_3^\circ(12.2, 298.15 \text{ K}) = (19.37 \pm 0.19)$ and $\Delta_r G_m^\circ(12.2, 298.15 \text{ K}) = -(110.57 \pm 1.09) \text{ kJ}\cdot\text{mol}^{-1}$ for the following equilibrium:



$$\Delta_r G_m^\circ(\text{NpO}_2(\text{CO}_3)_3^{4-}, 298.15) = -(2490.21 \pm 5.76) \text{ kJ}\cdot\text{mol}^{-1}$$

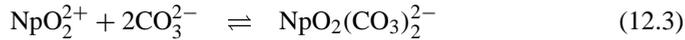
12.1.2.1.2.b Other mononuclear Np(VI) carbonate complexes

There is no reliable published work proposing formation constants for the mononuclear Np(VI) carbonate complexes other than $\text{NpO}_2(\text{CO}_3)_3^{4-}$. The lower complexes would be intermediate species in the sequential dissociation of this limiting complex (to NpO_2^{2+}) at low Np(VI) total concentrations (where the formation of polynuclear complexes will not occur). Maya [84MAY] interpreted his potentiometric titration data in terms of the species $\text{NpO}_2(\text{CO}_3)_2^{2-}$; but, in the course of the present review, it was found that the original experimental data may not have been reliable (due to supersaturation). The final interpretation proposed by Maya neglected $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$, which may have been important under the conditions used for some of the measurements. An alternate interpretation is proposed in this review (Appendix A). In the present review, only maximum values for the $\text{NpO}_2\text{CO}_3(\text{aq})$ and $\text{NpO}_2(\text{CO}_3)_2^{2-}$ formation constants are calculated from Maya's data (Table 12.1). In the same publication, Maya [84MAY] reported the variation of the Np(VI)/Np(V) redox potential with changes in the hydrogen ion concentration and $\text{CO}_2(\text{g})$ partial pressure. The formation constants he extracted from this electrochemical work were not entirely consistent with his interpretation of the potentiometric titration data, and although reasons were given for the discrepancy, these were not completely convincing. Reinterpretation of Maya's electrochemical measurements (Appendix A) suggests the observed variations were mainly due to the dissociation of the Np(V) limiting complex. A dissociation constant for the Np(VI) complex could be obtained by refitting the results (Table 12.1), but there is a large uncertainty in the calculated value, and the results are better used to define a limit.

Moskvin [75MOS], and more recently Pratopo, Moriyama and Higashi [93PRA/MOR, 95MOR/PRA], reported formation constant values for the lower carbonate complexes of Np(VI). However, their interpretations of the experimental results are completely in error (*cf.* Appendix A including the discussion of [98VIT/CAP]). Reinterpretation (when feasible) can give information only about the limiting complex, as it was the only major soluble Np(VI) carbonate complex present under the conditions of all these solubility measurements. Vitorge and Capdevila [98VIT/CAP] recently proposed values for the formation constants of $\text{NpO}_2\text{CO}_3(\text{aq})$ and $\text{NpO}_2(\text{CO}_3)_2^{2-}$ based on measurements of the solubility of $\text{NpO}_2\text{CO}_3(\text{s})$ in 3 M NaClO_4 media (Table 12.1). This work is accepted; and as was done by the original authors, this review calculates the values $\log_{10} \beta_1(12.4, 3 \text{ M NaClO}_4) = (8.72 \pm 0.52)$, $\log_{10} \beta_2(12.3, 3 \text{ M NaClO}_4) = (15.77 \pm 0.52)$ and the $\text{NpO}_2\text{CO}_3(\text{s})$ solubility product by curve fitting using fixed values of $\beta_3(12.2)$ and $\beta_{6,3}(12.6)$ (Appendix A). However,

the fixed β_3 (12.2) and $\beta_{6,3}$ (12.6) values used here are those selected in the present review (elsewhere in this section).

This is done, even though the values were determined from an overly sparse set of solubility measurements, as pointed out by the authors. In the extrapolation to zero ionic strength the following estimated specific interaction coefficients were used: $\varepsilon_{(\text{NpO}_2(\text{CO}_3)(\text{aq}), \text{Na}^+)} = 0 \text{ kg}\cdot\text{mol}^{-1}$ (as for all the uncharged species) and $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_2^{2-}, \text{Na}^+)} = -(0.02 \pm 0.14) \text{ kg}\cdot\text{mol}^{-1}$ which is the $\varepsilon_{(\text{UO}_2(\text{CO}_3)_2^{2-}, \text{Na}^+)}$ value with increased uncertainty. Therefore, for the reactions



the selected values of the formation constants are

$$\log_{10} \beta_2^\circ(12.3, 298.15 \text{ K}) = (16.52 \pm 0.73)$$

$$\log_{10} \beta_1^\circ(12.4, 298.15 \text{ K}) = (9.32 \pm 0.61)$$

Then,

$$\Delta_r G_m^\circ(12.3, 298.15 \text{ K}) = -(94.28 \pm 4.16) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r G_m^\circ(12.4, 298.15 \text{ K}) = -(53.20 \pm 3.48) \text{ kJ}\cdot\text{mol}^{-1}$$

and

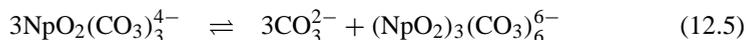
$$\Delta_f G_m^\circ(\text{NpO}_2(\text{CO}_3)_2^{2-}, 298.15 \text{ K}) = -(1946.01 \pm 7.03) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{NpO}_2\text{CO}_3, \text{aq}, 298.15 \text{ K}) = -(1377.04 \pm 6.62) \text{ kJ}\cdot\text{mol}^{-1}$$

12.1.2.1.2.c The carbonate trinuclear Np(VI) complex

The trinuclear complex $(\text{MO}_2)_3(\text{CO}_3)_6^{6-}$, was first identified for uranium ($M = \text{U}$) by Ciavatta *et al.* [81CIA/FER]. A few years later, during a sabbatical leave in Vitorge's laboratory, Grenthe worked with Riglet and Vitorge and used a spectrophotometric technique to demonstrate that neptunium and plutonium also form corresponding trinuclear complexes [86GRE/RIG, 90RIG].

For the neptunium complex, the stoichiometry determination, sensitivity analysis, uncertainty estimation and quantitative interpretation (*i.e.*, determination of the equilibrium constant value) were carried out using graphical methods. In the present review the original data tabulated in Riglet's thesis [90RIG] (from experiments in 3 M NaClO_4) were reanalyzed. The same equilibrium constant value (but with increased uncertainty limits) was found (Table 12.1) for the reaction



The trinuclear neptunium complex is less stable than the corresponding uranium complex, while the solid compounds of these two actinide(VI) ($\text{MO}_2\text{CO}_3(\text{s})$) are of

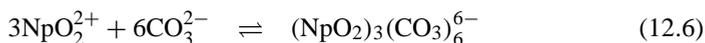
very similar stability. For this reason it is more difficult to obtain the Np(VI) trinuclear complex for equilibrium conditions than is the case for the corresponding uranium complex. Nevertheless, the trinuclear species was observed as the almost the sole neptunium solution species in supersaturated solutions. Thus the stoichiometry of this complex could be checked using a combination of classical and original graphical slope analyses (see [98VIT/CAP]). There is little other published data that shows evidence for the $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$ complex and that is of adequate quality to permit its formation constant to be calculated. Despite the problems discussed above and in Appendix A, one of Maya's potentiometric titrations [84MAY] was also used to calculate a value with a very large uncertainty, $\log_{10} K = -(8.81 \pm 1.08)$, for the reaction (12.5) at 1 M NaClO_4 . There are still only two values for the extrapolation to zero ionic strength. Analogy with uranium should not be used for ionic strength corrections for this type of equilibrium because complexes with very large negative charges (-5 or -6) often have been found to have unusual ε coefficients. This is probably due to ion pairing, and was found for the uranium trinuclear complex $(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$ [92GRE/FUG]. Rather than not selecting any value for the equilibrium constant for Reaction (12.5), a value having a large uncertainty is calculated using the only two available data, this gives ([84MAY], as reinterpreted by this review, and [90RIG]):

$$\begin{aligned}\log_{10} K^\circ(12.5, 298.15 \text{ K}) &= -(8.27 \pm 1.45) \\ \Delta_r G_m^\circ(12.5, 298.15 \text{ K}) &= (47.22 \pm 8.26) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Hence,

$$\Delta_f G_m^\circ(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}, 298.15) = -(5839.71 \pm 19.18) \text{ kJ}\cdot\text{mol}^{-1}$$

$\log_{10} \beta_{6,3}^\circ(12.6, 298.15 \text{ K}) = (49.84 \pm 1.56)$ and $\Delta_r G_m^\circ(12.6, 298.15 \text{ K}) = -(284.50 \pm 8.89) \text{ kJ}\cdot\text{mol}^{-1}$ are calculated for the equilibrium



From the extrapolation to zero ionic strength $\Delta\varepsilon(12.5) = (0.49 \pm 0.50) \text{ kg}\cdot\text{mol}^{-1}$; from which

$$\varepsilon_{((\text{NpO}_2)_3(\text{CO}_3)_6^{6-}, \text{Na}^+)} = -(0.46 \pm 0.73) \text{ kg}\cdot\text{mol}^{-1}$$

was derived and selected. This value is completely different from the corresponding uranium one [92GRE/FUG, 95GRE/PUI] $\varepsilon_{((\text{UO}_2)_3(\text{CO}_3)_6^{6-}, \text{Na}^+)} = (0.37 \pm 0.11) \text{ kg}\cdot\text{mol}^{-1}$; but as already pointed out [92GRE/FUG] the uranium value is itself quite unusual: negative ε values are usually observed for negatively charged complexes.

12.1.2.1.2.d Mixed hydroxide-carbonate complexes of Np(VI)

There is evidence from the work of Maya [84MAY] that mixed hydroxide-carbonate complexes can form, but as discussed above (Appendix A), the total Np(VI) concentration was not systematically varied in these experiments. Therefore, the stoichiometry of

polynuclear complexes could not be readily determined. In the present review some of Maya's reported formation constants (including some calculated for species that were eventually rejected), and some values recalculated in this review from Maya's data, are proposed as maximum possible values (Table 12.2).

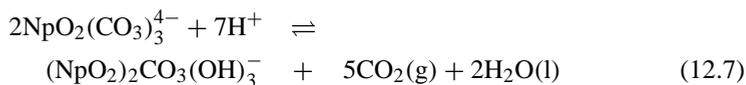
Table 12.2: Maximum possible values of formation constants. The formation of the Np(VI) species on the right-hand side of these equilibria has not been demonstrated unequivocally, *cf.* discussion of [71MOS2] and [93PRA/MOR, 95MOR/PRA] in Appendix A.

Method	Ionic Medium	t (°C)	$\log_{10} K$	Reference
$3\text{NpO}_2(\text{CO}_3)_3^{4-} + 7\text{H}_2\text{O}(\text{l}) \rightleftharpoons 7\text{H}^+ + 9\text{CO}_3^{2-} + (\text{NpO}_2)_3(\text{OH})_7^-$				
pot	1 M (NaClO ₄ , NaHCO ₃)	25	(62.35 ± 1.50) ≤ 63.33	[84MAY] ^(a)
$3\text{NpO}_2(\text{CO}_3)_3^{4-} + 8\text{H}_2\text{O}(\text{l}) \rightleftharpoons 8\text{H}^+ + 9\text{CO}_3^{2-} + (\text{NpO}_2)_3(\text{OH})_8^{2-}$				
pot	1 M (NaClO ₄ , NaHCO ₃)	25	≤ 55.45	[84MAY] ^{(a)(b)}
$3\text{NpO}_2(\text{CO}_3)_3^{4-} + 3\text{H}_2\text{O}(\text{l}) \rightleftharpoons 3\text{H}^+ + 8\text{CO}_3^{2-} + (\text{NpO}_2)_3\text{CO}_3(\text{OH})_3^+$				
pot	1 M (NaClO ₄ , NaHCO ₃)	25	≤ 75.42	[84MAY] ^(a)

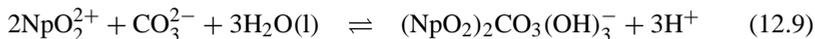
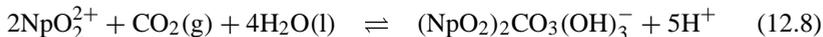
(a) Maximum possible value estimated in the present review from the data of [84MAY].

(b) The corresponding species was recently proposed for uranium [95PAL/NGU].

The only value accepted here (Table 12.1) is $\log_{10} K$ (12.7, 1 M NaClO₄) = (41.75 ± 1.46) for



Using data selected in this review, this corresponds to $\log_{10} K$ (12.8, 1 M NaClO₄) = $-(21.38 \pm 1.62)$ and $\log_{10} K$ (12.9, 1 M NaClO₄) = $-(4.16 \pm 1.60)$



As for the corresponding uranium species, the value $\varepsilon_{((\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-, \text{Na}^+)}$ = (0.00 ± 0.05) kg·mol⁻¹ is assumed and hence,

$$\log_{10} K^\circ (12.7, 298.15 \text{ K}) = (49.17 \pm 1.59)$$

$$\Delta_r G_m^\circ (12.7, 298.15 \text{ K}) = -(280.64 \pm 9.05) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ ((\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-, 298.15 \text{ K}) = -(2814.92 \pm 14.67) \text{ kJ}\cdot\text{mol}^{-1}$$

This corresponds to $\log_{10} K^\circ$ (12.9, 298.15 K) = $-(2.87 \pm 1.64)$ and $\log_{10} K^\circ$ (12.8, 298.15 K) = $-(21.02 \pm 1.64)$ which is less than $-(19.0 \pm 0.5)$, the uranium value [92GRE/FUG]. Hence, the mixed complex would be less stable for neptunium than for uranium.

Similar work on the uranium system by the same author, was found to overestimate formation constants of mixed uranium complexes (as selected in the uranium review [92GRE/FUG]). As a guideline, values selected for the formation constants of the U(VI) hydroxide-carbonate complexes by Grenthe *et al.* [92GRE/FUG] could also be used for the Np(VI) species.

12.1.2.1.2.e Temperature influence on the stability of the limiting carbonate complex of Np(VI)

Offerlé, Capdevila and Vitorge [95OFF/CAP] studied the Np(VI)/Np(V) redox equilibrium in solutions containing sodium carbonate (0.22 M to 2 M, variable ionic strength) at several different temperatures (5 to 60°C). The data are provided in [98VIT/CAP] together with results of an extrapolation to zero ionic strength at different temperatures. The data and the interpretation were rechecked and are accepted here. Details of the calculations are provided in Appendix A and in [98VIT/CAP]. From these, values of $\Delta_r S_m^\circ$, $\Delta_r H_m^\circ$ and $\Delta_r C_{p,m}^\circ$ at 25° were derived for each carbonate concentration and using the data previously extrapolated to zero ionic strength, the standard values were also calculated. In the temperature range of the study, the value of $\Delta_r C_{p,m}^\circ$ is not well defined by the experimental data. The results found in this review are consistent with those initially calculated by Offerlé, Capdevila and Vitorge [95OFF/CAP]. The results are given in Table VI.d of [98VIT/CAP].

$$\Delta_r H_m^\circ(12.1, 298.15 \text{ K}) = -(88.8 \pm 2.9) \text{ kJ}\cdot\text{mol}^{-1}$$

accepted in this review, $\Delta_r S_m^\circ(12.1, 298.15 \text{ K}) = -(188 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $\Delta_r C_{p,m}^\circ(12.1, 298.15 \text{ K}) = -(759 \pm 141) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This value, $\Delta_r S_m^\circ = -(188 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, is consistent with $\Delta_r S_m^\circ = -(188.33 \pm 9.89) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ calculated from the values $\Delta_r H_m^\circ = -(88.8 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r G_m^\circ = -(32.65 \pm 0.54) \text{ kJ}\cdot\text{mol}^{-1}$ selected above in this section.

As pointed out by Offerlé, Capdevila and Vitorge [95OFF/CAP], similar $\Delta_r S_m^\circ$ and $\Delta_r C_{p,m}^\circ$ values were found in the same laboratory for the corresponding uranium and plutonium equilibria using the same methodology. From the same experimental work, the influence of temperature on the value of $\Delta\varepsilon$ was studied [98VIT/CAP], but no temperature-dependent values of $\Delta\varepsilon$ from this analysis are selected in the present review.

The value of $\Delta_r H_m^\circ(12.2, 298.15 \text{ K})$ was measured by Schreiner, Friedman *et al.* [85SCH/FRI] and by Ullman and Schreiner [88ULL/SCH]. As was the case for their measurements on the corresponding uranium system, the enthalpy of sulphate complexation must be subtracted from their measurements [92GRE/FUG]. The value is then accepted by this review (Appendix A), but also needs to be corrected to zero ionic strength. These corrections were claimed to be negligible for uranium [92GRE/FUG].

In the present review, the influence of the ionic strength on the values was confirmed as being negligible from a calculation using the data at the end of the titration where the limiting complex had already formed, and only the ionic strength was being varied (Appendix A). The uncertainty was increased to the same value previously estimated for the uranium system [92GRE/FUG]

$$\Delta_r H_m^\circ(12.2, 298.15 \text{ K}) = -(41.9 \pm 4.1) \text{ kJ}\cdot\text{mol}^{-1}$$

From this value, $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, 298.15 \text{ K}) = -(860.7 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1}$ (Section 7.2) and $\Delta_f H_m^\circ(\text{CO}_3^{2-}, 298.15 \text{ K}) = -(675.23 \pm 0.25) \text{ kJ}\cdot\text{mol}^{-1}$ (Table 5.1)

$$\Delta_f H_m^\circ(\text{NpO}_2(\text{CO}_3)_3^{4-}, 298.15 \text{ K}) = -(2928.32 \pm 6.25) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated. From $\Delta_r H_m^\circ(12.2, 298.15 \text{ K}) = -(41.9 \pm 4.1) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r G_m^\circ(12.2, 298.15 \text{ K}) = -(110.57 \pm 1.09) \text{ kJ}\cdot\text{mol}^{-1}$ selected above in this section, $\Delta_r S_m^\circ(12.2, 298.15 \text{ K}) = (230.32 \pm 14.23) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ is calculated. This value is $(51.73 \pm 19.80) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ less than the corresponding uranium value $(282.05 \pm 13.79) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [92GRE/FUG]. $\Delta_r S_m^\circ(12.2, 298.15) = (230.32 \pm 14.23) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $S_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15) = -(92.4 \pm 10.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (Section 7.3) and $S_m^\circ(\text{CO}_3^{2-}, \text{aq}, 298.15 \text{ K}) = -(50 \pm 1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (Table 5.1) give

$$S_m^\circ(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{aq}, 298.15 \text{ K}) = -(12.07 \pm 17.92) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

which is $(46.0 \pm 23) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ less than the corresponding uranium value $S_m^\circ(\text{UO}_2(\text{CO}_3)_3^{4-}, \text{aq}, 298.15 \text{ K}) = (33.9 \pm 14.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ [92GRE/FUG].

12.1.2.1.2.f Discussion

The values selected in this review (see Table 12.3) for the Np(VI) carbonate complexes (and compound, see below) are quite similar to those for the corresponding uranium and plutonium species. Small regular variations are usually observed in the U, Np, Pu series. However, these can lead to real differences in behaviour of the species in solution as discussed above for the stability of the carbonate trinuclear complexes.

12.1.2.1.3 Np(V) carbonate and mixed hydroxide-carbonate complexes

As part of their study of potassium dioxoneptunium(V) carbonate solids Gorbenko-Germanov and Zenkova [66GOR/ZEN] published absorption spectra of their aqueous solutions. The spectra were later confirmed [75UEN/SAI] and can be interpreted as primarily resulting from the limiting complex $\text{NpO}_2(\text{CO}_3)_3^{5-}$ [90RIG]. Simakin [77SIM] deduced the correct stoichiometry of this limiting Np(V) carbonate complex, from solubility measurements of a hydrated $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ compound at constant ionic strength (3 M NaNO_3) in concentrated carbonate aqueous solutions. The full demonstration of this stoichiometry was only confirmed later (see Appendix A discussions for [77SIM, 90RIG]). Simakin's measurements were the first reliable work on

Table 12.3: Selected equilibrium constants in the dioxoneptunium(VI) carbonate system at 298.15 K and $I = 0$, including the mixed hydroxide-carbonate complexes.

Reaction		$\log_{10} K^\circ$
$\text{NpO}_2^{2+} + \text{CO}_3^{2-}$	\rightleftharpoons	$\text{NpO}_2\text{CO}_3(\text{aq})$ (9.32±0.61)
$\text{NpO}_2^{2+} + 2\text{CO}_3^{2-}$	\rightleftharpoons	$\text{NpO}_2(\text{CO}_3)_2^{2-}$ (16.52±0.73)
$\text{NpO}_2^{2+} + 3\text{CO}_3^{2-}$	\rightleftharpoons	$\text{NpO}_2(\text{CO}_3)_3^{4-}$ (19.37±0.19) ^(b)
$3\text{NpO}_2^{2+} + 6\text{CO}_3^{2-}$	\rightleftharpoons	$(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$ (49.84±1.56) ^(b)
$2\text{NpO}_2^{2+} + \text{CO}_3^{2-} + 3\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^- + 3\text{H}^+$ -(2.87±1.64) ^(b)
$\text{NpO}_2(\text{CO}_3)_3^{4-} + \text{e}^-$	\rightleftharpoons	$\text{NpO}_2(\text{CO}_3)_3^{5-}$ (0.338±0.006) ^(a)
Solubility product:		
$\text{NpO}_2\text{CO}_3(\text{s})$	\rightleftharpoons	$\text{NpO}_2^{2+} + \text{CO}_3^{2-}$ -(14.60±0.47)
$\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$	\rightleftharpoons	$\text{NpO}_2(\text{CO}_3)_3^{4-} + 4\text{K}^+$ -(7.03±0.88)
$(\text{NH}_4)_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$	\rightleftharpoons	$\text{NpO}_2(\text{CO}_3)_3^{4-} + 4\text{NH}_4^+$ -(7.44±0.30)

^(a) $E^\circ/(\text{V vs. SHE})$ ^(b) Calculated from selected data

dioxoneptunium(V) carbonates from which thermodynamic constant can be determined.

Billon [81BIL] provided further evidence of the formation of soluble complexes, and this preliminary work was extended in the same laboratory by Vitorge [84VIT], Riglet [90RIG] and in collaboration with Grenthe [86GRE/ROB]. Within the framework of the MIRAGE project, Kim [85CÔM, 85KIM] provided a summary of this work and that of Bidoglio, Tanet and Chatt [85BID/TAN] who used a liquid-liquid extraction technique. Billon's spectrophotometric observations can be explained in terms of the formation of the Np(V) carbonate complexes $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2(\text{CO}_3)_3^{3-}$. In the documents of the MIRAGE project contradictory formation constants were reported for these intermediary complexes. Meanwhile Maya [83MAY] deduced the Np(V) carbonate complexation constants from a solubility study of a hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ compound. In the present review, this is considered to be one of the most important papers for the selection of thermodynamic data for dioxoneptunium(V) carbonate complexes.

Varlashkin, Begun and Hobart [84VAR/BEG] reported Np(V) spectral variations on addition of NaOH to concentrated Np(V) carbonate aqueous solutions. These results were later confirmed by Riglet [90RIG] and Vitorge and Capdevila [98VIT/CAP], and interpreted as evidence of the formation of mixed Np(V) hydroxide-carbonate complexes. As work on this section of the review was nearing completion, further information about the nature of these species was also provided in similar work reported by Neck, Fanghänel and Kim [97NEC/FAN].

In her thesis work, Riglet [90RIG] used solubility and spectrophotometric

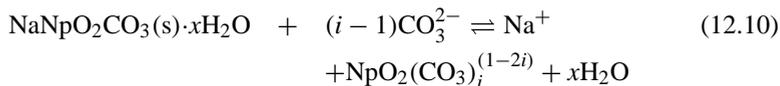
techniques with a range of Np(V) concentrations. She independently varied the chemical conditions of the aqueous carbonic acid/bicarbonate/carbonate/hydroxide system over a sufficiently large domain to confirm, extend or refute assumptions made in earlier work. Aside from the mixed hydroxide-carbonate complex(es), formed only in concentrated hydroxide-carbonate media, the Np(V) complexes in carbonic acid/bicarbonate/carbonate aqueous solutions are clearly mononuclear, and contain only carbonate ligands $(\text{NpO}_2(\text{CO}_3)_i)^{(1-2i)}$, $i = 1, 2, 3$.

Several other early experimental studies of Np(V) in bicarbonate or carbonate aqueous solution, were also published [71MOS2, 75UEN/SAI, 79MOS/POZ]. They cannot be used to propose selected thermodynamic values, but it can be shown (Appendix A) that no species beyond those selected in the present review is needed to understand these experimental results. For example, the species $\text{NpO}_2\text{HCO}_3(\text{aq})$ proposed by Moskvin and Gel'man [63MOS/GÉL], and $\text{NpO}_2\text{CO}_3\text{OH}^{2-}$ or $\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}$ proposed by Moskvin [71MOS2], can be shown to result from erroneous interpretations of the experimental observations.

More recently, results of further experimental work on these systems have been reported. Nitsche, Standifer and Silva [90NIT/STA], Kim *et al.* [91KIM/KLE], Meinrath [94MEI], and Neck *et al.* [94NEC/KIM, 94NEC/RUN, 95NEC/FAN, 95NEC/RUN] published values derived from spectrophotometric measurements at different ionic strengths (Na^+ , (ClO_4^-) or Cl^- media), and proposed complexation constant values extrapolated to zero ionic strength. Kim *et al.* [91KIM/KLE], Neck *et al.* [94NEC/KIM, 95NEC/RUN] and Runde *et al.* [96RUN/NEU] also determined values for the dioxoneptunium(V) carbonate complexation constants in various aqueous media from new solubility measurements (also see Section 12.1.2.1.3.b).

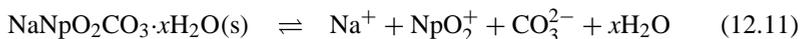
Lemire, Boyer and Campbell [93LEM/BOY] studied the influence of temperature on Np(V) solubility in carbonate media. They found their results appeared to be in contradiction with those of Visyashcheva *et al.* [74VIS/VOL], and that the data were difficult to interpret. The data indicate that there are problems in obtaining stable phases in these solubility experiments, especially during experiments carried out above room temperature. This is discussed in more detail in Section 12.1.2.2.2 and in Appendix A. Clark *et al.* [96CLA/CON] reported preliminary results on the temperature dependence of the complexation constants that also seemed to be in contradiction with the observations of Lemire, Boyer and Campbell.

Many of the more reliable complexation constant determinations have been obtained from solubility measurements. Solubility was typically controlled by the equilibria ($i = 1, 2$ and 3).

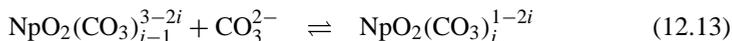


This interpretation assumes that no Np(V) carbonate polynuclear or mixed complexes are formed; a few studies have actually confirmed this [86GRE/ROB, 90RIG]. The treatment of the data (typically curve fitting) is equivalent to slope analysis of the $\log_{10}(\text{solubility})$ vs. $\log_{10}[\text{CO}_3^{2-}]$ plots to generate the equilibrium constants, $K_{s,i}$ (12.10) = $K_{s,0}$ (12.11) $\cdot \beta_i$ (12.12). The classical $K_{s,0}$ (12.11) and β_i (12.12) values

are then deduced for the equilibria



As discussed below and in Appendix A (see the discussions of [84VIT, 90RIG, 93LEM/BOY]) well-characterised hydrated solid phases are difficult to obtain. These solids may evolve during the course of the equilibrations, and, at least for conditions under which $\text{NpO}_2(\text{CO}_3)_3^{5-}$ is formed, the hydrated $\text{MNpO}_2\text{CO}_3(\text{s})$ solids are metastable with respect to others with stoichiometries such as $\text{M}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ [95NEC/RUN]. When enough experimental information is available [84VIT, 93LEM/BOY, 98VIT/CAP] these changes can be recognized, and are consistent with published X-ray diffraction patterns [94MEI, 95NEC/RUN, 96RUN/NEU, 98VIT/CAP]; these transformations could cause problems even within the same set of measurements by the same author. To avoid this problem, this review used another set of equilibria to interpret solubility measurements. One equilibrium must correspond to the solubility product (Eq. 12.10, $i = 0$), and its determination is not independent of these kinetic problems, but the other equilibria



corresponding to the stepwise complexation constants, $K_i = \beta_i/\beta_{i-1} = K_{s,i}$ (12.10)/ $K_{s,i-1}$ (12.10), are less dependent on the solid phase problem. These stepwise constants were also directly measured when using absorption spectrophotometry or liquid-liquid extraction techniques.

Several papers have recently appeared [94NEC/RUN, 95FAN/NEC, 95NEC/FAN, 95NOV/ROB, 95NEC/RUN, 96RUN/NEU] proposing and comparing extrapolations to zero ionic strength using the SIT (Appendix B) and the equations of Pitzer [73PIT]. As discussed below and in Appendix A references to these papers, the complexation constant and solubility product values as extrapolated to zero ionic strength are in reasonable agreement with those based on other publications. However, some of these results lead to inconsistencies in the derived SIT parameters (*cf.* Section 12.1.2.1.3.b). The differences may indicate experimental problems in some of these studies, or some of the earlier studies, or theoretical problems related to neglect of anion-anion interactions, or might result in part from some of the fitted parameters being highly correlated.

As discussed below small systematic deviations could not be ruled out for all the experimental measurements used in the present review to select thermodynamic data for the Np(V) carbonate system. To minimize the effect of these systematic deviations, this review selected procedures that enhanced cancellation of errors, reduced the errors as much as possible, or corrected them when feasible; similar weight was given to data originated from each laboratory because duplicating experiments decreases the random uncertainties, but not the systematic errors. A better treatment of the random uncertainties is generally obtained by equally weighting the values from each laboratory to select a given constant.

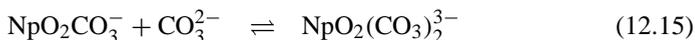
12.1.2.1.3.a Np(V) carbonate complexes

Three types of experimental measurements, liquid-liquid extraction, spectrophotometry and solubility, have been used to derive formation constants for dioxoneptunium(V) carbonate complexes.

Using a liquid-liquid extraction technique with 0.1 or 0.2 M NaClO₄ aqueous solutions, the equilibrium constants, $K_1 = \beta_1$, for



and $K_2 = \beta_2/\beta_1$, for



were measured by Bidoglio, Tanet and Chatt [85BID/TAN]. Their β_1 value does not correspond to the experimental data shown in figures of the publication, but even following re-evaluation in the present review (see Appendix A), none of these β_1 values, nor the K_2 value are in accord with other published work and with the thermodynamic data selected here. Inoue and Tochiyama [85INO/TOC] also used a liquid-liquid extraction technique to determine the values of β_1 and β_2 in 1 M NaClO₄. Within the small uncertainties assigned by the authors, the values are not in good agreement with those selected in the present review. Although larger uncertainties could be assumed (see Appendix A), this work was not used in the final selection of thermodynamic values in the present review.

Values for β_1 , K_2 and the stepwise complexation constant, $K_3 = \beta_3/\beta_2$, for



can be deduced from absorption spectrophotometric studies (see the discussion of [90RIG] in Appendix A); but, of these, the most difficult constant to determine is K_2 because the $\text{NpO}_2(\text{CO}_3)_2^{3-}$ complex cannot be obtained alone to measure its molar absorptivity (*cf.* Figure 12.5). This difficulty is even more important at high ionic strengths. This in turn introduces difficulties when treating the experimental data to obtain β_1 and K_3 values. Too low a solubility can also cause problems in the determination of values for β_1 and K_2 .

Riglet's β_1 values [90RIG] in 0, 0.5, 1 and 2 M NaClO₄ are lower than (but still within the stated uncertainties of) the values selected below in the present review, and the corresponding value of $\Delta\varepsilon_1$ is in fair agreement with the one selected here (see Table 12.5). In the present review only the β_1 value in 0.5 M NaClO₄ could be redetermined from the experimental information available in the thesis (see Appendix A) and was used in the present review to calculate the selected β_1° value. The extrapolation (using the SIT) to zero ionic strength using Riglet's spectrophotometric data, gave a value of $\log_{10} K_2^\circ$ and a corresponding $\Delta\varepsilon_2$ value in reasonable agreement with those selected below, but none of Riglet's K_2 values have been used because the experimental information available is insufficient to allow K_2 to be recalculated.

The spectrophotometric data used in determining K_3 were limited to those solutions in which the extent of dissociation of the limiting complex was not greater than 25%.

This minimized the systematic error due to the second dissociation. Riglet's K_3 values in 0, 0.5, 1 and 2 M NaClO₄ and 0.17 M Na₂CO₃, as redetermined in the present review (Appendix A), were extrapolated to zero ionic strength (using the SIT), which gave $\log_{10} K_3^\circ$ and corresponding $\Delta\varepsilon_3$ values. To avoid giving too much weight to values from a single laboratory, only the value at zero ionic strength was used in the calculation of the selected thermodynamic data. The ionic strength effect was still taken into account in this selection, because solubility data [86GRE/ROB] from the same laboratory, obtained at high ionic strength (3 M) were also used (see below). Riglet's data also indicate that the SIT is still useful even for Np(V) carbonate equilibria involving the highly charged (5^-) limiting complex in solutions with ionic strengths as great as $I = 3$ M NaClO₄, and this review did not find any experimental evidence for a difference between values of $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{Na}^+)}$ as determined in NaCl and NaClO₄ media [94NEC/KIM].

Nitsche, Standifer and Silva [90NIT/STA] did similar measurements in 0.1 M NaClO₄. Within the authors' stated uncertainties, the reported value β_1 is in agreement with some published values, but not with the value selected below. Other possible errors in the treatment of the experimental data were taken into account, and the value of β_1 was recalculated from the experimental information available in the paper [90NIT/STA] (see Appendix A). The value then found is in excellent agreement with other data accepted in the present review. The recalculated value of β_1 , with an increased uncertainty to allow for possible systematic errors as reflected in the different interpretations of the experimental data, is one of the values used in this review to select a value of β_1 at zero ionic strength.

Nitsche, Standifer and Silva [90NIT/STA] also extrapolated available literature values (along with their experimental value for β_1) to zero ionic strength using the SIT, but without reinterpreting the other values prior to carrying out this extrapolation. Their proposed β_1° value (Table 12.4) is not in accord with the value selected in the present review, although their value of $\Delta\varepsilon_1$ is in fair agreement with the value selected here.

Method	Ionic medium $I_c/\text{mol}\cdot\text{dm}^{-3}$	t (°C)	$\log_{10} K(I_c)$ reported	$\log_{10} K(I_c)$ recalculated	Reference
$\text{NpO}_2^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2\text{CO}_3^-$					
sp	0.016 M $\text{HCO}_3^- + ?$?	(5.5±0.5)		[81BIL] ^{(a)(b)}
dis	0.1 M NaClO_4	25	(4.13±0.03)	(3.80±0.36) ^(c)	[85BID/TAN]
sp	0.1 M NaClO_4	23	(4.34±0.11)	(4.56±0.67) ^{(c)(d)}	[90NIT/STA]
sp	0.1 M NaClO_4	25	(4.38±0.04)		[94NEC/RUN]
sol	0.1 M NaClO_4	25	(4.58±0.04) ^(e)	(4.51±0.22) ^(c)	[91KIM/KLE]
sol	0.1 M NaClO_4	25	(4.52±0.02)		[94MEI]
sp	0.1 M TBANO_3	23	(4.13±0.20)		[96CLA/CON]
sp	0.1 M TBANO_3	70	3.75 ^(f)		

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^(a) Calculated by this review, the data of this publication were not interpreted by the author(s).

^(b) Rough estimation.

^(c) Recalculated by this review, following the calculation of the author(s) of the publication.

^(d) Value selected by this review to determine the standard value (at $I = 0$) and eventually the ε coefficient.

^(e) Values are also published in [94NEC/KIM, 94NEC/RUN, 95NEC/RUN]. In [95NEC/RUN] a few of the reported uncertainties differ from those in the earlier references.

sp	0.1 M NaCl	23	(4.08±0.05)		[96RUN/NEU] ^{(c)(d)}
sol	0.1 M NaCl	23	(4.88±0.1)		[96RUN/NEU] ^(h)
sp	0.5 M NaClO ₄	22	(4.3±0.1)	(4.41±0.1) ^{(c)(d)}	[90RIG]
sol	0.5 M NaClO ₄	75	(4.8±0.28)		[93LEM/BOY] ^{(c)(b)}
sol	1 M NaClO ₄	25	(4.49±0.06)	(4.57±0.35) ^{(c)(d)}	[83MAY]
sol	1 M NaClO ₄	25		(4.6±0.1) ⁽ⁱ⁾	
dis	1 M NaClO ₄	25	(4.14±0.01)	(4.14±0.5) ^(c)	[85INO/TOC]
sp	1 M NaClO ₄	22	(4.3±0.2)		[90RIG]
sol	1 M NaClO ₄	25	(4.50±0.04) ^(e)	(4.48±0.36) ^(c)	[91KIM/KLE]
sol	1 M NaClO ₄	30	(4.7±0.1)	(4.77±0.51) ^{(c)(b)}	[93LEM/BOY]
sol	1 M NaClO ₄	50	(5.6±0.2)	(5.7±0.54) ^{(c)(b)}	
sol	1 M NaClO ₄	75	(5.80±0.58)	(5.2±0.54) ^{(c)(b)}	
sol	1 M NaCl	23	(4.32±0.07)		[96RUN/NEU] ^{(g)(h)}
sp	2 M NaClO ₄	22	(4.6±0.3)		[90RIG]
sol	3 M NaClO ₄	22	(5.09±0.57)	(5.25±0.29) ^{(c)(d)}	[86GRE/ROB] ⁽ⁱ⁾

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^(f) $\log_{10} \beta_1 = (1.335 \pm 0.084) + (829 \pm 27) \cdot T^{-1}$ ($303 < T < 343$ K)^(g) Cited in [96RUN/NEU] from a report that was not available to the reviewer: Runde W. and Kim J. I. (1994) RCM-01094, Institut für Radiochemie, TU München.^(h) Molal units⁽ⁱ⁾ Recalculated in the [93LEM/BOY] publication.^(j) The reference is noted [86GRE/ROB] for a series of Vitorge *et al.*'s publications that used the same experimental results [84VIT, 85CÔM, 85KIM, 90RIG, 98VIT/CAP].

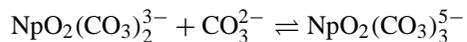
sol	5 M NaClO ₄	23	(4.76±0.04) ^(k)	(4.77±0.43) ^(c)	[91KIM/KLE]
sol	3 M NaCl	23	(4.3±0.1)		[96RUN/NEU] ^(h)
sp	3 M NaCl	23	(4.67±0.07)		[96RUN/NEU] ^{(g)(h)}
sol	5 M NaClO ₄	25	(5.00±0.05)	(4.92±0.81) ^(c)	[94NEC/KIM]
sol	5 M NaCl	23	(4.71±0.04)		[96RUN/NEU] ^{(g)(h)}
sp	5 M NaCl	23	(4.72±0.13)		[96RUN/NEU] ^{(g)(h)}
sol	5 M NaCl	25	5.70	4.68 ^(k)	[94NEC/KIM]
$\text{NpO}_2\text{CO}_3^- + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_2^{3-}$					
sp	0.008 M CO ₃ ²⁻ + ?	?		(2.5±0.5)	[81BIL] ^{(a)(b)}
dis	0.1 M HCO ₃ ⁻	?		(2.3±1.0)	[79MOS/POZ] ^(a)
sol	0.1 M NaClO ₄	25	(2.02±0.08) ^(e)	(2.08±0.22) ^(c)	[91KIM/KLE]
sp	0.1 M NaClO ₄	25	(2.02±0.3)		[94NEC/RUN]
sp	0.1 M TBANO ₃	23	1.98		[96CLA/CON]
sp	0.1 M TBANO ₃	70	1.99 ^(l)		
sp	0.04 M Na ₂ CO ₃	22		(1.4±0.3)	[90RIG] ^(c)
sol	0.05 M Na ₂ CO ₃			(2.08±0.29)	[75UEN/SAI] ^{(a)(b)}

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^(k) Corrected by the author for Cl⁻ complex formation^(l) $\log_{10} K_2 = 2.046 + 18 \cdot T^{-1}$, (303 < T < 343 K)

dis	0.2 M NaClO ₄	23	2.95	(3.42±1.0) ^(c)	[83BIL/IAN]
sp	0.16 M CO ₃ ²⁻	?		(1.4±1)	[81BIL] (a)(b)
sp	0.5 M NaClO ₄	22	(2.23±0.07)		[90RIG]
sol	0.5 M NaClO ₄	75		(2.40±0.36)	[93LEM/BOY] ^{(c)(b)}
sol	1 M NaClO ₄	25	(2.62±0.09)	(2.45±0.26) ^{(c)(d)}	[83MAY]
sol	1 M NaClO ₄	25		(2.5±0.14)	[83MAY] ⁽ⁱ⁾
dis	1 M NaClO ₄	25	(2.64±0.02)	(2.64±0.70) ^(c)	[85INO/TOC]
sp	1 M NaClO ₄	22	(2.38±0.07)		[90RIG]
sol	1 M NaClO ₄	25	(2.46±0.08) ^(e)	(2.49±0.36) ^(c)	[91KIM/KLE]
sol	1 M NaClO ₄	30	(2.3±0.14)	(2.7±0.22) ^{(c)(b)}	[93LEM/BOY] ^{(c)(b)}
sol	1 M NaClO ₄	50	(1.3±0.36)	(3.1±0.18) ^{(c)(b)}	
sol	1 M NaClO ₄	75	(3.0±1.52)	(2.1±0.28) ^{(c)(b)}	
sol	1 M NaCl	23	(2.17±0.13)		[96RUN/NEU] ^{(g)(h)}
sol	1 M KCl	75		(2.2±0.4) ^{(c)(b)}	[93LEM/BOY]
sp	2 M NaClO ₄	22	(2.54±0.07)		[90RIG]
sol	3 M NaClO ₄	22	(3.06±0.21)	(2.90±0.17) ^{(d)(c)}	[86GRE/ROB] ^(j)
sol	3 M NaClO ₄	25	(2.93±0.08) ^(e)	(2.93±0.46) ^(c)	[91KIM/KLE]
sol	3 M NaCl	23	(2.8±0.2)		[96RUN/NEU] ^(h)
sol	5 M NaClO ₄	25	(3.29±0.10)	(3.40±0.70) ^(c)	[94NEC/KIM]
sol	5 M NaCl	23	(2.83±0.06)		[96RUN/NEU] ^{(g)(h)}

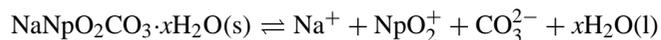
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sp	5 M NaCl	25	(2.91±0.20)		[96RUI/NEU] ^{(a)(b)}
sol	0.07 M Na ₂ CO ₃		(0.28±0.23)		[75UEN/SAI] ^{(a)(b)}
sol	0.1 M Na ₂ CO ₃		(0.56±0.23)		[75UEN/SAI] ^{(a)(b)}
sol	0.15 M Na ₂ CO ₃		(0.99±0.23)		[75UEN/SAI] ^{(a)(b)}
sp	0.16 M CO ₃ ²⁻ + ?		(1.4±1)		[81BIL] ^{(a)(b)}
sp	0.17 M Na ₂ CO ₃	22	(0.90±0.2)		[90RIG] ^(c)
sol	0.2 M Na ₂ CO ₃		(0.96±0.23)		[75UEN/SAI] ^{(a)(b)}
sol	0.3 M Na ₂ CO ₃		(1.14±0.23)		
sp	0.5 M NaClO ₄	22	(1.37±0.07)	(1.13±0.2) ^{(c)(d)}	[90RIG]
sol	0.5 M NaClO ₄	75		(1.35±0.42)	[93LEM/BOY] ^{(c)(b)}
sol	1 M NaClO ₄	25	(1.42±0.11)	(1.50±0.36) ^{(c)(d)}	[83MAY]
sol	1 M NaClO ₄	25		(1.4±0.14)	[83MAY] ⁽ⁱ⁾
sp	1 M NaClO ₄	22	(1.60±0.07)	(1.48±0.2) ^{(c)(d)}	[90RIG]
sol	1 M NaClO ₄	25	(1.71±0.12) ^(e)	(1.71±0.36) ^(c)	[91KIM/KLE]
sol	1 M NaClO ₄	30		(1.5±0.22) ^{(c)(b)}	[93LEM/BOY]
sol	1 M NaClO ₄	50	(1.7±0.42)	(1.5±0.34) ^{(c)(b)}	
sol	1 M NaClO ₄	75	(1.3±1.41)	(1.6±0.28) ^{(c)(b)}	

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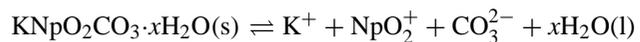
sol	1 M NaCl	25	(2.06±0.13)		[96RUN/NEU] ^(e)
sol	1 M KCl	75		(2.5±0.45) ^{(c)(b)}	
sp	2 M NaClO ₄	22	(2.47±0.07)	(1.96±0.2) ^{(c)(d)}	[90RIG]
sp	3 M NaClO ₄	22	(2.9±0.2)		
sol	3 M NaClO ₄	22	(2.31±0.14)	(2.49±0.07) ^{(c)(d)}	[86GRE/ROB] ^(j)
sol	3 M NaClO ₄	25	(2.61±0.12) ^(e)	(2.61±0.50) ^(c)	[91KIM/KLE]
sol	3 M NaCl	23	(2.1±0.3)		[96RUN/NEU]
sol	5 M NaClO ₄	25	(3.18±0.10)	(3.20±0.80) ^(c)	[94NEC/KIM]
sol	5 M NaCl	23	(2.09±0.07)		[96RUN/NEU] ^(g)
sol	5 M NaCl	25	2.50		[94NEC/KIM]



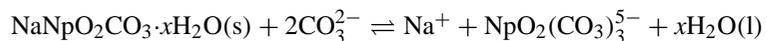
sol	0.1 M NaClO ₄	25	-(10.22±0.02)		[94MEI]
sol	0.1 M NaClO ₄	25	-(10.28±0.04) ^(e)	-(10.29±0.16) ^(c)	[91KIM/KLE]
sol	0.1 M NaCl	23	-(10.4±0.2)		[96RUN/NEU]
sol	0.5 M NaClO ₄	75		-(9.80±0.2) ^{(c)(b)}	[93LEM/BOY]
sol	1 M NaClO ₄	25	-(10.14±0.04)	-(10.12±0.35) ^(c)	[83MAY]
sol	1 M NaClO ₄	25		-(10.12±0.04)	[83MAY] ⁽ⁱ⁾
sol	1 M NaClO ₄	25	-(10.10±0.03) ^(e)	-(10.10±0.36) ^(c)	[91KIM/KLE]

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sol	1 M NaClO ₄	50	-(10.7±0.1)	-10.77 (c)(b)	[93LEM/BOY]
sol	1 M NaClO ₄	50	-(11.0±0.1)	-(11.1±0.2) (c)(b)	
sol	1 M NaClO ₄	75	-(10.94±0.29)	(10.5±0.5) (c)(b)	
sol	1 M NaCl	23	-(9.77±0.16)		[96RUN/NEU] (g)
sol	3 M NaClO ₄	22	-(10.56±0.34)	-(10.65±0.33) (c)	[86GRE/ROB] (j)
sol	3 M NaClO ₄	25	-(10.45±0.04) (e)	-(10.45±0.42) (c)	[91KIM/KLE]
sol	3 M NaCl	23	-(9.4±0.2)		[96RUN/NEU] (g)
sol	5 M NaClO ₄	25	-(11.06±0.06)	-(11.07±0.81) (c)	[94NEC/KIM]
sol	5 M NaCl	25	-9.52 (k)	-10.54	[94NEC/KIM]
sol	5 M NaCl	25	-(9.61±0.11)		[95NEC/RUN]



pot	diluted?	20		-(10.3±2.0)	[74VIS/VOL] (a)(b)
sol	1 M KCl	75		-(6.7±0.2)	[93LEM/BOY] (c)



sol	0.07 M Na ₂ CO ₃			-(3.04±1.25)	[75UEN/SAI] (a)(b)
sol	0.1 M Na ₂ CO ₃			-(2.92±0.92)	

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sol	0.15 M Na ₂ CO ₃			-(2.58±0.64)		
sol	0.2 M Na ₂ CO ₃			-(1.97±0.51)		
sol	0.3 M Na ₂ CO ₃			-(1.78±0.42)		
	0.4 M Na ₂ CO ₃			-(1.72±0.39)		
sol	0.5 M NaClO ₄	75		-(1.25±0.52)		[93LEM/BOY] ^{(c)(b)}
sol	1 M NaClO ₄	25	-(1.61±0.10)	-(1.60±0.41) ^(c)		[83MAY]
				-1.62 ⁽ⁱ⁾		
sol	1 M NaClO ₄	25	-(1.43±0.07)	-(1.42±0.68) ^(c)		[91KIM/KLE]
sol	1 M NaClO ₄	30		-(1.8±0.3)		[93LEM/BOY] ^{(c)(b)}
sol	1 M NaClO ₄	50	-(2.4±0.32)	-(0.8±0.59) ^{(c)(b)}		[93LEM/BOY]
sol	1 M NaClO ₄	75	-(0.84±1.39)	-(1.6±0.35) ^{(c)(b)}		
sol	1 M NaCl	23	-(1.34±0.19)			[96RUN/NEU] ^(g)
sol	3 M NaClO ₄	22	-(0.10±0.15)	-(0.01±0.17) ^(c)		[86GRE/ROB] ^(j)
sol	3 M NaClO ₄	25	-(0.15±0.10)	-(0.15±0.86) ^(c)		[91KIM/KLE]
sol	3 M NaCl	23	-(0.2±0.2)			[91KIM/KLE]
sol	5 M NaClO ₄	25	(0.41±0.10)	(0.45±1.39) ^(c)		[94NEC/KIM]
sol	5 M NaCl	23	(0.02±0.16)			[96RUN/NEU] ^(g)
sol	5 M NaCl	25		(0.14±1.27) ^(c)		[95NEC/RUN]
sol	5 M NaCl	25	0.21			[94NEC/KIM]

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sol	0.2 M K ₂ CO ₃	(20 ± 2)	−(3.0 ± 1.5)			[66GOR/ZEN] ^{(a)(b)}
sol	1 M KCl	75		−(2 ± 0.63)		[93LEM/BOY] ^{(c)(b)}
$\text{CsNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s}) + 2\text{CO}_3^{2-} \rightleftharpoons \text{Cs}^+ + \text{NpO}_2(\text{CO}_3)_3^{5-} + x\text{H}_2\text{O}(\text{l})$						
sol	0.2 M Cs ₂ CO ₃	(20 ± 2)	−(2.4 ± 1.5)			[66GOR/ZEN] ^{(a)(b)}
$\text{NH}_4\text{NpO}_2\text{CO}_3(\text{s}) + 2\text{CO}_3^{2-} \rightleftharpoons \text{NH}_4^+ + \text{NpO}_2(\text{CO}_3)_3^{5-} + x\text{H}_2\text{O}(\text{l})$						
sol	0.6 M (NH ₄) ₂ CO ₃	?		−(2.81 ± 0.4)		[71MOS2] ^{(b)(m)}
$\text{Na}_3\text{NpO}_2(\text{CO}_3)_2 \cdot y\text{H}_2\text{O}(\text{s}) + \text{CO}_3^{2-} \rightleftharpoons 3\text{Na}^+ + \text{NpO}_2(\text{CO}_3)_3^{5-} + y\text{H}_2\text{O}(\text{l})$						
sol	0.5 M NaClO ₄	75		−(4.70 ± 0.3)		[93LEM/BOY] ^{(c)(b)(n)}
sol	1 M NaClO ₄	30		−(4.5 ± 0.2)		

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^(m) Reinterpreted by this review, the author(s) proposed another interpretation of their data; but it was not correct.

⁽ⁿ⁾ The Na₃NpO₂(CO₃)₂(s) solid hydrated phase prepared at room temperature is expected to be partially dehydrated when the temperature is raised above 30°C. This stability constant is for this partially dehydrated solid phase.

sol	1 M NaClO ₄	50	–(4.3±0.37)	–(4.0±0.2)	[93LEM/BOY] ^{(c)(b)}
sol	1 M NaClO ₄	50	–(4.3±0.37)	–(4.5±0.3) ^{(c)(b)}	[93LEM/BOY] ⁽ⁿ⁾
sol	1 M NaClO ₄	75	–(4.3±0.83)	–(4.5±0.2) ^{(c)(b)}	
sol	1 M NaClO ₄	25	–(3.56±0.17)	–(3.57±0.30) ^(c)	[95NEC/RUN]
sol	0.5 M Na ₂ CO ₃			–3.72	[77SAI/UEN] ^{(a)(b)}
sol	0.75 M Na ₂ CO ₃			–2.92	
sol	1 M Na ₂ CO ₃			–2.42	
sol	3 M NaNO ₃	?		–(1.46±0.09)	[77SIM] ^{(o)(d)}
sol	3 M NaClO ₄	25	–(2.29±0.15)	–(1.67±0.50) ^(c)	[95NEC/RUN]
sol	3 M NaClO ₄	22	–1.98	–(1.17±0.79) ^(c)	[90RIG]
sol	1.35 M Na ₂ CO ₃			–1.86	[77SAI/UEN] ^{(a)(b)}
sol	1.6 M Na ₂ CO ₃			–1.42	
sol	5 M NaClO ₄	25	–(2.10±0.14)		[95NEC/RUN]
sol	5 M NaCl	25		–(1.50±0.86)	[95NEC/RUN] ^(o)
sol	1.85 M Na ₂ CO ₃			–1.07	[77SAI/UEN] ^{(a)(b)}
sol	2 M Na ₂ CO ₃			–0.87	

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^(o) Calculated by this review, the author(s) proposed a correct interpretation of their data; but he (they) did not calculate the corresponding equilibrium constant.

$\text{K}_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s}) + \text{CO}_3^{2-} \rightleftharpoons 3\text{K}^+ + \text{NpO}_2(\text{CO}_3)_3^{5-} + x\text{H}_2\text{O}(\text{l})$					
sol	1 M KCl	75		$-(4.7 \pm 0.2)$	[93LEM/BOY] ^{(c)(b)}
sol	1.2 M K_2CO_3	20		$-(3.4 \pm 0.5)$	[74VIS/VOL] ^{(a)(b)}
sol	1.2 M K_2CO_3	80		$-(3.1 \pm 0.5)$	
sol	5.57 M K_2CO_3	202		$-(1.4 \pm 1.5)$	[66GOR/ZEN] ^{(a)(b)}
$(\text{NH}_4)_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s}) + \text{CO}_3^{2-} \rightleftharpoons 3\text{NH}_4^+ + \text{NpO}_2(\text{CO}_3)_3^{5-} + x\text{H}_2\text{O}(\text{l})$					
sol	2.2 M $(\text{NH}_4)_2\text{CO}_3$?		$-(2.6 \pm 0.5)$	[71MOS2] ^{(m)(b)}
$\text{Na}_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s}) + (y - x)\text{H}_2\text{O} \rightleftharpoons \text{NaNpO}_2\text{CO}_3 \cdot y\text{H}_2\text{O}(\text{s}) + \text{CO}_3^{2-} + 2\text{Na}^+$					
sol	0.5 M NaClO_4	75		$-(3.45 \pm 0.42)$	[93LEM/BOY] ^{(c)(b)(n)}
sol	1 M NaClO_4	30		$-(2.7 \pm 0.23)$	
sol	1 M NaClO_4	30		$-(2.2 \pm 0.3)$	[93LEM/BOY] ^{(c)(b)}
sol	1 M NaClO_4	50	$-(1.9 \pm 0.2)$	$-(3.7 \pm 0.51)$	[93LEM/BOY] ^{(c)(b)(n)}
sol	1 M NaClO_4	75	$-(3.46 \pm 1.12)$	$-(2.9 \pm 0.28)$	[93LEM/BOY] ^{(c)(b)}
sol	1 M NaClO_4	25	-2.13	$-(2.15 \pm 0.88)$	[95NEC/RUN] ^(c)
sol	3 M NaClO_4	22	-1.88	$-(1.16 \pm 0.15)$	[90RIG] ^(j)

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sol	5 M NaClO ₄	25	-(2.14±0.18)	-(2.12±1.10) ^(c)	[93NEC/RUN]
sol	5 M NaClO ₄	25	-(2.51±0.17)	-(2.55±1.7) ^(c)	
sol	5 M NaCl	25	-(1.64±1.53)		
$\text{K}_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s}) + (y - x)\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{KNpO}_2\text{CO}_3 \cdot y\text{H}_2\text{O}(\text{s}) + \text{CO}_3^{2-} + 2\text{K}^+$					
sol	0.2 to 0.8 ^(p) M K ₂ CO ₃			-(0.6±0.9)	[74SIM/VOL] ^{(a)(b)}
sol	1 M KCl	75		-(2.7±0.6)	[93LEM/BOY] ^{(c)(b)}
$(\text{NH}_4)_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s}) + (y - x)\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4\text{NpO}_2\text{CO}_3 \cdot y\text{H}_2\text{O}(\text{s}) + \text{CO}_3^{2-} + 2\text{NH}_4^+$					
sol	1.5 to 2.2 ^(p) M (NH ₄) ₂ CO ₃	?		-(0.34±0.58)	[71MOS2] ^{(m)(b)}

^(p) In M₂CO₃ aqueous solution, the two M-Np(V)-CO₃ solid phases are at equilibrium for a unique [M₂CO₃] value, [M₂CO₃]_s; but, since thermodynamic cycles were used, the value of the equilibrium constant can be estimated in aqueous solution with M₂CO₃ concentration different from the [M₂CO₃]_s value. This is important only for ionic strength corrections.

Reference	$\log_{10} K_{s,0}^{\circ}$	$\log_{10} K_1^{\circ}$	$\log_{10} K_2^{\circ}$	$\log_{10} K_3^{\circ}$	ε_0	ε_1	ε_2	ε_3
[98VIT/CAP] ^(b,e)	-10.96	4.97	1.49	-1.20		-0.20	-0.40	-0.70
[90RIG] ^(c)		(4.80±0.11)	(1.50±0.01)	-(0.88±0.01)		-(0.16±0.10)	-(0.27±0.11)	-(0.61±0.11)
[90RIG] ^(b)				-(1.04±0.05)				-(0.16±0.05)
[98VIT/CAP] ^(g)	-(11.00±0.22)	(4.70±0.10)	(1.38±0.32)	-(0.86±0.13)	(0.25±0.05)	-(0.07±0.03)	-(0.28±0.03)	-(0.40±0.11)
[91KIM/KLE] ^(m)	-(10.96±0.05)	(5.04±0.06)	(1.55±0.11)	-(0.86±0.19)	(0.34±0.08) ^(j) (0.25±0.08) ^(k)	(0.09±0.10) ^(p)	-(0.06±0.09) ^(j) (0.03±0.18) ^(k)	-(0.23±0.21) ^(j) -(0.05±0.20) ^(k)
[94NEC/RUN] ^(m)	-(11.0±0.07)	(4.81±0.15)	(1.74±0.27)	-(1.01±0.25)	(0.31±0.08) ^(j) (0.22±0.08) ^(k)	-(0.05±0.11) ^(p)	-(0.16±0.10) ^(j) -(0.07±0.19) ^(k)	-(0.33±0.20) ^(j) -(0.15±0.19) ^(k) -(0.16±0.11) ^(s)
[94NEC/RUN] ^(c,m)	-(10.96±0.14) ^(d)	(4.98±0.16) ^(d)	(1.61±0.07) ^(d)	-0.92 ^(d)	(0.34±0.10) ^(j) (0.24±0.12) ^(k) (0.18±0.03) ^(c,l)	(0.08±0.13) ^(p)	-(0.06±0.13) ^(j) (0.03±0.21) ^(k)	-(0.24±0.25) ^(j) -(0.06±0.26) ^(k)
[94NEC/KIM] ^(m)					(0.20±0.05) ^(a)	(0.06±0.01) ^(a)	(0.12±0.30) ^(a)	(0.63±0.78) ^(a)
[95FAN/NEC] ^(h,m)	-(11.09±0.11) ⁽ⁿ⁾	(5.03±0.06)	(1.44±0.15)	-(1.10±0.39)	(0.09±0.01) ^(r)			
[95FAN/NEC] ^(a,h,q)					(0.09±0.08) ^(c,l,r)			
[94NEC/KIM] ^(q)								
[96RUN/NEU] ^(q)	-(11.05±0.05)	(5.18±0.17)	(1.01±0.48)	-(0.35±0.48)	(0.05±0.08) ^(r)	-(0.02±0.13)	-(0.36±0.12)	-(0.26±0.13)
[95NOV/ROB]	-11.3	5.39	0.41	-0.62	(0.21±0.07) ^(a)	(0.08±0.07) ^(a)	(0.01±0.45) ^(a)	(0.63±0.81) ^(a)
[96RUN/NEU] ^(h)	-10.89	5.06	1.43	-1.07	(0.17±0.01) ^(a)	(0.05±0.07) ^(a)	(0.08±0.10) ^(a)	(0.51±0.69) ^(a)
[90NIT/STA] ^(h)		(4.69±0.13)						
This review ^(b,i)		(4.92±0.03)	(1.58±0.09)	-(1.04±0.12)	(0.25±0.05)	-(0.22±0.06)	-(0.35±0.11)	-(0.59±0.13)
This review ^(b,f)	- (11.66±0.50)^(o)	(4.96±0.06)	(1.57±0.08)	-(1.06±0.11)	(0.25±0.05)	-(0.18±0.15)	-(0.33±0.16)	-(0.53±0.19)

^(a)Calculated in this review from the ion pair Pitzer parameters, neglecting higher order terms even when given in the original publication. Similar ε values were derived from the Pitzer parameters from different publications [95FAN/NEC, 95NEC/FAN, 95NOV/ROB, 96RUN/NEU], probably because the authors fitted parameters from similar sets of published equilibrium constants.

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- (f) Values selected in this review based on equally weighted recalculated values from the different studies.
- (g) These values (cited in [98VIT/CAP], p. 49), are from earlier calculations presented at the conference “Migration 91”.
- (h) Literature data were used for extrapolation to $I = 0$.
- (i) For extrapolation to $I = 0$, linear regression weighted by $1/(\text{uncertainty})$ was used.
- (j) ε_i is calculated in this review from the value published for $\Delta\varepsilon_i = \varepsilon_i - \varepsilon_0 - i\varepsilon(\text{CO}_3^{2-}, \text{Na}^+)$, using the ε_0 value on the same line, $\varepsilon(\text{CO}_3^{2-}, \text{Na}^+) = -(0.06 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ (this review (Appendix B) accepts $-(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$), and other required values as recalculated (in this review) from Pitzer ion pair parameters^(a) from the same laboratory [95FAN/NEC, 95NEC/FAN].
- (k) ε_i is calculated in this review from the value published for $\Delta\varepsilon_i = \varepsilon_i - \varepsilon_0 - i\varepsilon(\text{CO}_3^{2-}, \text{Na}^+)$, using the ε_0 value on the same line, $\varepsilon(\text{CO}_3^{2-}, \text{Na}^+) = +(0.03 \pm 0.09) \text{ kg}\cdot\text{mol}^{-1}$ (this review (Appendix B) accepts $-(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$), from other required values and from pH calibration information given in the original publication (from which $\log_{10} K_{p2}^\circ = (18.23 \pm 0.16)$ was estimated in this review; the value accepted in this review is (18.155 ± 0.03) (Table 5.2)). The difference in the results calculated using the procedure described in footnote (j) arises only from differences in the sets of auxiliary values for NaClO_4 media. These differences are in most cases within the statistical errors estimated in this review.
- (l) From liquid-liquid extraction measurements.
- (m) Equilibrium constants $K(I)$ (for $K = K_i$ and $K_{s,0}$) were proposed from a solubility study in 0.1, 1 and 3 M NaClO_4 , and $K(I)$ were extrapolated to $I = 0$ by SIT linear regression to obtain K° and $\Delta\varepsilon$ [91KIM/KLE]. From the same sets of measurements, and values later reported for $I = 5$ M for $K(I)$, K° and $\Delta\varepsilon$ were calculated using the SIT [94NEC/RUN, 95NEC/RUN], or the Pitzer formula in non-complexing [95NEC/FAN] or complexing [95FAN/NEC] aqueous solutions. In this later case, other published data for aqueous solutions up to $I = 5$ M in NaClO_4 were also used. Here only tabulated K° and ε values deduced from experimental measurements in 0.1 to 3 M NaClO_4 are used.
- (n) [95NEC/FAN]
- (o) $\log_{10} K_s^\circ = -(11.16 \pm 0.35)$ is also selected in this review for the freshly precipitated solid phase.
- (p) ε_i calculated^(j,k) in this review from $\Delta\varepsilon_i$; the auxiliary value $\varepsilon(\text{CO}_3^{2-}, \text{Na}^+)$ is not needed (or cancels) in this particular case.

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complex (Cl^- addition to $\text{NpO}_2\text{CO}_3^-$). Differences in ε_2 and ε_3 values originate in the differences in $\varepsilon_{(\text{CO}_3^{2-}, \text{Na}^+)}$ values used for Cl^- and ClO_4^- which are propagated in the ε_i values.

- (r) Here ε° represents $\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)}$. The values are italicised to stress $\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)}$ is not expected to have the same value as $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$.
- (s) From the solubility product of $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s, hyd})$.

Neck *et al.* also reported β_1 and β_2 values deduced from absorption spectrophotometry [94NEC/RUN]. The K_2 value (calculated as β_2/β_1) is exactly the same as the value reported from their solubility measurements in the same paper, and is in accord with the value selected in the present review, while their β_1 value is reasonably consistent with the value they determined from their solubility measurements (see the discussion of [91KIM/KLE] in Appendix A); the latter (extrapolated to $I = 0$) was used in the present review in selection of the values for the complexation constants. However, in the absence of sufficient experimental information to re-interpret the spectrophotometric measurements, those values are not used in the present review in the final selection of the values for the complexation constants.

Clark *et al.* [96CLA/CON] also reported β_1 and β_2 values deduced from absorption spectrophotometry from about 30 to 70°C. The K_2 value for 25°C is in accord with the value selected in the present review (within the uncertainty estimated by the authors), while the value of β_1 is not. These values are not used in the present review in the selection of formation constants because there was not enough experimental detail in the publication.

Complexation constants were also determined in several solubility studies in NaClO₄ or NaCl aqueous solutions. There are problems in the interpretation of solubility data to obtain values for the complexation constants. These problems are dealt with in more detail above and in the section on the selection of the values of the solubility products for alkali-Np(V)-carbonates (Section 12.1.2.2.2). Even though Maya [83MAY] and Grenthe, Robouch and Vitorge [86GRE/ROB] seem to have carried out two of the more reliable studies, the solid phases they used were probably somewhat different (see Section 12.1.2.2.2 and the discussion of [83MAY, 84VIT, 90RIG] in Appendix A). However, these problems should not have a direct influence on the selection of the stepwise complexation constants. Another potential problem is that the formation of the NpO₂CO₃⁻ complex over a MNpO₂CO₃(s) solid phase can result in a constant minimum total ²³⁷Np(V) solubility, which is not far from the usual analytical detection limits (for α - or γ -spectrometry or liquid scintillation methods); however, this does not seem to have caused any difficulties in any of the publications reviewed here (except perhaps for [93LEM/BOY]).

The Np(V) solubility tabulated in the report by Kim *et al.* [91KIM/KLE] for $I = 1$ M NaClO₄, can be plotted exactly on Maya's [83MAY] curve, even though the pH calibration may not have been done in the same way in the two sets of experiments. Moreover, the minimum solubility does not depend on the pH calibration, and the reported solubility values were the same, though the equilibration times were not. The Np(V) solubilities tabulated in the report by Kim *et al.* [91KIM/KLE] and other work by Neck *et al.* [94NEC/KIM, 94NEC/RUN, 95NEC/RUN], Fanghänel *et al.* [95FAN/NEC] and Runde *et al.* [96RUN/NEU] are slightly shifted toward higher [CO₃²⁻] when compared with the previous data of Grenthe, Robouch and Vitorge [86GRE/ROB]. This shift seems to be less important for the solubility of NaNpO₂CO₃(s) than for the solubility of hydrated Na₃NpO₂(CO₃)₂(s) (although this is an observation based on the sole value for the latter solid in [86GRE/ROB]). This might be evidence that the solubility was not controlled by the same solid

phases in both studies (see the discussion on the selection of solubility products in Section 12.1.2.2.2). Nevertheless, the solid phases in the later studies seem to be well characterized, as in the interconversion between hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ and hydrated $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ [95NEC/RUN].

The complexation constant values selected at $I = 3 \text{ M NaClO}_4$ are particularly important for selecting the standard K° value using the SIT (limited to $I \leq 3.5 \text{ m}$), because they have a critical influence on the selection of the values of $\Delta\varepsilon$ and ε . From their solubility measurements in perchlorate media, Kim *et al.* [91KIM/KLE, 94NEC/KIM] extrapolated their values for the dioxoneptunium(V) carbonate complexation constants to zero ionic strength using the SIT for $I \leq 3.5 \text{ m}$ and also carried out an extrapolation including literature data. The extrapolation of their own data resulted in values for β_1° and the corresponding $\Delta\varepsilon_1$ that are only in marginal agreement with the values proposed by the present review (see Table 12.5 and discussion in Appendix A). The difference in $\Delta\varepsilon_1$ ($-0.19 \text{ kg}\cdot\text{mol}^{-1}$ vs. $-0.35 \text{ kg}\cdot\text{mol}^{-1}$) is mostly due to the difference in $\log_{10}\beta_1$ for $I = 3 \text{ M}$ (0.33 in the original publications [86GRE/ROB, 91KIM/KLE], but somewhat larger if values recalculated in the present review are used). In the present review the value used for $I = 3 \text{ M}$ directly in assessing $\Delta\varepsilon_1$ for the dissolution equilibrium is from [86GRE/ROB]. However, values from Kim *et al.* [91KIM/KLE] are extrapolated to $I = 0$ where possible problems (see Appendix A) cancel, and then used in the data selection in the present review.

On the other hand, there are fewer problems in calculating values of the stepwise complexation constants, K_2° and K_3° , as extrapolated to $I = 0$ in the present review. The (relatively small) inconsistency in the β_1 values should most likely be attributed to problems with achieving equilibrium between the solutions and the solid compounds for conditions close to the solubility minimum. In the present review, to minimize the possible effects of systematic errors, values of each stepwise equilibrium constant from these papers [91KIM/KLE, 94NEC/KIM] have been extrapolated to zero ionic strength (Table 12.5). These $I = 0$ constants (only) are used (with values from other studies) in arriving at selected values.

The work of Neck, Runde and Kim [95NEC/RUN] and Runde, Neu and Clark [96RUN/NEU] shows that although in solutions with low concentrations of CO_3^{2-} the solubility of $\text{NaNpO}_2\text{CO}_3(\text{s})$ decreases markedly as the concentration of NaClO_4 is increased, the solubility changes only marginally as chloride concentrations are increased to 5 M.

The formation constants and interaction coefficients derived from the solubilities in sodium perchlorate solutions should also be applicable to solubilities in chloride solutions within the uncertainties in the activity coefficient equations. Although various authors [95FAN/NEC, 95NEC/FAN, 95NOV/ROB, 96RUN/NEU] have derived sets of Pitzer equation [73PIT] coefficients for the Np(V)-carbonate system, it seems that the SIT can still be used separately (within the experimental uncertainties) for solutions either 3 M in NaClO_4 or 3 M NaCl . However, it is then necessary to select a value for $\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)}$. Based on a solubility study of $\text{NpO}_2\text{OH}(\text{am})$, Roberts *et al.* [96ROB/SIL] proposed a value of $(0.08 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$. Analysis of the Pitzer coefficients proposed by Fanghänel, Neck *et al.* [95FAN/NEC, 95NEC/FAN], and by

Runde *et al.* [96RUN/NEU] leads to similar values (see the Appendix A discussion of this paper). In the present review, we select the value

$$\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)} = (0.09 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$$

Unfortunately, this value is not completely consistent with the solubility of the Np(V) sodium carbonate solids (*cf.* Section 12.1.2.1.3.b).

Therefore, despite the extensive work on these systems, for the reasons discussed above, there is still some doubt about the values selected in the present review for the formation constant of $\text{NpO}_2\text{CO}_3^-$, and especially the value of the specific interaction coefficient $\varepsilon_{(\text{Na}^+, \text{NpO}_2\text{CO}_3^-)}$. These then propagate into uncertainties about the cumulative formation constants (β 's) and specific interaction coefficients for the other carbonate complexes. For the reasons explained above (see Appendix A for more details), in the selection of final values for complexation constants in the present review, only one set of values was used from each laboratory. This avoids assigning too much weight to sets that might have common systematic errors or uncertainties (and all sets of data undoubtedly have some). Additional reliable experimental measurements are still required, especially near $I = 3$ M.

The first set of equilibrium constants for Np(V) carbonate complexes was proposed by Maya [83MAY] from solubility measurements in 1 M NaClO_4 aqueous solution, and these were confirmed by Grenthe, Robouch and Vitorge [86GRE/ROB] who used the same technique in 3 M NaClO_4 . Using the SIT extrapolation to zero ionic strength from these two determinations give stepwise complexation constants, K_i° , and corresponding $\Delta\varepsilon_i$ values that are compatible with others used in the selection of values in the present review (see Table 12.5).

For β_1° (12.14), the selected value was obtained using an SIT unweighted linear regression (Figure 12.2) of the results from these two solubility studies plus those of Kim *et al.* [91KIM/KLE] and Neck *et al.* [94NEC/KIM, 94NEC/RUN] re-extrapolated to $I = 0$ (see Appendix A) and the spectrophotometric determinations of Riglet [90RIG], and of Nitsche, Standifer and Silva [90NIT/STA] in 0.5 and 0.1 M NaClO_4 respectively (both reinterpreted in the present review as explained above and in Appendix A). As explained above, the liquid-liquid extraction data were not considered.

The selected value from the unweighted linear regression is

$$\log_{10}\beta_1^\circ(12.14) = (4.96 \pm 0.06)$$

Linear regression also gives $\Delta\varepsilon_1 = -(0.35 \pm 0.14) \text{ kg}\cdot\text{mol}^{-1}$ (Figure 12.2). Using this value, $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})} = -(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ (Table B.4), and $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.25 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ (Table B.3), the interaction coefficient

$$\varepsilon_{(\text{Na}^+, \text{NpO}_2\text{CO}_3^-)} = -(0.18 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$$

is calculated. The selected value $\log_{10}\beta_1^\circ$ corresponds to

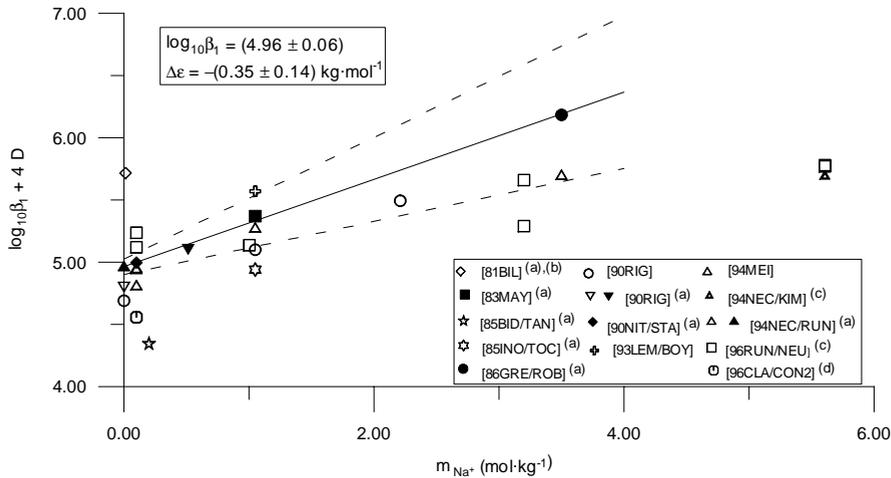
$$\Delta_r G_m^\circ(12.14, 298.15 \text{ K}) = -(28.32 \pm 0.35) \text{ kJ}\cdot\text{mol}^{-1}$$

and hence

$$\Delta_{\text{r}}G_{\text{m}}^{\circ}(\text{NpO}_2\text{CO}_3^-, 298.15 \text{ K}) = -(1463.99 \pm 5.65) \text{ kJ}\cdot\text{mol}^{-1}$$

For K_2° (12.15), the selected value (Figure 12.3) was based on the values from the

Figure 12.2: Extrapolation to $I = 0$ of the $\text{NpO}_2^+ + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2\text{CO}_3^-$ equilibrium constant β_1 , using the SIT with values from measurements in aqueous NaClO_4 accepted in the present review (filled symbols). Other literature experimental data (not used in determining the selected value) are also plotted for comparison (open symbols). Sets of values recalculated in the present review (*cf.* Appendix A) are marked (a). Measurements were done in NaClO_4 or in Na_2CO_3 (b), NaCl (c) or $(n\text{-CH}_4\text{H}_9)_4\text{NNO}_3$ (d) media as noted in the legend (in the latter case the x axis is $m_{(n\text{-C}_4\text{H}_9)_4\text{N}^+}$ and not m_{Na^+}).



solubility data of Maya [83MAY], Grenthe, Robouch and Vitorge [86GRE/ROB], and those of Kim *et al.* [91KIM/KLE] and Neck *et al.* [94NEC/KIM, 94NEC/RUN] re-extrapolated to $I = 0$ in the present review (excluding the data from $I = 5 \text{ M}$ where the SIT is probably not valid, although the reported values are still in accord with those selected by this review). The spectrophotometric determinations of Riglet [90RIG], in 0.5, 1 and 2 M NaClO_4 , respectively, have not been used (see above), but the results are in accord with the selected value, as is the calculated value. The liquid-liquid extraction data were not used, but those reported by Inoue and Tochiyama [85INO/TOC] at $I = 1 \text{ M}$ are in reasonable agreement with the selected values. The selected value from the unweighted linear regression is

$$\begin{aligned} \log_{10} K_2^{\circ} (12.15) &= (1.57 \pm 0.08) \\ \Delta_{\text{r}}G_{\text{m}}^{\circ} (12.15, 298.15 \text{ K}) &= -(8.97 \pm 0.47) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

From this, the selected value

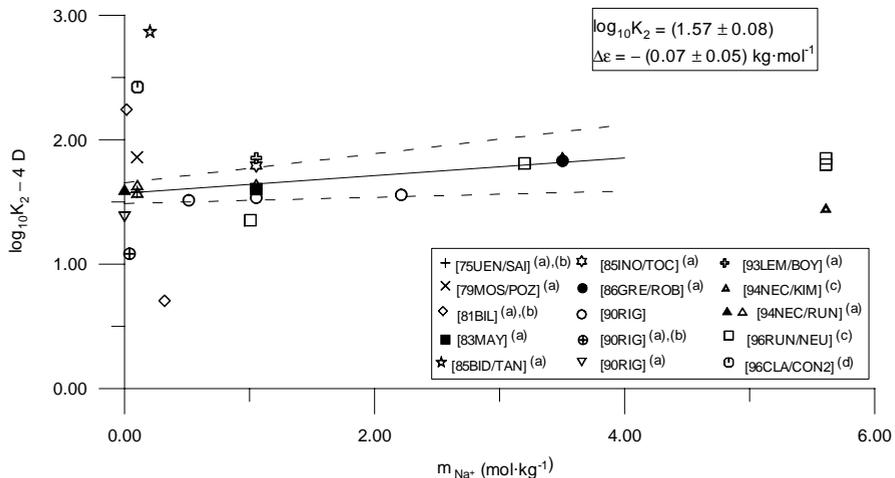
$$\Delta_f G_m^\circ(\text{NpO}_2(\text{CO}_3)_2^{3-}, 298.15 \text{ K}) = -(2000.86 \pm 5.69) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated. Linear regression also gives $\Delta\varepsilon(12.15) = -(0.07 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ (Figure 12.3). Using this value, $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})} = -(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ (Table B.4), and $\varepsilon_{(\text{Na}^+, \text{NpO}_2\text{CO}_3^-)} = -(0.18 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$ determined above, the interaction coefficient

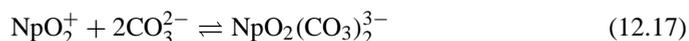
$$\varepsilon_{(\text{Na}^+, \text{NpO}_2(\text{CO}_3)_2^{3-})} = -(0.33 \pm 0.17) \text{ kg}\cdot\text{mol}^{-1}$$

is calculated.

Figure 12.3: Extrapolation to $I = 0$ of the $\text{NpO}_2\text{CO}_3^- + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_2^{3-}$ equilibrium constant K_2 , using the SIT with values from measurements in aqueous NaClO_4 accepted in the present review (filled symbols). Other literature experimental data (not used in determining the selected value) are also plotted for comparison (open symbols). Sets of values recalculated in the present review (*cf.* Appendix A) are marked (a). Measurements were done in NaClO_4 or in Na_2CO_3 (b), NaCl (c) or $(n - \text{C}_4\text{H}_9)_4\text{NNO}_3$ (d) media as noted in the legend (in the latter case the x axis is $m_{(n-\text{C}_4\text{H}_9)_4\text{N}^+}$ and not m_{Na^+}).



From the selected β_1° and K_2° values, $\beta_2^\circ = \beta_1^\circ \cdot K_2^\circ$ is calculated and $\log_{10} \beta_2^\circ(12.17, 298.15 \text{ K}) = (6.53 \pm 0.10)$, for



as is $\Delta_r G_m^\circ(12.17, 298.15 \text{ K}) = -(37.30 \pm 0.59) \text{ kJ}\cdot\text{mol}^{-1}$. For K_3° the selected value was chosen (Figure 12.4) using the solubility data of Maya [83MAY] and Grenthe, Robouch and Vitorge [86GRE/ROB], those of Kim *et al.* [91KIM/KLE] and Neck *et al.* [94NEC/KIM, 94NEC/RUN] re-extrapolated to $I = 0$ in the present review, and the spectrophotometric determinations of Riglet [90RIG] in 0.5 to 2 M NaClO₄ as re-interpreted in the present review. The solubility measurements actually were obtained for an equilibrium involving a metastable solid, and Maya's data really include only one measurement that is significant for the determination of the value of K_3 . Ionic strength corrections, deduced from Riglet's spectrophotometric data alone, are in accord with the selected value. To balance the selection between results from spectrophotometric and solubility experiments, results from both Grenthe, Robouch and Vitorge [86GRE/ROB] and Riglet [90RIG] were used even though they originated in the same laboratory. The selected value from the unweighted linear regression is

$$\begin{aligned}\log_{10} K_3^\circ(12.16, 298.15 \text{ K}) &= -(1.03 \pm 0.11) \\ \Delta_r G_m^\circ(12.16, 298.15 \text{ K}) &= (5.90 \pm 0.63) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

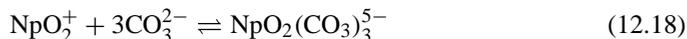
from which the selected value

$$\Delta_f G_m^\circ(\text{NpO}_2(\text{CO}_3)_3^{5-}, 298.15 \text{ K}) = -(2522.86 \pm 5.73) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated. Linear regression also gives $\Delta \varepsilon(12.16) = -(0.12 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ (Figure 12.4). Using this value, $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})} = -(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$, (Table B.4) and $\varepsilon_{(\text{Na}^+, \text{NpO}_2(\text{CO}_3)_2^{3-})} = -(0.33 \pm 0.17) \text{ kg}\cdot\text{mol}^{-1}$ determined above, the interaction coefficient

$$\varepsilon_{(\text{Na}^+, \text{NpO}_2(\text{CO}_3)_3^{5-})} = -(0.53 \pm 0.19) \text{ kg}\cdot\text{mol}^{-1}$$

is calculated. From the selected β_1° , K_2° and K_3° values $\log_{10} \beta_3^\circ(12.18, 298.15 \text{ K}) = (5.50 \pm 0.15)$ for



and $\Delta_r G_m^\circ(12.18, 298.15 \text{ K}) = -(31.39 \pm 0.86) \text{ kJ}\cdot\text{mol}^{-1}$.

A predominance diagram for the system at different ionic strengths is shown in Figure 12.5.

12.1.2.1.3.b Formation of carbonate complexes in chloride media – a conundrum

During the period this review was being written, several papers appeared on the behaviour of neptunium(V) in chloride media [94NEC/KIM, 95FAN/NEC, 95NEC/FAN, 95NEC/RUN, 95NOV/ROB, 96RUN/NEU, 96ROB/SIL]. Most of these focussed on the complexation of NpO_2^+ with carbonate or the hydrolysis of NpO_2^+ . For the most part the experimental work seems to have been carried out carefully and with proper attention to the myriad of experimental problems associated with solubility and potentiometric studies.

Figure 12.4: Extrapolation to $I = 0$ of the $\text{NpO}_2(\text{CO}_3)_2^{3-} + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-}$ equilibrium constant K_3 , using the SIT with values from measurements in aqueous NaClO_4 accepted in the present review (filled symbols). Other literature experimental data (not used in determining the selected value) are also plotted for comparison (open symbols). Sets of values recalculated in the present review (*cf.* Appendix A) are marked (a). Measurements were done in NaClO_4 or in Na_2CO_3 (b) or NaCl (c) media as noted in the legend.

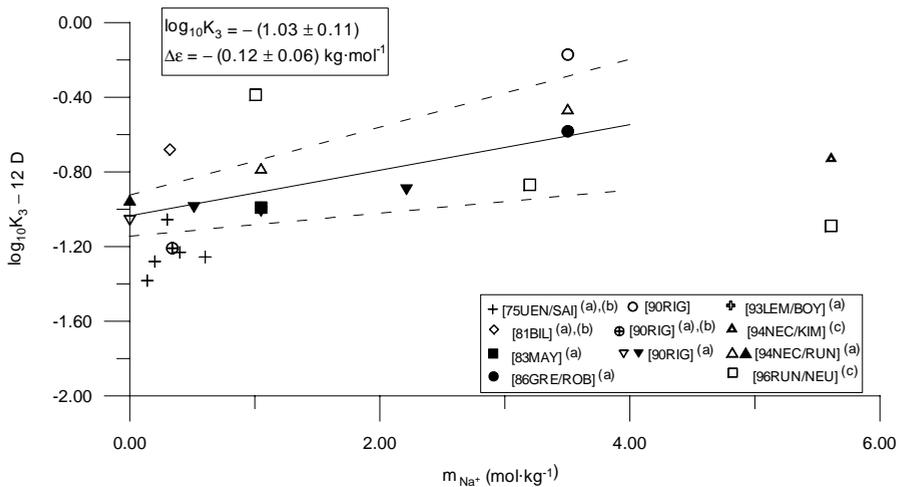
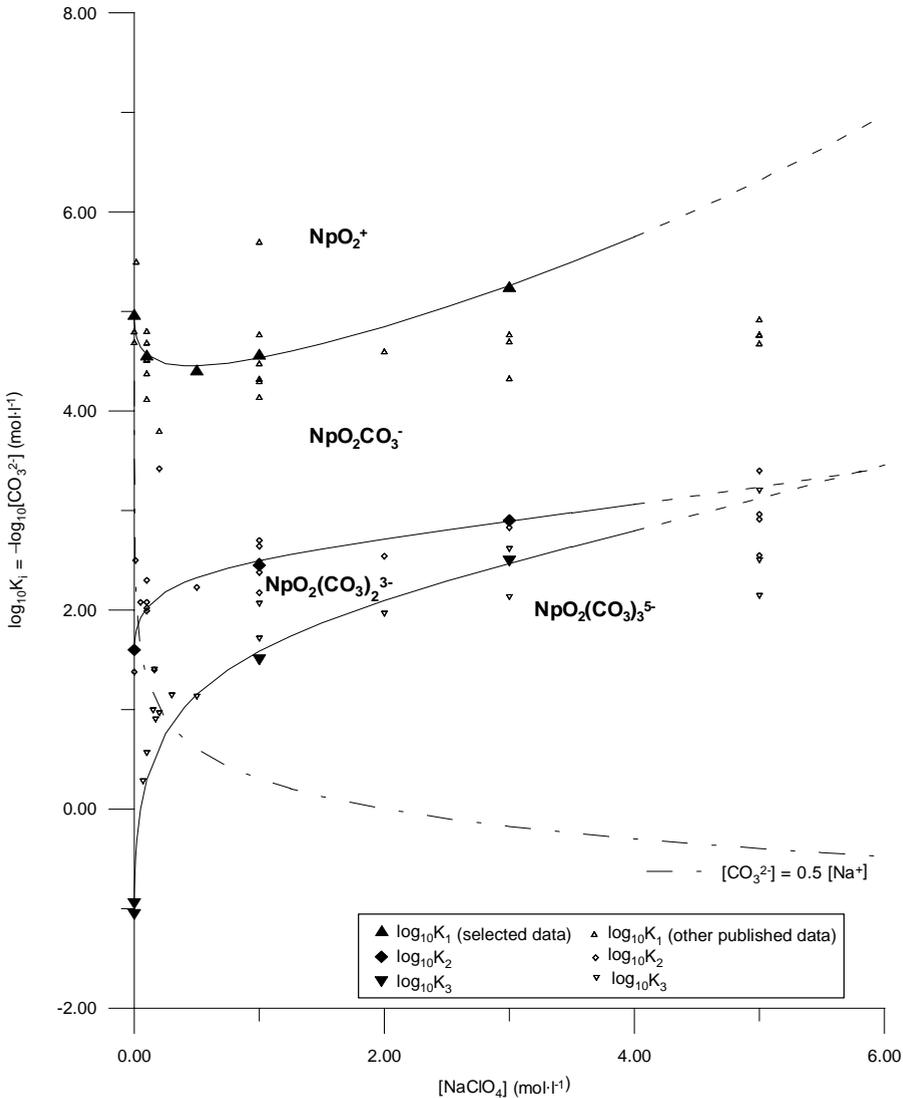


Figure 12.5: Predominance diagrams of Np(V) carbonate aqueous complexes at different ionic strengths in NaClO₄ aqueous solutions. The lines are calculated with data selected in the present review. The directly measured stepwise formation constants are also marked on the figure. Ionic strength corrections can be less than the scatter in the data. At high ionic strengths, the species NpO₂(CO₃)₂³⁻ has a very small region of predominance, while NpO₂(CO₃)₃⁵⁻ can be formed only in high ionic strength solutions. The domain below the line [CO₃²⁻]=0.5[Na⁺] cannot be reached experimentally; the line itself correspond to pure Na₂CO₃.



For studies of carbonate complexation in perchlorate media there are some minor differences between values reported in these papers and values from earlier studies. There might also be some differences of opinion regarding electrode calibration or characterization of the solids in the solubility studies. However, in most cases the differences are well within the experimental uncertainties.

Nevertheless, the studies in chloride media have raised some interesting questions. For example, the solubility for NpO_2OH was found to be slightly less than half an order of magnitude more soluble in 3 M NaCl than in 3 M NaClO_4 .



Using the SIT as outlined in Appendix B (with non-zero coefficients ε only for cation-anion interactions), this would suggest $\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)}$ is approximately $0.1 \text{ kg}\cdot\text{mol}^{-1}$ less positive than $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$. This is also consistent with the difference of $0.1 \text{ kg}\cdot\text{mol}^{-1}$ that can be calculated from the liquid-liquid extraction data reported by Neck *et al.* [95NEC/FAN]. However, in solutions containing low concentrations of carbonate, and with $\text{NaNpO}_2\text{CO}_3\cdot x\text{H}_2\text{O}$ as the controlling solid, the solubility of $\text{NaNpO}_2\text{CO}_3\cdot x\text{H}_2\text{O}$ in 3 M NaCl is found to be a full order of magnitude greater than in 3 M NaClO_4 .

The reaction(s) should be either

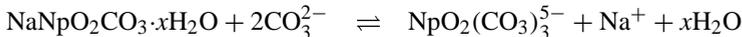


in which case (with the ε values given in Appendix B) the value of $\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)}$ is approximately $0.3 \text{ kg}\cdot\text{mol}^{-1}$ less positive than $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$ – not $0.1 \text{ kg}\cdot\text{mol}^{-1}$, or



which would suggest $\varepsilon_{(\text{Na}^+, \text{Cl}^-)} - \varepsilon_{(\text{Na}^+, \text{ClO}_4^-)} = -0.3 \text{ kg}\cdot\text{mol}^{-1}$ – a value inconsistent with the Appendix B value of $0.02 \text{ kg}\cdot\text{mol}^{-1}$, and a rather large value for the difference between interaction coefficients for Na^+ with two singly-charged small anions.

Finally, in high-carbonate concentration media, the solubilities of $\text{NaNpO}_2\text{CO}_3\cdot x\text{H}_2\text{O}$ in 3 M NaCl and in 3 M NaClO_4 are approximately equal for the reaction



and (again, assuming only anion-cation interactions) $\varepsilon_{(\text{Na}^+, \text{Cl}^-)}$ is approximately equal to $\varepsilon_{(\text{Na}^+, \text{ClO}_4^-)}$. Interaction parameters for $\text{NpO}_2(\text{CO}_3)_3^{5-}$ would have the same value in each medium (and the same would apply to $\text{NpO}_2(\text{CO}_3)_2^{3-}$).

Clearly, there is a problem. Either all the carbonate complexation results in chloride (or perchlorate) media are badly in error (which is possible, but unlikely), or some other aspects of the set of arguments presented above is wrong. There is a remote possibility radiolytic effects are important in the long-term solubility studies; the formation of mixed carbonatochloro complexes also seems possible, although this would be unexpected considering the apparent weakness of complexation of NpO_2^+ with chloride (Section 9.2.2.3).

Neck, Kim, Fanghänel and co-workers [94NEC/KIM, 95NEC/FAN, 95FAN/NEC] have suggested that anion-anion interactions need to be considered. Thus, the problem could arise from equating trace activity coefficients for ions such as CO_3^{2-} or $\text{NpO}_2\text{CO}_3^-$ in different media. In that case a Pitzer-treatment of the activity coefficients [95NEC/FAN, 95NOV/ROB, 96RUN/NEU] or a modified set of SIT coefficients [99NEC/FAN] could be invoked. It is clear that such an approach could resolve some of the difficulties. However, the large difference in the solubility of $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ in different media when the predominant reaction is expected to be



suggests that even this approach will not completely make the problem disappear.

These differences are smallest at zero ionic strength, where there is less uncertainty, hence they have no influence on any standard equilibrium constants selected in this review. Nor is there much of an effect in the calculated speciation in many groundwaters. Nevertheless, larger differences in solubilities might be generated in more concentrated Cl^- aqueous solutions, but this difference would certainly be within the uncertainties estimated in this review. However, solubility data indicate no difference between Cl^- and ClO_4^- media when the limiting complex $\text{NpO}_2(\text{CO}_3)_3^{5-}$, or its first dissociated complex $\text{NpO}_2(\text{CO}_3)_2^{3-}$, is formed - the problem is actually restricted to quite narrow domain of Cl^- concentration, assuming consistent auxiliary values are used to calculate $[\text{CO}_3^{2-}]$.

More data have been published for NaClO_4 solutions than for NaCl media, and statistical analysis is not very meaningful in this later medium. The ε SIT pair coefficients for Np(V) anions estimated in this review from their data in 0.1 to 3 M NaCl or NaClO_4 aqueous solutions, are the same within the uncertainties when different values for $\varepsilon_{(\text{CO}_3^{2-}, \text{Na}^+)}$ in ClO_4^- and Cl^- media are assumed (Table 12.5). This is not consistent with methodologies adopted in this review. All this does not mean the data in NaCl media are incorrect, typically determinations of values for the $\text{CO}_2(\text{g})/\text{CO}_3^{2-}$ equilibrium constant K_{p_2} , in both media differ by only 0.17 \log_{10} unit, and are consistent with the CODATA auxiliary value adopted in this review (see footnotes for Table 12.5). This 0.17 difference reflects the accuracy of the measurements, but it is more than the uncertainty of the K_{p_2} value adopted in the present review, and the difference propagates in the uncertainties of ε for the Np(V) interactions:

- From the determinations of K_{p_2} in 0.1 to 3 M NaClO_4 aqueous solution Kim *et al.* and Neck *et al.* [91KIM/KLE, 94NEC/RUN], and using $\varepsilon_{(\text{H}^+, \text{ClO}_4^-)} = (0.13 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$ deduced from Pitzer parameters [95FAN/NEC, 95NEC/FAN] (instead of (0.14 ± 0.02) (Table B.3)), we have calculated $\varepsilon_{(\text{CO}_3^{2-}, \text{Na}^+)} = (0.03 \pm 0.09) \text{ kg} \cdot \text{mol}^{-1}$ and $\log_{10} K_{p_2} = (18.23 \pm 0.16) \text{ kg} \cdot \text{mol}^{-1}$, while $-(0.08 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ (Table B.4) and $(18.15_5 \pm 0.03)$ (CODATA value) respectively are used in this review (also see [95GRE/PUI]). From this value and the solubility product K_s° for $\text{NaNpO}_2\text{CO}_3(\text{s})$ measured in similar conditions, this review then calculated $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.25 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}$ [91KIM/KLE] and $(0.24 \pm 0.12) \text{ kg} \cdot \text{mol}^{-1}$ [94NEC/RUN]. These values are in fair agreement with

the value (0.25 ± 0.05) used in this review (Table B.3), and $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.18 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ from liquid-liquid extraction data [94NEC/KIM]. Neck *et al.* [94NEC/KIM] proposed $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = 0.20$, possibly to be more consistent with their liquid-liquid extraction data.

- From similar calculations in NaCl media, this review calculated $\varepsilon_{(\text{CO}_3^{2-}, \text{Na}^+)} = -(0.07 \pm 0.09) \text{ kg}\cdot\text{mol}^{-1}$, $\log_{10} K_{p2} = (18.06 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)} = (0.05 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$ from the solubility data [94RUN/KIM, 96RUN/NEU], and $\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)} = (0.09 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$ from the liquid-liquid extraction data [94NEC/KIM].

This suggests the problem might be in the determination of K_{p2} at high ionic strength, and not in K_s° . This is consistent with the explanation of the authors who proposed using different $\varepsilon_{(\text{CO}_3^{2-}, \text{Na}^+)}$ in ClO_4^- and Cl^- media, or using a third order virial expansion, (*i.e.*, a Pitzer formula). All these ε values are in agreement within the uncertainties estimated in this review (as 1.96σ) for the experimental determinations of these authors. For this reason, and because of the lack of independent confirmation from other laboratories, this review did not change its auxiliary value for $\varepsilon_{(\text{CO}_3^{2-}, \text{Na}^+)}$ even though this problem might very well indicate it is needed; minimally the numerical value for $\varepsilon_{(\text{CO}_3^{2-}, \text{Na}^+)}$ now needs confirmation.

At this time we have chosen to select a value for $\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)}$ based solely on the $\text{NpO}_2\text{OH}(\text{c})$ solubility studies, with the full knowledge that this provides an inadequate representation of the best current solubility measurements for $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$ in chloride media. A better resolution must be found in the future.

12.1.2.1.3.c Temperature influence on Np(V) carbonate complexation

Corbenko-Germanov and Zenkova [66GOR/ZEN] reported Np(V) solubilities at 20 and 80°C, but it is not known whether the solid phases were the same for the two measurements. These measurements were not used in the present review to propose thermodynamic values, nor the temperature dependence of the solubility for the reasons explained below (Section 12.1.2.2.2).

Lemire, Boyer and Campbell studied Np(V) solubility in alkali-carbonate media at 30 to 75°C [93LEM/BOY]. Essentially, constant solubilities were found over a wide range of chemical conditions. This was due to the offsetting effects of changes in carbonate complexation (that increased solubility with $[\text{CO}_3^{2-}]$), and solid phase transformations that were difficult to control. Values of β_1 , K_2 and K_3 determined by Lemire, Boyer and Campbell at 30°C are in reasonable agreement with those selected in the present review for 25°C. Curve fitting performed by the author and graphical reinterpretations attempted as part of the present review (see Appendix A) were unsuccessful in determining enthalpies for the complexation reactions because of the scatter in the experimental data, and ambiguities as to the nature of the solid phases.

In an overview paper by Clark *et al.* [96CLA/CON] a spectrophotometric technique was used to propose values of β_1 and β_2 as a function of temperature. The method used

in this work is promising. A figure shows there is little scatter in the complexation constants, and demonstrates a linear variation of the logarithm of the formation constant values with $1/T$. From these plots the authors deduced $\Delta_r H$ values. Some data proposed for 25°C in this paper are not consistent with values selected in the present review. In the absence of details and original data, no values for the enthalpies of the complexation reactions involving Np(V) carbonato complexes from this work, have been selected in the present review.

However, from $\Delta_r H_m^\circ$ (12.1, 298.15 K) = $-(88.8 \pm 2.9)$ kJ·mol⁻¹ (Section 12.1.2.1), $\Delta_r H_m^\circ$ (12.2, 298.15 K) = $-(41.9 \pm 4.1)$ kJ·mol⁻¹ (Section 12.1.2.1) and $\Delta_r H_m^\circ$ (7.4, 298.15 K) = $-(117.4 \pm 0.6)$ kJ·mol⁻¹ (Section 7.2), the value $\Delta_r H_m^\circ$ (12.18, 298.15 K) = $-(13.25 \pm 5.06)$ kJ·mol⁻¹ is calculated. Using $\Delta_f H_m^\circ$ (NpO₂⁺, 298.15 K) selected in this review and $\Delta_f H_m^\circ$ (CO₃²⁻, 298.15 K) from Table 5.1,

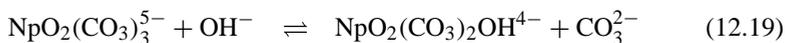
$$\Delta_f H_m^\circ(\text{NpO}_2(\text{CO}_3)_3^{5-}, 298.15 \text{ K}) = -(3017.12 \pm 6.89) \text{ kJ}\cdot\text{mol}^{-1}$$

From $\Delta_r H_m^\circ$ (12.18, 298.15 K) = $-(13.25 \pm 5.06)$ kJ·mol⁻¹ and $\Delta_r G_m^\circ$ (12.18, 298.15 K) = $-(31.39 \pm 0.86)$ kJ·mol⁻¹ selected in this section, $\Delta_r S_m^\circ$ (12.18, 298.15 K) = (60.84 ± 17.21) J·K⁻¹·mol⁻¹ is calculated. Using the selected values for S_m° (NpO₂⁺, 298.15 K) and S_m° (CO₃²⁻, 298.15 K)

$$S_m^\circ(\text{NpO}_2(\text{CO}_3)_3^{5-}, 298.15 \text{ K}) = -(135.05 \pm 20.47) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

12.1.2.1.3.d Mixed Np(V) hydroxide-carbonate complexes

Varlashkin, Begun and Hobart [84VAR/BEG, 84VAR/HOB] observed spectral variations on adding concentrated NaOH to concentrated Na₂CO₃ aqueous solutions containing Np(V). Riglet [90RIG] and Vitorge and Capdevila [98VIT/CAP] repeated and extended this work and showed the changes were evidence of formation of a mixed hydroxide-carbonate complex, possibly NpO₂(CO₃)₂OH⁴⁻ or NpO₂CO₃(OH)₂³⁻.



The stoichiometry of the mixed species could not be unambiguously established, and there was evidence of a transient species that formed prior to (or concurrently with) the predominant complex (the somewhat unlikely species NpO₂(CO₃)₂(OH)₂⁵⁻ has been proposed [98VIT/CAP]). Most of the experimental data were discussed at the Migration'91 Conference and were reported in [98VIT/CAP].

Neck, Fanghänel and Kim [97NEC/FAN] also recently reported a similar spectrophotometric study of the dissociation of the carbonate limiting complex in alkaline media. As explained in that reference, the measurements to identify the complexes are quite difficult, and evidence was presented for formation of NpO₂(CO₃)₂OH⁴⁻ and NpO₂CO₃(OH)₂³⁻.

Despite the extensive scatter in the experimental measurements, it is clear the first dissociation step of the limiting carbonate complex $\text{NpO}_2(\text{CO}_3)_3^{5-}$ is not associated with any polymerization reaction. This scatter could be explained by kinetics, $\text{NpO}_2(\text{CO}_3)_3^{5-}$ might react to form a transient species detected by Riglet [90RIG] who used an experimental method (direct addition of reactant in the spectrophotometric cuvette) that gave more rapid results. For electrostatic reasons, it would be surprising if a negatively charged ligand is added to the limiting hydroxide complex $\text{NpO}_2(\text{OH})_2^-$. Exchange of carbonate from a carbonato complex for hydroxide anions (or a hydroxide anion) seems more likely.

Beside the species involved in equilibrium 12.19, the formation of other monomeric mixed-hydroxide complexes has been suggested [90RIG, 97NEC/FAN]. Neck, Fanghänel and Kim [97NEC/FAN] attributed a broad shoulder at about 1025 nm to the presence of colloids and to formation of a second complex. However, their stoichiometry could not be clearly established, and evidence for additional soluble monomeric species is not clear. As suggested (but eventually rejected, see Appendix A) by Neck, Fanghänel and Kim [97NEC/FAN] in the qualitative discussion of their spectrophotometric results, formation of $\text{NpO}_2(\text{OH})_2^-$ and precipitation of a hydroxide compound might be sufficient to explain most of the experimental observations in more alkaline media. This has also been shown by experiments to determine the influence of changes in total neptunium(V) concentration [97NEC/FAN, 98VIT/CAP]. In the course of precipitation a new polymeric species, or equally well a metastable colloid, may be formed. The influence of all these possible reactions on the spectrum cannot easily be distinguished.

The values $\log_{10} K(12.19, 3\text{M Na}^+) = (0.47 \pm 0.27)$ and (0.12 ± 0.05) are calculated from the data of [90RIG] and [97NEC/FAN], respectively. The molar absorptivity at 1010 nm is estimated to be $(101 \pm 17) \text{ l}\cdot\text{mol}^{-1}\text{cm}^{-1}$. These numbers are not consistent within the reported uncertainties; the uncertainties are quite small only because a limited set of data could be used. From all the published data (also including results of Gorgeon reported recently by Vitorge and Capdevila [98VIT/CAP]), this review calculates $\log_{10} K(12.19, 3\text{M Na}^+) = (0.14 \pm 0.75)$. Assuming $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}, \text{Na}^+)} = \varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+)} = -(0.40 \pm 0.19) \text{ kg}\cdot\text{mol}^{-1}$,

$$\log_{10} K^\circ(12.19, 298.15\text{K}) = (3.20 \pm 1.16)$$

$$\Delta_r G_m^\circ(12.19, 298.15\text{K}) = -(18.24 \pm 6.64) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r G_m^\circ(\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}, 298.15\text{K}) = -(2170.42 \pm 8.78) \text{ kJ}\cdot\text{mol}^{-1}$$

are calculated and selected. Using values selected in this review, $\log_{10} K(12.20, 298.15\text{K}) = (8.70 \pm 1.17)$ and $\log_{10} K(12.19, 3\text{M Na}^+, 298.15\text{K}) = (10.75 \pm 0.76)$ are calculated for the equilibrium



The value $\log_{10} K(12.19, 3\text{M NaClO}_4, 298.15\text{K}) = (10.06 \pm 0.11)$ recently proposed [97NEC/FAN] is in agreement with this (10.75 ± 0.76) value, even though different auxiliary data (for the limiting carbonate complex) were used; its uncertainty

should be increased for the reasons explained in Appendix A. No values are selected for $\text{NpO}_2(\text{OH})_2\text{CO}_3^{3-}$, though the value $\log_{10}\beta = 9.56$ ($I = 3 \text{ M NaClO}_4$) from [97NEC/FAN] can be used as a guideline.

12.1.2.1.4 Np(IV) carbonate complexes

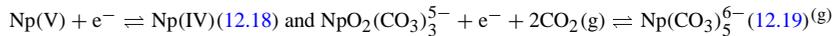
Published values for formation of monomeric carbonate complexes of Np(IV) are summarized in Table 12.6. Moskvin [71MOS2] showed spectral evidence of Np(IV) complexation in concentrated carbonate aqueous solutions, but the stoichiometry and formation constants proposed by Moskvin are “completely erroneous” according to Rai and Ryan [85RAI/RYA]. This Np(IV) spectrum was later confirmed [77SAI/UEN, 81WES/SUL, 84VAR/HOB, 93LI/KAT, 96DEL/VIT]. Li, Kato and Yoshida [93LI/KAT] observed that the Np(IV) spectrum changes when the total concentration of Na_2CO_3 is decreased from 1 to 0.2 M at pH 10.1. This observation was later reproduced by Delmau, Vitorge and Capdevila [96DEL/VIT], who demonstrated that the dissociation of the limiting complex involved the loss of only one carbonate (and no OH^- addition). They showed that only two species were necessary to describe their spectra and all published spectral information for Np(IV) in concentrated carbonate/bicarbonate aqueous solutions. This is consistent with the solubility experiments of Rai and Ryan [85RAI/RYA] and Rai *et al.* [99RAI/HES] and with the reported behaviour of Pu(IV) (Section 21.1.2.1.3) and U(IV) [92GRE/FUG]. Fedoseev, Peretruxhin and Krot only proposed a rough estimate for the formal potential of the Np(V)/Np(IV) redox couple in 1 M Na_2CO_3 , because they could not obtain steady emf measurements. Delmau, Vitorge and Capdevila [96DEL/VIT] prepared Np(IV) by electrochemical reduction of Np(V) in 0.3 to 1.5 M Na_2CO_3 aqueous solutions. They obtained steady emf measurements, and calculated the stability of the Np(IV) limiting complex, assuming its stoichiometry to be $\text{Np}(\text{CO}_3)_5^{6-}$ in parallel to those proposed for the Th(IV) [97FEL/RAI], U(IV) [92GRE/FUG] and Pu(IV) analogues [98CLA/CON]. Rai and Ryan showed that no detectable carbonate or mixed hydroxide-carbonate complex of Np(IV) was formed when the total concentration of carbonate was less than 0.01 M, regardless of the value of the pH [85RAI/RYA]. They also suggested “upper limits” for the stability constants of species proposed elsewhere in the literature [71MOS2, 89MOR/PRA, 90PRA/MOR] on the basis of solubility measurements that could not reasonably be used to deduce any thermodynamic information. Other information about the carbonate complexes of Np(IV) is not reliable or is erroneous as discussed previously [85RAI/RYA, 95VIT, 96DEL/VIT]. Recently Rai *et al.* studied the solubility of tetravalent hydroxides of actinides in concentrated bicarbonate and carbonate solutions [95RAI/FEL, 97FEL/RAI]. They concluded pentacarbonate complexes were present in their aqueous actinide solutions, consistent with the interpretation used in this review for the carbonate complexes of tetravalent actinides.

In two very recent papers, this group has also presented new experimental data and proposed new stability constant values for the U(IV) [98RAI/FEL] and Np(IV) [99RAI/HES] systems. Copies of these papers were received late in the course of the review for neptunium, and provide more reliable data for the Np(IV) system ¹ (*cf.* the discussion on Np analogues at the end of this section).

¹ Nevertheless, the information in these papers was reviewed and this led us to revise and add to the selected values for Np(IV) carbonate complexes; however the papers were published too late to completely redraft the discussion in Section 12.1.2.1.4.

$\text{Np}(\text{CO}_3)_4^{4-} + \text{CO}_3^{2-} \rightleftharpoons \text{Np}(\text{CO}_3)_5^{6-}$				
sp	0.2 M Na_2CO_3 , pH=10.8	room t	> (1.3 ± 0.5)	[93LI/KAT] ^(a)
sp	0.4 M Na^+ , CO_3^{2-} , HCO_3^- ^(b)	(21 ± 2)	1.47	[96DEL/VIT] ^(c)
sp	0.6 M Na^+ , CO_3^{2-} , HCO_3^- ^(b)	(21 ± 2)	1.63	
sp	0.8 M Na^+ , CO_3^{2-} , HCO_3^- ^(b)	(21 ± 2)	1.80	
sp	1 M Na^+ , CO_3^{2-} , HCO_3^- ^(b)	(21 ± 2)	1.79	
sp	1.2 M Na^+ , CO_3^{2-} , HCO_3^- ^(b)	(21 ± 2)	2.21	
sp	$I = 0$	(21 ± 2)	-(1.06 ± 0.20)	
$\text{NpO}_2(\text{am, hyd}) + 4\text{CO}_3^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{Np}(\text{CO}_3)_4^{4-} + 4\text{OH}^-$				
sol	0.033 to 0.11 m KHCO_3	(23 ± 2)	-(17.36 ± 0.12) ^(d)	[99RAI/HES] ^(e)
$\text{NpO}_2(\text{am, hyd}) + 5\text{CO}_3^{2-} + 2\text{H}_2\text{O} \rightleftharpoons \text{Np}(\text{CO}_3)_5^{6-} + 4\text{OH}^-$				
sol	1.78 m KHCO_3	(23 ± 2)	-(11.66 ± 0.35) ^(d)	[99RAI/HES] ^(f)
$\text{Np}^{4+} + 5\text{CO}_3^{2-} \rightleftharpoons \text{Np}(\text{CO}_3)_5^{6-}$				
sol	$I = 0$	(23 ± 2)	33.79	[99RAI/HES]
sol	$I = 0$	(23 ± 2)	(35.64 ± 1.07) ^(f)	

(Continued on next page)



pot	1 M Na ₂ CO ₃ ^(h)	room t	(0.1 ± 0.2) ⁽ⁱ⁾	0.514 ^(j)		[79FED/PER]
pot	0.3 M Na ₂ CO ₃	25	0.267 ^(k)	0.641 ^(j)		[96DEL/VIT]
pot	0.6 M Na ₂ CO ₃	25	0.188 ^(k)	0.694 ^(j)	-0.00206 ^(m)	
pot	1 M Na ₂ CO ₃	25	0.226 ^(k)	0.641 ^(j)	-0.00217 ^(m)	
	pH=10.27			0.535		
pot	1.5 M Na ₂ CO ₃	25	0.207 ^(k)	0.620 ^(j)	-0.00224 ^(m)	
pot	<i>I</i> = 0	25	0.124	(0.436 ± 0.116)		

Redox equilibria

Method	Ionic medium (mol · dm ⁻³)	<i>t</i> (°C)	<i>E</i> ^{o'} (V vs. SHE)	Reference
$\text{Np}(\text{CO}_3)_5^{6-} + \text{e}^- \rightleftharpoons \text{Np}(\text{CO}_3)_3^{3-} + 2\text{CO}_3^{2-} \text{ (n)}$				
vlt	1 M Na ₂ CO ₃	room t	-(1.32 ± 0.1)	[79FED/PER]
vlt	1 M K ₂ CO ₃	room t	-(1.3 ± 0.1)	[84VAR/HOB]
vlt	2 M Na ₂ CO ₃	room t	-(1.2 ± 0.1)	

(Continued on next page)

$\text{Np}^{4+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{Np}(\text{CO}_3)_3^{2-}$					
sol	NaHCO_3 , in air	room t	(37.0 ± 1.2)	< 33	[89MOR/PRA]
$\text{Np}^{4+} + 2\text{CO}_3^{2-} + 2\text{OH}^- \rightleftharpoons \text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$					
sol	0.01 M $(\text{CO}_3^{2-} + \text{HCO}_3^-)$, Na^+	room t	(45.69 ± 0.44)	$< 42^{(d)}$	[90PRA/MOR]
sol	$I = 0$	(23 ± 2)	43.17	< 42	[99RAI/HES]
$\text{Np}^{4+} + \text{CO}_3^{2-} + 4\text{OH}^- \rightleftharpoons \text{Np}(\text{CO}_3)(\text{OH})_4^{2-}$					
sol	0.1 to 2.2 M $(\text{NH}_4)_2\text{CO}_3$	room t	(53.05 ± 0.02)	$< 47^{(d)}$	[71MOS2]
sol	0.5 M NaClO_4	20	(49.2 ± 0.5)		[93ERI/NDA]
$\text{Np}^{4+} + 2\text{CO}_3^{2-} + 4\text{OH}^- \rightleftharpoons \text{Np}(\text{CO}_3)_2(\text{OH})_4^{4-}$					
sol	0.01 M $(\text{CO}_3^{2-} + \text{HCO}_3^-)$, Na^+	room t	(53.07 ± 0.44)	$< 48^{(d)}$	[90PRA/MOR]
$\text{Np}^{4+} + \text{CO}_3^{2-} + 3\text{OH}^- \rightleftharpoons \text{NpCO}_3(\text{OH})_3^-$					
sol	0.5 M NaClO_4	20	(45.8 ± 0.5)		[93ERI/NDA]

^(a)Estimated in the present review from data of this study (not interpreted by the original authors).

^(b) $\log_{10}K$ determined in chemical conditions where $\log_{10}[\text{CO}_3^{2-}] = -\log_{10}K$.

^(c)Data tabulated on pages 57 and 58 of [96DEL/VIT].

^(d)Molal units.

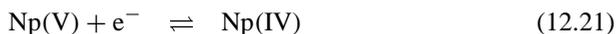
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- (^h) 1 M K_2CO_3 is written in Table I of [79FED/PEK] which is probably an error.
- (i) Uncertainty assigned in the present review.
- (j) Assuming equilibrium with the air.
- (k) Recalculated from the data tabulated on page 58 of [96DEL/VIT]; corrected for the [Np(V)]/[Np(IV)] ratio.
- (l) Maximum possible value estimated in this review from the work of the reference, or from [85RAI/RYA].
- (^m) Temperature coefficients from linear regression of $E^{\circ'}$ vs. T .
- (ⁿ) The stoichiometry $\text{Np}(\text{CO}_3)_3^{3-}$ for the Np(III) limiting complex, is assumed by analogy with Am(III) [95SIL/BID], but further confirmation is needed.

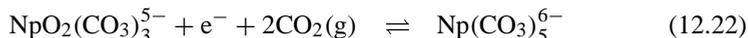
In this review the stoichiometry of the Np(IV) limiting complex was assumed to be $\text{Np}(\text{CO}_3)_5^{6-}$, despite the lack of experimental confirmation of this stoichiometry. A quantitative interpretation of the (relatively poor) experimental data leads to a rough estimate of the stability of $\text{Np}(\text{CO}_3)_5^{6-}$ based on the formal potential of the Np(V)/Np(IV) redox couple. However, recent, solubility data are used to calculate the value of the formation constant selected for $\text{Np}(\text{CO}_3)_4^{4-}$. Spectrophotometric data for the dissociation of the limiting complex are used to calculate the equilibrium constant for the reaction and the stability constant for $\text{Np}(\text{CO}_3)_5^{6-}$. The model assumed here seems to be sufficient to explain all published data. The species $\text{Np}(\text{OH})_4(\text{aq})$, $\text{Np}(\text{CO}_3)_5^{6-}$ and $\text{Np}(\text{CO}_3)_4^{4-}$ are probably formed in concentrated carbonate/bicarbonate media. There are insufficient data to allow selection of formation constant values for other complexes, but that does not mean they do not exist.

12.1.2.1.4.a The limiting Np(IV) carbonate complex

Fedoseev, Peretrukhin and Krot [79FED/PER] proposed the rough value $E^\circ(12.21, 1 \text{ M Na}_2\text{CO}_3) = 0.1 \text{ V/SHE}$ for the redox potential of the equilibrium



A reasonable assessment of the uncertainty in this value is probably $\pm 0.2 \text{ V}$ (Appendix A). Delmau, Vitorge and Capdevila [96DEL/VIT] later obtained a steady measurement in the same medium and determined $E^\circ(12.21, 1 \text{ M Na}_2\text{CO}_3, \text{pH}=10.12) = 0.244 \text{ V/SHE}$. The major redox equilibrium can now be interpreted in terms of the limiting carbonate complexes of Np(IV) and Np(V) whose stoichiometries and stabilities in these chemical conditions are now reasonably well established (see below in this section and Section 12.1.2.1.3.a respectively).



The potential of the Np(V)/Np(IV) redox couple $E(12.21)$, is corrected for $\text{CO}_2(\text{g})$ partial pressure to obtain the formal potential $E^\circ(12.22)$. This is the main source of uncertainty: when a closed 1 M Na_2CO_3 solution ($p_{\text{CO}_2} = 10^{-6.3} \text{ atm}$ [95VIT]) is contacted with air ($p_{\text{CO}_2} = 10^{-3.5} \text{ atm}$), p_{CO_2} can progressively increase, decreasing pH and shifting the redox potential of the solution by as much as +330 mV. Conversely, water reduction produced OH^- anion in the course of the electrochemical preparation of Np(IV) from Np(V). $E^\circ(12.22, 1 \text{ M Na}_2\text{CO}_3, p_{\text{CO}_2} = 1 \text{ atm}) = 0.514$ and 0.535 V/SHE are calculated by this review from the above values $E^\circ(12.21, 1 \text{ M Na}_2\text{CO}_3) = 0.1 \text{ V/SHE}$ [79FED/PER] assuming equilibrium with air, and from $E^\circ(12.21, 1 \text{ M Na}_2\text{CO}_3, \text{pH } 10.12) = 0.244 \text{ V/SHE}$ [96DEL/VIT] respectively. Further discussion is provided in Appendix A. From the mean of the two values, $E^\circ(12.22, 1 \text{ M Na}_2\text{CO}_3, p_{\text{CO}_2} = 1 \text{ atm}, 298.15 \text{ K}) = (0.524 \pm 0.101) \text{ V/SHE}$ (the uncertainty reflects the inaccuracy in the value of p_{CO_2}), this review calculates $\log_{10}\beta_5(12.23, 1 \text{ M Na}_2\text{CO}_3, \gamma_{\text{Np}^{4+}} = 1, 298.15 \text{ K}) = (41.96 \pm 1.70)$ in molal units for the equilibrium



using the standard potential of the $\text{NpO}_2^+/\text{Np}^{4+}$ couple $E^\circ(7.6, 298.15 \text{ K}) = (0.604 \pm 0.007) \text{ V/SHE}$ (Section 7.3), the formation constant of the limiting complex of Np(V) $\log_{10} \beta_3^\circ(12.14, 298.15 \text{ K}) = (5.50 \pm 0.15)$, determined above, the $\text{CO}_3^{2-}/\text{CO}_2(\text{g})$ equilibrium constant $\log_{10} K^\circ = (18.155 \pm 0.035)$ (Table 5.2), $\varepsilon_{(\text{Na}^+, \text{NpO}_2(\text{CO}_3)_3^{5-})} = -(0.53 \pm 0.19) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})} = -(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ (Table B.4).

Delmau, Vitore and Capdevila did not measure pH at equilibrium in the course of their measurements of the redox potential of the $\text{Np(V)}/\text{Np(IV)}$ couple in 0.3, 0.6 and 1.5 M Na_2CO_3 (see Appendix A). Hence pH was different and unknown in each different solution. The uncertainty in $E^\circ(12.22)$ due to the uncertainty in $p\text{CO}_2$ is assumed to partially cancel in extrapolating these data to zero ionic strength by linear regression; $\Delta\varepsilon(12.22, 298.15\text{K}) = -(0.54 \pm 0.50) \text{ kg}\cdot\text{mol}^{-1}$. From this value and $\varepsilon_{(\text{Na}^+, \text{NpO}_2(\text{CO}_3)_3^{5-})} = -(0.53 \pm 0.19) \text{ kg}\cdot\text{mol}^{-1}$ determined above, $\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_5^{6-})} = (0.00 \pm 0.54) \text{ kg}\cdot\text{mol}^{-1}$ is calculated for 0.3 to 1.5 M Na_2CO_3 .

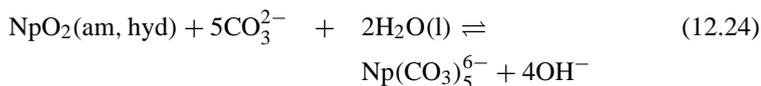
Using $\Delta\varepsilon(12.25) = (0.38 \pm 0.18) \text{ kg}\cdot\text{mol}^{-1}$ determined below by linear regression from data in 0.2 to 0.5 M Na_2CO_3 , $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})} = -(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ (Table B.4) and $\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_4^{4-})} = \varepsilon_{(\text{Na}^+, \text{U}(\text{CO}_3)_4^{4-})} = -(0.09 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ (Table B.4), an estimate for $\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_5^{6-})} = (0.21 \pm 0.21) \text{ kg}\cdot\text{mol}^{-1}$ in this lower ionic strength region is calculated. This value is consistent with the high ionic strength estimate $\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_5^{6-})} = (0.00 \pm 0.54) \text{ kg}\cdot\text{mol}^{-1}$ within the large uncertainties, although there is no reason this should be the case (the SIT assumption that $\Delta\varepsilon(\text{I})$ is constant is not necessarily accurate at high ionic strength for -5 and -6 anions [90RIG, 92GRE/FUG]). However, the approximate agreement in the two $\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_5^{6-})}$ values is important only in that it means variation in ionic strength effects cannot be invoked to explain differences between the Np and the U and Pu systems as discussed below.

Using $\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_5^{6-})} = (0.00 \pm 0.52) \text{ kg}\cdot\text{mol}^{-1}$, this review extrapolates $E^\circ(12.22, 1 \text{ M Na}_2\text{CO}_3, p\text{CO}_2 = 1 \text{ atm}, 298.15 \text{ K}) = (0.524 \pm 0.101) \text{ V/SHE}$ and $\log_{10} \beta_5(12.23, 1 \text{ M Na}_2\text{CO}_3, \gamma_{\text{Np}^{4+}} = 1, 298.15 \text{ K}) = (41.96 \pm 1.70)$ values (discussed above) to zero ionic strength; $E^\circ(12.22, p\text{CO}_2 = 1 \text{ atm}, 298.15 \text{ K}) = (0.436 \pm 0.116) \text{ V/SHE}$ and $\log_{10} \beta_5^\circ(12.23, 298.15 \text{ K}) = (38.98 \pm 1.97)$ are obtained. The latter is consistent with the upper limit of β_5 deduced from Rai and Ryan's first solubility measurement [85RAI/RYA] (Appendix A), and with the formal potential of the $\text{Np(IV)}/\text{Np(III)}$ redox couple assuming analogy between the Np(III) and Am(III) limiting complexes $\text{M}(\text{CO}_3)_3^{3-}$ (see Section 12.1.2.1.5). However, $E^\circ(12.22, p\text{CO}_2 = 1 \text{ atm}, 298.15 \text{ K}) = (0.240 \pm 0.091) \text{ V/SHE}$ and $\log_{10} \beta_5^\circ(12.23, 298.15 \text{ K}) = (35.62 \pm 1.07)$ are calculated from values selected in this review, and even these values may be slight overestimates. The E° values are in marginal agreement, while the β_5° values differ by slightly more than the combined uncertainties.

Hence, consistent estimations of β_5 are obtained for Np(IV) using two different thermodynamic cycles, one of them with data from two different laboratories using different methods to prepare Np(IV) in carbonate solutions. Nevertheless, this value is

only an estimate; it is much larger than the corresponding uranium ($\log_{10} \beta_5^\circ = (34.1 \pm 1.0)$ [95GRE/PUI]), and plutonium ($\log_{10} \beta_5^\circ = (32.2 \pm 2.0)$) values as estimated by Vitorge [95VIT] from Capdevila's data [92CAP] (see also Paragraph 21.1.2.1.3 and [96CAP/VIT]). As suggested previously, this discrepancy could be due to problems in the measurements of the Np(V)/Np(IV) formal potential [79FED/PER] or in their interpretation [96DEL/VIT]; it could also be due to the formation of mixed hydroxocarbonato complexes. For the highly negatively charged $M(\text{CO}_3)_5^{6-}$ complexes ($M = \text{Th, U, Np, Pu, Am}$), strict analogy of ionic strength effects (and, hence, specific interaction coefficients), is not expected. Nevertheless the observed difference between β_5° values (within the actinide series) seems too large to be attributed to the procedures for extrapolation to zero ionic strength. Capdevila *et al.* estimated U, Np and Pu β_5 values for an ionic medium close to those used in the experimental determinations (3 M NaClO₄) [96CAP/VIT]. They also found the value for the formation constant of the neptunium species to be 4 to 5 orders of magnitude greater than the formation constants of the corresponding uranium and plutonium species. For this reason, the uncertainty in $\log_{10} \beta_5^\circ(12.23, 298.15 \text{ K}) = 38.98$ could be increased to ± 7 (also see the discussion on actinide analogues at the end of this section).

Very recently Rai *et al.* [99RAI/HES] estimated $\log_{10} K_{s,5}^\circ(12.24) = -21.15$



and then $\log_{10} \beta_5^\circ(12.23) = 33.79$ (or 33.32, using for $^*K_{s,0}^\circ$ the value selected in Section 8.2.5.2) from a study of Np(IV) solubility in KOH/K₂CO₃/KHCO₃ aqueous solutions, and confirmed the stoichiometry of $\text{Np}(\text{CO}_3)_5^{6-}$ using X-ray Absorption Spectroscopy. However, the selected value

$$\Delta_f G_m^\circ(\text{Np}(\text{CO}_3)_5^{6-}, 298.15 \text{ K}) = -(3334.57 \pm 8.43) \text{ kJ}\cdot\text{mol}^{-1}$$

was obtained, and $\log_{10} K_{s,5}^\circ(12.24, 298.15\text{K}) = -(18.86 \pm 0.37)$ is calculated from values selected below in this review: $\log_{10} K_5^\circ(12.25) = -(1.07 \pm 0.30)$ and $\log_{10} K_{s,4}^\circ(12.26, 298.15\text{K}) = -(17.79 \pm 0.22)$. From the $K_{s,5}^\circ$ value and $\log_{10} ^*K_{s,0}^\circ(8.13) = (1.53 \pm 1.00)$ selected in Section 8.2.5.2, $\log_{10} \beta_5^\circ(12.23) = (35.62 \pm 1.07)$ is obtained. This selected stability constant for $\text{Np}(\text{CO}_3)_4^{4-}$ may be an overestimate (see Section 12.1.2.1.4.b). If so, this would propagate to other values deduced from $K_{s,4}^\circ(12.26, 298.15 \text{ K})$, namely $\Delta_f G_m^\circ(\text{Np}(\text{CO}_3)_5^{6-})$ and $K_{s,5}^\circ(12.24)$, which would also be overestimated. However, the values would certainly still be within the stated uncertainties (see the discussion of [99RAI/HES] in Appendix A).

The selected value is less than $\log_{10} \beta_5^\circ = 38.98$ estimated (but not selected) above in this section from emf measurement by more than the combined uncertainties (and confirms the assigned uncertainty of the emf measurement is probably too small), but it is also 2.27 greater than the value determined by Rai *et al.* The sources of the latter discrepancy are the higher weight given in this review to data in KHCO₃ media, the different procedures used for extrapolation to the standard state, and difficulties in the interpretation (different assumptions for the stoichiometry of the predominant complex in KHCO₃ aqueous solutions). None of the available procedures are likely to be

satisfactory for -6 charged species in high ionic strength media (1-5 m K_2CO_3). The values for $\log_{10} \beta_5^\circ$ for the neptunium value and uranium [95GRE/PU] complexation constants are within their combined uncertainties.

The value of $K_{s,4}^\circ$ (12.26) selected in this section from the solubility data of Rai *et al.* in KHCO_3 media, and K_5° (12.25) selected below (Section 12.1.2.1.4.b) reproduce the other solubility data they reported for concentrated $\text{K}_2\text{CO}_3 + \text{KOH}$ media reasonably well (see Appendix A). The value

$$\Delta\varepsilon(12.24) = -(0.45 \pm 0.68) \text{ kg}\cdot\text{mol}^{-1}$$

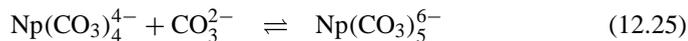
is calculated in this review from the data. From that $\Delta\varepsilon$ value the selected interaction coefficient

$$\varepsilon_{(\text{Np}(\text{CO}_3)_5^{6-}, \text{K}^+)} = -(0.73 \pm 0.68) \text{ kg}\cdot\text{mol}^{-1}$$

is calculated. The value for $\varepsilon_{(\text{Np}(\text{CO}_3)_4^{4-}, \text{K}^+)}$ (see Appendix A) has little influence on solubilities calculated for KHCO_3 media such as those used in the experiments adopted in the selection of $K_{s,4}^\circ$ (12.26). However, the value of $\varepsilon_{(\text{Np}(\text{CO}_3)_5^{6-}, \text{K}^+)}$ does have a dramatic influence on solubilities calculated for the $\text{K}_2\text{CO}_3 + \text{KOH}$ media. The difficulty in interpreting these data, and the way they are reinterpreted in this review, may result in systematic errors. These would mainly be reflected in the value fitted for $\varepsilon_{(\text{Np}(\text{CO}_3)_5^{6-}, \text{K}^+)}$, which has a large uncertainty.

12.1.2.1.4.b Dissociation of the limiting Np(IV) carbonate complex

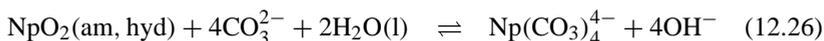
In a spectrophotometric study starting with the limiting Np(IV) complex in 0.2 to 0.6 M Na_2CO_3 aqueous solutions, Delmau, Vitorge and Capdevila [96DEL/VIT] found that only two species were necessary to describe their observations. They determined in these media, the values $K_5(12.25, x \text{ M Na}_2\text{CO}_3)$ of the constant of the equilibrium



and extrapolated them to zero ionic strength with the same methodology used in this review (Appendix B). These data, and calculations to test the effects of exclusion of the measurement at the highest ionic strength and different methods of estimating the mean ionic strength, were presented elsewhere [95VIT, (pp. 35 – 36)], [96CAP/VIT], resulting in values of $\log_{10} K_5^\circ(12.25) = -(1.27 \text{ to } -0.98)$, and $\Delta\varepsilon(12.25) = (0.05 \text{ to } 0.44) \text{ kg}\cdot\text{mol}^{-1}$. Excluding the measurement in 0.6 M Na_2CO_3 they calculated $\log_{10} K_5^\circ(12.25) = -(1.06 \pm 0.20)$, and $\Delta\varepsilon(12.25) = (0.39 \pm 0.18) \text{ kg}\cdot\text{mol}^{-1}$ (uncertainty calculated as 1.96σ). Reanalysis in the present review leads to approximately the same values:

$$\begin{aligned} \log_{10} K_5^\circ(12.25, 298.15\text{K}) &= -(1.07 \pm 0.30) \\ \Delta\varepsilon(12.25) &= (0.38 \pm 0.18) \text{ kg}\cdot\text{mol}^{-1} \\ \Delta_r G_m^\circ(12.25, 298.15 \text{ K}) &= (6.11 \pm 1.71) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

This is accepted as the best estimate of $\log_{10} K_5^\circ(12.25)$ at 25°; the uncertainty in $\log_{10} K_5^\circ(12.25)$ has been increased from 0.14 (= 1.96 σ) to 0.30 because the quality of the spectrophotometric and pH measurements is not as good as for the similar study from the same laboratory on the corresponding plutonium system [96CAP/VIT]. Very recently Rai *et al.* [99RAI/HES] found a dramatic increase in Np(IV) solubility with increasing KHCO₃ molality. Recalculations (Appendix A) indicate a slope of +4 for the log-log plot, and the data can be interpreted in terms of the equilibrium



Using the low ionic strength experimental data (molal units) reported in [99RAI/HES], the molal constant, $\log_{10} K_{s,4}(12.26)$, 0.033 to 0.11 m KHCO₃, has a value of $-(17.36 \pm 0.12)$, from which the selected standard values

$$\begin{aligned} \log_{10} K_{s,4}^\circ(12.26, 298.15 \text{ K}) &= -(17.79 \pm 0.22) \\ \Delta_r G_m^\circ(12.26, 298.15 \text{ K}) &= (101.55 \pm 1.26) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

are obtained. The selected value

$$\Delta_f G_m^\circ(\text{Np}(\text{CO}_3)_4^{4-}, 298.15 \text{ K}) = -(2812.78 \pm 8.24) \text{ kJ}\cdot\text{mol}^{-1}$$

is obtained from this $K_{s,4}^\circ$ value, $\log_{10} {}^*K_{s,0}(8.13, 298.15 \text{ K}) = (1.53 \pm 1.00)$, $\Delta_f G_m^\circ(\text{Np}^{4+}, 298.15 \text{ K}) = -(491.77 \pm 5.59) \text{ kJ}\cdot\text{mol}^{-1}$ selected in Sections 8.2.5.2 and 7.4, and $\Delta_f G_m^\circ(\text{CO}_3^{2-}, 298.15 \text{ K}) = -(527.9 \pm 0.39) \text{ kJ}\cdot\text{mol}^{-1}$ (Table 5.1) and $\log_{10} \beta_4^\circ(12.27) = (36.69 \pm 1.03)$ is calculated for the equilibrium



Neglecting possible formation of mixed hydroxide-carbonate complexes, and systematic errors in selection of $\Delta \varepsilon(12.26)$, a relatively unimportant quantity for these low ionic strengths, might result in overestimation of the stability of $\text{Np}(\text{CO}_3)_4^{4-}$. This in turn would result in overestimation of the stability of $\text{Np}(\text{CO}_3)_5^{6-}$, and of the standard potential $E^\circ(12.21)$ for the Np(V)/Np(IV) redox couple.

12.1.2.1.4.c Other Np(IV) carbonate or mixed hydroxide-carbonate complexes

Rai and Ryan [85RAI/RYA] measured Np(IV) solubility in neutral media and concluded that no detectable anionic complex was formed in their conditions. This observation is consistent with the values for the stability constants of $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$ selected above (see also the discussion of [85RAI/RYA] in Appendix A). Rai and Ryan also excluded the soluble complexes of Np(IV) proposed by Moskvina [71MOS2] to interpret his solubility study. Pratopo and Moriyama have tried to reproduce Rai and Ryan's measurements under exactly the same conditions [89MOR/PRA] or similar conditions [90PRA/MOR]. They found higher solubilities and interpreted this as evidence of new carbonate or mixed hydroxide carbonate soluble complexes. As explained in Appendix A the results were too scattered and cannot reasonably be

used to deduce any thermodynamic information or, indeed, any information at all on the solution species. Eriksen *et al.* [93ERI/NDA] also proposed two mixed complexes based on a single series of experiments. This review accepts the conclusions of Rai and Ryan [85RAI/RYA] and of Vitorge [95VIT] that solubility studies published up to and including 1990 [71MOS2, 85RAI/RYA, 89MOR/PRA, 90PRA/MOR] show no firm evidence of any soluble carbonate or mixed hydroxide Np(IV) carbonate complex. When such species were proposed in literature, they are the result of incorrect experimental methodology and treatment of data. An efficient reducing agent must be used for Np(IV) solubility measurements in neutral solutions or in solutions containing low concentrations of carbonate/bicarbonate [85RAI/RYA], to avoid oxidation of complexes and changes in the solid phase during solubility measurements. According to the following equilibria



the plot of experimental $\log_{10}(\text{solubility})$ as a function of $(\log_{10}[\text{CO}_3^{2-}] - (4/x)\log_{10}[\text{OH}^-])$ should be linear with the slope x , when $\text{Np(CO}_3)_x^{(4-2x)}$ soluble complex predominate. In the present review, $x = 5$ and 4 are used and the corresponding $4/x$ values are 0.8 and 1 . It is noted, however, that a line can be drawn through data reported in [89MOR/PRA, 90PRA/MOR] with a slope that might indicate formation of $\text{Np(CO}_3)_4^{4-}$ (or $\text{Np(CO}_3)_2(\text{OH})_2^{2-}$ [99RAI/HES]). The scatter in the experimental data could be due to the formation of colloidal $\text{NpO}_2(\text{am, hyd})$. However, such species would be important only under a very limited range of conditions. Possible formation of other species cannot be excluded [93ERI/NDA] (also *cf.* the Appendix A entry for [99RAI/HES]).

12.1.2.1.4.d Temperature influence

Delmau, Vitorge and Capdevila [96DEL/VIT] measured the influence of temperature on the Np(V)/Np(IV) couple. By varying temperature up and down over several weeks, they obtained reasonable precision (± 10 or 20 mV), when compared to previous work [79FED/PER, 84VAR/BEG]. As discussed above (Section 12.1.2.1.4.a), the main uncertainty was lack of correct pH measurements and this could induce shifts of as much as 330 mV. Since reproducible data were obtained during temperature cycles on a single solution, it is clear that eventually each solution was buffered. Hence the main source of uncertainty cancels when calculating the enthalpy of reaction. The authors calculated, by linear regression, $\partial E^\circ/\partial T$ (12.21) = -2.0584 , -2.1676 and -2.2409 $\text{mV}\cdot\text{K}^{-1}$ in 0.6 , 1 and 1.5 M Na_2CO_3 respectively. This data treatment neglected heat capacity, hence assuming entropy and enthalpy changes were independent of temperature. This review calculates $\Delta_r H_m$ (12.21) = -82.40 , -85.86 , -86.91 $\text{kJ}\cdot\text{mol}^{-1}$ respectively. Extrapolation to zero ionic strength using the SIT and linear regression [94GIF/VIT] gives $\Delta_r H_m^\circ$ (12.21, 298.15 K) = $-(84.39 \pm 4.38)$ $\text{kJ}\cdot\text{mol}^{-1}$ and $T^\circ(d\Delta\varepsilon(12.21))/dT = (0.50 \pm 0.34)$ $\text{kg}\cdot\text{mol}^{-1}$, where T° is the standard temperature (298.15 K).

For comparison purposes, the simple mean of these enthalpy of reaction values at different ionic strengths is $-(85.06 \pm 4.63) \text{ kJ}\cdot\text{mol}^{-1}$. From $\Delta_r H_m^\circ(12.21, 298.15 \text{ K}) = -(84.39 \pm 4.38) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{NpO}_2(\text{CO}_3)_3^{5-}, 298.15 \text{ K}) = -(3017.12 \pm 6.89) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\circ(\text{Np}(\text{CO}_3)_5^{6-}, 298.15 \text{ K}) = -(3888.53 \pm 8.17) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated. From these values, $\Delta_r H_m^\circ(12.23, 298.15 \text{ K}) = (43.54 \pm 9.27) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated, which is very different from the corresponding (calorimetrically determined) uranium value $-(20.0 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}$ [92GRE/FUG]. For this reason the calculated enthalpy of formation value for $\text{Np}(\text{CO}_3)_5^{6-}$ is not selected.

12.1.2.1.4.e Discussion: Using Np analogues to estimate missing data

Table 12.7 provides a summary of equilibrium constant and enthalpy of reaction values for carbonate complexation as selected in the TDB volumes for U [92GRE/FUG, 95GRE/PUI], Np, Pu and Am [95SIL/BID]. Besides the values selected in this review, it seems reasonable to use trends in the numerical values of equilibrium constants measured within the actinide series (Th, U, Np, Pu and Am have been prepared in the +4 oxidation state in bicarbonate-carbonate media) by the same author, even when each value is not exactly the one selected in the present review. In such cases, several systematic errors should cancel. Rai *et al.* [95RAI/FEL, 97FEL/RAI, 98RAI/FEL] recently published data from solubility measurements of Th(IV) and U(IV). Results from similar Np(IV) studies [99RAI/HES] from this group were made available for this review prior to publication. Vitorge *et al.* [95VIT, 96CAP/VIT, 96DEL/VIT] published reliable data from spectrophotometric measurements or literature review on U(IV) and Pu(IV). They also estimated values for Np(IV), but with poorer accuracy. Hence, their Np(IV) data are not used below.

$\Delta_r H_m$		(5.0±2.0)			
$\log_{10} \beta_2$	$\text{MO}_2^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{MO}_2(\text{CO}_3)_2^{2-}$	(16.94±0.12)	(16.52±0.73)	(14.5±2.6)	
$\Delta_r H_m$		(18.5±4.0)		-(27.0±4.0)	
$\log_{10} \beta_3$	$\text{MO}_2^{2+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{MO}_2(\text{CO}_3)_3^{4-}$	(21.60±0.05)	(19.37±0.19)	(17.7±0.9)	
$\Delta_r H_m$		-(32.9±4.1)	-(41.9±4.1)	-(38.6±2.0)	
$\log_{10} \beta_{36}$	$3\text{MO}_2^{2+} + 6\text{CO}_3^{2-} \rightleftharpoons (\text{MO}_2)_3(\text{CO}_3)_6^{6-}$	(54.0±1.0)	(49.84±1.54)		
$\Delta_r H_m$		-(62.7±2.4)			
$\log_{10} (\beta_{36}/\beta_3^3)$	$3\text{MO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons (\text{MO}_2)_3(\text{CO}_3)_6^{6-} + 3\text{CO}_3^{2-}$	-(10.8±1.0)	-(8.27±1.45)		
	$2\text{UO}_2(\text{CO}_3)_3^{4-} + \text{MO}_2(\text{CO}_3)_3^{4-} \rightleftharpoons (\text{UO}_2)_2\text{MO}_2(\text{CO}_3)_6^{6-} + 3\text{CO}_3^{2-}$	-(10.8±1.0)	-(8.99±2.69)	-(8.2±1.3)	
$\log_{10} {}^* \beta_{2,1,3}$	$2\text{MO}_2^{2+} + \text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{MO}_2)_2\text{CO}_3(\text{OH})_3^- + 5\text{H}^+$	-(19.01±0.50)	-(21.38±1.62)		
$\log_{10} {}^* \beta_{3,1,3}$	$3\text{MO}_2^{2+} + \text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{MO}_2)_3\text{HCO}_3\text{O}(\text{OH})_2^+ + 5\text{H}^+$	-(17.5±0.5)			
$\log_{10} {}^* \beta_{11,6,12}$	$11\text{MO}_2^{2+} + 6\text{CO}_2(\text{g}) + 18\text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{MO}_2)_{11}(\text{CO}_3)_6(\text{OH})_{12}^{2-} + 24\text{H}^+$	-(19.01±0.50)			
$\log_{10} K_{s,0}$	$\text{MO}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{MO}_2^{2+} + \text{CO}_3^{2-}$	-(14.47±0.04)	-(14.60±0.47)	-(14.2±0.3)	
$\log_{10} K_{s,3}$	$\text{Na}_4\text{MO}_2(\text{CO}_3)_3(\text{s}) \rightleftharpoons 4\text{Na}^+ + \text{MO}_2(\text{CO}_3)_3^{4-}$	-(5.34±0.16)			
$\log_{10} K_{s,3}$	$\text{K}_4\text{MO}_2(\text{CO}_3)_3(\text{s}) \rightleftharpoons 4\text{K}^+ + \text{MO}_2(\text{CO}_3)_3^{4-}$			-(7.03±0.88)	
$\log_{10} K_{s,3}$	$(\text{NH}_4)_4\text{MO}_2(\text{CO}_3)_3(\text{s}) \rightleftharpoons 4\text{NH}_4^+ + \text{MO}_2(\text{CO}_3)_3^{4-}$			-(7.44±0.30)	
$\log_{10} (\beta_3^{\text{VI}}/\beta_3^{\text{V}})$	$\text{MO}_2^{2+} + \text{MO}_2(\text{CO}_3)_3^{5-} \rightleftharpoons \text{MO}_2^+ + \text{MO}_2(\text{CO}_3)_3^{4-}$	(14.19±0.26)	(13.87±0.12)	(13.0±0.6)	(13.9±1.6)
$\log_{10} \beta_1$	$\text{MO}_2^+ + \text{CO}_3^{2-} \rightleftharpoons \text{MO}_2\text{CO}_3^-$		(4.96±0.06)	(5.12±0.14)	
$\log_{10} \beta_2$	$\text{MO}_2^+ + 2\text{CO}_3^{2-} \rightleftharpoons \text{MO}_2(\text{CO}_3)_2^{3-}$		(6.53±0.10)		

(Continued on next page)

$\log_{10} K_{s,0}$	$\text{NaMO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}(\text{s, fresh}) \rightleftharpoons \text{Na}^+ + \text{MO}_2^+ + \text{CO}_3^{2-} + 3.5\text{H}_2\text{O}$			$-(11.16 \pm 0.35)$
$\log_{10} K_{s,0}$	$\text{NaMO}_2\text{CO}_3(\text{s, hyd, aged}) \rightleftharpoons \text{Na}^+ + \text{MO}_2^+ + \text{CO}_3^{2-}$			$-(11.66 \pm 0.50)$
$\log_{10} K_{s,0}$	$\text{Na}_3\text{MO}_2(\text{CO}_3)_2(\text{s, hyd}) \rightleftharpoons 3\text{Na}^+ + \text{MO}_2^+ + 2\text{CO}_3^{2-}$			$-(14.70 \pm 0.66)$
$\log_{10}(\beta_3^{\text{V}}/\beta_5^{\text{IV}})$	$\text{MO}_2^+ + \text{M}(\text{CO}_3)_5^{6-} \rightleftharpoons \text{M}^{4+} + \text{MO}_2(\text{CO}_3)_3^{5-} + 2\text{CO}_3^{2-}$	$-(26.5 \pm 1.0)$		$-(30.12 \pm 1.16)$
$\log_{10}\beta_5$	$\text{M}^{4+} + 5\text{CO}_3^{2-} \rightleftharpoons \text{M}(\text{CO}_3)_5^{6-}$	(33.9 ± 1.0)	(35.62 ± 1.15)	(39.3 ± 2.1)
$\Delta_r H_m$		$-(20.0 \pm 4.0)$		
$\log_{10} K_5$	$\text{M}(\text{CO}_3)_4^{4-} + \text{CO}_3^{2-} \rightleftharpoons \text{M}(\text{CO}_3)_5^{6-}$	$-(1.12 \pm 0.25)$	$-(1.07 \pm 0.30)$	$-(1.36 \pm 0.09)$
$\log_{10}(\beta_3^{\text{IV}}/\beta_3^{\text{III}})$	$\text{M}^{4+} + \text{M}(\text{CO}_3)_3^{3-} + 2\text{CO}_3^{2-} \rightleftharpoons \text{M}^{3+} + \text{M}(\text{CO}_3)_5^{6-}$		(19.96 ± 2.27)	(20.1 ± 0.9)
$\log_{10}\beta_1$	$\text{M}^{3+} + \text{CO}_3^{2-} \rightleftharpoons \text{MCO}_3^+$			(7.8 ± 0.3)
$\log_{10}\beta_2$	$\text{M}^{3+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{M}(\text{CO}_3)_2^-$			(12.3 ± 0.4)
$\log_{10}\beta_3$	$\text{M}^{3+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{M}(\text{CO}_3)_3^{3-}$		(15.66 ± 2.51)	(15.2 ± 0.6)
$\log_{10} K_{s,0}$	$\text{M}(\text{CO}_3)_{1.5}(\text{s}) \rightleftharpoons \text{M}^{3+} + 1.5\text{CO}_3^{2-}$			$-(16.7 \pm 1.1)$
$\log_{10} K_{s,0}$	$\text{MCO}_3\text{OH}(\text{s}) \rightleftharpoons \text{M}^{3+} + \text{CO}_3^{2-} + \text{OH}^-$			$-(21.2 \pm 1.4)$

Capdevila *et al.* [96CAP/VIT] showed that the dissociation of the Pu(IV) limiting complex (12.25) gave results similar to those for the corresponding U(IV) [89BRU/GRE, 92GRE/FUG] and Np(IV) [95VIT, 96DEL/VIT] systems. At high ionic strength, they estimated $\log_{10} K_5$ (12.25, 3M NaClO₄) decreased by $(1.09 \pm 0.35) \log_{10}$ unit from U to Pu. At zero ionic strength the corresponding decrease is (0.26 ± 0.27) . The $\log_{10} K_5^\circ$ value selected in the present review is also the same (within uncertainty) as those for U and Pu as selected in this series of reviews ([92GRE/FUG, 95GRE/PU], and Section 21.1.2.1.3 of the present review). Hence the differences in K_5 values within the actinide series from U to Pu are certainly not much more than the scatter of the data originated from different laboratories (when available). Nevertheless other dissociation schemes have been proposed in literature, typically for the limiting complex of Th(IV) [94OST/BRU, 97FEL/RAI, 98RAI/FEL]; experimental verification is therefore needed.

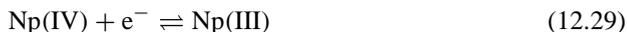
Clark *et al.* [98CLA/CON] and Rai *et al.* [95RAI/FEL, 97FEL/RAI, 98RAI/FEL] were able to explain their EXAFS spectra in terms of the $M(\text{CO}_3)_5^{6-}$ stoichiometry, and demonstrated that the limiting Pu(IV) carbonate complex is $\text{Pu}(\text{CO}_3)_5^{6-}$, thus confirming the interpretation used in this review. Rai *et al.* also produced solubility data confirming the steep increase of MO₂(am) solubility associated with $M(\text{CO}_3)_5^{6-}$ formation as predicted by Vitorge [95VIT]. Rai *et al.* reported $\log_{10} \beta_5^\circ$ (12.23) = 31.29, 33.79 and 34.18 for the U(IV), Np(IV) and Pu(IV) complexes, respectively [98RAI/FEL, 99RAI/HES, 99RAI/HES2]. The variation found by this group may be within the uncertainties, but there appears to be a slight increase of $\log_{10} \beta_5^\circ$ (12.23) from uranium to plutonium. The same group also determined a much smaller value for the corresponding Th(IV) complex [97FEL/RAI]. Capdevila *et al.* [96CAP/VIT] estimated a (1.1 ± 1.4) decrease in $\log_{10} \beta_5$ (12.23, 3M NaClO₄) at high ionic strength from U to Pu, and Vitorge [95VIT] also estimated the same trend at zero ionic strength. This decrease (1.8 ± 2.2) in $\log_{10} \beta_5^\circ$ (12.23) from U to Pu is also certainly within the uncertainties in the results (at least two orders of magnitude), and again no definite trend can be discerned. The same conclusion stands for the value selected in the present review for the Np complex at zero ionic strength; it is larger than the corresponding U and Pu values by (1.7 ± 1.5) and (2.4 ± 2.3) , respectively. Silva *et al.* [95SIL/BID], based [89ROB] on data from the redox study of Bourges *et al.* [83BOU/GUI], estimated a $\log_{10} \beta_5^\circ$ (12.23) value for Am(IV) larger by (5.3 ± 2.3) than the value for the corresponding uranium(IV) reaction (not unlike the result for Np(IV) discussed above for some of the calculations performed in the course of doing this review). It is clear that further experimental confirmation of the stoichiometry of the limiting complex and its stability constant are needed.

12.1.2.1.5 Np(III) carbonate complexes

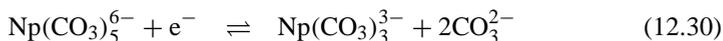
Np³⁺ can be prepared and stabilised in non-complexing (acidic) reducing aqueous solutions. For kinetic reasons, Np(III) is formed in some cases as an intermediary in the preparation of Np(IV) in carbonate solutions (see the discussions of [84VAR/HOB] in Appendix A and [96DEL/VIT, 95VIT]). Nevertheless, Np(III) complexes that may be formed in carbonate aqueous solutions, are probably not stable. As is the case for

Am^{3+} [95SIL/BID], the Np^{3+} cation is expected to be complexed by the carbonate anion in near-neutral or basic aqueous solutions. In such conditions, $\text{Np}(\text{OH})_4(\text{aq})$ or other $\text{Np}(\text{IV})$ complexes strongly stabilise neptunium in the +4 oxidation state, and $\text{Np}(\text{III})$ is usually oxidised to $\text{Np}(\text{IV})$ by water. For this reason, there have been no reliable experimental studies that can be used to propose thermodynamic values for the formation of intermediary $\text{Np}(\text{III})$ complexes in bicarbonate/carbonate media. Thus, no values for such complexes are selected in the present review. As a guideline, complexation constants of americium(III) [95SIL/BID] or lanthanide(III) chemical analogues could be used as reasonable approximations.

For the redox potential of the equilibrium,

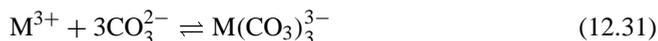


Fedoseev, Peretruckhin and Krot [79FED/PER] measured $E^\circ(12.29, 1 \text{ M K}_2\text{CO}_3) = -1.32 \text{ V/SHE}$. Varlashkin *et al.* [84VAR/HOB] measured similar values: $E^\circ(12.29, 1 \text{ M K}_2\text{CO}_3) = -1.3 \text{ V/SHE}$ and $E^\circ(12.29, 2 \text{ M Na}_2\text{CO}_3) = -1.2 \text{ V/SHE}$. These values confirm that $\text{Np}(\text{III})$ at equilibrium is oxidised by water in these media. As for the Am analogue [95SIL/BID], this review assumed the stoichiometry $\text{Np}(\text{CO}_3)_3^{3-}$ for the $\text{Np}(\text{III})$ limiting complex, and hence:



The stoichiometry $\text{M}(\text{CO}_3)_4^{5-}$ has been proposed for other $\text{M}(\text{III})$ analogues ($\text{M}=\text{Cm}$ or lanthanides); but was excluded for Am^{3+} . Silva *et al.* [95SIL/BID] concluded the limiting americium(III) species is $\text{Am}(\text{CO}_3)_3^{3-}$, and formation of $\text{Np}(\text{CO}_3)_3^{3-}$ is assumed in this review because $\text{Am}(\text{III})$ is usually the closest analogue for $\text{Np}(\text{III})$. However further confirmation is required.

From the shift between $E^\circ(12.29, 1 \text{ M K}_2\text{CO}_3) = 1.32 \text{ V/SHE}$ and the $\text{Np}^{4+}/\text{Np}^{3+}$ standard potential $E^\circ(7.9) = (0.219 \pm 0.010) \text{ V/SHE}$ (Section 7.5), $\log_{10}(\beta_{5(\text{IV})}(12.23)/\beta_{3(\text{III})}(12.31))(\text{M} = \text{Np}, 1 \text{ M Na}_2\text{CO}_3, \gamma_{\text{Np}^{4+}} = 1, \gamma_{\text{Np}^{3+}} = 1) = (26.08 \pm 1.70)$ (molal units) is calculated. Using $\log_{10}(\beta_{5(\text{IV})}(12.23), 1 \text{ M Na}_2\text{CO}_3, \gamma_{\text{Np}^{4+}} = 1, 298.15\text{K}) = (41.96 \pm 1.70)$ in molal units (Section 12.1.2.1.4.a), and assuming the same ionic strength corrections in K^+ and Na^+ media, $\log_{10}\beta_3(12.31, \text{M} = \text{Np}, 1 \text{ M K}_2\text{CO}_3, \gamma_{\text{Np}^{3+}} = 1) = (15.87 \pm 2.40)$ (molal units) is calculated for the equilibrium



while $\log_{10}\beta_3(12.31, \text{M} = \text{Am}, 1 \text{ M Na}_2\text{CO}_3, \gamma_{\text{Am}^{3+}} = 1) = (14.20 \pm 0.79)$ is calculated for $\text{Am}(\text{III})$ from $\log_{10}\beta_3^\circ(12.31, \text{M} = \text{Am}) = (15.2 \pm 0.6)$ and $\varepsilon_{(\text{Na}^+, \text{Am}(\text{CO}_3)_3^{3-})} = -(0.15 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ [95SIL/BID]. Using the same ionic strength corrections for $\text{Am}(\text{III})$ and $\text{Np}(\text{III})$ and for Na^+ and K^+ , $\log_{10}\beta_3^\circ(12.31, \text{M} = \text{Np}) = (16.9 \pm 2.5)$ is calculated. The $\text{Am}(\text{III})$ and $\text{Np}(\text{III})$ values are in reasonable agreement. A smaller value is expected for the smaller $\text{Am}(\text{III})$ cation. No value of $\beta_3(12.31)$ could be selected from these data.

However, as this review neared completion, a new study on Np(IV) solubility was used to select data from which $\log_{10} \beta_5^\circ(\text{IV})$ (12.23) = (35.62 ± 1.07) and $\varepsilon_{(\text{Np}(\text{CO}_3)_5^{6-}, \text{K}^+)} = -(0.73 \pm 0.68) \text{ mol}\cdot\text{kg}^{-1}$ were obtained (Section 12.1.2.1.4). By extrapolation of E° (12.29, 1 M K_2CO_3) to zero ionic strength (assuming $\varepsilon_{(\text{K}^+, \text{Np}(\text{CO}_3)_3^{3-})} = \varepsilon_{(\text{Na}^+, \text{Am}(\text{CO}_3)_3^{3-})}$)

$$E^\circ(12.30, 298.15 \text{ K}) = -(0.962 \pm 0.134) \text{ V/SHE}$$

$$\Delta_r G_m^\circ(12.30, 298.15 \text{ K}) = (92.82 \pm 12.93) \text{ kJ}\cdot\text{mol}^{-1}$$

are calculated and selected. From the latter, $\Delta_f G_m^\circ(\text{Np}(\text{CO}_3)_5^{6-}, 298.15 \text{ K})$ (Section 12.1.2.1.4) and $\Delta_f G_m^\circ(\text{CO}_3^{2-}, 298.15 \text{ K})$ (Table 5.1)

$$\Delta_f G_m^\circ(\text{Np}(\text{CO}_3)_3^{3-}, 298.15 \text{ K}) = -(2185.95 \pm 15.45) \text{ kJ}\cdot\text{mol}^{-1}$$

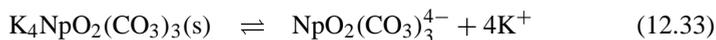
Then using values of E° (12.30) and the standard potential of the $\text{Np}^{4+}/\text{Np}^{3+}$ redox couple E° (7.9) as selected in this review (Section 7.5), $\log_{10}(\beta_5^\circ(\text{IV})/\beta_3^\circ(\text{III}), M = \text{Np}) = (19.96 \pm 2.27)$ and $\log_{10} \beta_3^\circ(12.31, M = \text{Np}) = (15.66 \pm 2.51)$ are calculated. The corresponding values for the americium system [95SIL/BID] are (20.1 ± 0.9) and (15.2 ± 0.6) , respectively.

12.1.2.2 Solid neptunium carbonates

12.1.2.2.1 Solid neptunium(VI) carbonates

There have been several publications on neptunium(VI) solubility in carbonate/bicarbonate aqueous solutions. The available experimental information is summarised in Table 12.1, where the results of reanalysis of data carried out in the present review are also provided.

In this review the solubility measurements of Gorbenko-Germanov and Klimov [66GOR/KLI] have been interpreted, and those of Moskvina [71MOS2] have been re-interpreted (see Table 12.1), as discussed by Vitorge and Capdevila [98VIT/CAP] considering the following equilibria:



This was done even though the solid phase $\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$ was not properly characterized. The corresponding equilibrium constants (Table 12.1) were extrapolated to zero ionic strength (see Appendix A) by performing linear SIT regressions with $\Delta\varepsilon$ (12.32), $-(0.70 \pm 0.14) \text{ kg}\cdot\text{mol}^{-1}$ and $\Delta\varepsilon$ (12.33) $-(0.54 \pm 0.37) \text{ kg}\cdot\text{mol}^{-1}$ from which

$$\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{NH}_4^+)} = -(0.78 \pm 0.25) \text{ kg}\cdot\text{mol}^{-1}$$

$$\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{K}^+)} = -(0.62 \pm 0.42) \text{ kg}\cdot\text{mol}^{-1}$$

were derived. The standard state equilibrium constants are

$$\log_{10} K_{s,3}^{\circ}(\text{12.32}, 298.15 \text{ K}) = -(7.44 \pm 0.30)$$

$$\log_{10} K_{s,3}^{\circ}(\text{12.33}, 298.15 \text{ K}) = -(7.03 \pm 0.88)$$

Hence

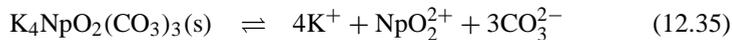
$$\Delta_r G_m^{\circ}(\text{12.32}, 298.15 \text{ K}) = (42.49 \pm 1.70) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r G_m^{\circ}(\text{12.33}, 298.15 \text{ K}) = (40.15 \pm 5.00) \text{ kJ}\cdot\text{mol}^{-1}$$

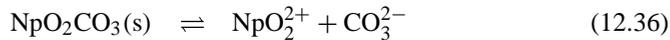
$$\Delta_f G_m^{\circ}((\text{NH}_4)_4\text{NpO}_2(\text{CO}_3)_3(\text{s}), 298.15 \text{ K}) = -(2850.29 \pm 6.11) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^{\circ}(\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s}), 298.15 \text{ K}) = -(3660.39 \pm 7.64) \text{ kJ}\cdot\text{mol}^{-1}$$

From these selected values of $\log_{10} K_{s,3}^{\circ}$ (12.32) and $\log_{10} K_{s,3}^{\circ}$ (12.33) and the value of $\log_{10} \beta_3^{\circ}$ (12.2) = (19.37 ± 0.19) (Section 12.1.2.1.2), the values $\log_{10} K_{s,0}^{\circ}$ (12.34) = -(26.81 ± 0.35) and $\log_{10} K_{s,0}^{\circ}$ (12.35) = -(26.40 ± 0.90) are calculated for



Vitorge and Capdevila's estimate of the solubility product for $\text{NpO}_2\text{CO}_3(\text{s})$ [98CAP/VIT] is recalculated in this review using the same method as the authors; but with the fixed β_3 (12.2) and $\beta_{6,3}$ (12.6) values selected by this review as was done when selecting the $\text{NpO}_2\text{CO}_3(\text{aq})$ and $\text{NpO}_2(\text{CO}_3)_2^{2-}$ formation constants (*cf.* Section 12.1.2.1.2). This value, $\log_{10} K_{s,0}^{\circ}$ (12.36, 3 M NaClO_4), is corrected to zero ionic strength using ϵ coefficients in Appendix B.



$$\log_{10} K_{s,0}^{\circ}(\text{12.36}, 298.15 \text{ K}) = -(14.60 \pm 0.47)$$

Hence,

$$\Delta_r G_m^{\circ}(\text{12.36}, 298.15 \text{ K}) = (83.32 \pm 2.68) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^{\circ}(\text{NpO}_2\text{CO}_3(\text{s}), 298.15 \text{ K}) = -(1407.16 \pm 6.23) \text{ kJ}\cdot\text{mol}^{-1}$$

As this review was nearing completion, further evidence for this solid was also reported by Kato *et al.* [96KAT/KIM]. Their measurement of the solubility product, as corrected in this review (Appendix A), is in agreement with the selected value.

12.1.2.2.2 Solid alkali metal neptunium(V) carbonate hydrates

A summary of the experimental information on neptunium(V) solubility in carbonate/bicarbonate aqueous solutions, and results of reanalysis of these data as carried out as part of the present review are provided in Tables 12.4 and 12.5.

The first publication discussing neptunium chemistry in carbonate media was a paper by Nigon *et al.* [54NIG/PEN] in which the preparation of a hydrated $\text{KNpO}_2\text{CO}_3(\text{s})$ solid was described. Keenan and Kruse [64KEE/KRU] later characterised a compound with the same stoichiometry. Keenan [65KEE] claimed that he prepared a $\text{CsAmO}_2\text{CO}_3(\text{s})$ compound, but not the corresponding $\text{Np}(\text{V})$ that should be easier to prepare (see Appendix A). Gorbenko-Germanov and Zenkova [66GOR/ZEN] precipitated $\text{M-Np}(\text{V})\text{-CO}_3$ solid compounds ($\text{M} = \text{K}, \text{Cs}$), with different stoichiometries, including $\text{K}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$, but equilibrium was probably not obtained, and the hydrated solid phases probably were changing during the course of the experiments (see Appendix A). Moskvina [71MOS2] prepared $\text{NH}_4\text{NpO}_2\text{CO}_3(\text{s})$ hydrated compounds, and Kharitonov and Moskvina [73KHA/MOS] reported an infrared spectrum, but the compounds were not characterised. The monoammonium solid was transformed into another (more stable) solid, possibly hydrated $(\text{NH}_4)_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$, when the aqueous $(\text{NH}_4)_2\text{CO}_3$ concentration was greater than 1.5 M (transformation may even have occurred in 0.6 M $(\text{NH}_4)_2\text{CO}_3$, see Appendix A). Volkov *et al.* later proposed a structure for this type of alkali metal carbonate compound ($\text{Np}(\text{V})$, $\text{Pu}(\text{V})$ and $\text{Am}(\text{V})$), in which alkali metal cations could be exchanged for the NH_4^+ or possibly divalent cations. However, as discussed in Appendix A, questions remain about some of the compounds and structures proposed in this series of papers (*e.g.*, [74VIS/VOL, 81VOL/VIS]).

Compounds for which published information is available, but for which no thermodynamic data can be derived include:

- $\text{MNpO}_2\text{CO}_3(\text{s})$ compounds for $\text{M}^+ = \text{Li}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+$ and NH_4^+ , [74VOL/KAP, 81VOL/VIS3];
- $\text{M}_{0.5}\text{NpO}_2(\text{CO}_3)_2(\text{s})$ hydrated compounds for $\text{M}^{2+} = \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}$ and Ba^{2+} [81VOL/VIS3] that were claimed to form from $\text{NaNpO}_2\text{CO}_3(\text{s})$ in concentrated MCl_2 or $\text{M}(\text{NO}_3)_2$ aqueous solutions;
- the hydrated compound $\text{Na}_{0.6}\text{NpO}_2(\text{CO}_3)_{0.8}$ that was proposed [79VOL/VIS]; but which might not be stable in contact with aqueous solutions [84VIT, 98VIT/CAP].

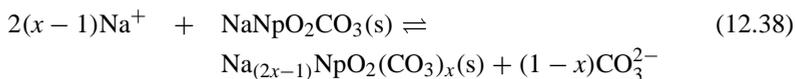
Simakin [77SIM] was the first author to use this qualitative information to measure and correctly interpret a solid/liquid equilibrium in the $\text{Np}(\text{V})$ carbonate system. He studied the equilibrium



In this review the value of the equilibrium constant $K_{s,3}$ (12.37) was calculated and selected (see Appendix A). Earlier (but indirect) evidence that solubility measurements

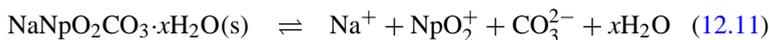
could be used to estimate the $\text{NaNpO}_2\text{CO}_3(\text{s})$ solubility product (and then $\Delta_r G$) came from Ueno and Saito [75UEN/SAI] as interpreted in Appendix A of the present review (the authors did not interpret their observations). As discussed in Appendix A, the results of these solubility measurements in 0.05 to 0.4 M Na_2CO_3 aqueous solutions can be reproduced using thermodynamic values selected in the present review from later work on aqueous $\text{Np}(\text{V})$ complexation. For solutions at higher CO_3^{2-} concentrations, similar to those in which Simakin prepared hydrated $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$, equilibrium was not obtained.

Maya [83MAY] first proposed a reliable solubility product value for a hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ compound in 1 M NaClO_4 aqueous solution. This value was used in the present review, but with an increased uncertainty (see Appendix A). Vitorge and co-workers [85CÔM, 85KIM, 86GRE/ROB, 90RIG, 98VIT/CAP] pointed out that characterisation of the solid phase was not straightforward. The X-ray diffraction patterns of his compounds could equally well be attributed to the $\text{Na}_{0.6}\text{NpO}_2(\text{CO}_3)_{0.8}(\text{s})$ compound, as prepared by Volkov *et al.* [79VOL/VIS2], that had received a thermal treatment (see Appendix A). Volkov *et al.* proposed an ion exchange reaction that can be written as

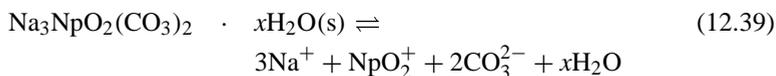


However, Vitorge [84VIT, 98VIT/CAP] showed that the solubilities could be interpreted in terms of gradual conversion of “freshly” precipitated hydrated $\text{Na}_{0.72}\text{NpO}_2(\text{CO}_3)_{0.86}(\text{s})$, to a compound having a stoichiometry closer to $\text{NaNpO}_2\text{CO}_3(\text{s})$ (see Appendix A). The equilibration time required for conversion at room temperature was found to be at least several weeks — more than the time reported in most other similar studies (also see [95NEC/RUN]). Thus, at least some of the solid compounds prepared by Volkov’s group were poorly crystallized, and equilibrium conditions with an aqueous phase were not always obtained. For $\text{MNpO}_2\text{CO}_3(\text{s})$ compounds, complex X-ray powder diffraction patterns with broad overlapping peaks have been used to propose structures, but single crystals have never been prepared. The patterns may also simply indicate the solids have low symmetry, are poorly crystallized or may even be mixtures of several compounds. The variations between the different X-ray diffraction patterns have been interpreted as resulting from variation in the lattice distances. This could be correlated with variation in the number of water molecules in the compounds [81VOL/VIS4], perhaps with the differences depending on how strongly the water in the solid is coordinated to the specific alkali metal cations (the heavier alkali metal cations are normally less hydrated). This is a reasonable explanation, but more experimental confirmation is needed. The proposed structures could also explain the reported ionic exchange properties but, as discussed above, other explanations based on kinetics are possible. These kinetic problems can induce variations in the solubility product measurements (lower values are expected for ripened, better crystallized solid phases). Although such differences are generally greater than corrections for ionic strength effects, they do not affect the value of the solubility product by much more than a factor of 10.

Kim *et al.* [91KIM/KLE], Meinrath [94MEI] and Neck and co-workers [94NEC/KIM, 94NEC/RUN, 95FAN/NEC, 95NEC/FAN, 95NEC/RUN] did not report any such problems with the solid phase they used for their solubility measurements. As discussed above in the selection of formation constants for the aqueous complexes (see Appendix A), the reported values for the $\text{NaNpO}_2\text{CO}_3(\text{s})$ solubility product, $K_{\text{s},0}$ (12.11) are first extrapolated to zero ionic strength, and the resulting standard value, $K_{\text{s},0}^\circ$ (12.11), is used in this review to derive the selected value.



The value of the corresponding $\Delta\varepsilon$ for Eq. 12.11 fitted in this review from these $K_{\text{s},0}$ (12.11) determinations at $I = 0.1$ to 3 M (see Appendix A) [91KIM/KLE, 94NEC/RUN], and using the values of $\varepsilon_{(\text{Na}^+, \text{ClO}_4^-)}$ and $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})}$ from Appendix B, results in the calculated value $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.34 \pm 0.10) \text{ kg} \cdot \text{mol}^{-1}$, while $(0.18 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ is calculated in the present review from the liquid-liquid extraction data of Neck *et al.* [94NEC/KIM, 95NEC/FAN]. Similar values can be obtained from calculated parameters proposed by the authors (*e.g.*, the values $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.31 \pm 0.08)$ or $(0.20 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$ from $\Delta\varepsilon = (0.21 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ [94NEC/RUN] or from the Pitzer parameters [95FAN/NEC], respectively). The mean, $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.255 \pm 0.185) \text{ kg} \cdot \text{mol}^{-1}$, of the two recalculated (statistically inconsistent) values from the two different experimental studies is in agreement with the value used in the present review $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.25 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$. Differences in the estimates of $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$ probably originated, at least in part, in the $\varepsilon_{(\text{CO}_3^{2-}, \text{Na}^+)}$ auxiliary values (Table 12.5). The ionic strength corrections proposed by the authors were not used in the present review. It cannot be ruled out that whatever problems is at the origin of the apparent inconsistency in the $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$ values extracted from the solubility product determinations, $K_{\text{s},0}$ (12.11), was also present in the rest of the solubility work. For this reason similar ionic strength corrections for the complexation constants, calculated from these solubility studies, were not used in this review (see Section 12.1.2.1.3.a). The same type of problem was found for the determinations of $K_{\text{s},0}$ (12.39), the solubility product for



Information in the one of the later papers from this group [96FAN/NEC] suggested that there may still be some minor systematic problems in their calibration procedures. As suggested by the authors, it is also possible that their work indicates a need to eventually revise auxiliary data (*e.g.*, the value for $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})}$) used in the present review (see the discussion of [96FAN/NEC] in Appendix A).

Lemire, Boyer and Campbell [93LEM/BOY] carried out solubility experiments with hydrated sodium and potassium Np(V) carbonate salts at 30 to 75°C, but their data are very scattered, especially at higher temperatures. They attributed this to slow

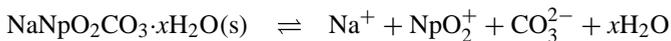
solid phase transformations, as was confirmed by X-ray analysis of their solids after liquid-solid equilibration (see also [84VIT, 98VIT/CAP]).

Such an explanation is also suggested by published complex X-ray diffraction patterns for $\text{NaNpO}_2\text{CO}_3(\text{s})$ (e.g., [96RUN/NEU]) which have broad overlapping bands (this is not the case for the diffraction pattern of $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$), and is in accord with other reported observations [84VIT, 86GRE/ROB, 90RIG, 98VIT/CAP] (but not with those of Neck *et al.* [94NEC/RUN], as discussed above, who claimed they did not have this problem). Lemire, Boyer and Campbell came to the conclusion that at least two different hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ solids were formed in the course of their experiments, possibly corresponding to one or more of the pairs of solids involved in the transformations suggested by Volkov, Visyashcheva and Kapshukov [77VOL/VIS]. This is possibly correct, but further confirmation is needed.

Therefore, it is concluded that in most of, if not all, the published solubility studies the hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ compound ripened gradually near 25°C , and a solid phase transformation is suspected just above room temperature. It is not clear whether this is a kinetic problem or whether (at least) two solubility products should be selected, however the corresponding scatter in the calculated solubility product values is not very large (about ± 0.5 in $\log_{10} K_s$, see the discussions of [84VIT, 93LEM/BOY] in Appendix A). The value of $\Delta\varepsilon$ has not been determined in the present review based on published experimental determinations of the solubility products, $K_{s,0}$ (12.11), at different ionic strengths (or of $K_{s,i}$ (12.10) = $K_{s,0}$ (12.11) β_i (12.12)), since the influence of this parameter is not much more than that due to the probable solid phase transformation. Instead, the $\Delta\varepsilon$ value is calculated from other (independent) sources (see above), and is used to compare the $K_{s,i}$ (12.10) ($i = 0, 1, 2$ and 3) determinations and to propose the following selected values:

$$\begin{aligned} \log_{10} K_{s,0}^\circ(12.11, x=3.5, 298.15 \text{ K}) &= -(11.16 \pm 0.35) \\ &\text{for freshly precipitated} \\ &\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}(\text{s}) \\ \Delta_r G_m^\circ(12.11, x=3.5, 298.15 \text{ K}) &= (63.68 \pm 2.01) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}(\text{s}), 298.15 \text{ K}) &= -(2591.29 \pm 5.99) \text{ kJ}\cdot\text{mol}^{-1} \\ \log_{10} K_{s,0}^\circ(12.11, x=0, 298.15 \text{ K}) &= -(11.66 \pm 0.50) \\ &\text{for aged or less hydrated NaNpO}_2\text{CO}_3(\text{s}) \\ \Delta_r G_m^\circ(12.11, x=0, 298.15 \text{ K}) &= (66.54 \pm 2.86) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{NaNpO}_2\text{CO}_3(\text{s}), 298.15 \text{ K}) &= -(1764.16 \pm 6.33) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

corresponding to the equilibrium 12.11



where x is unknown for the “aged or less hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ compound” (no H_2O molecule is taken into account when calculating ΔG_m values involving this last solid phase). These selected values are consistent with all published data, but, as for the $\text{Np}(\text{V})$ carbonate aqueous species, and as discussed in Appendix A (e.g.,

[94NEC/RUN]), for the work of Kim *et al.* [91KIM/KLE] and Neck and co-workers [94NEC/RUN, 95NEC/RUN] only the values extrapolated to zero ionic strength were used. The smallest reported solubility product value (near room temperature) was obtained at 30°C [93LEM/BOY], and the low value may be associated with the appearance of a new solid phase. The next lowest value was obtained in the work that probably used the longest equilibration time at room temperature [86GRE/ROB, 98VIT/CAP], reasonably followed by Maya's value [83MAY] as Maya probably used the shortest equilibration time. It is somewhat surprising that the ($I = 0$) solubility product value of Neck *et al.* [94NEC/RUN] corresponds to the more soluble compound. Although the value they reported for $I = 1$ M is the same as Maya's, their value for $I = 3$ M, is less than the value measured by Grenthe, Robouch and Vitorge [86GRE/ROB]. The reported effects of temperature on solubility [93LEM/BOY] were not used in this review to estimate $\Delta_r H$ for reactions involving these solid compounds, since solid phase transformations certainly cannot be neglected.

This review compared the published solubility product determinations (Figure 12.6) by plotting the experimentally determined $\log_{10} K_{s,0}^\circ$ (12.11) values minus the Debye-Hückel contribution (see Appendix B) as a function of the Na^+ molality. The scatter in the published values is likely primarily due to solid phase transformation. The lines are calculated from the data selected by this review — determinations in 1 and 3 M NaClO_4 aqueous solutions [83MAY, 86GRE/ROB] and from another set of data [94NEC/RUN] using only the values as extrapolated to $I = 0$. The other values are shown for comparison. The solid line corresponds to the solubility product for the freshly precipitated hydrated compound (the most probable value for the hydration number x is 3.5). The lower line corresponds to a more aged solid. The value of [93LEM/BOY] was determined at 30°C while the others were at 25°C or room temperature. Several values were recalculated in the course of the present review (Appendix A) from information in the original papers. As explained above, no linear regression is performed on the values shown in the figure; the slopes of the lines are, $-\Delta\varepsilon - 3.5r$, where $\Delta\varepsilon$ is calculated from the parameters of Appendix B, and r is the mean value of $(\log_{10} a_{\text{H}_2\text{O}})/m$.

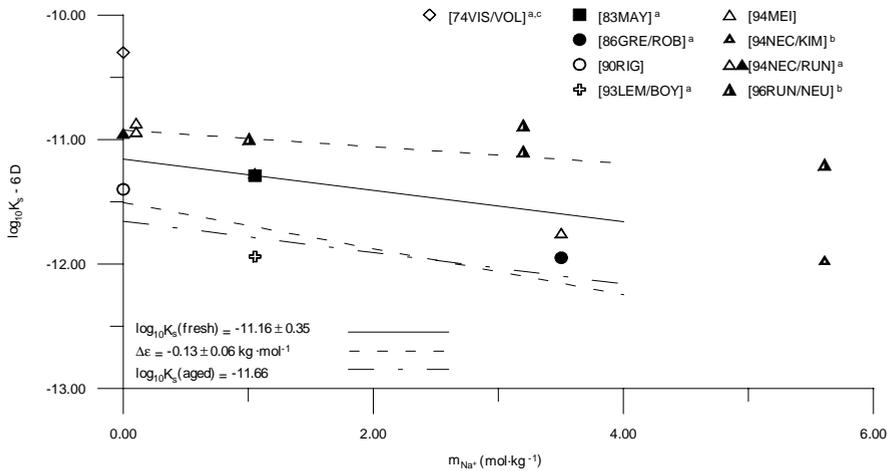
The same type of treatment to derive solubility products is done from the results of experiments using hydrated $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$. However, in this case it is not clear if there is a true solid phase dehydration transformation with increasing temperature between solids otherwise having the same stoichiometry, or whether there might be solid phases with stoichiometries between $\text{NaNpO}_2\text{CO}_3(\text{s})$ and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ (see Appendix A, [93LEM/BOY]).

The results for the equilibrium 12.37



are in Table 12.4 (see also Figure 12.7), but the extent of hydration of the solid is not known. The $K_{s,3}$ (12.37) value proposed in the present review is determined from Simakin's data [77SIM] and interpretation (see Appendix A), but is calculated by this review. The equilibrium constant value at $I = 3$ M NaNO_3 ,

Figure 12.6: Comparison of values of the solubility product, $K_{s,0}$ (12.11, $\text{mol}^3 \cdot \text{kg}^{-3}$), directly measured at room temperature, 25°C or 30°C ([93LEM/BOY]), and at different ionic strengths under conditions where the contribution of NpO_2^+ to the solubility is large ($\log_{10}[\text{CO}_3^{2-}] \leq -4$). The slopes $-\Delta\varepsilon$ of the lines (for aqueous NaClO_4 solutions) are calculated from ε values tabulated in Appendix B, not from linear regression. $K_s(\text{fresh})$ is the solubility product of the fresh precipitate $\text{NaNpO}_2\text{CO}_3(\text{s}) \cdot 3.5\text{H}_2\text{O}$; the mean value of $\log_{10}(a_{\text{H}_2\text{O}})/m$ is included in $\Delta\varepsilon$ and the uncertainty is shown by the dashed lines. For the aged precipitate (---, uncertainties not shown) the stoichiometry $\text{NaNpO}_2\text{CO}_3(\text{s})$ is assumed, and the slope is also $-\Delta\varepsilon = -0.13 \text{ kg} \cdot \text{mol}^{-1}$. As noted in the legend, values, some recalculated in this review (a), cf. Appendix A, were determined from measurements in NaClO_4 , in NaCl (b) or in dilute K^+ media (c) (in contact with hydrated $\text{KNpO}_2\text{CO}_3(\text{s})$). In this latter case, $x = m_{\text{K}^+}$ and not m_{Na^+} .



$\log_{10} K_{s,3}$ (12.37) = $-(1.46 \pm 0.09)$, is greater than the mean values estimated by Vitorge and co-workers [85CÔM, 85KIM, 86GRE/ROB, 90RIG, 98VIT/CAP], and this is clearly due to evolution of the solid. The value selected in the present review,

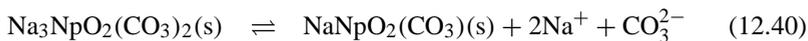
$$\begin{aligned}\log_{10} K_{s,3}^{\circ}(\text{12.37}, 298.15\text{K}) &= -(9.20 \pm 0.65) \\ \Delta_r G_m^{\circ}(\text{12.37}, 298.15\text{K}) &= (52.52 \pm 3.70) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^{\circ}(\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s}), 298.15\text{K}) &= -(2833.33 \pm 6.84) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

and hence,

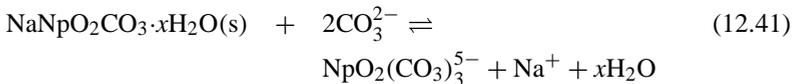
$$\begin{aligned}\log_{10} K_{s,0}^{\circ}(\text{12.39}, 298.15\text{K}) &= -(14.70 \pm 0.66) \\ \Delta_r G_m^{\circ}(\text{12.39}, 298.15\text{K}) &= (83.91 \pm 3.80) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

(based on Simakin's work [77SIM]) refers to the freshly precipitated compound. The value from data at $I = 3$ M as determined by Kim *et al.* and Neck *et al.* [91KIM/KLE, 94NEC/RUN] is even smaller, but is in accord with that of Simakin when extrapolated to zero ionic strength (see also comments in Appendix A concerning possible systematic errors at high ionic strength). Some solubilities measured by Lemire, Boyer and Campbell [93LEM/BOY] at 30°C and some values reported by Vitorge and co-workers for 25°C are even smaller, probably because a new phase was formed (see the discussion of [93LEM/BOY] in Appendix A). The mean value of $\log_{10} K_{s,0}^{\circ}$ (12.39) based on all the reported determinations [77SIM, 86GRE/ROB, 93LEM/BOY, 95NEC/RUN, 98VIT/CAP] is $-(9.68 \pm 1.01)$ (maximum -8.67 , minimum -10.67).

Values from some references [85CÔM, 85KIM, 86GRE/ROB, 90RIG, 98VIT/CAP] cannot be used because the solubility was changing with time. The equilibrium constant for transformation of hydrated $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ into hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$



can be calculated from the two solubility products $K_{s,3}$ (12.37) and $K_{s,3}$ (12.41)



($\log_{10} K^{\circ}$ (12.40, 298.15K) = $\log_{10} K_{s,3}^{\circ}$ (12.37) - $\log_{10} K_{s,3}^{\circ}$ (12.41, $x = 3.5$) = $-(3.54 \pm 0.75)$) or directly (Figure 12.8). Hence, $\Delta_r G_m^{\circ}$ (12.40, 298.15K) = $(20.23 \pm 4.29) \text{ kJ}\cdot\text{mol}^{-1}$.

Thermodynamic equilibrium between the two solid phases and 1 M NaClO_4 aqueous solutions is obtained for $\log_{10}[\text{CO}_3^{2-}] = -2.3$. This value is consistent with experimental observations [93LEM/BOY, 86GRE/ROB, 95NEC/RUN]; but equilibrium is difficult to obtain for kinetic reasons [93LEM/BOY, 98VIT/CAP].

In the present review, values for $K_{s,3}$ (12.41) and $K_{s,3}$ (12.37) are also estimated for the corresponding K^+ [66GOR/ZEN, 93LEM/BOY], Cs^+ [66GOR/ZEN] and NH_4^+ [71MOS2] compounds in various media (Table 12.4). However, no values have been

Figure 12.7: Comparison of values (some recalculated (a) in the present review, *cf.*, Appendix A) of $K_{s,3}$ (12.37, $\text{mol}^3 \cdot \text{kg}^{-3}$), directly measured at room temperature, 25°C or 30°C ([93LEM/BOY]), and at different ionic strengths under conditions where the contribution of $\text{NpO}_2(\text{CO}_3)_5^{3-}$ to the solubility is large ($\log_{10}[\text{CO}_3^{2-}] \geq -2$). The values of $\log_{10}K_{s,3}$ minus the Debye-Hückel correction, and corrected for the appropriate M^+ specific interaction coefficient, are plotted as a function of the M^+ molality ($M^+ = \text{Na}^+, \text{K}^+$ or NH_4^+). The slope of the line (for aqueous NaClO_4 solutions), $\Delta\varepsilon = -(0.45 \pm 0.19) \text{ kg} \cdot \text{mol}^{-1}$, is calculated using the data selected in the present review and in Appendix B. The intercept is $\log_{10}K_{s,3}^0 = -(9.20 \pm 0.65)$. Effects related to the extent of hydration of the solid $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}$ are small; — $x = 0$; — — $x = 3.5$. Values were determined from measurements in NaClO_4 , or in NaNO_3 (b), Na_2CO_3 (c), K_2CO_3 (d) or $(\text{NH}_4)_2\text{CO}_3$ (e) media as noted in the legend.

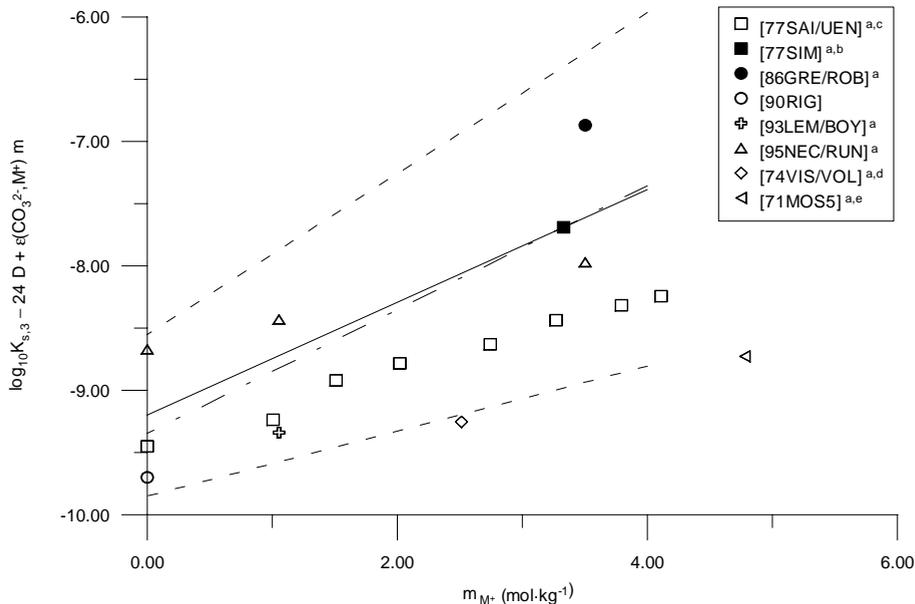
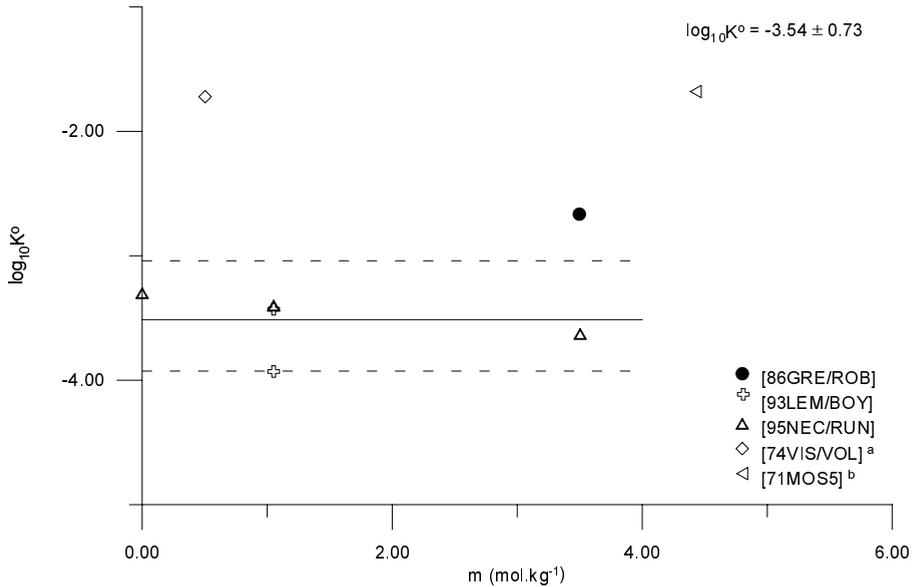


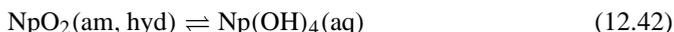
Figure 12.8: Comparison of values of K (12.40). Plotted values are from published data for NaClO_4 media, re-evaluated in the present review and corrected to $I=0$. The line, $\log_{10}K^\circ = -(3.54 \pm 0.73)$ is calculated using the $K_{s,3}$ (12.37) and $K_{s,3}$ (12.41) values selected in the present review. Any effects related to water of hydration have been neglected. Data for other media are also shown ((a) K_2CO_3 and (b) $(\text{NH}_4)_2\text{CO}_3$; see legend). On the x axis, $m = m_{\text{K}^+}$, m_{Na^+} or $m_{\text{NH}_4^+}$.



selected for standard conditions because: (a) the solid phases were undoubtedly changing during the solubility measurements, and (b) the ion interaction coefficients, ε , could not be accurately estimated for solutions containing cations other than Na^+ as the predominant cation, especially for reactions involving the highly charged limiting complex.

12.1.2.2.3 Np(IV) Solid phases equilibrated with carbonate / bicarbonate aqueous solutions

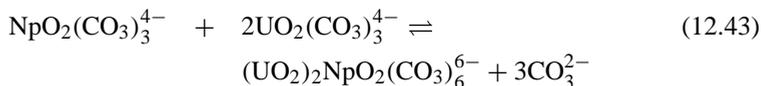
Np(IV) solubility in neutral media is $10^{-(8.3 \pm 0.3)} \text{mol} \cdot \text{dm}^{-3}$ (Section 8.1.4) and was interpreted in terms of the equilibrium



[85RAI/RYA]. Hence, in these conditions, no carbonate solid phase containing Np(IV) was formed. In more concentrated alkali metal carbonate media, the solubility [71MOS2, 77SAI/UEN, 93LI/KAT, 99RAI/HES] increased as a result of $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$ formation [95VIT]. This is undoubtedly limited by some new solid phase or phases [77SAI/UEN, 95VIT], possibly including alkali metal cations and $\text{Np}(\text{CO}_3)_6^{5-}$ anions. No thermodynamic data could be estimated for these possible solid phases.

12.1.2.3 Mixed actinide carbonate complexes

Values for the equilibrium constants for formation of complexes of the type $(\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^{6-}$ according to the reaction



have been discussed previously in this series of reviews [92GRE/FUG, 95GRE/PUJ]. The assessed values were $\log_{10} K^\circ = -(9.4 \pm 1.3)$ for the Np equilibrium, and $-(8.2 \pm 1.3)$ for the plutonium equilibrium (also *cf.* Section 21.1.2.1.1.e). These selections were based on Grenthe, Riglet and Vitorge's spectrophotometric determination for the neptunium containing species $\log_{10} K(12.43, 3\text{MNaClO}_4) = -(10.0 \pm 0.2)$ [86GRE/RIG, 90RIG]. This work is also accepted in the present review, but with an increased uncertainty, equal to the uncertainty assigned in the re-evaluation for the pure Np(VI) trinuclear complex. The earlier work used the same ionic strength corrections for all the formation constants of complexes of the type $(\text{UO}_2)_2\text{MO}_2(\text{CO}_3)_6^{6-}$ ($\text{M} = \text{U}, \text{Np}, \text{Pu}$). This correction, using $\Delta\varepsilon = (0.16 \pm 0.36) \text{kg} \cdot \text{mol}^{-1}$ [95GRE/PUJ], was only measured for the pure uranium trinuclear complex ($\text{M}=\text{U}$). Instead of $-(9.4 \pm 1.3)$, $\log_{10} K^\circ(12.43) = -(9.2 \pm 1.3)$ is calculated for formation constant of the mixed U-Np trinuclear carbonate complex, using $\Delta\varepsilon = (0.49 \pm 0.50) \text{kg} \cdot \text{mol}^{-1}$ estimated in the present review for the pure neptunium trinuclear complex. This review estimates

$$\varepsilon_{((\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^{6-}, \text{Na}^+)} = (0.09 \pm 0.71) \text{kg} \cdot \text{mol}^{-1}$$

as the weighted mean of the uranium and neptunium corresponding values $\varepsilon_{((\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^-, \text{Na}^+)} = (2\varepsilon_{((\text{UO}_2)_3(\text{CO}_3)_6^-, \text{Na}^+)} + \varepsilon_{((\text{NpO}_2)_3(\text{CO}_3)_6^-, \text{Na}^+)})/3$. Then $\Delta\varepsilon(12.43) = (0.27 \pm 0.77) \text{ kg}\cdot\text{mol}^{-1}$ is calculated and used to extrapolate the above value, $\log_{10} K(12.43, 3 \text{ M NaClO}_4) = -(10.0 \pm 0.3)$ to zero ionic strength:

$$\log_{10} K^\circ(12.43, 298.15\text{K}) = -(8.99 \pm 2.69)$$

Hence,

$$\Delta_r G_m^\circ(12.43, 298.15\text{K}) = (51.29 \pm 15.36) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ((\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^-, 298.15\text{K}) = -(6174.31 \pm 16.98) \text{ kJ}\cdot\text{mol}^{-1}$$

$\log_{10} K^\circ(12.44, 298.15\text{K}) = (53.59 \pm 2.70)$ and $\Delta_r G_m^\circ(12.44, 298.15\text{K}) = -(305.87 \pm 15.40) \text{ kJ}\cdot\text{mol}^{-1}$ are calculated for the equilibrium



from the above selected values.

12.1.3 Neptunium cyanide complexes

Formation constants ($\log_{10} \beta_n = 2.90, 3.23, 4.81, 5.11$ and $5.94, n=1-5$) for cyano complexes of dioxoneptunium(V), $\text{NpO}_2(\text{CN})_n^{1-n}$ ($n = 1-5$) at 25°C , $I = 5$ ($\text{mol}\cdot\text{dm}^{-3}$) have been reported [77CUI/MUS, 78MUS/MAR], based on a spectroscopic study (970 to 1060 nm) at pH values between 6.2 and 9.4. Insoluble complex solids, tentatively identified as $\text{NaNpO}_2(\text{CN})_2\cdot x\text{H}_2\text{O}$ and $\text{NpO}_2\text{CN}\cdot y\text{H}_2\text{O}$ were also found to form in concentrated solutions of $\text{NaCN}(\text{aq})$, and solubilities in 2M NaCN ($5\text{M Na}^+(\text{aq})$) were reported. As discussed in Appendix A, although there is good evidence for complex formation, the results of this work cannot be used to derive serviceable values for $I = 0$, and the stoichiometries of the major complexes and solids need to be confirmed by other experiments.

12.1.4 Neptunium thiocyanate complexes

12.1.4.1 Aqueous Np(IV) thiocyanate complexes

The formation of thiocyanate complexes of Np(IV) has been studied by Rao *et al.* [78RAO/BAG2] using solvent extraction. This is a careful and comprehensive study (see discussion in Appendix A). The authors reported equilibrium constants for three reactions of the type:



Their results are summarized in Table 12.8.

For extrapolation of the 1:1 and 1:2 data to $I = 0$, we use the $\Delta\varepsilon$ values that were used for the corresponding U(IV) system,

Table 12.8: Experimental equilibrium data for the neptunium(IV) thiocyanate system, pH = 0.

Method	Ionic medium	t (°C)	$\log_{10} \beta_q^{(a)}$	$\log_{10} \beta_q^{\circ(b)}$	Reference
$\text{Np}^{4+} + \text{SCN}^- \rightleftharpoons \text{NpSCN}^{3+}$					
dis-TTA	2 M (H, Na)ClO ₄	10	(1.53 ± 0.01)		[78RAO/BAG2]
	2 M (H, Na)ClO ₄	25	(1.49 ± 0.07)	3.03 ^(c)	
	2 M (H, Na)ClO ₄	40	(1.40 ± 0.01)		
dis-DNNS	2 M (H, Na)ClO ₄	25	(1.48 ± 0.06)	3.02 ^(c)	
$\text{Np}^{4+} + 2 \text{SCN}^- \rightleftharpoons \text{Np}(\text{SCN})_2^{2+}$					
dis-TTA	2 M (H, Na)ClO ₄	10	(2.25 ± 0.03)		[78RAO/BAG2]
	2 M (H, Na)ClO ₄	25	(2.06 ± 0.08)	4.02 ^(c)	
	2 M (H, Na)ClO ₄	40	(2.13 ± 0.03)		
dis-DNNS	2 M (H, Na)ClO ₄	25	(2.26 ± 0.05)	4.22 ^(c)	
$\text{Np}^{4+} + 3 \text{SCN}^- \rightleftharpoons \text{Np}(\text{SCN})_3^+$					
dis-TTA	2 M (H, Na)ClO ₄	10	(2.61 ± 0.03)		[78RAO/BAG2]
	2 M (H, Na)ClO ₄	25	(2.53 ± 0.02)	4.81 ^(c)	
	2 M (H, Na)ClO ₄	40	(2.34 ± 0.04)		
dis-DNNS	2 M (H, Na)ClO ₄	25	(2.50 ± 0.03)	4.78 ^(c)	

^(a) $\log_{10} \beta_q$ refers to the equilibrium and the ionic strength given in the table.

^(b) $\log_{10} \beta_q^{\circ}$ is the corresponding value corrected to $I = 0$ at 298.15 K.

^(c) The uncertainties given by the authors do not include systematic errors and have therefore not been propagated to zero ionic strength.

$\Delta\varepsilon(12.45, q = 1) = -(0.13 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ and $\Delta\varepsilon(12.45, q = 2) = -(0.56 \pm 0.19) \text{ kg}\cdot\text{mol}^{-1}$, after increasing the uncertainties by ± 0.05 due to the estimation by analogy. For the 1:3 reaction, we use $\varepsilon_{(\text{Np}(\text{SCN})_3^+)} \approx \varepsilon_{(\text{AmF}_2^+)} = 0.17 \text{ kg}\cdot\text{mol}^{-1}$, which results in $\Delta\varepsilon(12.45, q = 3) = -(0.82 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}$, after increasing the uncertainty by ± 0.05 due to the analogy made. The resulting values at $I = 0$ are listed in Table 12.8. The values at 25°C determined with TTA and DNNS agree well. We estimate that the uncertainties of these values, taking systematic errors into account, are around ± 0.1 logarithmic units for the formation of the 1:1 complex and ± 0.2 for the 1:2 and 1:3 complexes. We select the average of these values and assign uncertainties that reflect the fact that no independent study is available on this system.

$$\log_{10} \beta_1^\circ(12.45, q = 1, 298.15 \text{ K}) = 3.0 \pm 0.3$$

$$\log_{10} \beta_2^\circ(12.45, q = 2, 298.15 \text{ K}) = 4.1 \pm 0.5$$

$$\log_{10} \beta_3^\circ(12.45, q = 3, 298.15 \text{ K}) = 4.8 \pm 0.5$$

Rao *et al.* [78RAO/BAG2] performed their measurements at 10, 25 and 40°C, *cf.* Table 12.8. From the temperature dependence of the resulting equilibrium constants, they derived enthalpy values, *cf.* Appendix A. The values of β_2 at different temperatures show no steady variation, which gives an indication of appreciable uncertainty. Due to lack of information, we assume the enthalpies to be independent of the ionic strength and assign the uncertainties accordingly.

$$\Delta_r H_m^\circ(12.45, q = 1, 298.15 \text{ K}) = -(7 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m^\circ(12.45, q = 2, 298.15 \text{ K}) = -(9 \pm 9) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m^\circ(12.45, q = 3, 298.15 \text{ K}) = -(13 \pm 9) \text{ kJ}\cdot\text{mol}^{-1}$$

The thermodynamic formation data are derived from these constants and the selected data for Np^{4+} and SCN^- :

$$\Delta_f G_m^\circ(\text{NpSCN}^{3+}, \text{aq}, 298.15 \text{ K}) = -(416 \pm 7) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Np}(\text{SCN})_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(330 \pm 10) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Np}(\text{SCN})_3^+, \text{aq}, 298.15 \text{ K}) = -(241 \pm 14) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{NpSCN}^{3+}, \text{aq}, 298.15 \text{ K}) = -(487 \pm 7) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{Np}(\text{SCN})_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(412 \pm 13) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{Np}(\text{SCN})_3^+, \text{aq}, 298.15 \text{ K}) = -(340 \pm 16) \text{ kJ}\cdot\text{mol}^{-1}$$

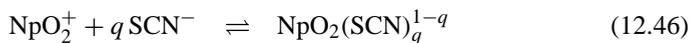
$$S_m^\circ(\text{NpSCN}^{3+}, \text{aq}, 298.15 \text{ K}) = -(248 \pm 25) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^\circ(\text{Np}(\text{SCN})_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(90 \pm 51) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^\circ(\text{Np}(\text{SCN})_3^+, \text{aq}, 298.15 \text{ K}) = (55 \pm 66) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

12.1.4.2 Aqueous Np(V) thiocyanate complexes

Formation constants of Np(V) thiocyanate complexes according to the reaction:



have been reported in four papers [77CUI/MUS, 77MUS/MAR, 79RAO/GUD, 81PAT/RAM]. Rao *et al.* [79RAO/GUD] have verified that Np(V) keeps its oxidation state during the experiments, although a reduction to Np(IV) by SCN^- would be thermodynamically favoured. The published experimental data are summarized in Table 12.9. High thiocyanate concentrations are necessary for these complexes to form. In two studies, complexes with $q > 2$ were proposed [77CUI/MUS, 77MUS/MAR], but the effects leading to these results, probably also for $q = 2$, could equally well be interpreted in terms of activity factor changes.

A comparison of the results of the two earlier studies [77CUI/MUS, 77MUS/MAR] shows a marked decrease of the stability constants from $I = 9 \text{ M}$ to $I = 5 \text{ M}$, suggesting that activity factor effects have a substantial impact on the results. No valid model is available to extrapolate the high ionic strength results to $I = 0$. The constant determined at $I = 2 \text{ M}$ originates from a reliable study [79RAO/GUD] (*cf.* Appendix A). An attempt to extrapolate this value to $I = 0$, using $\Delta\varepsilon(12.46, q = 1) = -(0.30 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$ from the corresponding ε values in Appendix B, yields $\log_{10} \beta_1^\circ(12.46, q = 1) = (0.08 \pm 0.30)$ where the uncertainty is an estimate. This value may be used as a guideline, but it is not recommended by the present review.

12.1.4.3 Aqueous Np(VI) thiocyanate complexes

No experimental data are available on the formation of Np(VI) thiocyanate complexes. Rao *et al.* [78RAO/BAG2] expected the study of Np(VI) thiocyanate complexing to be rather difficult, because Np(VI) would be reduced in the presence of SCN^- .

Table 12.9: Experimental equilibrium data for the neptunium(V) thiocyanate system.

Method	Ionic medium	t (°C)	$\log_{10} \beta_q^{(a)}$	Reference
$\text{NpO}_2^+ + \text{SCN}^- \rightleftharpoons \text{NpO}_2\text{SCN}(\text{aq})$				
sp	5 M (NaClO ₄)	25	0.86	[77CUI/MUS]
pot	9 M (NaClO ₄)	25	1.03	[77MUS/MAR]
sp	9 M (NaClO ₄)	25	1.23	
dis	2 M (H, Na)ClO ₄	25	(0.32 ± 0.02)	[79RAO/GUD]
dis	8.5 M (H, Na)ClO ₄	25	0.91	[81PAT/RAM]
$\text{NpO}_2^+ + 2 \text{SCN}^- \rightleftharpoons \text{NpO}_2(\text{SCN})_2^-$				
sp	5 M (NaClO ₄)	25	1.05	[77CUI/MUS]
pot	9 M (NaClO ₄)	25	1.56	[77MUS/MAR]
sp	9 M (NaClO ₄)	25	1.91	
dis	8.5 M(H, Na)ClO ₄	25	1.07	[81PAT/RAM]
$\text{NpO}_2^+ + 3 \text{SCN}^- \rightleftharpoons \text{NpO}_2(\text{SCN})_3^{2-}$				
sp	5 M (NaClO ₄)	25	0.89	[77CUI/MUS]
pot	9 M (NaClO ₄)	25	1.60	[77MUS/MAR]
sp	9 M (NaClO ₄)	25	2.04	
$\text{NpO}_2^+ + 4 \text{SCN}^- \rightleftharpoons \text{NpO}_2(\text{SCN})_4^{3-}$				
sp	5 M (NaClO ₄)	25	-0.11	[77CUI/MUS]
pot	9 M (NaClO ₄)	25	1.56	[77MUS/MAR]
sp	9 M (NaClO ₄)	25	1.72	
$\text{NpO}_2^+ + 5 \text{SCN}^- \rightleftharpoons \text{NpO}_2(\text{SCN})_5^{4-}$				
sp	9 M (NaClO ₄)	25	0.46	[77MUS/MAR]

^(a) $\log_{10} \beta_q$ refers to the equilibrium and the ionic strength given in the table.

Chapter 13

Neptunium group 2 (alkaline-earth) compounds

Several ternary oxides of alkaline earth elements with neptunium have been reported, and general synthesis and X-ray diffraction data for these compounds have been summarised by Fahey [86FAH] and references therein. However, chemical thermodynamic data for these compounds are relatively limited.

The thermodynamic quantities calculable from the available experimental data are exclusively enthalpies of formation. Gibbs energies would, of course, be more useful for thermodynamic modelling. However, in this review no entropy (or Gibbs energy) values are estimated for the mixed alkaline earth/neptunium oxides nor for the mixed alkali metal/neptunium oxides (Chapter 14). Entropies determined experimentally for uranium solids (*e.g.* γ – $\text{UO}_3(\text{cr})$) give a clear indication that entropies for M(VI) oxides are likely to be greater than those predicted based on “Latimer type” contributions derived from entropies of M(III) or M(IV) solids (see [92GRE/FUG], especially Appendix D). However, $\text{NpO}_3(\text{cr})$ does not exist, and no information is available from direct measurements on the hydrated Np(VI) oxides.

13.1 Neptunium strontium compounds

13.1.1 $\text{Sr}_3\text{NpO}_6(\text{cr})$

Morss *et al.* [83MOR/WIL] measured the enthalpy of solution of $\text{Sr}_3\text{NpO}_6(\text{cr})$ in 1.0 M HCl, obtaining $\Delta_f H_m^\circ(\text{Sr}_3\text{NpO}_6, \text{cr}, 298.15 \text{ K}) = -(3125.3 \pm 5.8) \text{ kJ}\cdot\text{mol}^{-1}$. Using CODATA compatible auxiliary data the value

$$\Delta_f H_m^\circ(\text{Sr}_3\text{NpO}_6, \text{cr}, 298.15 \text{ K}) = -(3125.8 \pm 5.9) \text{ kJ}\cdot\text{mol}^{-1}$$

is obtained from a recalculation in this review. The value is accepted here.

13.2 Neptunium barium compounds

13.2.1 $\text{Ba}_3\text{NpO}_6(\text{cr})$

Morss *et al.* [83MOR/WIL] measured the enthalpy of solution of $\text{Ba}_3\text{NpO}_6(\text{cr})$ in 1.0 M HCl, obtaining $\Delta_f H_m^\circ(\text{Ba}_3\text{NpO}_6, \text{cr}, 298.15 \text{ K}) = -(3086.0 \pm 7.7) \text{ kJ}\cdot\text{mol}^{-1}$. Using

CODATA compatible auxiliary data the value

$$\Delta_f H_m^\circ(\text{Ba}_3\text{NpO}_6, \text{cr}, 298.15 \text{ K}) = -(3085.6 \pm 9.6) \text{ kJ}\cdot\text{mol}^{-1}$$

is obtained from a recalculation in this review. The value is accepted here.

13.2.2 Barium alkaline-earth compounds

Enthalpy of formation data have been reported for three barium alkaline-earth compounds, the perovskite-type oxides of the form $\text{Ba}_2\text{MNpO}_6(\text{cr})$ with $\text{M} = \text{Mg}, \text{Ca}$ and Sr .

No entropy or Gibbs energy values are available for these compounds.

13.2.2.1 $\text{Ba}_2\text{MgNpO}_6(\text{cr})$

Based on the enthalpy of reaction of $\text{Ba}_2\text{MgNpO}_6(\text{cr})$ with 1 M HCl reported by Morss, Fuger and Jenkins [82MOR/FUG] and auxiliary data discussed in Appendix A,

$$\Delta_f H_m^\circ(\text{Ba}_2\text{MgNpO}_6, \text{cr}, 298.15 \text{ K}) = -(3096.9 \pm 8.2) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated and accepted in this review.

13.2.2.2 $\text{Ba}_2\text{CaNpO}_6(\text{cr})$

The value of the heat of solution of $\text{Ba}_2\text{CaNpO}_6(\text{cr})$ in 1 M HCl was reported by Gens *et al.* [85GEN/FUG] from nine replicate measurements on two well-characterised samples. From this and auxiliary data in Appendix A, the recommended value

$$\Delta_f H_m^\circ(\text{Ba}_2\text{CaNpO}_6, \text{cr}, 298.15 \text{ K}) = -(3159.3 \pm 7.9) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated.

13.2.2.3 $\text{Ba}_2\text{SrNpO}_6(\text{cr})$

The value of the heat of solution of $\text{Ba}_2\text{SrNpO}_6(\text{cr})$ in 1 M HCl was reported by Gens *et al.* [85GEN/FUG] from nine replicate measurements on two well-characterised samples. From this and auxiliary data in Appendix A, the recommended value

$$\Delta_f H_m^\circ(\text{Ba}_2\text{SrNpO}_6, \text{cr}, 298.15 \text{ K}) = -(3122.5 \pm 7.8) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated.

Chapter 14

Neptunium group 1 (alkali) compounds

Several ternary oxides of alkali metal elements with neptunium have been reported, and general synthesis and X-ray diffraction data for these compounds have been summarised by Fahey [86FAH] and references therein. However, chemical thermodynamic data for these compounds are relatively limited.

14.1 Neptunium lithium compounds

14.1.1 Li_2NpO_4 (cr)

The value

$$\Delta_f H_m^\circ(\text{Li}_2\text{NpO}_4, \text{cr}, 298.15 \text{ K}) = -(1828.2 \pm 5.8) \text{ kJ}\cdot\text{mol}^{-1}$$

is accepted, based on a recalculation (*cf.* Appendix A) of the value reported by Goudiakas, Jemine and Fuger [91GOU/JEM] from measurements of the enthalpy of solution of the solid in 1 M HCl.

14.1.2 $\text{Li}_2\text{Np}_2\text{O}_7$ (cr)

Fuger [85FUG] reported that the attempted synthesis of $\text{Li}_2\text{Np}_2\text{O}_7$ (cr) was unsuccessful.

14.2 Neptunium sodium compounds

14.2.1 α - Na_2NpO_4

The value

$$\Delta_f H_m^\circ(\text{Na}_2\text{NpO}_4, \alpha, 298.15 \text{ K}) = -(1763.8 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1}$$

is accepted, based on a recalculation (*cf.* Appendix A) of the value reported by Goudiakas, Jemine and Fuger [91GOU/JEM] from measurements of the enthalpy of solution of the solid in 1 M HCl.

14.2.2 β -Na₂NpO₄

The value

$$\Delta_f H_m^\circ(\text{Na}_2\text{NpO}_4, \beta, 298.15 \text{ K}) = -(1748.5 \pm 6.1) \text{ kJ}\cdot\text{mol}^{-1}$$

is accepted, based on a recalculation (*cf.* Appendix A) of the value reported by Goudiakas, Jemine and Fuger [91GOU/JEM] from measurements of the enthalpy of solution of the solid in 1 M HCl. The difference in the enthalpies of solution of the α - and β -forms, $(15.3 \pm 3.5) \text{ kJ}\cdot\text{mol}^{-1}$, is similar to that for the corresponding uranium compounds $(13.1 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$ [92GRE/FUG].

14.2.3 β -Na₄NpO₅

Fuger [85FUG] reported a preliminary value of $\Delta_f H_m^\circ(\text{Na}_4\text{NpO}_5, \beta, 298.15 \text{ K}) = -(2311.7 \pm 7.2) \text{ kJ}\cdot\text{mol}^{-1}$ based on two preparations with five determinations on each. He cautioned that the result was suspect because the enthalpy of solution results (dissolution in 1 M HCl) from solids from the two preparations differed by $5 \text{ kJ}\cdot\text{mol}^{-1}$. The details were not published, and the value is not accepted in the present review. Nevertheless, the results are in good agreement with those from another set of experiments from the same group $\Delta_f H_m^\circ(\text{Na}_4\text{NpO}_5, \beta, 298.15 \text{ K}) = -(2315.7 \pm 5.3) \text{ kJ}\cdot\text{mol}^{-1}$ [91GOU/JEM]). After adjustment of the auxiliary data to values consistent with those used in the present review (*cf.* Appendix A), the value

$$\Delta_f H_m^\circ(\text{Na}_4\text{NpO}_5, \beta, 298.15 \text{ K}) = -(2315.4 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1}$$

is selected.

14.2.4 Na₂Np₂O₇(cr)

Judge, Brown and Fuger, as cited by Fuger [85FUG], measured the enthalpy of solution of Na₂Np₂O₇(cr) in aqueous HCl (1 M). From this and auxiliary data discussed in Appendix A, the standard enthalpy of formation of Na₂Np₂O₇(cr) is calculated to be

$$\Delta_f H_m^\circ(\text{Na}_2\text{Np}_2\text{O}_7, \text{cr}, 298.15 \text{ K}) = -(2894 \pm 11) \text{ kJ}\cdot\text{mol}^{-1}$$

This value is accepted in this review.

No data on S_m° and $\Delta_f G_m^\circ$ of Na₂Np₂O₇(cr) appear to be available.

14.3 Neptunium potassium compounds

14.3.1 K₂NpO₄(cr)

The value

$$\Delta_f H_m^\circ(\text{K}_2\text{NpO}_4, \text{cr}, 298.15 \text{ K}) = -(1784.3 \pm 6.4) \text{ kJ}\cdot\text{mol}^{-1}$$

is accepted, based on a recalculation (*cf.* Appendix A) of the value reported by Goudiakas, Jemine and Fuger [91GOU/JEM] from measurements of the enthalpy of solution of the solid in 1 M HCl.

14.3.2 $\text{K}_2\text{Np}_2\text{O}_7(\text{cr})$

Judge, Brown and Fuger, as cited by Fuger [85FUG], measured the enthalpy of solution of $\text{K}_2\text{Np}_2\text{O}_7(\text{cr})$ in aqueous HCl (1 M). From this and auxiliary data discussed in Appendix A, the standard enthalpy of formation of $\text{K}_2\text{Np}_2\text{O}_7(\text{cr})$ is calculated to be

$$\Delta_f H_m^\circ(\text{K}_2\text{Np}_2\text{O}_7, \text{cr}, 298.15 \text{ K}) = -(2932 \pm 11) \text{ kJ}\cdot\text{mol}^{-1}$$

This value is accepted in this review.

No data on S_m° and $\Delta_f G_m^\circ$ of $\text{K}_2\text{Np}_2\text{O}_7(\text{cr})$ appear to be available.

14.4 Neptunium rubidium compounds

14.4.1 $\text{Rb}_2\text{Np}_2\text{O}_7(\text{cr})$

Judge, Brown and Fuger, as cited by Fuger [85FUG], measured the enthalpy of solution of $\text{Rb}_2\text{Np}_2\text{O}_7(\text{cr})$ in aqueous HCl (1 M). From this and auxiliary data discussed in Appendix A, the standard enthalpy of formation of $\text{Rb}_2\text{Np}_2\text{O}_7(\text{cr})$ is calculated to be

$$\Delta_f H_m^\circ(\text{Rb}_2\text{Np}_2\text{O}_7, \text{cr}, 298.15 \text{ K}) = -(2914 \pm 12) \text{ kJ}\cdot\text{mol}^{-1}$$

This value is accepted in this review.

No data on S_m° and $\Delta_f G_m^\circ$ of $\text{Rb}_2\text{Np}_2\text{O}_7(\text{cr})$ appear to be available.

14.5 Neptunium caesium compounds

14.5.1 $\text{Cs}_2\text{NpO}_4(\text{cr})$

The value

$$\Delta_f H_m^\circ(\text{Cs}_2\text{NpO}_4, \text{cr}, 298.15 \text{ K}) = -(1788.1 \pm 5.7) \text{ kJ}\cdot\text{mol}^{-1}$$

is accepted, based on a recalculation (*cf.* Appendix A) of the value reported by Goudiakas, Jemine and Fuger [91GOU/JEM] from measurements of the enthalpy of solution of the solid in 1 M HCl.

14.5.2 $\text{Cs}_2\text{Np}_2\text{O}_7(\text{cr})$

Judge, Brown and Fuger, as cited by Fuger [85FUG], synthesised a solid that was primarily $\text{Cs}_2\text{Np}_2\text{O}_7(\text{cr})$, but between 9 and 21% of the neptunium was Np(V). The measured enthalpies of solution were not reported, and no thermodynamic values are available for this compound.

Part IV

Discussion of plutonium data selection

Chapter 15

Elemental plutonium

15.1 Plutonium crystal and liquid

15.1.1 Crystal structure and phase transitions

Plutonium is unique among the metallic elements in having six allotropic modifications stable at atmospheric pressure. Above 30 kbar, only the two monoclinic, most highly f-bonded phases (α and β), and the liquid are stable. The crystal structures, given in Table 15.1, are based on studies by Zachariasen and Ellinger [63ZAC/ELL], Jette [55JET], and Ellinger [56ELL]. The lattice parameters are those selected by Weigel, Katz and Seaborg ([86WEI/KAT], pp. 600-601), from which the densities have been recalculated.

There is little uncertainty in the transition temperatures. Earlier work has been summarised by Oetting *et al.* [76OET/RAN], but the preferred values are those suggested by Oetting and Adams [83OET/ADA] which incorporate more recent calorimetric work by themselves and data measurements by Rolon and Gallegos [81ROL/GAL]. These are also very close to the further data measurements given by Foltyn [90FOL].

15.1.2 Heat capacity and entropy

Early work on the low-temperature heat capacity of plutonium were plagued with the effects of self-heating and radiation damage. Work up to 1975 has been summarised by Oetting *et al.* [76OET/RAN]. Subsequently, Gordon *et al.* [76GOR/HAL] made measurements on both ^{240}Pu and ^{242}Pu , with good agreement. The derived heat capacity and entropy for α -Pu are:

$$\begin{aligned}C_{p,m}^{\circ}(\text{Pu}, \alpha, 298.15 \text{ K}) &= (31.49 \pm 0.40) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\S_{\text{m}}^{\circ}(\text{Pu}, \alpha, 298.15 \text{ K}) &= (54.46 \pm 0.80) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\end{aligned}$$

Oetting *et al.* [76OET/RAN] have summarised the work on heat capacities of the various allotropes (mainly due to Engel [67ENG] and Kay and Loasby [64KAY/LOA]), where there were disagreements of the order of 10%. The recent study from 330 to 700 K (Oetting and Adams [83OET/ADA]), using very pure ^{239}Pu in an adiabatic calorimeter, merge well with the low-temperature data of Gordon *et al.* [76GOR/HAL] and the high-temperature data of Engel [67ENG], and have been preferred to the earlier values. The coefficients of the expression $C_{p,m}^{\circ} = a + b(T/\text{K})$ are given in Table 15.2.

Table 15.1: Allotropy of plutonium

Phase	Stability range/K	Structure type and space group	Lattice parameters 10^{10} m	Z	Density $\text{g}\cdot\text{cm}^{-3}$
α	below 397.6	monoclinic $P2_1/m$	$a = 6.183$ $b = 4.822$ $c = 10.963$ $\beta = 101.79$ at 294 K	16	19.85
β	397.6 to 487.9	bc monoclinic $I2/m$	$a = 9.284$ $b = 10.463$ $c = 7.859$ $\beta = 93.13$ at 463 K	34	17.71
γ	487.9 to 593.1	orthorhombic $Fddd$	$a = 3.159$ $b = 5.768$ $c = 10.162$ at 508 K	8	17.15
δ	593.1 to 736.0	fc cubic $Fm3m$	$a = 4.6371$ at 593 K	4	15.92
δ'	736.0 to 755.7	bc tetragonal $I4/mmm$	$a = 3.34$ $c = 4.44$ at 738 K	2	16.03
ε	755.7 to 913.0	bc cubic $Im3m$	$a = 3.6361$ at 763 K	2	16.51

Table 15.2: Plutonium allotropes: Heat capacity coefficients and transformation data

Phase	$C_{p,m}^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ $= a + b(T/\text{K})$		T_{trs}/K	$\Delta_{\text{trs}}H_m^\circ / \text{J}\cdot\text{mol}^{-1}$
	a	$b \times 10^3$		
α	18.1258	44.820	397.6	(3706 ± 100)
β	27.4160	13.060	487.9	(478 ± 20)
γ	22.0233	22.959	593.1	(713 ± 40)
δ	28.4781	10.807	736.0	(84 ± 20)
δ'	35.560	0	755.7	(1841 ± 100)
ε	33.720	0	913.0	(2824 ± 100)
liquid	42.248	0	–	–

The concordant transition temperatures and enthalpies measured by Oetting and Adams [83OET/ADA], who found very sharp inflections in their curves, and by Rolon and Gallegos [81ROL/GAL] are preferred over the earlier measurements summarised by Oetting *et al.* [76OET/RAN] with which the agreement is in any case good. For consistency, the values recommended by Oetting and Adams [83OET/ADA] have been taken for the temperatures and enthalpies of transition, with increased (usually) uncertainties. Their values for the enthalpies of the $\delta - \delta'$, $\delta' - \varepsilon$ and ε -liquid transitions are in any case those recommended by Oetting *et al.* [76OET/RAN].

15.2 Plutonium ideal monatomic gas

Less than 300 energy levels were known when Benton [64BEN] and Feber and Herrick [65FEB/HER] made the first statistical-mechanical calculations of the thermal functions of Pu(g). In subsequent calculations, Oetting *et al.* [76OET/RAN] used 1075 levels up to 40000 cm^{-1} provided by Fred [75FRE]; Glushko *et al.* [82GLU/GUR] used the levels (including estimates of some unidentified levels, see below) for 11 so-called valence state configurations (plus two others), while Ward *et al.* [86WAR/KLE] used the 98 levels up to 20000 cm^{-1} given by Brewer [84BRE], based on listings provided by Fred and Blaise [83FRE/BLA]. Blaise and Wyart [92BLA/WYA] have recently published a comprehensive listing of the known energy levels of all the actinide gases, which contains 1190 levels for Pu(g). These are in fact identical with the 1192 levels given by Blaise and Fred [86BLA/FRE] except for the deletion of two high energy levels from the list given by the latter authors. These 1190 levels include all those expected up to at least 20000 cm^{-1} [84BRE], so as pointed out by Brewer, the uncertainty in Gibbs energy function $-\{G_m - H_m(298.15 \text{ K})/T\}$ at low temperatures ($<1000 \text{ K}$) is little greater than that from the uncertainties in the Fundamental Constants and the atomic mass of plutonium. However, Rand [80RAN] has pointed out that there is a very large number of unidentified energy levels for Pu(g), and showed from the approximate calculations that their effects need to be considered above *ca.* 3000 K.

The revised values of the thermal functions have been calculated from the 1190 levels tabulated by Blaise *et al.* [92BLA/WYA]; the Gibbs energy functions begin to differ from those given by Oetting and Rand [76OET/RAN] by more than 0.005 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ at about 2000K.

The values at 298.15 K for the ^{239}Pu isotope (molar mass=239.0522 $\text{g}\cdot\text{mol}^{-1}$ [86BRO/FIR]) are:

$$\begin{aligned} C_{p,m}^{\circ}(\text{Pu, g, 298.15 K}) &= (20.854 \pm 0.010) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ S_m^{\circ}(\text{Pu, g, 298.15 K}) &= (177.167 \pm 0.005) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

The following equations represent the heat capacities of Pu(g) from 298.15 to 2000 K:

$$\begin{aligned} C_{p,m}^{\circ}(\text{Pu, g, } T) &= (20.52 - 9.3914 \times 10^{-3}T + 2.57547 \times 10^{-5}T^2 \\ &\quad + 7.512 \times 10^{-4}T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

from 298.15 to 500 K, and

$$C_{p,m}^{\circ}(\text{Pu, g, } T) = (4.592 + 3.31521 \times 10^{-2}T - 5.64466 \times 10^{-6}T^2 + 7.0159 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 500 to 1100 K, and

$$C_{p,m}^{\circ}(\text{Pu, g, } T) = (-9.588 + 4.60885 \times 10^{-2}T - 8.63248 \times 10^{-6}T^2 + 5.01446 \times 10^6 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 1100 to 2000 K.

15.2.1 Enthalpy of formation

Work on the vapour pressure prior to 1976 has been summarised by Oetting *et al.* [76OET/RAN]. There has been one additional study since then (Bradbury and Ohse, [79BRA/OHS]) which was carried out at higher temperatures (giving pressures up to 1303 Pa), partially to test the upper limit of the Knudsen effusion regime. The vapour pressure equations from the five studies, and the derived second- and third-law values for $\Delta_f H_m^{\circ}$ (298.153 K), are given in Table 15.3; there is a good agreement between the second and third law analyses and between the five studies, probably because, unlike the earlier actinides, the monoxide gas is only a minor species in the evaporation of oxygen-contaminated plutonium. The selected value for the enthalpy of formation is:

Table 15.3: Vaporisation of Pu(g) and the enthalpy of formation at 298.15 K

Reference	T/K	$\log_{10}(p/\text{bar})^{(a)}$		$\Delta_f H_m^{\circ}/(\text{kJ}\cdot\text{mol}^{-1})$	
		A	B	2nd-law	3rd-law
[56PHI/SEA]	1392-1793	-17587	5.020	355.2	347.6
[66MUL]	1133-1792	-17420	4.919	352.1	347.8
[69KEN]	1426-1658	-17420	4.871	352.0	349.0
[75ACK/RAU]	1210-1620	-17120	4.598	346.2	351.0
[79BRA/OHS]	1724-2219	-17066	4.666	343.5	349.4
Selected value: $(349.0 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$					

$$^{(a)} \log_{10}(p/\text{bar}) = A(T/\text{K})^{-1} + B$$

$$\Delta_f H_m^{\circ}(\text{Pu, g, } 298.15 \text{ K}) = (349.0 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$$

The calculated Gibbs energy of formation thus becomes

$$\Delta_f G_m^{\circ}(\text{Pu, g, } 298.15 \text{ K}) = (312.415 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$$

Chapter 16

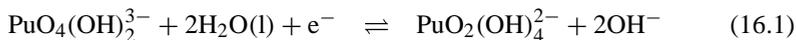
Plutonium aqua ions

Plutonium in aqueous solution can exist in the oxidation states, III, IV, V, VI, and VII. In acidic solution, the reduction potentials of the $\text{Pu}^{4+}/\text{Pu}^{3+}$, $\text{PuO}_2^+/\text{Pu}^{4+}$, $\text{PuO}_2^{2+}/\text{Pu}^{4+}$, and $\text{PuO}_2^{2+}/\text{PuO}_2^+$ couples lie relatively close to each other, and multiple oxidation states can coexist in solution. Thus, the determination of molar enthalpies, Gibbs energies and entropies of reaction may be hampered by the presence of plutonium in oxidation states that are unrelated to the redox couple under investigation, and the presence of the plutonium in these other oxidation states may remain undetected by the potential measurements. In solutions less than 1 M in acid, tetravalent plutonium slowly undergoes disproportionation to Pu(III) and Pu(VI). Also, it is partially hydrolyzed even in 1 M acid solution. Pentavalent plutonium disproportionates to Pu(III), Pu(IV) and Pu(VI) in acidic solutions, and if the acid concentration is of the order of 0.1 M or less, Pu(IV) may also be precipitated. The selected thermodynamic quantities for Pu^{3+} , Pu^{4+} , PuO_2^+ and PuO_2^{2+} are strongly connected, and there is a minimum amount of redundant information to provide confirmation for these values. The selection process used in the present review relies primarily on values for Pu^{3+} derived from solubility and enthalpy of solution measurements. Values for Pu^{4+} are based on potential measurements of the $\text{Pu}^{4+}/\text{Pu}^{3+}$ couple. Next, for PuO_2^{2+} , the equilibrium constant for the disproportionation reaction of Pu(IV) to Pu(VI) and Pu(III) and values for the $\text{Pu}^{4+}/\text{Pu}^{3+}$ couple and the enthalpy of oxidation of Pu(III) to Pu(VI) are used. Finally, values for PuO_2^+ are based on potential measurements of the $\text{PuO}_2^{2+}/\text{PuO}_2^+$ couple. It is assumed, that the value of the enthalpy of a reaction at $I = 0$ is equal to that in 1 M HClO_4 within the uncertainties of the measurements. This approximation leads to the differences between values of the formal potentials in 1 M $\text{HClO}_4(\text{aq})$ and the standard potentials being assigned primarily to entropy differences. The assumption is undoubtedly incorrect (and would actually be consistent with temperature-independent activity coefficients) but, used consistently, in the absence of experimental information, is probably subject to smaller errors than would be introduced by some of the other possible assumptions.

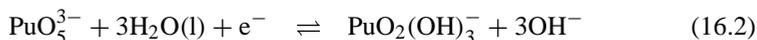
16.1 Pu(VII) and redox potentials in alkaline solutions

Heptavalent plutonium is only stable in strongly basic solution. The formal potential in 1 M NaOH for the Pu(VII)/Pu(VI) couple was measured by Krot *et al.*, [70KRO/GEL] and by Peretrukhin *et al.* [72PER/KRO] as $E^{\circ'} = 0.95$ V and 0.85 V, respectively, for

the proposed reaction



Musante [75MUS] measured $E^\circ(1 \text{ M Bu}_4\text{NOH}) = 1.12 \text{ V}$ for the proposed reaction



These measurements probably refer to the same reaction.

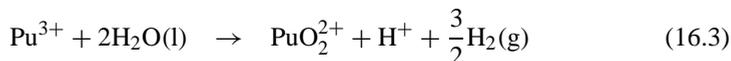
There are few thermochemical data available on plutonium in alkaline solution. The alkaline chemistry of transuranium elements was recently reviewed by Peretrukhin *et al.* [95PER/SHI]. Table 16.1 gives the reported formal redox potentials for plutonium in 1 M NaOH.

Table 16.1: Formal potentials for plutonium in 1 M NaOH(aq) at 298.15 K as reported from the review of Peretrukhin *et al.* [95PER/SHI].

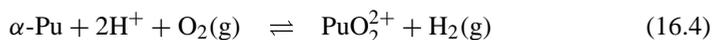
Formal potential (V, vs. SHE)			
VII/VI	VI/V	V/IV	IV/III
0.85	0.12	-0.67	-0.96

16.2 PuO_2^{2+}

Values for the standard molar enthalpy of formation, the Gibbs energy of formation, and the molar entropy of the dioxoplutonium(VI) cation were extensively reviewed in the IAEA review of Fuger and Oetting [76FUG/OET]. Small deviations from the values of Fuger and Oetting may occur in some instances due to the slightly different new (revised [89COX/WAG]) CODATA values used by this review. The average value for $\Delta_f H_m^\circ(16.3) = (341.4 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1}$



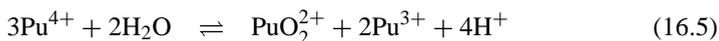
was derived by Fuger and Oetting [76FUG/OET] from two independent calorimetric determinations in aqueous (0.5 and 1.0 M) HClO_4 [49EVA, 59AXE/IHL, 60IHL/AXE]. Using this, the value of $\Delta_f H_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K})$ and the CODATA value of $\Delta_f H_m^\circ(\text{H}_2\text{O}(\text{l}), 298.15 \text{ K})$, and with the assumption that the heat of transfer to infinite dilution is negligible, they obtained the value $\Delta_r H_m^\circ(16.4) = -(822.2 \pm 6.7) \text{ kJ}\cdot\text{mol}^{-1}$ for the reaction



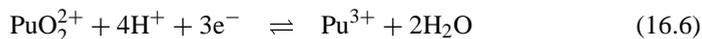
After incorporating changes in the auxiliary data, and using the selected value of $\Delta_f H_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K})$ (*cf.* Section 16.5), the present review accepts

$$\Delta_f H_m^\circ(\text{PuO}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(822.0 \pm 6.6) \text{ kJ}\cdot\text{mol}^{-1}$$

We also adopt the approach of the IAEA review that based their standard molar entropy value for PuO₂²⁺ on data of Connick and McVey [53CON/MCV] and Rabideau [53RAB] for the Pu⁴⁺ disproportionation equilibrium reaction, $\Delta_r G_m^\circ(16.5, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (11.68 \pm 0.54) \text{ kJ}\cdot\text{mol}^{-1}$,



and on $E^\circ(\text{Pu}^{4+}/\text{Pu}^{3+})$, and $S_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K})$ (*cf.* Section 16.5). Capdevila and Vitorge [92CAP/VIT, 95CAP/VIT] recently confirmed the disproportionation equilibrium constant and derived $E^\circ = -(0.988 \pm 0.020) \text{ V}$ for the standard potential according to Reaction (16.6).



Because of the large uncertainty in this standard potential, this review prefers to derive $\Delta_r G_m^\circ(16.6, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (295.95 \pm 0.56) \text{ kJ}\cdot\text{mol}^{-1}$ and $\log_{10} K(16.6, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(51.85 \pm 0.10)$ by combining the value of the formal Gibbs energy of reaction for the Pu⁴⁺ disproportionation equilibrium Reaction (16.5) with the formal Gibbs energy of reaction corresponding to the Pu⁴⁺/Pu³⁺ redox potential (0.9821 V, see Section 16.4). The values are converted to molality units and extrapolated to the standard condition, $I = 0$, using the specific interaction theory (SIT). In the absence of reliable values for the interaction coefficients for Pu³⁺ and PuO₂²⁺ with ClO₄⁻, the values of the homologous ions Nd³⁺, $\varepsilon_{(\text{Nd}^{3+}, \text{ClO}_4^-)} = (0.49 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ [83SPA, 95SIL/BID], and UO₂²⁺, $\varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)} = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ are used, but with the uncertainties of the interaction coefficients estimated by analogy raised to 0.05 kg·mol⁻¹ (values of several interaction coefficients [92GRE/FUG, 95SIL/BID] involving plutonium species have been revised in the present review for reasons discussed in footnotes to Appendix B).

The following selected values are obtained (the contribution to this potential of conversion to a standard pressure of 1 bar (+0.00017 V) is within the uncertainty of the value):

$$\begin{aligned} \log_{10} K^\circ(16.6, 298.15 \text{ K}) &= (50.97 \pm 0.15) \\ E^\circ(16.6, 298.15 \text{ K}) &= (1.005 \pm 0.003) \text{ V} \\ \Delta_r G_m^\circ(16.6, 298.15 \text{ K}) &= -(290.91 \pm 0.85) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

$E^\circ(\text{PuO}_2^{2+}/\text{Pu}^{3+}) = (0.988 \pm 0.020) \text{ V}$ for the reduction potential that was derived by Capdevila and Vitorge [92CAP/VIT] is consistent with the selected value $E^\circ(16.6, 298.15 \text{ K}) = (1.005 \pm 0.003) \text{ V}$. The Gibbs energy of reaction $\Delta_r G_m^\circ(16.6,$

298.15 K) = $-(290.91 \pm 0.85)$ kJ·mol⁻¹ is used to calculate $\Delta_f G_m^\circ$ from the values selected for Pu³⁺ and CODATA auxiliary values.

$$\Delta_f G_m^\circ(\text{PuO}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(762.4 \pm 2.8) \text{ kJ}\cdot\text{mol}^{-1}$$

Using the Gibbs-Helmholtz relation and $\Delta_r H_m^\circ = -(822.0 \pm 6.6)$ kJ·mol⁻¹, $\Delta_r S_m^\circ(16.4, 298.15 \text{ K}) = -(200.2 \pm 22.1)$ J·K⁻¹·mol⁻¹. From this number, the standard molar entropy value of PuO₂²⁺ is calculated as:

$$S_m^\circ(\text{PuO}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(71.2 \pm 22.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

using $S_m^\circ(\text{Pu}, \alpha, 298.15 \text{ K}) = (54.46 \pm 0.80)$ J·K⁻¹·mol⁻¹ from this review and CODATA auxiliary values.

Lemire and Campbell [96LEM/CAM] have used the results of their study of apparent molar heat capacities of NpO₂ClO₄(aq) with values of the partial molar heat capacities of other electrolytes [89HOV/NGU, 96LEM/CAM2] to estimate the variation of the potential of the Pu(VI)/Pu(V) couple as a function of temperature. The apparent molar heat capacities of PuO₂²⁺ and PuO₂⁺ as a function of temperature were assumed equal to those for UO₂²⁺ and NpO₂⁺, respectively [89HOV/NGU, 96LEM/CAM].

The mean value proposed by Capdevila and Vitorge [95CAP/VIT] for $\Delta_r C_{p,m}(16.8)$ is approximately -400 J·K⁻¹·mol⁻¹. This was calculated by double differentiation of a smoothed function of $E_{\text{VI/V}}^\circ(T)$ (based on experimental potential measurements for temperature from 5 to 65°C), and is much more negative than the -70 J·K⁻¹·mol⁻¹ calculated by the method of Lemire and Campbell [96LEM/CAM]. The uncertainties in that method cannot accommodate the Capdevila and Vitorge value [95CAP/VIT], and suggest the uncertainty in the entropy value proposed for that work should also be increased. To a first approximation, this review accepts that the partial molar heat capacities of all the aqueous dioxoactinide(V) and dioxoactinides(VI) ions can be assumed identical to those determined for UO₂²⁺ and NpO₂⁺, respectively [89HOV/NGU, 96LEM/CAM].

16.3 PuO₂⁺

The standard Gibbs energy of formation of the dioxoplutonium(V) cation is calculated by this review from the standard potential of the reaction



Several independent determinations of the PuO₂²⁺/PuO₂⁺ potential in perchloric acid solution are available. They are summarised in Table 16.2. The formal potentials in 1 M HClO₄ at 25°C were determined by Rabideau [56RAB], and by Capdevila *et al.* [92CAP, 92CAP/VIT, 95CAP/VIT], as $E^{\circ'} = (0.9164 \pm 0.0002)$ V, and (0.912 ± 0.007) V, respectively.

The value of Riglet, Robouch and Vitorge [89RIG/ROB], (0.941 ± 0.0052) V, was determined at 20°C, and not at 25°C, the standard temperature. They derived

Table 16.2: Experimental formal potentials in 1 M HClO_4 , derived standard potentials, and temperature coefficients for the $\text{PuO}_2^{2+}/\text{PuO}_2^+$ couple at 298.15 K (at 1 atm. except for the standard value selected in this review which is at 1 bar).

Method	Formal potential (V. vs. SHE)	Standard potential (V. vs. SHE)	$\partial E^\circ/\partial T$ ($\text{V}\cdot\text{K}^{-1}$)	Reference
Redox couple: $\text{PuO}_2^{2+}/\text{PuO}_2^+$, according to $\text{PuO}_2^{2+} + \frac{1}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{PuO}_2^+ + \text{H}^+$				
pot	(0.9164 ± 0.0002)		-0.0003	[56RAB]
rev		$(1.016 \pm 0.050)^{\text{(a)}}$		[76FUG/OET]
sol		(0.956 ± 0.025)		[84RAI]
emf			0.00065	[84BLA/MAD] ^(e)
vlt	$(0.941 \pm 0.005)^{\text{(b)}}$	$(0.954 \pm 0.010)^{\text{(b)}}$		[89RIG/ROB]
vlt	(0.912 ± 0.007)	(0.938 ± 0.010)	(0.00019 ± 0.00004)	[92CAP] ^(d)
vlt	(0.913 ± 0.005)	(0.938 ± 0.010)	expansion function ^(c)	[92CAP/VIT] ^(d)
rev	(0.913 ± 0.005)	(0.936 ± 0.005)	(0.0000 ± 0.0002)	this review

(a) Estimated correction of Rabideau's [56RAB] $E^{\circ'}$ value by 0.1 V [76FUG/OET].

(b) Value at 20°C.

(c) Expansion about a reference temperature T° : $E(T) = E(T^\circ) + (\Delta S(T^\circ)/F) \times (T - T^\circ) + (\Delta C_p(T^\circ)/2T^\circ F) \times (T - T^\circ)^2$, $\Delta S^\circ/F = (0.00034 \pm 0.00004) \text{ V}\cdot\text{K}^{-1}$ and $\Delta C_p^\circ/F = -(0.00404 \pm 0.00090) \text{ V}\cdot\text{K}^{-1}$.

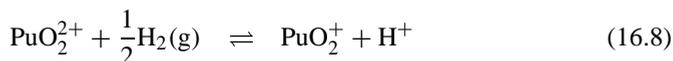
(d) Same experimental data set.

(e) $\partial E^\circ/\partial T$

$E^\circ = (0.954 \pm 0.010)$ V by applying the SIT to data from cyclic voltammetry measurements at 0.5, 1, 2, and 3 M ionic strengths. Rai [84RAI] reported $E^\circ = (0.956 \pm 0.025)$ V from solubility measurements. Capdevila's value of $E^\circ = (0.938 \pm 0.010)$ V was also derived by applying the SIT treatment to their data. They calculated the ion interaction parameter $\Delta\varepsilon = (0.22 \pm 0.03)$ kg·mol⁻¹ (similar to the values for the reactions involving the corresponding uranium and neptunium species (Appendix B)). Although these three values for the standard potential lie within their combined uncertainties, we do not select the data because the measurements of Riglet, Robouch and Vitorge were hampered by experimental problems (*cf.* Appendix A) as was pointed out in a later publication [95CAP/VIT] by one co-author of the initial investigation. Rai's value was derived solely from solubility measurements and carries, therefore, the large uncertainty of 0.025 V. Because the value of Capdevila *et al.* also has a relatively large uncertainty of 0.010 V, we derive the formal potential $E^\circ(16.7, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (0.913 \pm 0.005)$ V, $\log_{10}K(16.7, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (15.43 \pm 0.08)$ and $\Delta_r G_m^\circ(16.7, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(88.09 \pm 0.48)$ kJ·mol⁻¹ by combining the raw data of Capdevila and Vitorge [95CAP/VIT] and Rabideau [56RAB]. These data are corrected to standard conditions using the SIT $\Delta\varepsilon (= (0.22 \pm 0.03)$ kg·mol⁻¹) value of Capdevila and Vitorge [95CAP/VIT]. The following values are obtained:

$$\begin{aligned} E^\circ(16.7, 298.15 \text{ K}) &= (0.936 \pm 0.005) \text{ V} \\ \log_{10}K^\circ(16.8, 298.15 \text{ K}) &= (15.82 \pm 0.09) \\ \Delta_r G_m^\circ(16.8, 298.15 \text{ K}) &= -(90.29 \pm 0.51) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

for the reaction



The correction to the standard pressure of 1 bar lies within the uncertainty of the values. The estimate of Fuger and Oetting [76FUG/OET], $E^\circ = (1.016 \pm 0.05)$ V, appears to be too high in light of these results, and the less positive value, $E^\circ = 0.936$ V, is used here. Therefore,

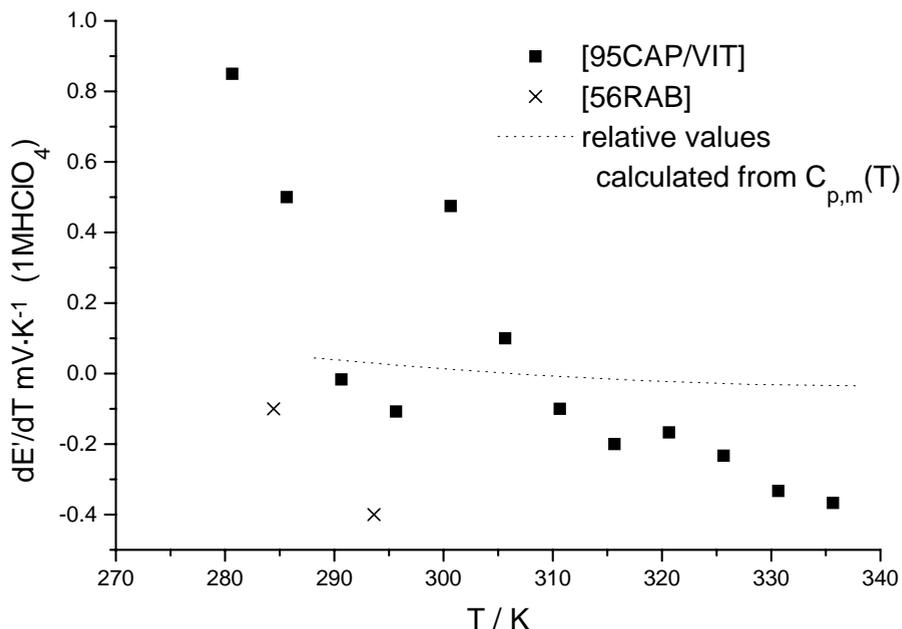
$$\Delta_f G_m^\circ(\text{PuO}_2^+, \text{aq}, 298.15 \text{ K}) = -(852.6 \pm 2.9) \text{ kJ}\cdot\text{mol}^{-1}$$

is derived from $\Delta_r G_m^\circ(16.8, 298.15 \text{ K})$ and the selected value of $\Delta_f G_m^\circ(\text{PuO}_2^{2+}, \text{aq}, 298.15 \text{ K})$.

The change in enthalpy for Reaction (16.8) is obtained from the temperature coefficient of the potential. Figure 16.1 shows the temperature variation of the derivative with respect to temperature of the $\text{PuO}_2^{2+}/\text{PuO}_2^+$ couple formal potential (1.0 M HClO₄) for Rabideau's [56RAB] and Capdevila and Vitorge's [95CAP/VIT] data. Because of the conflicts in the trends in temperature variation, $(\partial E^\circ/\partial T) = (0.0000 \pm 0.0002)$ V·K⁻¹ is selected by this review. This is consistent with the variation of the temperature coefficient between the different investigators listed in Table 16.2. Rabideau [56RAB] reported a very small negative coefficient, whereas Capdevila and Vitorge, as well as

Blanc and Madic [84BLA/MAD], reported positive values. The uncertainty, though smaller than the experimental scatter, is selected to maintain consistency with entropy differences for analogous reactions. (e.g., [92GRE/FUG]).

Figure 16.1: Temperature variation of the derivative of the formal potential (1.0 M HClO₄) of the PuO₂²⁺/PuO₂⁺ couple with respect to temperature. The data are taken from [56RAB] and [95CAP/VIT]. The values used to construct the dotted line are based on values for UO₂²⁺ and NpO₂⁺ in perchlorate media [96LEM/CAM].



We calculate the change in enthalpy for Reaction (16.8, 1 M HClO₄) from E° and $\partial E^{\circ}/\partial T$ with the Gibbs-Helmholtz relation, neglect the small heat of transfer to infinite dilution [94CAP/VIT, 95CAP/VIT] (however, an extra uncertainty equal to 30% of the uncertainty in $\partial E^{\circ}/\partial T$ was incorporated), and obtain

$$\Delta_r H_m^{\circ}(\text{16.8, 298.15 K}) = -(88.09 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1}$$

Using $\Delta_f H_m^{\circ}(\text{PuO}_2^{2+}, \text{aq, 298.15 K})$, cf. Section 16.2, the selected value

$$\Delta_f H_m^{\circ}(\text{PuO}_2^{+}, \text{aq, 298.15 K}) = -(910.1 \pm 8.9) \text{ kJ}\cdot\text{mol}^{-1}$$

is derived.

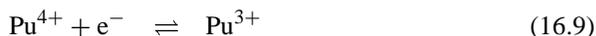
The standard molar entropy value is derived from $\Delta_r S_m^{\circ}(\text{16.8, 298.15 K}) = (7.4 \pm 20.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ that is calculated from the Gibbs-Helmholtz relation,

$S_m^\circ(\text{PuO}_2^{2+}, \text{aq}, 298.15 \text{ K})$, *cf.* Section 16.2, and CODATA auxiliary data

$$S_m^\circ(\text{PuO}_2^+, \text{aq}, 298.15 \text{ K}) = (1 \pm 30) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

16.4 Pu⁴⁺

The standard Gibbs energy of formation of the plutonium(IV) cation is calculated by this review from the standard potential of the reaction



and the standard Gibbs energy of formation of Pu³⁺ (*cf.* Section 16.5). Eight independent experimental determinations of the Pu⁴⁺/Pu³⁺ potential are available: six in perchloric acid and two in hydrochloric acid solutions. The results are summarised in Table 16.3.

Riglet, Robouch and Vitorge [89RIG/ROB] determined the formal potential of the Pu⁴⁺/Pu³⁺ couple in 1 M HClO₄ at 293.15 K by cyclic voltammetry, using a platinum electrode, as $E^{o'}(293.15 \text{ K}) = (0.959 \pm 0.005) \text{ V}$. Using the same method, Capdevila, Vitorge and Giffaut [92CAP/VIT], Capdevila [92CAP] and Capdevila and Vitorge [95CAP/VIT] derived $E^{o'} = (0.973 \pm 0.007) \text{ V}$, $E^{o'} = (0.978 \pm 0.007) \text{ V}$, and $E^{o'} = (0.978 \pm 0.005) \text{ V}$, respectively. Connick and McVey [51CON/MCV] and Rabideau and Lemons [51RAB/LEM] determined for the Pu⁴⁺/Pu³⁺ couple the formal potentials of $E^{o'} = (0.982 \pm 0.002) \text{ V}$ and $E^{o'} = (0.9821 \pm 0.0005) \text{ V}$, respectively. The data of these investigators are derived from junction potential-free emf measurements which are precise and accurate. To compare the non-standard (293.15 K) formal potential of Riglet, Robouch and Vitorge [89RIG/ROB] to the potentials derived at standard temperature, this review applies $(dE/dT)_{\text{isotherm}} = (0.00149 \pm 0.00004) \text{ V}\cdot\text{K}^{-1}$, which is the selected value for the temperature coefficient of the potential. The correction for the temperature change of the formal potential from 293.15 to 298.15 K gives Riglet, Robouch and Vitorge's formal Pu⁴⁺/Pu³⁺ potential at standard temperature, $E^{o'} = (0.966 \pm 0.005) \text{ V}$. This potential is 16 mV smaller than Connick and McVey's, and Rabideau and Lemons' potentials. It is 7 and 12 mV smaller than the potentials reported by Capdevila *et al.* and Capdevila, respectively. This discrepancy in the value of the formal potential reported by Riglet, Robouch and Vitorge [89RIG/ROB] was traced to experimental problems [95CAP/VIT] (also, *cf.* Appendix A). Therefore the value is rejected in the present review.

Based on the consistency of the data of Connick and McVey and of Rabideau and Lemons, this review selects $E^{o'} = (0.9821 \pm 0.0005) \text{ V}$ given by Connick and McVey and accepts the identical value for the 1 bar standard state (the difference is within the assigned uncertainty). Within its relatively large uncertainty limit, Capdevila and Vitorge's potential is in agreement with the selected value. Rabideau [57RAB] obtained $E^{o'} = 0.9817 \text{ V}$ in 1 M HClO₄/1 M LiClO₄ solution at $I = 2$. In 1 M HCl, Rabideau and Cowan [55RAB/COW] measured $E^{o'} = (0.9701 \pm 0.0118) \text{ V}$ which is significantly lower than the selected value due to chloride complexing. The potential given by Schwabe and Nebel [62SCH/NEB] was determined in 0.1 M HCl. They calculated the

Table 16.3: Experimental formal potentials in 1 M HClO₄ (unless otherwise noted), derived standard potentials, and temperature coefficients for the Pu⁴⁺/Pu³⁺ couple at 298.15 K. (at 1 atm. except for the standard value selected in this review which is at 1 bar)

Method	Formal potential (V, vs. SHE)	Standard potential (V, vs. SHE)	$\partial E^\circ/\partial T$ (V·K ⁻¹)	Reference
Redox couple: Pu ⁴⁺ /Pu ³⁺ , according to $\text{Pu}^{4+} + \frac{1}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{Pu}^{3+} + \text{H}^+$				
emf	(0.982±0.002)		(0.00125±0.00004)	[51CON/MCV]
emf	(0.9821±0.0005)			[51RAB/LEM]
emf	(0.9701±0.0118) ^(a)		(0.00117±0.00001)	[55RAB/COW]
emf	(0.9817) ^(b)		(0.00147±0.00012)	[57RAB]
pol		(1.006±0.003) ^(c)		[62SCH/NEB]
emf			(0.0019±0.0004)	[84BLA/MAD] ^(h)
vlt	(0.959±0.005) ^(d)	(1.010±0.010) ^(d)		[89RIG/ROB]
	(0.966±0.005) ^(e)	(1.017±0.010) ^(e)		
vlt	(0.973±0.007)	(1.044±0.010)	(0.00184±0.00010)	[92CAP] ^(f) [92CAP/VIT] ^(f)
vlt	(0.978±0.005)	(1.044±0.010)	(0.00147±0.00011)	[95CAP/VIT] ^(f)
rev	(0.9821±0.0005)	(1.006±0.003)		[76FUG/OET]
rev	(0.9821±0.0005)	(1.047±0.003)	(0.00149±0.00008)	this review ^(g)

(a) Measured in 1 M HCl.

(b) Measured in 1 M HClO₄/1 M LiClO₄, $I = 2$ M.

(c) Measured in 0.1 M HCl and corrected for HCl activity.

(d) Value at 20°C.

(e) Corrected to 25°C by this review.

(f) Same experimental data set. The heat capacity was neglected in [92CAP, 92CAP/VIT]. It was fitted with a constant value in [95CAP/VIT].

(g) 1 bar standard state.

(h) $\partial E^\circ/\partial T$

standard potential using an activity correction for 0.1 M HCl, but no correction was made for the formation of hydrolyzed plutonium(IV) species. For these reasons, the data are not considered. The SIT treatment is used to correct the selected formal potential to standard conditions with the SIT $\Delta\varepsilon$ (16.9, 298.15 K) (= 0.33 ± 0.04 kg·mol⁻¹) value of Capdevila and Vitorge [95CAP/VIT]. The selected value in this review for the Pu⁴⁺/Pu³⁺ couple is the standard potential obtained from the extrapolation to $I = 0$

$$\begin{aligned} E^\circ(16.9, 298.15 \text{ K}) &= (1.047 \pm 0.003) \text{ V} \\ \log_{10} K^\circ(16.9, 298.15 \text{ K}) &= 17.69 \pm 0.04 \end{aligned}$$

The conversion of this potential from a standard pressure of 1 atm to 1 bar (-0.00017 V) is within the uncertainty of the value. The value agrees with Capdevila and Vitorge's value but has a much smaller uncertainty. It also agrees with $E^\circ = (1.046 \pm 0.011)$ V, that can be derived by applying the correction $E^\circ - E'^\circ = (0.064 \pm 0.011)$ V to the selected formal Pu⁴⁺/Pu³⁺ potential, which was determined by Riglet, Robouch and Vitorge for the Np⁴⁺/Np³⁺ couple.

From the selected E° , we calculate for Reaction (16.9), $\Delta_r G_m^\circ(16.9, 298.15 \text{ K}) = -(101.0 \pm 0.3)$ kJ·mol⁻¹. Using the selected values for $\Delta_r G_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K})$ we calculate

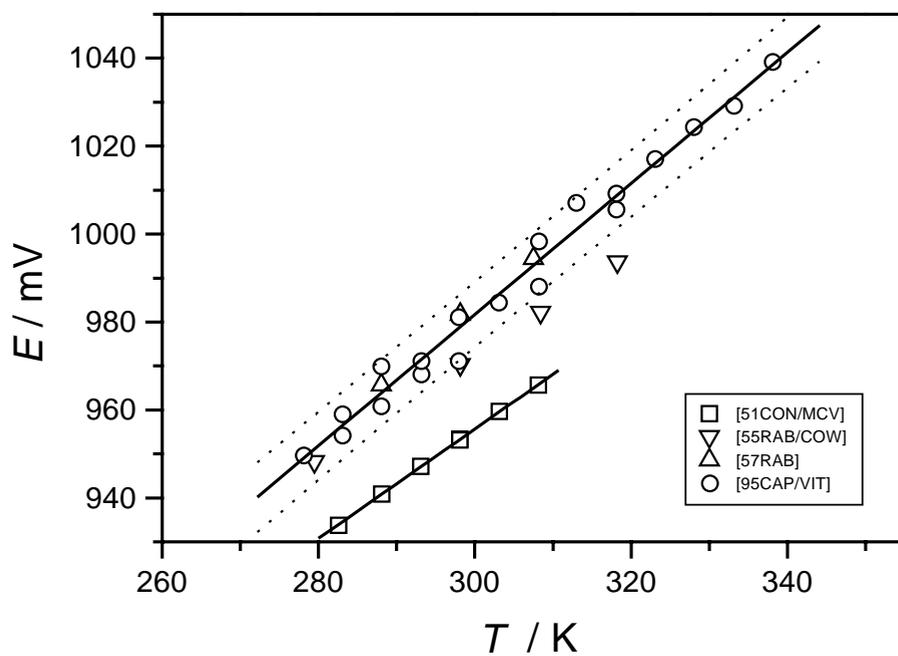
$$\Delta_f G_m^\circ(\text{Pu}^{4+}, \text{aq}, 298.15 \text{ K}) = -(478.0 \pm 2.7) \text{ kJ}\cdot\text{mol}^{-1}$$

$\Delta_r S_m(16.9, 1 \text{ M HClO}_4)$ is calculated from the temperature coefficient of the Pu⁴⁺/Pu³⁺ potential. The data are summarised in Table 16.3. Four independent data sets were measured by (1) Connick and McVey [51CON/MCV] in 1 M HClO₄ from 9.41 to 35.01°C; (2) Rabideau and Cowan [55RAB/COW] in 1 M HCl from 6.32 to 45.11°C; (3) Rabideau [57RAB] in 1 M HClO₄/1 M LiClO₄ at $I = 2$ M from 14.90 to 34.36°C; and, (4) Capdevila and Vitorge [95CAP/VIT] in 1 M HClO₄ from 5 to 65°C. The data are shown in Figure 16.2. The potentials of Connick and McVey are raw data from an electrochemical cell containing 1.18×10^{-3} M Pu(ClO₄)₄ and 3.50×10^{-3} M Pu(ClO₄)₃. No correction to unit concentration was made here because it will only offset the potential and not change the temperature coefficient. Rabideau and Cowan's measurements in 1 M HCl were not considered because it is possible that the temperature coefficient in chloride solution might differ from that in perchlorate solution due to chloride complexation.

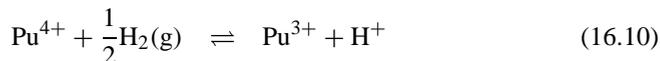
This review selects the data of Capdevila and Vitorge which covers a much wider temperature range than Connick and McVey's measurements, and combines it with Rabideau's data [57RAB] assuming a negligible change of the temperature coefficient due to the increased ionic strength of 2 M.

Through linear regression analysis, the selected values for this review $\partial E'^\circ/\partial T = (0.00149 \pm 0.00008)$ V·K⁻¹ and $\Delta_r S_m(16.9, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (143.8 \pm 7.7)$ J·K⁻¹·mol⁻¹ are obtained. From this and $\Delta_r G_m(16.9, 1 \text{ M HClO}_4, 298.15 \text{ K}) = -(94.76 \pm 0.05)$ kJ·mol⁻¹, the value of $\Delta_r H_m$ is derived. We assume that the enthalpy change to standard conditions is negligible (however, an extra uncertainty equal to 30% of the uncertainty in $\partial E'^\circ/\partial T$ was incorporated) to obtain

Figure 16.2: Formal potential of the Pu⁴⁺/Pu³⁺ couple as a function of the temperature. The data are taken from [51CON/MCV], [55RAB/COW], [57RAB] and [95CAP/VIT].



$$\Delta_r H_m^\circ(16.10, 298.15 \text{ K}) = -(51.9 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}.$$



The review by Rand [66RAN] derived $\Delta_r H_m(16.10, 0.5 \text{ M HClO}_4, 298.15 \text{ K}) = -50.2 \text{ kJ}\cdot\text{mol}^{-1}$ from Evans' [49EVA] calorimetric measurements of the oxidation of both Pu^{3+} and Fe^{2+} in 0.5 M HClO_4 , which is in closer agreement with the value calculated by this review than with values based on temperature coefficients ($-(56.5 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$) used previously [66RAN]. Using the value based on $\partial E^{o'}/\partial T$ and $\Delta_f H_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K})$, we determine

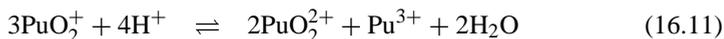
$$\Delta_f H_m^\circ(\text{Pu}^{4+}, \text{aq}, 298.15 \text{ K}) = -(539.9 \pm 3.1) \text{ kJ}\cdot\text{mol}^{-1}$$

The standard entropy of Reaction (16.10) is derived from the standard enthalpy and the Gibbs energy, $\Delta_r S_m^\circ(16.10, 298.15 \text{ K}) = (164.68 \pm 8.12) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, from which we obtain the selected

$$S_m^\circ(\text{Pu}^{4+}, \text{aq}, 298.15 \text{ K}) = -(414.5 \pm 10.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

using $S_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K})$ and the auxiliary data.

The irreversible redox potentials were recently reviewed by Capdevila [92CAP]. Rabideau [56RAB] reported for the Pu(VI)/Pu(IV) potential in 1 M HClO_4 $E^{o'} = 1.0433 \text{ V}$. Capdevila *et al.* [92CAP/VIT] obtained this potential from their measurements of the reversible plutonium couples ($\text{PuO}_2^{2+}/\text{PuO}_2^+$, $\text{Pu}^{4+}/\text{Pu}^{3+}$) and the equilibrium constants for the respective disproportionation reactions of Pu^{4+} and PuO_2^+ . Their values are $E^{o'} = (1.033 \pm 0.022) \text{ V}$ and $E^{o'} = (1.022 \pm 0.030) \text{ V}$ depending on the use of the disproportionation constant $K(16.5)$ or $K(16.11)$, respectively.



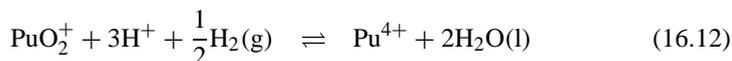
Using the SIT treatment, the authors obtained $\log_{10}(K^\circ(16.11)) = 2.6 \pm 0.5$ for the disproportionation equilibrium of PuO_2^+ at infinite dilution and the interaction coefficient $\Delta\varepsilon = (0.09 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$. From their data, they then calculated $E^\circ = (0.965 \pm 0.035) \text{ V}$. Using the potential values $E^\circ(16.6)$ and $E^\circ(16.9)$ as selected above, we obtained for the Pu(VI)/Pu(IV) redox couple

$$E^\circ = (0.983 \pm 0.004) \text{ V}$$

which agrees within the uncertainty limits with Capdevila's value. Capdevila obtained for the Pu(V)/Pu(IV) potential in 1 M HClO_4 , $E^{o'} = (1.154 \pm 0.050) \text{ V}$ or $E^{o'} = (1.134 \pm 0.050) \text{ V}$ using their $K(16.5)$ or $K(16.11)$ values, respectively, and $E^\circ = (0.991 \pm 0.060) \text{ V}$. From the selected values of this review,

$$E^\circ = (1.031 \pm 0.010) \text{ V}$$

is calculated for the reaction



16.5 Pu³⁺

The values of the standard molar enthalpy of formation, the Gibbs energy of formation, and the molar entropy of the plutonium(III) cation were very thoroughly reviewed by Fuger and Oetting [76FUG/OET]. Their selected value $\Delta_f H_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K}) = -(592.0 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$, was derived from calorimetric measurements of the enthalpies of solution of Pu and PuCl₃(cr) in HCl(aq) [76FUG/OET]. Their analysis used the value of Robinson and Westrum [49ROB/WES] for the enthalpy of solution of PuCl₃(cr) in 6 M HCl(aq) $(-92.68 \pm 0.42) \text{ kJ}\cdot\text{mol}^{-1}$ and the result of the extrapolation of the enthalpy of solution of PuCl₃(cr) in HCl(aq) to infinite dilution $(-133.47 \pm 0.84) \text{ kJ}\cdot\text{mol}^{-1}$ by the same authors. For the enthalpy of solution of Pu(cr, α) in 6 M HCl(aq) Akhachinskij's [66AKH] value of $(-592.04 \pm 1.67) \text{ kJ}\cdot\text{mol}^{-1}$ was accepted. Using revised auxiliary data (*cf.* Section 18.1),

$$\Delta_f H_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K}) = -(591.8 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$$

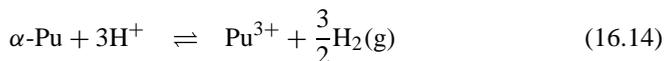
Based on the Gibbs energy and enthalpy values for the dissolution reaction,



$(-30.125 \pm 0.840) \text{ kJ}\cdot\text{mol}^{-1}$ and $(-34.60 \pm 0.64) \text{ kJ}\cdot\text{mol}^{-1}$, as discussed in Sections 18.1.3.3.a and 18.1.3.3.b, $\Delta_r S_m^\circ(16.13) = -(15.01 \pm 3.53) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. From this value and using new CODATA auxiliary data and values from this review for $S_m^\circ(\text{Cl}^-, \text{aq}, 298.15 \text{ K}) = (56.60 \pm 0.20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $S_m^\circ(\text{PuCl}_3 \cdot 6\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (420 \pm 5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, *cf.* Section 18.1.3.3,

$$S_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K}) = -(184.5 \pm 6.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Then, using $S_m^\circ(\text{Pu}, \text{cr}, 298.15 \text{ K}) = (54.46 \pm 0.80) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ as selected by this review (*cf.* Section 15.1.2), $\Delta_r S_m^\circ(16.14) = -(42.95 \pm 6.21) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was calculated.



From this and the selected value of $\Delta_f H_m^\circ$, the selected value

$$\Delta_f G_m^\circ(\text{Pu}^{3+}, \text{aq}, 298.15 \text{ K}) = -(579.0 \pm 2.7) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated. The standard potential for the $\alpha\text{-Pu}/\text{Pu}^{3+}$ couple, $E^\circ(16.15)$,



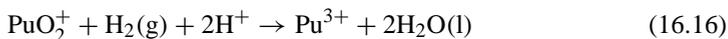
is then calculated as

$$E^\circ(16.15) = -(2.000 \pm 0.009) \text{ V}.$$

For the value of the Pu(VI)/Pu(III) redox couple, Capdevila [92CAP, 92CAP/VIT, 95CAP/VIT] obtained $E^\circ(16.6, 1 \text{ M HClO}_4) = (1.013 \pm 0.017) \text{ V}$ from $K(16.5)$, and

$E^{\circ}(\text{16.6}, 1 \text{ M HClO}_4) = (1.006 \pm 0.017) \text{ V}$ from $K(\text{16.11})$. From these, $E^{\circ}(\text{16.6}) = (0.988 \pm 0.020) \text{ V}$ is obtained. Rabideau [56RAB] calculated $E^{\circ}(\text{16.6}, 1 \text{ M HClO}_4) = 1.0228 \text{ V}$. These values can be compared with the standard potential, $E^{\circ}(\text{16.6}) = (1.005 \pm 0.003) \text{ V}$, selected in this review (*cf.* Section 16.2), and the value of the formal potential, $E^{\circ}(\text{16.6}, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (1.022 \pm 0.002) \text{ V}$, that is calculated from the selected values of the formal potential for Pu(IV)/Pu(III) couple and the disproportionation constant of Pu(IV), $K(\text{16.5})$.

Similarly, Capdevila reported $E^{\circ} = (1.063 \pm 0.030) \text{ V}$, and $E^{\circ} = (1.053 \pm 0.022) \text{ V}$ and $E^{\circ} = (1.014 \pm 0.025) \text{ V}$ from $K(\text{16.5})$ and $K(\text{16.11})$ for the Pu(V)/Pu(III) potential. From the selected values of this review, we calculate for



$$E^{\circ}(\text{16.16}, 1 \text{ M HClO}_4, 298.15 \text{ K}) = (1.077 \pm 0.004) \text{ V}$$

$$E^{\circ}(\text{16.16}) = (1.040 \pm 0.005) \text{ V}$$

16.6 Summary

Table 16.4 summarises the NEA selected thermodynamic constants for the plutonium aqua ions.

Table 16.4: NEA selected chemical thermodynamic values for plutonium aqua ions.

	$\Delta_f H_m^{\circ}$ (kJ·mol ⁻¹)	$\Delta_f G_m^{\circ}$ (kJ·mol ⁻¹)	S_m° (J·K ⁻¹ ·mol ⁻¹)
PuO ₂ ²⁺ (aq)	-(822.0 ± 6.6)	-(762.4 ± 2.8)	-(71 ± 22)
PuO ₂ ⁺ (aq)	-(910.1 ± 8.9)	-(852.6 ± 2.9)	(1 ± 30)
Pu ⁴⁺ (aq)	-(539.9 ± 3.1)	-(478.0 ± 2.7)	-(414.5 ± 10.2)
Pu ³⁺ (aq)	-(591.8 ± 2.0)	-(579.0 ± 2.7)	-(184.5 ± 6.2)

Figure 16.3: Standard potentials ($I = 0$, 25°C) for plutonium, in units of V vs. SHE.

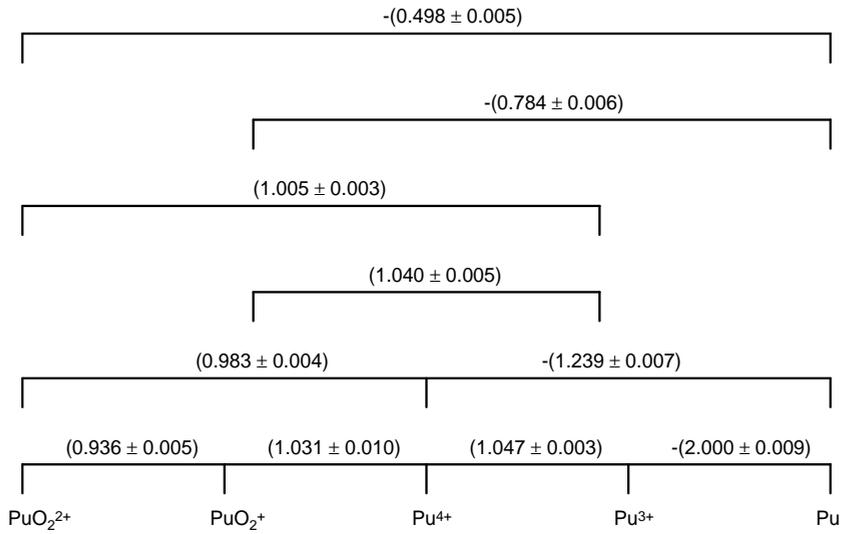
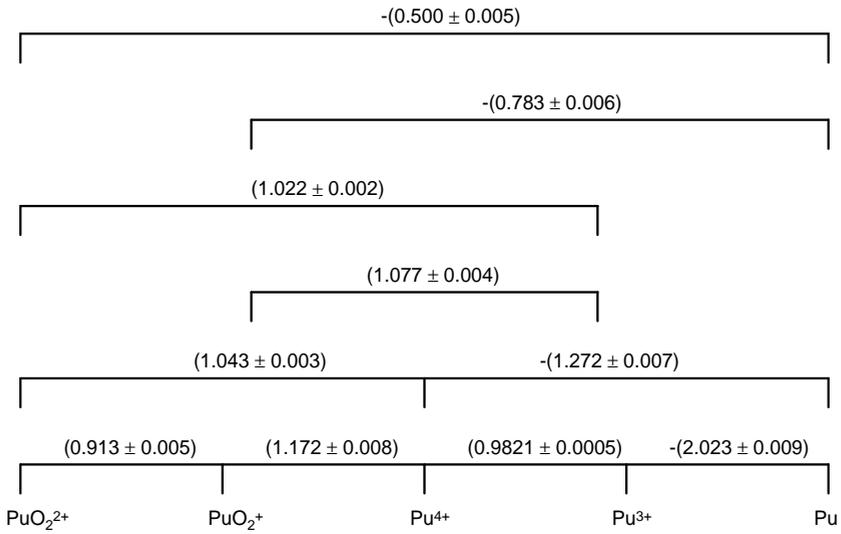


Figure 16.4: Formal potentials (1 M HClO₄, 25°C) for plutonium, in units of V vs. SHE.



Chapter 17

Plutonium oxygen and hydrogen compounds and complexes

17.1 Aqueous plutonium hydroxide complexes

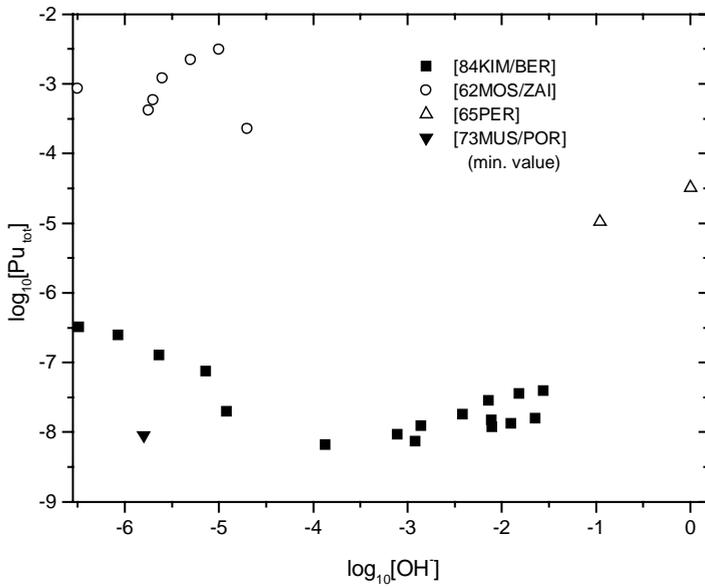
17.1.1 Plutonium(VI) hydroxide complexes

Even the earliest studies on this system [44O'C, 49KRA/DAM2] reported experimental problems caused by the slow kinetics of some of the hydrolysis reactions in neutral and basic solutions. This has been confirmed in later potentiometric [75SCH] and spectrophotometric [93OKA/REE] studies, and means results from most of these studies cannot be used to determine equilibrium constants without some reservations. The situation has been well summarised by Pashalidis *et al.* [93PAS/KIM2]: "In solutions that are initially more basic than pH 5 and have total Pu(VI) concentrations 10^{-3} mol·dm⁻³ or greater, the time dependent reactions preclude the use of thermodynamic calculations unless there are inordinately long time intervals between consecutive additions of base."

In addition, radiolysis is caused by the α -decay of plutonium in solution. This leads to species that cause the reduction of Pu(VI) (initially to Pu(V)) in perchloric acid solutions. The extent of radiolytic reduction depends on the isotope of plutonium used, the effects decreasing with increasing half lives (²³⁸Pu($t_{1/2}$ = 87.74 a); ²³⁹Pu($t_{1/2}$ = 24100 a); ²⁴²Pu($t_{1/2}$ = 376000 a) [79SHI/LED]). The extent of radiolytic reduction increases with increasing concentrations of plutonium solution species and also depends on the medium. Thus, reasonably concentrated plutonium in aqueous perchlorate solutions near neutral pH cannot be left long enough for equilibrium to be established without the solutions also undergoing autoreduction. Although other types of studies exist, the bulk of the information concerning Pu(VI) hydrolysis comes from solubility, spectroscopic and potentiometric experiments.

The stable hydrolytic solid containing Pu(VI) is probably PuO₂(OH)₂·H₂O (see Section 17.2.2.1). There are at least four solubility studies in the literature [62MOS/ZAI, 65PER, 73MUS/POR, 84KIM/BER], that report hydrolysis constants for Pu(VI). The study of Perez-Bustamante [65PER] was restricted to strongly basic solutions. Based on the published hydrolysis constants for Pu(VI) (Figure 17.1) and solubility product, it appears the solubilities of Musante and Porthault must have been similar to those of Kim *et al.* (within about an order of magnitude, although the pH of the minimum solubility differs somewhat).

Figure 17.1: Comparison of experimental solubilities of hydrated Pu(VI) oxide solids from studies to determine hydrolysis constants of Pu(VI) (*cf.* Appendix A for the source of the value plotted for [73MUS/POR]).



The solubilities of Moskvina and Zaitseva [62MOS/ZAI] are several orders of magnitude higher at all overlapping values of pH. Although their reported solubility product based on a solution at low pH may be reasonable, it is clear that their equilibration times were too short to provide usable equilibrium solubilities (and hydrolysis constants) at high pH values.

The data of Kim *et al.* [84KIM/BER] were reanalysed in the present review using a non-linear least squares treatment (Appendix A). A set of four equations was derived relating the solubility product and five hydrolysis constants. From the solubility data alone, it is not possible mathematically to distinguish contributions to the solubility by different species having the same total charge. Thus, the ratios of the equilibrium concentrations of PuO_2^{2+} to $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ and PuO_2OH^+ to $(\text{PuO}_2)_x(\text{OH})_{2x-1}^+$ remain constant at all values of pH. If the dimeric species $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ is a major species in equilibrium with the solid at some pH, the values of $K_{s,0}$, and $\beta_{2,2}$ cannot be separated in the absence of other data. In their calculations, Kim *et al.* [84KIM/BER] used fixed values for $K_{s,0}$ and β_1 [86LIE/KIM]. The set of equations must be used with qualitative and quantitative information from potentiometric and spectrophotometric studies to derive hydrolysis constants and a solubility product consistent with the solubilities.

The spectrophotometric and potentiometric hydrolysis studies lead to the conclusion that, compared to the uranium species $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3(\text{OH})_5^+$, the first polymeric hydrolysis species formed for plutonium are relatively unstable. Thus, these species do not extensively enhance the dissolution of a stable solid. The results of Okajima *et al.* [90OKA/REE] and Pashalidis *et al.* [93PAS/KIM2] underscore the slow nature of the secondary hydrolysis reactions. The solubility studies, suggest the spectrophotometric and potentiometric studies were all (or almost all) done using solutions supersaturated with respect to $\text{PuO}_2(\text{OH})_2(\text{s})$.

Debate has continued over the years as to whether, in solutions containing Pu(VI) at concentrations greater than 10^{-5} mol·kg⁻¹, the first hydrolysis species is the monomer or the dimer. Much of the spectrophotometric and potentiometric data in the literature can be equally well interpreted in terms of either PuO_2OH^+ or $(\text{PuO}_2)_2(\text{OH})_2^{2+}$, and assuming the other species to be absent. Okajima *et al.* [91OKA/REE] interpreted their UV spectroscopic data in terms of PuO_2OH^+ , but reinterpreted them in terms of $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ in a later paper [93OKA/REE]. Even the data from extensive potentiometric study of Schedin [75SCH] is ambiguous as to whether significant quantities of the monomeric hydrolysis species is formed.

The most direct evidence that the initial hydrolysis species of PuO_2^{2+} is polymeric, at least at high solution concentrations of plutonium, comes from the Raman study of Madic *et al.* [84MAD/BEG]. No modification of the band for PuO_2^{2+} was found for a solution 0.1 mol·dm⁻³ in aqueous plutonium for pH values below 3.77. The first hydrolysis species was tentatively identified as $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ ($\log_{10}^*\beta_{2,2} = 8.01$), both by analogy with $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and because the shift between the MO_2^{2+} band and that of the first hydrolysis species was approximately the same in both systems. The band from a second plutonium hydrolysis species was assigned to $(\text{PuO}_2)_4(\text{OH})_7^+$ ($\log_{10}^*\beta_{7,4} = -29.32$) rather than an alternative 5:3 species, but the stoichiometry of the species was not firmly established (see Appendix A). Using the spectra for

0.1 M Pu(VI) in a 1.0 M ionic strength medium (0.26 M ClO_4^- , adjusted with NaCl, apparently room temperature measurements), formation constants were calculated for the 2:2 and 7:4 species. No evidence for a 1:1 hydrolysis species was found in these rather concentrated solutions.

Only the potentiometric study of Cassol *et al.* [72CAS/MAG] provides evidence that PuO_2OH^+ and $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ coexist, although the solubility study of Kim *et al.* [84KIM/BER] was interpreted as being consistent with that conclusion.

It appears the higher polymeric species deduced from the potentiometric studies, $(\text{PuO}_2)_3(\text{OH})_5^+$ and $(\text{PuO}_2)_4(\text{OH})_7^+$, are metastable if they exist at all [93PAS/KIM2], although other polymers may exist. The existence of both PuO_2OH^+ and $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ seems reasonable, although even the dimer may be metastable [95PAS/KIM]. If $\log_{10}^*\beta_1$ and $\log_{10}^*\beta_{2,2}$ have values near -5.5 and -7.5 , respectively, much of the spectroscopic and potentiometric data can be rationalised. One of the exceptions to this would be the solubility data of Kim *et al.* [84KIM/BER].

The results of Pashalidis *et al.* [95PAS/KIM] lead to a formation constant for $\text{PuO}_2(\text{OH})_2(\text{aq})$ of $\log_{10}^*\beta_{2,1} = -(13.15 \pm 0.18)$ at 22°C (Appendix A). This would mean the species is more stable than predicted in other work (*e.g.* [93PAS/KIM2]), and would be consistent with the polymeric Pu(VI) hydrolysis species being metastable except under very specific conditions.

Woods *et al.* [78WOO/MIT] reported Pu(VI) solutions, 10^{-3} to 10^{-4} M, 0.15 M in NaClO_4 were stable at a pH value of 11.4 for as long as two months. However, the nature of the hydrolysis species formed at high pH (13.3) was not established in the Raman study of Madic and Begun [84MAD/BEG]. From NIR spectroscopy, Tananaev [89TAN] suggested there was evidence for the existence of $\text{PuO}_2(\text{OH})_4^{2-}$ (in 1 M LiOH) and $\text{PuO}_2(\text{OH})_3^-$ in less basic solutions, however, no values were proposed for the hydrolysis constants. Moskvina and Zaitseva [62MOS/ZAI], Perez-Bustamante [65PER], Kim *et al.* [84KIM/BER] and Musante and Porthault all reported evidence for increased solubility of plutonium(VI) in basic solutions. None of these authors tried to interpret their data by including polymeric anionic species in their models. Such species have been proposed for the U(VI) system [92GRE/FUG]. With the possible exception of the last two studies, no useful thermodynamic information was reported in these papers (see Appendix A).

This review recommends

$$\log_{10}^*\beta_1^\circ = -(5.5 \pm 0.5)$$

(essentially identical to the value of Pashalidis *et al.* [95PAS/KIM]) and

$$\log_{10}^*\beta_{2,2}^\circ = -(7.5_{-1.0}^{+0.5})$$

For the neutral monomeric hydrolysis species, $\text{PuO}_2(\text{OH})_2(\text{aq})$, the 22°C value from Pashalidis *et al.* [95PAS/KIM] is accepted at 25°C , but with increased (and unsymmetrical) uncertainties,

$$\log_{10}^*\beta_{2,1}^\circ = -(13.2_{-1.5}^{+0.5})$$

The data for the the anionic species in basic solutions, are too uncertain for hydrolysis constants to be recommended at this time.

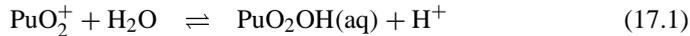
$$\begin{aligned}\Delta_f G_m^\circ(\text{PuO}_2\text{OH}^+, \text{aq}, 298.15 \text{ K}) &= -(968.1 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ((\text{PuO}_2)_2(\text{OH})_2^{2+}, \text{aq}, 298.15 \text{ K}) &= -(1956.2_{-8.0}^{+6.1}) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{PuO}_2(\text{OH})_2, \text{aq}, 298.15 \text{ K}) &= -(1161.3_{-9.0}^{+3.9}) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Based on the work of Rizkalla *et al.* [94RIZ/RAO], but with an increased uncertainty (*cf.* Appendix A), the value $\Delta_r H_m^\circ$ (Appendix A, Equation A.76, $a = 1$) = $(28 \pm 15) \text{ kJ}\cdot\text{mol}^{-1}$ is accepted. Hence:

$$\Delta_f H_m^\circ(\text{PuO}_2\text{OH}^+(\text{aq})) = -(1080 \pm 16) \text{ kJ}\cdot\text{mol}^{-1}$$

17.1.2 Plutonium(V) hydroxide complexes

There are few studies of the hydrolysis of the Pu(V). This is due to problems associated with possible disproportionation or precipitation in the pH range where hydrolysis is likely to occur. One series of studies [46KRA/DAM, 48KRA/NEL, 49KRA/DAM, 56KRA] provides a limiting value of $\log^* \beta_1^\circ = -9.7$ for the first hydrolysis constant:



A recent thesis and paper [90BEN, 92BEN/HOF] proposes $\log^* \beta_1^\circ(298 \text{ K}) \approx \log^* \beta_1(296 \text{ K}, 0.1 \text{ M})$ is $-(9.73 \pm 0.10)$, but for reasons outlined in Appendix A entry for [90BEN], this value probably reflects an upper limit for the stability of this complex. The selected upper limit

$$\log^* \beta_1^\circ(17.1, 298 \text{ K}) \leq -9.73$$

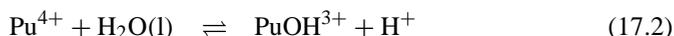
from [90BEN, 92BEN/HOF] is consistent with the value selected for the analogous Np(V) species ($\log^* \beta_1^\circ(8.1) = -(11.3 \pm 0.7)$). If a value is required for $\log_{10}^* \beta_1^\circ(17.1)$ rather than a limit, a value equal to that for the corresponding neptunium reaction but with an increased uncertainty, $\log_{10}^* \beta_1^\circ(17.1) = -(11.3 \pm 1.5)$, would be reasonable.

Recently Peretrukhin, David and Maslennikov [94PER/DAV] determined $E^\circ = -0.6 \text{ V}$ for the reduction on Pu(V) to Pu(IV) in 1 M LiOH, indicating Pu(V) is unlikely to disproportionate in basic solutions. Their work also suggested possible formation of an anionic Pu(V) hydrolysis species in strongly basic solutions ($> 0.5 \text{ M LiOH}$), but provides no quantitative evidence of the stability of this or these species. Further work is required on the stability of Pu(V) hydrolysis products. Peretrukhin, David and Maslennikov [94PER/DAV] and Neu *et al.* [94NEU/HOF], have concluded that significant solution concentrations of Pu(V) species can be found in basic and neutral aqueous solutions of plutonium.

17.1.3 Plutonium(IV) hydroxide complexes

There have been a number of potentiometric [51RAB/LEM, 57RAB], solubility [90PAZ/KUD], extraction [74SOL, 76MET/GUI] and spectroscopic [50KRA/NEL, 60RAB/KLI, 96NIT/SIL] studies of the first hydrolysis constant of Pu(IV). These are discussed in Appendix A. Measured values may be time dependent because of slow oxidation, disproportionation, radiolysis, or polymerization reactions. Therefore, the hydrolysis constant can be found only from studies in which the electrochemical potential was carefully controlled, or in which the equilibrium total plutonium(IV) in solution was measured, or the measurements were carried out rapidly.

The values of ${}^*\beta_1$ for reaction:



reported from the two extraction studies [74SOL, 76MET/GUI], are in relatively good agreement, but the source of Solovkin's values [74SOL] is not clear (see Appendix A). Metivier and Guillaumont's value [76MET/GUI] differs by an order of magnitude from the value found potentiometrically in a similar medium [51RAB/LEM]. Conversely, the spectrophotometric results of Rabideau and Kline [60RAB/KLI] are almost half an order of magnitude larger than the value reported from potential measurements by Rabideau [57RAB]. In this complicated system, spectrophotometric measurements are probably less prone than extraction or potentiometric measurements to some of the possible systematic errors that can originate from slow disproportionation of Pu(IV). There is only one study in chloride solution. Even for perchlorate solutions there are insufficient data, and the data are too badly scattered, to calculate an interaction $\Delta\varepsilon$ term for the hydrolysis reaction. An estimated value of $\varepsilon_{(\text{PuOH}^{3+}, \text{ClO}_4^-)} = 0.50 \text{ kg}\cdot\text{mol}^{-1}$ was used to calculate $\Delta\varepsilon = -0.18 \text{ kg}\cdot\text{mol}^{-1}$ and used with the experimental $\log_{10}{}^*\beta_1$ values from the three spectroscopic studies in perchlorate media [50KRA/NEL, 60RAB/KLI, 96NIT/SIL] (equally weighted) to obtain the selected

$$\log_{10}{}^*\beta_1^\circ(17.2, 298.15 \text{ K}) = -(0.78 \pm 0.60)$$

The uncertainty has been increased to overlap with the values from the potentiometric studies [51RAB/LEM, 57RAB]. Within the uncertainties, the value is the same as those selected for corresponding reactions involving uranium [92GRE/FUG] and neptunium (Section 8.1.4) species. Hence,

$$\Delta_f G_m^\circ(\text{PuOH}^{3+}, \text{aq}, 298.15 \text{ K}) = -(710.7 \pm 4.4) \text{ kJ}\cdot\text{mol}^{-1}$$

Two studies [57RAB, 60RAB/KLI] provide information on the temperature dependence of the first hydrolysis constant of Pu^{4+} . The reported values of $\Delta_r H_m$ for the reaction 17.2 are (30.5 ± 2.1) [57RAB] and (35.6 ± 3.8) [60RAB/KLI], both determined in perchlorate media of approximately 2 M ionic strength. Both these values were obtained from changes in equilibrium constants over quite small temperature differences, and the actual hydrolysis constants reported in the two studies are only in

marginal agreement. However, the values are in moderately good agreement with the value of $(46.9 \pm 9.0) \text{ kJ}\cdot\text{mol}^{-1}$ recently selected for the enthalpy of reaction in the corresponding uranium system [92GRE/FUG]. For the sake of consistency, the value

$$\Delta_f H_m^\circ(17.2, 298.15 \text{ K}) = (36 \pm 10) \text{ kJ}\cdot\text{mol}^{-1},$$

based on the spectrophotometric study [60RAB/KLI], is selected in the present review. The uncertainty is an estimate. From this,

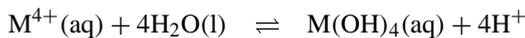
$$S_m^\circ(\text{PuOH}^{3+}, \text{aq}, 298.15 \text{ K}) = -(239 \pm 37) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

None of the available studies provide good thermodynamic data for higher hydrolysis species of Pu(IV). Equilibrium measurements are difficult to obtain, and radiolytic reactions can be important. The study of Metivier and Guillaumont is probably the best available. It is probable that in moderate to weakly acidic solutions ($\leq 0.1 m_{\text{H}^+}$), in a 1 M perchlorate medium, disproportionation relegates the higher cationic hydrolysis species of Pu(IV) to being minor components (subject to constraints imposed by slow reaction kinetics and possible radiolysis reactions) in the absence of a holding reduction/oxidation agent. For reasons discussed in Appendix A, the values from the solubility study of Yamaguchi *et al.* [94YAM/SAK] were not found to be useful. The studies of Rai and coworkers [80RAI/SER2, 80RAI/SER, 81RAI/SWA, 82RAI/RYA] established that at near neutral pH similar total plutonium concentrations were found regardless of whether the initial solid was “ $^{239}\text{Pu}(\text{OH})_4(\text{am})$ ” or $^{239}\text{PuO}_2(\text{cr})$. The stable solution plutonium species over this solid (designated by the authors as “less crystalline”) tended to be Pu(IV) or Pu(V) species – approximately 1% of the plutonium was found to be Pu(IV) plus Pu(III). Rai concluded that, near neutral pH, measurements of E_h for plutonium solutions were unreliable because the potential in the system was unpoised. Therefore, at best, only a limiting value can be calculated from these studies for the stability of $^{239}\text{Pu}(\text{OH})_4(\text{aq})$. Calculations indicate that for an unpoised system with respect to potential [84RAI], using the selected value for $\Delta_f G_m^\circ$ (hydrated PuO_2 , aged, 298.15 K) (*cf.* Section 17.2.2.3), the value

$$\Delta_f G_m^\circ(\text{Pu}(\text{OH})_4(\text{aq}), 298.15 \text{ K}) = -1387 \text{ kJ}\cdot\text{mol}^{-1}$$

is compatible with the results of the experimental study.

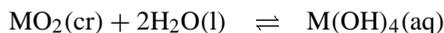
If this is accepted, the values of $\log_{10}K$ for the reactions



with $\text{M} = \text{U}, \text{Np}$ and Pu are -4.5 [92GRE/FUG], -9.8 (*cf.* Table 3.1) and -6.9 respectively (after this review was completed, a more negative value, < -10 , was reported [99RAI/HES2] for the plutonium reaction). It might be expected that the hydrolysis constants for these ions would be similar (within 1-2 orders of magnitude). If the stability of $\text{U}(\text{OH})_4(\text{aq})$ was less than the [92GRE/FUG] estimate by about four orders of magnitude (as suggested by work of Rai, Felmy and Ryan [90RAI/FEL] and Yajima, Kawamura and Ueta [95YAJ/KAW], but see also the discussion in [92GRE/FUG]), $\log_{10}K$ for the uranium reaction would be -8.5 . This appears to be a more reasonable

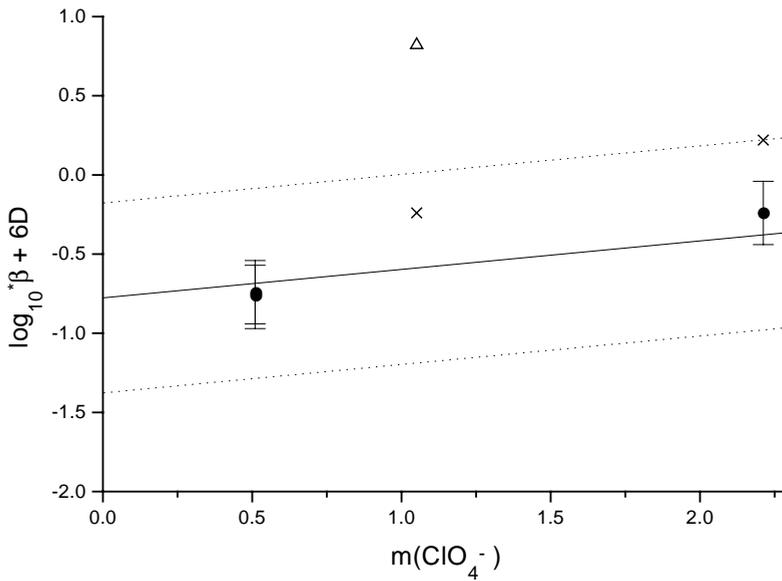
value, and the remaining spread of almost three orders of magnitude is possibly within the experimental uncertainties.

The Gibbs energies of reaction of M^{4+} ions ($M = U, Np, Pu$) with water to form the corresponding MO_2 crystalline oxides (26.1, 55.7 and 45.8 $\text{kJ}\cdot\text{mol}^{-1}$, respectively), show a large variation that is much greater than the accepted uncertainties. This variation is reflected in the values of $\log_{10}K$ for the reaction



Values for $M = U, Np$ and Pu are -9.4 [92GRE/FUG] (or -13.4 estimated from [90RAI/FEL]), -19.6 (*cf.* Table 3.1) and -14.9 respectively. It would be expected that this same variation of 5-10 orders of magnitude should be reflected in actinide(IV) “solubilities” measured in near-neutral, reducing solutions over “amorphous” or “hydrated” MO_2 (*cf.* Sections 8.2.5.2 and 17.6). The observed restricted range of solubility values (or similar “solubility limits”, *e.g.*, [85RAI/RVA], [90RAI/FEL] and also the recently published [99RAI/HES2]) is most likely due to inadequate detection limits, but is also possibly due to the differences in important experimental variables, one of which could be the nature of the solid phases.

Figure 17.2: Spectroscopically determined $\log_{10}^*\beta$ values [50KRA/NEL, 60RAB/KLI, 96NIT/SIL] of the first hydrolysis constant for Pu^{4+} (●), and the SIT plot (—) with estimated uncertainties (⋯) ($\varepsilon_{(\text{PuOH}^{3+}, \text{ClO}_4^-)}$ estimated as $0.50 \text{ kg}\cdot\text{mol}^{-1}$). Values from the potentiometric studies [51RAB/LEM, 57RAB] (×) and the extraction study of Metivier and Guillaumont [76MET/GUI] (Δ) are shown for comparison.



1:1				-5.71	[49KRA/DAM2]
1:2				-11.42	
1:1	pot	RT	0.186 mM HNO ₃	-3.33	[59KRE/NIK]
2:1				-7.38	
1:1	sol	25	1 M (Na)ClO ₄	-3.39	[62MOS/ZAI]
2:1				-8.64	
3:2				-17.77	
5:2				-31.50	
5:2	sol		var. KOH	-29.4	[65PER]
2:2	pot	25	3 M (Na)ClO ₄	-8.21 ^(a)	[71SCH]
1:1	pot	25	1 M (Na)ClO ₄	-5.97	[72CAS/MAG]
2:2				-8.51	
5:3				-22.16	
2:2	pot	25	3 M (Na)ClO ₄	-8.24	[75SCH]
7:4				-29.13	
1:1	tc	23	self 0.0005 M	-6.3	[83SCH/GOR]
1:1	sol	RT	0.1 M NaClO ₄	(log ₁₀ K ₁ = 8.26) ^(b)	[84KIM/BER]
2:1				(log ₁₀ β _{2,1} = 14.91)	
3:1				(log ₁₀ β _{3,1} = 16.90)	
2:2				(log ₁₀ β _{2,2} = 21.98)	
5:3				(log ₁₀ β _{5,3} = 56.28)	
				(log ₁₀ K _{s,0} = -23.00) ^(b)	
2:2	Raman	RT	1.0 M Cl ⁻ /ClO ₄ ⁻	-8.01	[84MAD/BEG]
7:4				-29.32	
(5:3)				-21.33) ^(c)	

(Continued on next page)

2:2	LPAS	25	0.1 M NaClO_4	-7.3	$-(7.33 \pm 0.09)$	[93OKA/REE]
	vis				$-(7.73 \pm 0.08)$	
1:1	nir	20	1.0 M NaClO_4	$(\log_{10} K_1 = 8.82)^{(e)}$	$-(4.76 \pm 0.3)$	[93PAS/KIM2]
2:1				$(\log_{10} \beta_{2,1} = 17.9)^{(e)}$		
1:1	uv/vis	22	0.1 M NaClO_4	$(\log_{10} K_1 = 8.20)^{(e)}$	$-(5.48 \pm 0.15)$	[95PAS/KIM]
2:1				$(\log_{10} \beta_{2,1} = 14.45)^{(e)}$	$-(13.15 \pm 0.18)$	
				$(\log_{10} K_{s,0} = -21.3)^{(e)}$	$\log_{10} {}^*K_{s,0} = (6.3 \pm 0.1)$	

(a) Reanalysed by the author in [75SCH] with additional data.

(b) The values of these parameters were fixed for the purposes of the calculations [86LIE/KIM]. See Appendix A.

(c) This alternate species with the noted value was reported by the authors.

(d) This value was repudiated by the authors in [93OKA/REE].

(e) Recalculated in this review (see Appendix A)

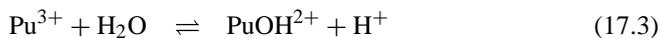
Table 17.2: Hydrolysis and solubility data for PuO_2^+

$n : m$	Methods	t (°C)	Ionic strength (medium)	$\log_{10}^* \beta_{n,m}$	$\log_{10}^* \beta_{n,m}^\circ$	Reference
	sol	RT	var. Cl^-	$(\log_{10} K_{s,0} = -8.6)$		[48KRA/NEL]
	sol	RT	self ClO_4^-	$(\log_{10} K_{s,0} = -9.3)$		[64GEL/ZAI] [68ZAI/ALE]
1:1	pot	RT	$3 \times 10^{-3} \text{ M}$ ClO_4^-	-9.7	-9.7	[49KRA/DAM]
1:1	LPAS	23	0.1 M ClO_4^-	-9.73	-9.73	[92BEN/HOF]

17.1.4 Plutonium(III) hydroxide complexes

Pu(III) is unstable in aqueous solutions towards oxidation by air and becomes less stable as the pH increases. Excluding air and/or adding a reductant will lead to rather stable Pu(III) solutions in the absence of species that can form strong complexes with Pu(IV). Solvent extraction with strongly complexing extractants (like HTTA), will shift the equilibrium towards the IV state.

Table 17.4 summarises the $^* \beta_1$ Pu(III) hydrolysis data for the reaction



There are really only six experimental studies (although two different values are reported on the basis of one of them [46KRA/DAM2, 49KRA/DAM3]). There are three kinds of data: (i) potentiometric titrations done at Oak Ridge and Los Alamos ([46KRA/DAM2], [49KRA/DAM3], [50BUS/COW]) during the U.S. Manhattan Project, (ii) a potentiometric titration [82NAI/CHA] done at Trombay, and (iii) studies done using the radio-tracer solvent extraction technique ([75HUB/HUS, 76HUB/HUS]).

The potentiometric measurements by Kraus *et al.* were carried out using Pu solutions in $\leq 0.002 \text{ M}$ NaCl or NaClO_4 at (probably) room temperature. Kraus *et al.* also studied the hydrolysis (and complexation) of plutonium in all oxidation states, so this group was familiar with problems resulting from oxidation state changes, precipitation, as well as possible polymerization during hydrolysis at these Pu concentrations (see Appendix A). The titrations were carried out with a protective atmosphere, avoiding carbonate in the titrant, and using spectrophotometry to control the relative concentrations of Pu(III) and Pu(IV) species. The experiments seem very reliable up to $\text{pH} \leq 7$, when precipitation began to occur. With modifications, the experiments were repeated several times with the same result. Studies of Am(III) suggest such solutions may be supersaturated [95SIL/BID]. The potentiometric titrations by [82NAI/CHA] were carried out in an inert atmosphere up to $\text{pH} 6$, when the solutions became opalescent due to “oxidation and precipitation” of Pu(IV). The Pu concentration was rather low, 0.04 mM, which would required high precision in order to yield reliable hydrolysis data up to a ligand number of 0.7. When the derived $\log_{10}^* \beta_1 = -(5.55 \pm 0.03)$ is

Table 17.3: Hydrolysis data for Pu⁴⁺

$n : m$	Methods	t (°C)	Ionic strength (medium)	$\log_{10}^*\beta_{n,m}$	Reference
1:1	sp	25	0.5 M Na/HCl	-1.66	[48KRA/NEL2] [50KRA/NEL]
1:1	sp	25	0.5 M Na/HClO ₄	-1.60 -1.80 ^(a)	[48KRA/NEL2] [50KRA/NEL]
1:1	pot	25.1	1.0 M Na/HClO ₄	-1.51	[51RAB/LEM]
1:1	pot	14.9	2.0 M Li/HClO ₄	-1.41	[57RAB]
1:1	pot	25.0		-1.26	
1:1	pot	34.4		-1.06	
1:1	sp	15.4	2.0 M Na/HClO ₄	-1.77	[60RAB/KLI]
1:1	sp	25.0		-1.70	
1:1	sp	15.4	2.0 M Na/DClO ₄	-2.17	[60RAB/KLI]
1:1	sp	25.0	in D ₂ O	-1.93	
1:1	ext	RT	1 M H/LiClO ₄	-0.45	[72MET/GUI]
2:1				-0.75	[73MET]
3:1				-3.3	[76MET/GUI]
4:1				-6.3	
1:1	ext/theor	RT	0.5-4.5 M NO ₃ ⁻	-0.67	[74SOL] ^(b)
2:1				-0.01	
3:1				0.8	
4:1	ext/theor			1.0	[80SOL/ZAK] ^(b)
1:1	sol	RT	3 M H/NaClO ₄	-1.52	[90PAZ/KUD]
2:1				-3.72	
3:1				-6.47	
4:1				-9.58	
1:1	sp	22	0.5 M Na/HClO ₄	-1.57 -1.84 ^(a)	[96NIT/SIL]

(a) Recalculated in the present review.

(b) The authors reported values for β_1° (for I=0) and indicate they used $K_w = 1.27 \times 10^{-14}$ in their calculations (for 22°C). However, at 22°C, $K_w = 8 \times 10^{-15}$ [59ROB/STO]. The values tabulated here for $\log_{10}^*\beta^\circ$ were calculated using the value for K_w indicated by Solovkin [74SOL].

Table 17.4: Data for the Pu(III) hydroxide system. ${}^*\beta_1$ refers to $\text{Pu}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{PuOH}^{2+} + \text{H}^+$.

t (°C)	Method	Medium	$\log_{10} {}^*\beta_1^{(b)}$	$\log_{10} {}^*\beta_1^\circ$	Reference
room?	pot (gl)	0.069 M NaClO ₄	-7.12	-6.73	[46KRA/DAM2] [48KRA/NEL2] [49HIN/AME]
room?	pot (gl?)	0.069 M NaClO ₄	-7.22	-6.83	[49KRA/DAM3]
room?	pot (gl?)	0.024 M NaCl	-7.37	-7.06 ^(a)	[49KRA/DAM3]
room?	pot (gl?)	0.040 M NaCl	-7.25	-6.86 ^(a)	[50BUS/COW]
23	dis (hydrazine)	0.20 M LiClO ₄	-3.80	-3.26	[75HUB/HUS]
23	dis (red?)	0.10 M LiClO ₄	-3.80	-3.36	[76HUB/HUS]
25	pot (gl?)	1.00 M NaClO ₄	-5.55	-4.74	[82NAI/CHA]

(a) Including corrections for Cl⁻ complexation (0.05 and 0.08, respectively).

(b) For discussion of uncertainties see text

used to calculate the titration curve, systematic deviations occur from the experimental points. It is not possible for the reviewer to explain the discrepancy, as too many explanations are possible. If Pu(IV), which hydrolyses much more easily (*i.e.*, at a lower pH), was present, this would account for the difference between the calculated and observed experimental values and yield too large a value for $\log_{10} {}^*\beta_1$ of Pu(III).

The third group, using radio-tracer solvent extraction with the extractant HTTA, obtained even larger hydrolysis constants than groups (i) and (ii), indicating that the hydrolysis starts at much lower pH values when using this technique (as compared to using potentiometric titrations). There should be no such discrepancy between the two techniques, but in this kind of study there can be many difficulties with radio-tracer solvent extraction. The results in [75HUB/HUS] are discussed in Appendix A. The main difficulty is to avoid the oxidation of Pu(III) to Pu(IV); the reviewer believes that Pu(IV) was present and interfered with the results, even though care was taken to avoid oxidation (excluding air and adding hydroxylamine as a reductant). The plutonium concentration was quite low, 10^{-5} to 10^{-8} M, and the amount of Pu(IV) was not measured during the experiments, which also showed unexpected kinetics. Hubert *et al.* [76HUB/HUS] did a slightly different experiment, carried out at lower ionic strength (0.1 instead of 0.2 M LiClO₄) and in the presence of citrate, which gave approximately the same equilibrium constant. In both cases, the statistical treatment of the data was unsatisfactory. Table 17.4 shows that it would be unwise to try to estimate $\Delta\varepsilon$ by a SIT plot. However, using $\Delta\varepsilon = (0.04 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ estimated by analogy with lanthanide systems [95SIL/BID], would yield a $\log_{10} {}^*\beta_1^\circ(17.4, I = 0) = -7.0$.



The average value of the potentiometric measurements (excluding the result from [82NAI/CHA]) is -6.73 at $I \leq 0.05$ M after corrections for temperature and chloride complexation. In this review

$$\log_{10} {}^*\beta_1^\circ(17.4, I = 0) = -(6.9 \pm 0.3)$$

is recommended where the uncertainties have been expanded. This is consistent with the value expected considering the value of the first hydrolysis constant of Am(III) selected by Silva *et al.* [95SIL/BID] is $-(6.4 \pm 0.2)$. Hence,

$$\Delta_f G_m^\circ(\text{PuOH}^{2+}, \text{aq}, 298.15\text{K}) = -(776.7 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}$$

17.2 Solid plutonium oxides and hydroxides

17.2.1 The plutonium-oxygen system

17.2.1.1 Phase diagram

The phase diagram and the non-stoichiometry of the oxide phases will not be dealt with in any detail in this volume, but the broad outlines of the system will be summarised. Despite a number of studies, the phase equilibria are not well established. This may be because the truly stable system shows many of the complexities of some of the lanthanide oxide systems at low temperatures, but the stable phase behaviour is disturbed by the inevitable radiation damage found in plutonium compounds. Figure 17.3 shows a diagram which is consistent with most of the observations, particularly those by Chikkalla *et al.* [64CHI/MCN], Gardner *et al.* [65GAR/MAR], Sari *et al.* [68SAR/BEN], Roulet [71ROU], and Boivineau [76BOI]. The two well defined oxides are the fcc dioxide and the hexagonal sesquioxide. In addition there are two bcc phases, one with a composition close to, and perhaps extending to, the sesquioxide composition, and one usually designated $\text{PuO}_{1.61}$ stable only above *ca.* 600 K, with a composition extending from $\text{PuO}_{1.61}$ probably to $\text{PuO}_{1.70}$. Above *ca.* 1000 K the fluorite dioxide phase can exist, presumably with oxygen vacancies, down to *ca.* $\text{PuO}_{1.71}$, but as seen on the figure, there are miscibility gaps and diphasic regions below this temperature. The phase boundaries above 1200 K are not well defined; although Roulet [71ROU] suggested that boundaries of the $\text{PuO}_{1.61}$ and PuO_{2-x} move to much lower O/Pu values at higher temperatures, the studies of Messier [68MES] and to a lesser extent Ohse and Ciani [68OHS/CIA] seem to confirm that the lower phase boundary of $\text{PuO}_{1.61}$ phase is not lower than $\text{PuO}_{1.60}$ from 2000 to 2300 K. The lower phase boundary of the sesquioxide is also certainly less than $\text{PuO}_{1.5}$ at high temperature (Tetenbaum [83TET] and Besmann and Lindemer [83BES/LIN]).

The solid monoxide reported in the earlier literature was in fact an oxy-carbonitride; the maximum oxygen content of the oxy-carbide is about $\text{PuC}_{0.3}\text{O}_{0.7}$ [65MUL/ELL].

Stakebake, Larson and Haschke [93STA/LAR] reported the reaction of plutonium with water vapour at 20 Pa to form an oxidised surface film, determined by photoelectron spectroscopy (XPS) to have a composition near $\text{PuO}_{2.2}$. It was suggested this phase may have a field of stability below 25°C.

17.2.1.2 PuO₂ (cr)

17.2.1.2.a Crystal structure

PuO₂ has the fluorite fcc structure (space group Fm3m) with $a = 5.396 \times 10^{-10}$ m; the X-ray density is $11.46 \text{ g}\cdot\text{cm}^{-3}$. As noted in a detailed discussion [67IAE], the lattice parameter increases with time owing to radiation damage.

17.2.1.2.b Heat capacity and entropy

Early measurements of the low-temperature heat capacity of ²³⁹PuO₂(cr) suffered from problems associated with radiation damage, and it was not until Flotow *et al.* [76FLO/OSB] made studies using oxides of the much less radioactive isotopes ²⁴²Pu (down to 12 K) and ²⁴⁴Pu (from 4 to 25 K) that reliable values of $C_{p,m}^{\circ}$ and S_m° (298.15 K) were obtained. Even so, the values below 25 K are uncertain by about 10-20%. Their most reliable measurements, extending from 12 to 347 K give:

$$\begin{aligned} C_{p,m}^{\circ}(\text{PuO}_2, \text{cr}, 298.15 \text{ K}) &= (66.25 \pm 0.26) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ S_m^{\circ}(\text{PuO}_2, \text{cr}, 298.15 \text{ K}) &= (66.13 \pm 0.26) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

High-temperature enthalpy increments, using ²³⁹PuO₂(cr), have been measured by Kruger and Savage [68KRU/SAV] from 298 to 1404 K, Ogard [70OGA] from 1500 to 2715 K, and Oetting and Bixby [82OET] from 353 to 1610 K. Ogard's measurements suggest a rapid increase in $C_{p,m}^{\circ}$ above 2370 K, but this is almost certainly because the sample was partially molten due to interaction with the tungsten container. Their values above 2370 K have been given zero weight. These measurements have been examined by Fink [82FIN] who fitted the enthalpy measurements to an expression representing two heat capacity contributions – a lattice contribution (taken to be a classical Einstein harmonic oscillator) and a term proportional to T , representing the contribution from lattice expansion and anharmonic terms, subject to the constraint of $C_{p,m}^{\circ}(298.15 \text{ K}) = 66.25 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ as given by Flotow *et al.* [76FLO/OSB]. Fink's values have been refitted to the extended Kelley polynomial (with a slightly relaxed constraint), to give:

$$\begin{aligned} C_{p,m}^{\circ}(\text{PuO}_2, \text{cr}, T) &= (84.4950 + 10.6390 \times 10^{-3}T \\ &\quad - 6.1136 \times 10^{-7}T^2 - 19.00564 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ &\quad (T = 298.15 - 2500 \text{ K}) \end{aligned}$$

The corresponding enthalpy expression fits all the experimental data below 2370 K to better than 3% (standard deviation). The thermal functions are close to those assessed by Glushko *et al.* [82GLU/GUR], which predate the study by Oetting and Bixby (1982).

Since stoichiometric PuO₂(cr) loses oxygen before melting, the melting point is not well defined, and the enthalpy of fusion is estimated. We have accepted the values given by Glushko *et al.* [82GLU/GUR] but increased the uncertainty:

$$\begin{aligned} T_{\text{fus}} &= (2663 \pm 40) \text{ K} \\ \Delta_{\text{fus}}H_m &= (67 \pm 15) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

These are based on measurements by Riley [70RIL] in 1 atm oxygen, Lyon and Bailey [67LYO/BAI], Chikalla *et al.* [64CHI/MCN], and comparison with urania. We have also taken for the value of the heat capacity of liquid PuO₂

$$C_{p,m}^{\circ}(\text{PuO}_2, \text{l}) = 131 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

as suggested by Glushko *et al.* [82GLU/GUR]. It should be emphasised again that PuO₂ will only melt congruently at very high pressures of oxygen.

17.2.1.2.c Enthalpy and Gibbs energy of formation

There is very good agreement between the several values for the enthalpy of combustion of plutonium in oxygen by Popov and Ivanov [57POP/IVA] $(-1056.0 \pm 4.0) \text{ kJ}\cdot\text{mol}^{-1}$, Holley *et al.* [58HOL/MUL] $(-1058.0 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$ and Johnson *et al.* [69JOH/DEV] $(-1055.70 \pm 0.71) \text{ kJ}\cdot\text{mol}^{-1}$. We select the value:

$$\Delta_f H_m^{\circ}(\text{PuO}_2, \text{cr}, 298.15 \text{ K}) = -(1055.8 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$$

given by Glushko *et al.* [82GLU/GUR], which is biased towards the appreciably more precise value by Johnson *et al.* [69JOH/DEV]. The derived Gibbs energy of formation of PuO₂(cr) is thus

$$\Delta_f G_m^{\circ}(\text{PuO}_2, \text{cr}, 298.15 \text{ K}) = -(998.113 \pm 1.031) \text{ kJ}\cdot\text{mol}^{-1}$$

17.2.1.2.d Solubility measurements

The ratios of the solubility products of PuO₂(cr) and hydrated PuO₂(cr) found in the studies of Kim and Kanellakopulos [89KIM/KAN2] and Rai *et al.* [80RAI/SER] appear to be similar. The value from Rai *et al.* [80RAI/SER] is subject to the same problems as the value for hydrated PuO₂ from the same study [84RAI] (*cf.* Section 17.2.2.3). The solubility product reported by Kim and Kanellakopulos [89KIM/KAN2] for PuO₂(cr) appears to be a good measurement for a batch experiment on a radioactive solid. However, it is not surprising that the value of $K_{s,0}$ is greater than the thermodynamic constant based on bulk (rather than surface) properties of the crystalline material (see Section 17.2.2.3).

17.2.1.3 Pu₂O₃ (cr)

17.2.1.3.a Crystal structure

Pu₂O₃(cr) has the hexagonal type-A rare earth sesquioxide structure (space group P3m1) with $a = 3.841 \times 10^{-10} \text{ m}$, $c = 5.958 \times 10^{-10} \text{ m}$ and a calculated density of $11.47 \text{ g}\cdot\text{cm}^{-3}$. As discussed in [67IAE], there is some evidence for the occurrence of a disordered variant of this structure in some samples of Pu₂O₃(cr), but it is not known whether this is due to the presence of impurities or a change in composition.

17.2.1.3.b Heat capacity and entropy

Flotow and Tetenbaum [81FLO/TET] have measured the heat capacity of a sample of $^{242}\text{Pu}_2\text{O}_3(\text{cr})$ from 8 to 350 K. A fairly sharp λ -type anomaly in the heat capacity occurs at 17.65 K, associated with an anti-ferromagnetic transition. The derived thermodynamic values at 298.15 K are:

$$\begin{aligned} C_{p,m}^\circ(\text{Pu}_2\text{O}_3, \text{cr}, 298.15 \text{ K}) &= (117.0 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ S_m^\circ(\text{Pu}_2\text{O}_3, \text{cr}, 298.15 \text{ K}) &= (163.0 \pm 0.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

There are no measurements of the thermal properties of $\text{Pu}_2\text{O}_3(\text{cr})$ at high temperatures, but estimates of $C_{p,m}^\circ$ have been given by [67IAE], Glushko *et al.* [82GLU/GUR], and Besmann and Lindemer [83BES/LIN]. The values from the last two estimations are very similar, since both used the known value at 298.15 K as a starting estimate. Since the equation given by Besmann and Lindemer does not reproduce the tabulated values of the Gibbs energy function (and leads to an unusual expression for $C_{p,m}^\circ$) we have preferred the values from Glushko *et al.* [82GLU/GUR]:

$$\begin{aligned} C_{p,m}^\circ(\text{Pu}_2\text{O}_3, \text{cr}, T) &= (169.466 - 79.98 \times 10^{-3}T \\ &\quad - 25.459 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ &\quad (298.15 \text{ to } 350 \text{ K}) \end{aligned}$$

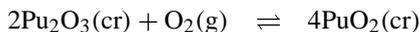
$$\begin{aligned} C_{p,m}^\circ(\text{Pu}_2\text{O}_3, \text{cr}, T) &= (122.953 + 28.548 \times 10^{-3}T \\ &\quad - 15.012 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ &\quad (350 \text{ to } 2358 \text{ K}) \end{aligned}$$

Although it is not known whether or not $\text{Pu}_2\text{O}_3(\text{cr})$ melts congruently, the melting point and enthalpy of fusion given by Glushko *et al.* [82GLU/GUR] are accepted here:

$$\begin{aligned} T_{\text{fus}} &= (2358 \pm 25) \text{ K} \\ \Delta_{\text{fus}}H_m &= (113 \pm 20) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

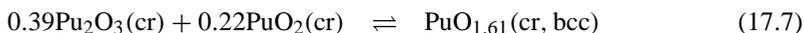
17.2.1.3.c Enthalpy and Gibbs energy of formation

There are no direct measurements of the enthalpy of formation of Pu_2O_3 and the value has been derived indirectly from the partial molar Gibbs energies and enthalpies of oxygen in the single phase oxides and diphasic fields between $\text{PuO}_{1.5}(\text{cr})$ and $\text{PuO}_2(\text{cr})$. Markin and Rand [66MAR/RAN] and [67IAE] presented a thorough analysis of the oxygen potential measurements of Markin *et al.* [64MAR/BON], giving a consistent analysis of the thermodynamic data and the phase diagram as envisaged at that time and giving values of the integrated enthalpy and entropy of the reaction:



Although further oxygen potential measurements have been made since then, notably by Atlas and Schlehman [66ATL/SCH], Woodley [81WOO], and Tetenbaum [83TET], none of these covers the whole region from $\text{PuO}_{1.5}$ to PuO_2 . However, the partial molar enthalpies of solution of oxygen presented by Chereau *et al.* [77CHE/DEA] indicate that the partial molar enthalpies and entropies derived from the EMF measurements by Markin and Rand [66MAR/RAN], although broadly correct, need some adjustments. This is also indicated by the appreciable difference in the integrated entropy for reaction (17.5) given by Markin and Rand, $\Delta_r S_m(1150 \text{ K}) = -180 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and that calculated from the thermal functions, $\Delta_r S_m(1150 \text{ K}) = -224 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Clearly an extensive reoptimisation of all the thermodynamic and phase diagram data, using appropriate models for the non-stoichiometric phases, is required. Until this considerable work is undertaken, the approximate treatment in the following paragraph must suffice.

Although, as noted above, some of the enthalpies and entropies given by Markin and Rand [66MAR/RAN] may be somewhat in error, their values of the oxygen potentials have been in general substantiated by subsequent studies, even those at higher temperatures than the measurements reported by Markin *et al.* [64MAR/BON] (see Tetenbaum [83TET], for example). We have therefore used the Gibbs energies, but not the enthalpies given by Markin and Rand, as items to be input into the assessment of the enthalpy of formation of $\text{Pu}_2\text{O}_3(\text{cr})$. Since data for the diphasic equilibrium $\text{Pu}_2\text{O}_3(\text{cr}) + \text{PuO}_{1.61}(\text{cr}, \text{bcc})$ are an important part of the overall assessment, values for the enthalpy of formation and entropy of the $\text{PuO}_{1.61}(\text{cr}, \text{bcc})$ phase at 298.15 K are also derived from the analysis, as noted below in the discussion of this phase. The final values chosen for $\text{Pu}_2\text{O}_3(\text{cr})$ and $\text{PuO}_{1.61}(\text{cr}, \text{bcc})$ are those which provided the best compromise between the experimental values given in Table 17.5, for the three reactions:



Considering the many approximations made in this brief analysis, particularly the neglect of the non-stoichiometry of the $\text{PuO}_{1.61}(\text{cr}, \text{bcc})$ phase and the simplifications in the phase diagram inherent in using Markin and Rand's original analysis, the agreement between the data is thought to be quite good. The derived value for the enthalpy of formation of $\text{Pu}_2\text{O}_3(\text{cr})$ is:

$$\Delta_f H_m^\circ(\text{Pu}_2\text{O}_3, \text{cr}, 298.15 \text{ K}) = -(1656 \pm 10) \text{ kJ}\cdot\text{mol}^{-1}$$

This is identical with that selected by Besmann and Lindemer [83BES/LIN] who used the oxygen potentials assessed by Markin and Rand [66MAR/RAN] to estimate $\Delta_f H_m^\circ(\text{Pu}_2\text{O}_3(\text{cr}))$. This value is consistent within the given uncertainties, with the approximate enthalpy of formation of $\text{PuO}_{1.52}(\text{cr}, \text{bcc})$ derived from the measurements by Chereau *et al.* [77CHE/DEA] of the enthalpies of combustion of two uncharacterised oxides of composition $\text{PuO}_{1.51}(\text{cr})$ and $\text{PuO}_{1.57}(\text{cr})$, as discussed briefly below.

Table 17.5: Thermochemical properties for interconversion reactions (17.5), (17.6), and (17.7) between plutonium oxides

Quantity	Value (kJ·mol ⁻¹)		Reference
	Experimental	Assessed	
$\Delta_r G_m(17.5)$ (1150 K)	-624.8	-639.5	[66MAR/RAN]
$\Delta_r H_m(17.5)$ (1373 K)	-875.6	-879.2	[77CHE/DEA]
$\Delta_r H_m(17.6)$ (1373 K)	-826.5	-824.1	[77CHE/DEA]
$\Delta_r G_m(17.6)$ (2250 K)	-547.8	-548.0	[83TET]
$\Delta_r G_m(17.6)$ (1600 K)	-623.8	-619.2	[66MAR/RAN] ^(a)
$\Delta_r G_m(17.6)$ (1100 K)	-687.8	-660.0	[66MAR/RAN]
$\Delta_r G_m(17.7)$ (573 K)	-0.2	<i>ca.</i> 0	[65GAR/MAR] (phase diagram)

(a) adjusted

The derived Gibbs energy of formation of Pu₂O₃(cr) is thus

$$\Delta_f G_m^\circ(\text{Pu}_2\text{O}_3, \text{cr}, 298.15 \text{ K}) = -(1580.375 \pm 10.013) \text{ kJ}\cdot\text{mol}^{-1}$$

17.2.1.4 PuO_{1.61} (cr, bcc)

17.2.1.4.a Crystal structure

This phase probably has a range of homogeneity with O/Pu extending from less than 1.61 to about 1.70; it exists only above 573 K. As summarised in [67IAE], the true structure of this phase is not known, but it is certainly closely related to the bcc C-type rare-earth structure, but with a smaller lattice parameter than the PuO_{1.52}(cr, bcc) phase.

17.2.1.4.b Heat capacity and entropy

Lacking experimental data, we have estimated $C_{p,m}^\circ$ to be approximately the weighted sum of Pu₂O₃(cr) and PuO₂(cr):

$$C_{p,m}^\circ(\text{PuO}_{1.61}, \text{bcc}, T) = 65.91 + 13.85 \times 10^{-3}T - 8.757 \times 10^5 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ (298.15 - 2300 \text{ K})$$

The entropy, as deduced in the analysis described under Pu₂O₃(cr), is slightly higher than that for 0.5 Pu₂O₃(cr), as expected for a phase which is stable only at higher temperatures:

$$S_m^\circ(298.15 \text{ K}) = (83.0 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

17.2.1.4.c Enthalpy and Gibbs energy of formation

There are no direct thermodynamic measurements of $\text{PuO}_{1.61}(\text{cr}, \text{bcc})$ but values have been deduced in the analysis described under $\text{Pu}_2\text{O}_3(\text{cr})$:

$$\Delta_f H_m^\circ(298.15 \text{ K}) = -(875.5 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$$

The derived Gibbs energy of formation of $\text{PuO}_{1.61}(\text{cr}, \text{bcc})$ is thus

$$\Delta_f G_m^\circ(\text{PuO}_{1.61}, \text{cr}, 298.15 \text{ K}) = -(834.771 \pm 10.113) \text{ kJ}\cdot\text{mol}^{-1}$$

17.2.1.5 $\text{PuO}_{1.52}(\text{cr}, \text{bcc})$

There are no thermodynamic measurements on this phase, except for enthalpies of combustion by Chereau *et al.* [77CHE/DEA] of uncharacterised samples of $\text{PuO}_{1.51}(\text{cr})$ and $\text{PuO}_{1.57}(\text{cr})$, which may have been rich in this phase. If the latter is assumed to be a mixture of $\text{PuO}_{1.52}(\text{cr}, \text{bcc})$ and $\text{PuO}_2(\text{cr})$, the measured values correspond to an enthalpy of formation of about $-(845 \pm 10) \text{ kJ}\cdot\text{mol}^{-1}$ for $\text{PuO}_{1.52}(\text{cr}, \text{bcc})$, which within the given uncertainties, is reasonably consistent with the assessed value for $\text{Pu}_2\text{O}_3(\text{cr})$. Other approximate values of its stability can be calculated from the (rather uncertain) phase diagram information, but since this phase is not of major importance for our considerations, this has not been attempted.

17.2.2 Hydrated plutonium oxides and hydroxides

17.2.2.1 Plutonium(VI) hydrated oxides and hydroxides

Cleveland [70CLE2] characterised the solid precipitated by ammonia from aqueous Pu(VI) as $\text{PuO}_2(\text{OH})_2\cdot\text{H}_2\text{O}$, and prepared a similar compound (less well characterised with respect to the extent of its hydration) by precipitation with pyridine. There are at least five solubility studies in the literature [62MOS/ZAI, 65PER, 73MUS/POR, 84KIM/BER, 95PAS/KIM], although the study of Perez-Bustamante [65PER] was restricted to strongly basic solutions. In none of the solubility studies was the solid thoroughly characterised, and in this review we have assumed the solid in each case was Cleveland's $\text{PuO}_2(\text{OH})_2\cdot\text{H}_2\text{O}(\text{cr})$. Musante and Porthault [73MUS/POR] reported $\log_{10} K_{s,0}^\circ = -(24.04 \pm 0.19)$, but did not provide details as to how this was determined. The value of Moskvin and Zaitseva [62MOS/ZAI], $\log_{10} K_{s,0}^\circ = -22.7$ was apparently based on a single solubility measurement for "ammonium diplutonnate" after equilibration for four to six hours at room temperature. The value from Kim *et al.* [84KIM/BER], is apparently not an experimental value at all [86LIE/KIM], but is an estimated value selected to be consistent with hydrolysis constant values calculated from the solubility study (see Appendix A). Pasaïdis *et al.* [95PAS/KIM] found that $\text{PuO}_2\text{CO}_3(\text{cr})$ was converted to a solid, presumably $\text{PuO}_2(\text{OH})_2(\text{cr})$, and spectroscopic measurements were used to determine the concentration and extent of hydrolysis of Pu(VI) over this solid (pH values from 4.8 to 6.0, 22°C, 0.1 M NaClO_4). After correction to $I = 0$ (Appendix A), the value $\log_{10}^* K_{s,0}^\circ = (6.3 \pm 0.1)$ is calculated. Based on the published hydrolysis constants and solubility product, it appears the solubilities

of Musante and Porthault must have been similar to those of Kim *et al.* (within about an order of magnitude, although the pH of the minimum solubility differs somewhat). The solubilities of Moskvin and Zaitseva are several orders of magnitude higher at all overlapping values of pH. However, the short equilibration period probably limited changes to the solution caused by radiolysis. Therefore, their reported solubility product (obtained from experiments at low pH where hydrolysis was unlikely) is probably toward the high end of the range of possible values. The solubility data of Kim *et al.* [84KIM/BER] are inconsistent with any value smaller than that of Moskvin and Zaitseva (see Appendix A). This is possibly indicative of problems with the Kim *et al.* study at low pH rather than a larger solubility product. However, the value from Pashalidis *et al.* [95PAS/KIM] suggests a somewhat lower stability for the solid even though the results were obtained after allowing for hydrolysis, and though the oxidation state of the plutonium in solution was carefully checked. This value could be consistent with the lower pH value measurements for Kim *et al.* In the present review we select

$$\log_{10}^* K_{s,0}^{\circ} = (5.5 \pm 1.0)$$

for the reaction



and hence,

$$\Delta_f G_m^{\circ}(\text{PuO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(1442.4 \pm 6.4) \text{ kJ} \cdot \text{mol}^{-1}$$

There are no reports in the literature of experimental values for the entropy or enthalpy of formation of $\text{PuO}_2(\text{OH})_2(\text{cr})$ or its hydrates. For the neptunium $\text{NpO}_2(\text{OH})_2(\text{cr})$ $S_m^{\circ} = (129 \pm 27) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ has been calculated (*cf.* Section 8.2.3.2) with the note that the value might actually be somewhat larger. If the contribution of $44.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for an extra water of hydration is considered [92GRE/FUG], S_m° becomes $(170 \pm 38) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The value $S_m^{\circ}(\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr})) = (188.54 \pm 0.38) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was reported by Tasker and O'Hare [88TAS/O'H]. By analogy, we select

$$S_m^{\circ}(\text{PuO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (190 \pm 40) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The heat capacity of $\text{PuO}_2(\text{OH})_2(\text{cr})$ was estimated as $112 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ by Lemire and Tremaine [80LEM/TRE] based on a Kopp's law calculation as outlined by Sturtevant [59STU]. If the solid were actually $\text{PuO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{cr})$ (and these materials were not distinguished in the earlier review [80LEM/TRE]), the estimated value would have been $148 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. This value is markedly smaller than the value $\text{UO}_3 \cdot \text{H}_2\text{O}(\text{cr})$, $(172.07 \pm 0.34) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ [88TAS/O'H]. However, in general, experimental heat capacity values for actinide solids tend to be somewhat greater than the Kopp's law estimates, and in the present review

$$C_{p,m}^{\circ}(\text{PuO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (170 \pm 20) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

is accepted, based on the heat capacity of the plutonium compound being similar to that for the uranium compound.

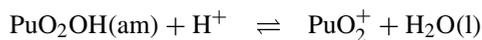
Bagnall and Laidler [64BAG/LAI] prepared a less hydrated compound with the stoichiometry $\text{PuO}_3 \cdot 0.8\text{H}_2\text{O}$ by passing ozonised oxygen through a suspension of Pu(IV) hydroxide at 90°C and vacuum drying the resulting solid at 130°C . On standing in air at room temperature, the compound took up water until it reached the composition $\text{PuO}_3 \cdot \text{H}_2\text{O}$. The X-ray diffraction pattern showed the compound is not iso-structural with any known uranium trioxide hydrates or, so far as could be determined, $\text{NpO}_3 \cdot \text{H}_2\text{O}$ [64BAG/LAI]. On the basis of the infrared spectra, Cleveland [70CLE2] suggested the compound of Bagnall and Laidler [64BAG/LAI] is probably structurally different from the compound precipitated from Pu(VI) solutions, $\text{PuO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$. This is also the case for the corresponding neptunium compounds [75BEL/IL'] (*cf.* Section 8.2.3.2). No thermodynamic data have been reported for $\text{PuO}_3 \cdot \text{H}_2\text{O}$.

17.2.2.2 Hydrated $\text{PuO}_2\text{OH}(\text{am})$

Kraus and Nelson [48KRA/NEL] reported a value of $\log_{10} K_{s,0} = -8.6$, ($\log_{10}^* K_{s,0} = 5.4$), for the solubility product for hydrated $\text{PuO}_2\text{OH}(\text{am})$ based on the data of Kraus and Dam [46KRA/DAM]. This value may be somewhat suspect, as the authors found considerable amounts of Pu(VI) and Pu(IV) in solution after redissolving the solids from these experiments. Reported values of $\log_{10} K_{s,0}$ in their study ranged from -8.3 to -9.5 (but see also Appendix A). Zaitseva *et al.* reported a solubility product of $\log_{10} K_{s,0} = -9.3$, ($\log_{10}^* K_{s,0} = 4.7$), based on the initial pH of precipitation from a 2.1×10^{-3} M Pu(V) solution. In the present review, we recommend a value of

$$\log_{10}^* K_{s,0} = (5.0 \pm 0.5)$$

for the reaction



for 298.15 K. This value is similar to the values selected (Section 8.2.4.2) for the solubility products of “fresh” and “aged” $\text{NpO}_2\text{OH}(\text{am})$. From the selected solubility product value

$$\Delta_f G_m^\circ(\text{PuO}_2\text{OH}, \text{am}, 298.15 \text{ K}) = -(1061.2 \pm 4.0) \text{ kJ} \cdot \text{mol}^{-1}$$

$S_m^\circ(\text{PuO}_2\text{OH}(\text{am}), 298.15 \text{ K}) = 87 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was estimated [80LEM/TRE] as the sum of $S_m^\circ(\text{PuO}_2)$ and an entropy contribution for an OH^- group attached to a singly charged metal ion. With the value for the entropy contribution given in Appendix D of the uranium review [92GRE/FUG], the value would be $S_m^\circ(\text{PuO}_2\text{OH}(\text{am}), 298.15 \text{ K}) = 97 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Hence, in the present review,

$$S_m^\circ(\text{PuO}_2\text{OH}, \text{am}, 298.15 \text{ K}) = (97 \pm 15) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

is accepted.

The heat capacity of $\text{PuO}_2\text{OH}(\text{am})$ was estimated as $86 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ by Lemire and Tremaine [80LEM/TRE] based on a Kopp's law calculation as outlined by Sturtevant [59STU]. In the absence of any experimental value, this is accepted in the present review with an estimated uncertainty of $20 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

$$C_{p,m}^{\circ}(\text{PuO}_2\text{OH}, \text{am}, 298.15 \text{ K}) = (86 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

17.2.2.3 $\text{Pu}(\text{OH})_4(\text{am})$ ($\text{PuO}_2 \cdot x \text{H}_2\text{O}$)

As shown in Table (17.6), there have been a number of reports on the solubility of solids resulting from hydrolysis of plutonium(IV) [49KAS, 65PER, 67DAV, 80RAI/SER, 84PER/SAP, 84RAI, 86LIE/KIM, 86EWA/HOW, 89KIM/KAN, 92EWA/SMI]. Some of these studies (*e.g.*, [65PER, 67DAV, 84PER/SAP]) have been done under poorly defined conditions, others are based on limited data (*e.g.*, [49KAS]). Even in this early study of Kasha, it was recognised that, except in strongly acidic solutions, only a small percentage of the total plutonium in aqueous solution at equilibrium over a plutonium(IV) hydrolytic solid would be plutonium(IV) species. This problem has apparently been ignored in some later studies (*e.g.*, [65PER, 67DAV, 84PER/SAP, 90PAZ/KUD]).

Table 17.6: Solubility data for plutonium(IV) oxide and hydroxide

Solid	Methods	t (°C)	Ionic strength (medium)	$\log_{10} K_{s,0}$	$\log_{10} K_{s,0}^{\circ}$ (recalc.)	Reference
$\text{Pu}(\text{OH})_4$	sol	RT	?	-55.5		[49KAS]
$\text{Pu}(\text{OH})_4$	sol	RT	0.062 M HCl	-55.1		[49KAS]
$\text{Pu}(\text{OH})_4$	sol	RT	1 M HClO_4	-55.2		[49KAS]
$\text{Pu}(\text{OH})_4$	sol	RT		-47.3 to -56.3		[65PER]
$\text{Pu}(\text{OH})_4$	sol	RT	ads. + ultfil	-50.2		[67DAV]
$\text{Pu}(\text{OH})_4$	sol	RT	ultrafil.	-54.7		[67DAV]
$\text{Pu}(\text{OH})_4$	sol	RT	0.0015 M CaCl_2	-50.2		[80RAI/SER]
PuO_2	sol	RT	0.0015 M CaCl_2	-52.2 -51.8		[80RAI/SER] (ex [89KIM/KAN])
$\text{Pu}(\text{OH})_4$	sol	RT		-53.0		[84PER/SAP]
$\text{PuO}_2(\text{hyd})$	sol	RT	corr. $I = 0$	-56.85	-57.4	[84RAI]
$\text{Pu}(\text{OH})_4$	sol	RT		-53.7		[86LIE/KIM]
$\text{Pu}(\text{OH})_4$	sol	20	corr. $I = 0$	-57.85	-58.8	[89KIM/KAN]
$\text{PuO}_2(\text{cr})$	sol	20	corr. $I = 0$	-60.20	-61.2	[89KIM/KAN]
$\text{Pu}(\text{OH})_4$	sol	25		-51.4		[90PAZ/KUD]
$\text{Pu}(\text{OH})_4$ (hyd, aged)	est.	25		-(58 ± 1)		this review
$\text{PuO}_2(\text{cr})$	calc.	25		-(64.0 ± 0.5)		this review

Radiolytic effects influence the solubility experiments. The crystalline dioxide, $^{239}\text{PuO}_2$, when contacted with water over a period of time, is slowly converted to

(or coated with a small amount of) a less crystalline form. The hydrated, amorphous form of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ is gradually converted to a similar, slightly crystalline, form, but the “Ostwald ripening” apparently does not continue past this stage [82RAI/RYA]. If $^{238}\text{PuO}_2$ is contacted with water, the crystalline solid is converted to the amorphous solid [82RAI/RYA]. Also, moderately acidic plutonium(IV) solutions frequently contain a colloidal plutonium species, probably finely dispersed $\text{PuO}_2 \cdot x\text{H}_2\text{O}$. This material can complicate solubility studies, leading to high apparent solubilities.

The total solubilities of plutonium aqueous species at a series of comparable pH values were reported by Perez-Bustamante [65PER] (perchlorate medium) and Rai [84RAI] (nitrate medium). These values differ by one to two orders of magnitude. The lower experimental solubilities in the earlier study might indicate the use of a more stable form of the hydroxide or hydrous oxide, but more likely were the result of the slow dissolution kinetics and a shorter equilibration time – the calculated solubility products ($\log_{10} K_{s,0}^\circ$) reported by Rai are more negative than those reported by Perez-Bustamante only because Rai treated activity coefficient effects differently, and also allowed for hydrolysis and complexation. The pH independence of this solubility difference suggests it is not simply the result of different oxidation state distributions. Kasha’s value (perchlorate medium) [49KAS] is comparable to those of Rai [84RAI], even though Kasha reported some colloid formation before the end of the experiment.

This so-called “plutonium(IV) polymer” or “plutonium hydrous polymer” has been found [78LLO/HAI] to consist of small (approximately 0.2 nm) colloiddally dispersed particles which can be either crystalline or amorphous. As is normal for a polymeric colloid, it has a distinctive absorption spectrum. The colloid is stabilized by anions such as nitrate or chloride when the molar ratio of the stabilizing anion to plutonium is between 0.8 and 4. The colloid can be prepared by partially acidifying precipitated “ $\text{Pu}(\text{OH})_4$ ”, by allowing Pu(IV) to form hydrolytic polymers in 0.1 M nitrate solutions, by heating moderately acidic solutions of Pu(IV), or by removing HNO_3 from aqueous $\text{Pu}(\text{NO}_3)_4\text{-HNO}_3$ solutions by extraction [86WEI/KAT]. It also appears to be formed by auto-radiolysis of $^{238}\text{PuO}_2(\text{cr})$ [82RAI/RYA] in aqueous suspension. When conditions are altered such that the colloid is destabilized, the particles may form insoluble aggregates that are primarily crystalline PuO_2 . Although there is at least one attempt in the literature to calculate a value of $\Delta_f G_m^\circ$ (“plutonium polymer”) per mole Pu(IV) [83SIL], this is not a meaningful (equilibrium) thermodynamic quantity.

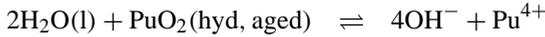
Kim and Kanellakopulos [89KIM/KAN] reported solubilities of $\text{Pu}(\text{OH})_4(\text{am})$ and $\text{PuO}_2(\text{cr})$ in 1 M HClO_4 . Their values are markedly lower than those of Rai [84RAI], or even those of Perez-Bustamante [65PER]. Kim and Kanellakopulos attributed this to unfilterable colloidal material (<1 nm) suspended in the solutions of Rai and Perez-Bustamante, however, Rai determined his Pu(IV) solution concentrations by extraction with TTA, and did not rely strictly on the gross α analysis. On the other hand, Kim and Kanellakopulos also verified their spectroscopically determined solution concentration of Pu(IV) by TTA extraction. The concentration determined by extraction was about 50% greater than the value from spectroscopy.

In view of the difficulties in establishing equilibrium, measuring the concentrations of Pu^{4+} (especially considering possible sorption effects) and maintaining constant temperatures while equilibrating and sampling the solutions, the results of Rai [84RAI]

and Kim and Kanellakopoulos [89KIM/KAN2] are actually in quite good agreement. The tendency of Pu(IV) to disproportionate under the experimental conditions was carefully taken into consideration. On the basis of these two studies, a value of

$$\log_{10} K_{s,0}^{\circ} = -(58 \pm 1)$$

is recommended for the solubility product of well aged hydrated PuO₂ (or Pu(OH)₄(am)).



Because the solid itself is not a thermodynamically stable solid that can be prepared reproducibly, any value for $\Delta_f G_m^{\circ}$ can only be approximate. Based on the selected solubility product, $\Delta_f G_m^{\circ}(\text{hydrated PuO}_2, \text{aged}, 298.15 \text{ K}) = -(963.7 \pm 6.3) \text{ kJ}\cdot\text{mol}^{-1}$ for hydrated oxide. This value is accepted for the precipitated solid, aged for several months near room temperature. The value of $\Delta_f G_m^{\circ}$ for freshly precipitated material may be 10 to 20 $\text{kJ}\cdot\text{mol}^{-1}$ more positive.

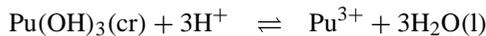
As this review was being completed, a preprint was received of a spectrophotometric study by Capdevila and Vitorge [98CAP/VIT] in which the concentrations of plutonium aqueous species in 0.1 M HClO₄(aq) over Pu(OH)₄(am) were measured at different ionic strengths. From the behaviour of the equilibria between the ions in different oxidation states, the authors calculated the concentration of Pu⁴⁺, a species that could not be detected spectrophotometrically in these solutions, and determined the solubility product of the Pu(IV) solid. Though it was not used in the present evaluation, the reported value for the solubility product $\log_{10} K_{s,0}^{\circ} = -(58.3 \pm 0.5)$ is in good agreement with the value selected in this review.

17.2.2.4 Pu(OH)₃(s)

Experimental studies on the solubility products of the actinide(III) hydroxides are very sparse. It is not obvious how the often cited [52LAT, 56KRA] value for the solubility product of Pu(OH)₃(s) was calculated from the original data of Busey and Cowan [50BUS/COW] (see Appendix A), nor is it clear the data are adequate for useful recalculations. Certainly no systematic study of $^*K_{\text{sp}}$ (the acidic solubility product) as a function of temperature has been done. Based on a recent study by Felmy *et al.* [89FEL/RAI] the value

$$\log_{10} ^*K_{s,0} = (15.8 \pm 1.5)$$

is accepted in the present review for the reaction



Hence,

$$\Delta_f G_m^{\circ}(\text{Pu}(\text{OH})_3, \text{s}, 298.15 \text{ K}) = -(1200 \pm 9) \text{ kJ}\cdot\text{mol}^{-1}$$

This solubility product is consistent with the values selected [95SIL/BID] for Am(OH)₃(s), $\log_{10} ^*K_{s,0} = (17.0 \pm 0.6)$ for the amorphous form and $\log_{10} ^*K_{s,0} = (15.2 \pm 0.6)$ for the crystalline form.

Chapter 18

Plutonium group 17 (halogen) compounds and complexes

18.1 Plutonium halide compounds

18.1.1 Introduction

There are experimental data for the enthalpies of formation at 298.15 K of some of the more important plutonium halides, but those of some technologically important compounds, such as PuF_4 and PuF_6 have still to be estimated from non-calorimetric observations, and thus are relatively uncertain. The only halides for which low temperature heat capacity measurements (and thus reliable standard entropies) are available are $\text{PuF}_3(\text{cr})$ and $\text{PuF}_4(\text{cr})$, so that the entropies of all the other halides have had to be estimated. The lack of a precise value for the standard entropy of PuCl_3 is particularly noteworthy.

There are precise determinations of the vapour pressures of PuF_3 , PuF_6 , PuCl_3 and PuBr_3 . The derived entropies of sublimation and vaporisation of the first three are in excellent accord with those predicted from the thermal functions (often estimated), but those of PuBr_3 are appreciably higher than anticipated, for reasons which are not clear.

18.1.2 Plutonium fluoride compounds

18.1.2.1 $\text{PuF}(\text{g})$ and $\text{PuF}_2(\text{g})$

18.1.2.1.a Enthalpy of formation

Kent [68KEN] has studied the equilibria involving $\text{Pu}(\text{g})$, $\text{PuF}(\text{g})$, $\text{PuF}_2(\text{g})$ and $\text{PuF}_3(\text{g})$ evaporating from a tantalum Knudsen cell, containing a mixture of PuF_3 and electro-refined plutonium metal, attached to a mass-spectrometer. The PuF_2^+ ion was formed from both $\text{PuF}_2(\text{g})$ and $\text{PuF}_3(\text{g})$ present in the vapour, but the fractions arising from the two species were estimated by making measurements at different accelerating voltages. The ion current analogues of the equilibrium constants for the two reactions



were plotted as a function of reciprocal temperature to give the enthalpies of these reactions: $\Delta_r H_m(18.1, 1414 \text{ K}) = (97.9 \pm 19.2) \text{ kJ}\cdot\text{mol}^{-1}$ and

$\Delta_r H_m(18.2, 1417 \text{ K}) = (120.0 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$. The corrections to 298.15 K using the thermal functions discussed in the next section, are respectively +34.1 and +23.7 $\text{kJ}\cdot\text{mol}^{-1}$, giving $\Delta_r H_m^\circ(18.1, 298.15 \text{ K}) = (132.0 \pm 20.0) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r H_m^\circ(18.2, 298.15 \text{ K}) = (143.7 \pm 11.0) \text{ kJ}\cdot\text{mol}^{-1}$. With the relatively precise values of $\Delta_f H_m^\circ(\text{Pu}, \text{g}, 298.15 \text{ K}) = (349.0 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$ (Section 15.2) and $\Delta_f H_m^\circ(\text{PuF}_3, \text{g}, 298.15 \text{ K}) = -(1167.8 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}$ (Section 18.1.2.3), these give the selected values

$$\begin{aligned}\Delta_f H_m^\circ(\text{PuF}, \text{g}, 298.15 \text{ K}) &= -(112.6 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f H_m^\circ(\text{PuF}_2, \text{g}, 298.15 \text{ K}) &= -(614.3 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

where the uncertainties have been increased to allow for uncertainties in the thermal functions and in the fraction of the overall PuF_2^+ ion due to the parent $\text{PuF}_2(\text{g})$ and $\text{PuF}_3(\text{g})$ species.

18.1.2.1.b Standard entropy and heat capacity

The thermal functions of $\text{PuF}(\text{g})$ and $\text{PuF}_2(\text{g})$ were calculated assuming the molecular parameters discussed in Rand and Fuger [2000RAN/FUG]. These are essentially those suggested by Hildenbrand *et al.* [85HIL/GUR], namely values similar to those estimated for $\text{UF}(\text{g})$ and $\text{UF}_2(\text{g})$ by Glushko *et al.* [82GLU/GUR], but with no electronic contributions. The Pu-F interatomic distances were taken to be 2.03×10^{-10} and 2.10×10^{-10} m respectively for $\text{PuF}(\text{g})$ and $\text{PuF}_2(\text{g})$. These assumptions give

$$\begin{aligned}S_m^\circ(\text{PuF}, \text{g}, 298.15 \text{ K}) &= (251 \pm 5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{PuF}, \text{g}, 298.15 \text{ K}) &= (33.5 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ S_m^\circ(\text{PuF}_2, \text{g}, 298.15 \text{ K}) &= (297 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{PuF}_2, \text{g}, 298.15 \text{ K}) &= (51.5 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\end{aligned}$$

Full tables of the estimated thermal functions of these species up to 2000 K are given by Rand and Fuger [2000RAN/FUG].

18.1.2.2 PuF₃ (cr)

18.1.2.2.a Enthalpy of formation

The enthalpy of formation of $\text{PuF}_3(\text{cr})$ is based on the enthalpy of precipitation of (hydrated) PuF_3 from 1.5 M HCl by $\text{HF} \cdot 1.925\text{H}_2\text{O}$ ($-(30.1 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1}$), measured by Westrum and Eyring [49WES/EYR]. The precipitate is assumed to contain $0.4\text{H}_2\text{O}$, based on the detailed study by Jones [53JON]. The value for the integral enthalpy of formation of the precipitating solution $\text{HF} \cdot 1.925\text{H}_2\text{O}$, was interpolated from the data of Johnson *et al.* [73JOH/SMI] by a quadratic function of $m^{1/2}$, for the range $m^{1/2} = 5.0 - 5.6$ for $m^{1/2} = 5.3699$ to be $-320.11 \text{ kJ}\cdot\text{mol}^{-1}$. As noted by Parker [76PAR], no correction is required for the fact that the value for $\Delta_f H_m^\circ(\text{HF}, \text{aq}, 298.15 \text{ K})$ used by Johnson *et al.* [73JOH/SMI], $-(335.64 \pm 0.29) \text{ kJ}\cdot\text{mol}^{-1}$, was slightly different from

the CODATA Key Value [89COX/WAG] $-(335.35 \pm 0.65) \text{ kJ}\cdot\text{mol}^{-1}$, the difference being accommodated in the enthalpies of dilution from the lowest concentration used by [73JOH/SMI] and infinite dilution.

Hence, for the reaction



$$\Delta_r H_m^\circ(298.15 \text{ K}) = -(1582.93 \pm 3.00) \text{ kJ}\cdot\text{mol}^{-1}$$

The enthalpy of dehydration of $\text{PuF}_3\cdot 0.4\text{H}_2\text{O}(\text{cr})$ has been taken to be

$$\Delta_r H(\text{dehydration}) = -(3.8 \pm 2.1) \text{ kJ}\cdot\text{mol}(\text{PuF}_3)^{-1}$$

as discussed by Fuger *et al.* [83FUG/PAR].

Hence,

$$\Delta_f H_m^\circ(\text{PuF}_3, \text{cr}, 298.15 \text{ K}) = -(1586.7 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}$$

18.1.2.2.b Standard entropy and heat capacity

The standard entropy and heat capacity at 298.15 K are taken from the low-temperature heat capacity measurements of Osborne *et al.* [74OSB/FLO], using a sample containing nearly isotopically pure ^{242}Pu , to minimise problems from self-heating at very low temperatures.

$$S_m^\circ(\text{PuF}_3, \text{cr}, 298.15 \text{ K}) = (126.11 \pm 0.36) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}^\circ(\text{PuF}_3, \text{cr}, 298.15 \text{ K}) = (92.64 \pm 0.28) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.2.2.c High temperature heat capacity

There are no measured values of the heat capacity above 350 K. Values have been estimated to be similar to those of $\text{UF}_3(\text{cr})$, assessed by Grenthe *et al.* [92GRE/FUG], with the constraint that they merge smoothly with the experimental values from 298.15 to 350 K from [74OSB/FLO]:

$$C_{p,m}^\circ(\text{PuF}_3, \text{cr}, T) = (104.078 + 0.707 \times 10^{-3}T - 10.355 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 K to 1700 K.

18.1.2.2.d Fusion data

The melting point is taken to be $(1700 \pm 3) \text{ K}$, corrected from the experimental value of $(1699 \pm 3) \text{ K}$ (assumed to be on the IPTS68 Temperature scale) given by Westrum and Wallmann [51WES/WAL]. The enthalpy of fusion $((35.4 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ and the heat capacity of the liquid $((130 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ have been estimated and given by Rand and Fuger [2000RAN/FUG].

18.1.2.3 PuF₃ (g)

18.1.2.3.a Enthalpy of formation

There are three Knudsen effusion studies of the vapour pressure of PuF₃(cr), contained in tantalum cells, by Phipps *et al.* [50PHI/SEA], Carniglia and Cunningham [55CAR/CUN] and Kent [68KEN], with excellent agreement. These have all been corrected to the 1990 Temperature scale and 1986 Fundamental constants. In addition small corrections have been applied to the first two measurements for conversion to the current recommended half-life of ²³⁹Pu (24110 y) [86BRO/FIR]. The amount of effusate in the experiments by Kent [68KEN] was determined by weighing, so no half-life corrections were required.

The least square fits to the data give for $\log_{10}(p/\text{bar}) = a/T + b$ and $\Delta_{\text{sub}}S_{\text{m}}^{\circ}$ are summarised in [2000RAN/FUG].

Third law treatment of all data using thermal functions estimated below gives

$$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (418.9 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$$

and hence,

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuF}_3, \text{g}, 298.15 \text{ K}) = -(1167.8 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}$$

18.1.2.3.b Standard entropy and heat capacity

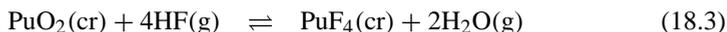
The thermal functions of PuF₃(g) were calculated assuming the molecular parameters given by Rand and Fuger [2000RAN/FUG], using the rigid-rotator, harmonic oscillator approximation. The molecule is assumed to be pyramidal, with C_{3v} symmetry. These give

$$\begin{aligned} S_{\text{m}}^{\circ}(\text{PuF}_3, \text{g}, 298.15 \text{ K}) &= (336.11 \pm 10.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{PuF}_3, \text{g}, 298.15 \text{ K}) &= (72.24 \pm 5.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

18.1.2.4 PuF₄ (cr)

18.1.2.4.a Enthalpy of formation

This has been estimated from two experimental observations and one correlation. Johns, [45JOH] measured the equilibrium constants for the reaction



at 673 and 873 K, giving the Gibbs energies of reaction:

$$\begin{aligned} \Delta_{\text{r}}G_{\text{m}}^{\circ}(18.3, 673 \text{ K}) &= -1.736 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_{\text{r}}G_{\text{m}}^{\circ}(18.3, 873 \text{ K}) &= 10.461 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

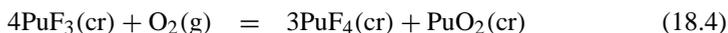
The entropy of reaction calculated from the thermal functions for the reaction is very different from the experimental value, and the third law

values for $\Delta_r H_m^\circ(298.15 \text{ K})$ are -161.2 and $-198.7 \text{ kJ}\cdot\text{mol}^{-1}$. With $\Delta_f H_m^\circ(\text{PuO}_2, \text{cr}, 298.15 \text{ K}) = -(1055.8 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$ from [82GLU/GUR] and the current review and CODATA values [89COX/WAG] for $\text{HF}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, the first derived value for the enthalpy of formation of $\text{PuF}_4(\text{cr})$, the mean of the two third-law values, is:

$$\Delta_f H_m^\circ(\text{PuF}_4, \text{cr}, 298.15 \text{ K}) = -(1844.3 \pm 30.0) \text{ kJ}\cdot\text{mol}^{-1}$$

from [45JOH].

Dawson and Elliott [54DAW/ELL] measured oxygen pressures close to equilibrium values at 783 and 1073 K for the reaction



which gives

$$\begin{aligned} \Delta_r G_m^\circ(18.4, 783 \text{ K}) &= -30.25 \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_r G_m^\circ(18.4, 1073 \text{ K}) &= -20.54 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Again, there is a considerable difference between the third law enthalpies for $\Delta_r H_m^\circ(298.15 \text{ K})$ of the reaction calculated using estimated thermal functions, -182.4 and $-223.3 \text{ kJ}\cdot\text{mol}^{-1}$. With the mean value and $\Delta_f H_m^\circ(\text{PuO}_2, \text{cr}, 298.15 \text{ K}) = -(1055.8 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$ from [82GLU/GUR] and the current review and our current value for $\text{PuF}_3(\text{cr})$, the second derived value for the enthalpy of formation of $\text{PuF}_4(\text{cr})$ is:

$$\Delta_f H_m^\circ(\text{PuF}_4, \text{cr}, 298.15 \text{ K}) = -(1831.3 \pm 20.0) \text{ kJ}\cdot\text{mol}^{-1}$$

from [54DAW/ELL], where the uncertainty is increased to allow for the possible lack of true equilibrium.

The third estimate is derived from the correlation between the difference of the enthalpies of formation of the actinide tetrahalides and the aqueous M^{4+} ions and the ionic radius of the M^{4+} , as discussed in detail by Fuger *et al.* [83FUG/PAR] and Rand and Fuger [2000RAN/FUG]. The extrapolated value of $\Delta_f H_m^\circ(\text{PuF}_4, \text{cr}, 298.15 \text{ K}) - \Delta_f H_m^\circ(\text{Pu}^{4+}, \text{aq}, 298.15 \text{ K})$ therefrom is $-(1319.5 \pm 13.0) \text{ kJ}\cdot\text{mol}^{-1}$, which with $\Delta_f H_m^\circ(\text{Pu}^{4+}, \text{aq}, 298.15 \text{ K}) = -(539.9 \pm 3.1) \text{ kJ}\cdot\text{mol}^{-1}$ gives finally

$$\Delta_f H_m^\circ(\text{PuF}_4, \text{cr}, 298.15 \text{ K}) = -(1859.4 \pm 13.4) \text{ kJ}\cdot\text{mol}^{-1}$$

from the correlation.

The selected value from these three fairly consistent estimates $-(1844.3 \pm 30.0)$, $-(1831.3 \pm 20.0)$ and $-(1859.4 \pm 13.4) \text{ kJ}\cdot\text{mol}^{-1}$ is

$$\Delta_f H_m^\circ(\text{PuF}_4, \text{cr}, 298.15 \text{ K}) = -(1850 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$$

but this can only be regarded as a provisional value. This value is consistent with the observation of Johnson *et al.* [61JOH/FIS] that $\text{SF}_4(\text{g})$ does not reduce $\text{PuF}_4(\text{cr})$ to $\text{PuF}_3(\text{cr})$ at 773K, which implies that $\Delta_f H_m^\circ(\text{PuF}_4, \text{cr}, 298.15 \text{ K})$ is more negative than *ca.* $-1815 \text{ kJ}\cdot\text{mol}^{-1}$.

18.1.2.4.b Standard entropy and heat capacity

The standard entropy and heat capacity at 298.15 K are taken from the low-temperature heat capacity measurements of Osborne *et al.* [75OSB/FLO], using a sample containing nearly isotopically pure ^{242}Pu , to minimise problems from self-heating at very low temperatures.

$$\begin{aligned} S_{\text{m}}^{\circ}(\text{PuF}_4, \text{cr}, 298.15 \text{ K}) &= (147.25 \pm 0.37) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{PuF}_4, \text{cr}, 298.15 \text{ K}) &= (116.19 \pm 0.29) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

18.1.2.4.c High temperature heat capacity

Osborne *et al.* [75OSB/FLO] estimated the heat capacity of $\text{PuF}_4(\text{cr})$ above 350 K, and we have accepted this estimate with a minor change to reproduce their experimental $C_{p,\text{m}}^{\circ}(298.15 \text{ K})$:

$$C_{p,\text{m}}^{\circ}(\text{PuF}_4, \text{cr}, T) = (127.53 + 3.114 \times 10^{-3}T - 10.91 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

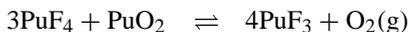
from 298.15 K to 1300 K.

18.1.2.4.d Fusion data

The melting point, $(1300 \pm 20) \text{ K}$, the enthalpy of fusion $(47 \pm 10) \text{ kJ}\cdot\text{mol}^{-1}$ and the heat capacity of the liquid $((165 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})$ have been estimated by Rand and Fuger [2000RAN/FUG].

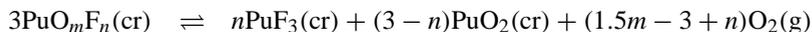
18.1.2.5 $\text{PuF}_4(\text{g})$

As noted by Rand [66RAN], the early work on the behaviour of PuF_4 at high temperatures is unsatisfactory, due either to the use of unsuitable container material (*e.g.*, tantalum) or, probably, the presence of PuO_2 either as an initial impurity or from adventitious reaction with air or water vapour. The presence of PuO_2 permits the auto-reduction reaction (*cf.* Dawson *et al.* [54DAW/ELL] noted above).



With the selected data for PuF_3 and PuF_4 , the pressure of oxygen generated by this reaction is calculated to be $3 \times 10^{-3} \text{ bar}$ at 1100 K and $3 \times 10^{-2} \text{ bar}$ at 1200 K, so that reaction would be rapid in a vacuum system at these temperatures. Work by Chudinov and Choporov [70CHU/CHO2], noted in more detail below, has clarified some of these aspects. They were able to measure reproducible vapour pressures, consistent with an enthalpy of sublimation similar to that of UF_4 , up to about 1100 K, but above that temperature, the pressures fell, possibly in steps, to those shown by PuF_3 . This was attributed to the possible formation of oxyfluorides; they postulate $\text{Pu}(\text{OH})\text{F}_3$ as an intermediary species. There are no known oxyfluorides of $\text{Pu}(\text{IV})$, but it is possible that PuOF_3 (for which there is some thermochromatographic evidence [79JOU/LEG]), or

less probably PuOF_4 or PuO_2F_2 , could be formed. These higher oxyfluorides would give a mixture of $\text{PuF}_3(\text{g})$ and $\text{PuF}_4(\text{g})$ in the vapour, (with total Pu-bearing pressures intermediate between those of PuF_3 and PuF_4) and would in turn decompose to condensed phase PuF_3 and oxygen,



when the Pu-containing vapour pressure would be the same as that of pure PuF_3 . Clearly additional work is required on the stability of condensed PuF_4 at high temperatures in the strict absence of PuO_2 .

18.1.2.5.a Enthalpy of formation

There are three studies which purport to measure the vapour pressure of PuF_4 . However, as noted by Rand [66RAN], the study by Mandleburg and Davies [61MAN/DAV] has to be discounted, since they used a tantalum effusion cell, which would certainly reduce PuF_4 to PuF_3 . It also seems likely that reduction (or other reactions as noted above) occurred in the measurements by Berger and Gaumann [61BER/GAU], from 1038 to 1308 K using a platinum cell, with a large orifice, since their measured pressure at 1038 K is close to that of Mandleburg and Davies [61MAN/DAV], and although the pressures at higher temperatures increase more rapidly, the entropy of sublimation (*ca.* $109 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) is still too small to correspond to a sublimation process.

The more detailed data in the first three runs up to 1125 K by Chudinov and Choporov [70CHU/CHO2], discussed above, however, seem more reliable, since the entropy change is reasonable for a sublimation process, and the vapour pressures are slightly larger than, rather than a small fraction of, those of UF_4 . As noted below, we have not included any electronic contribution to the entropy of $\text{PuF}_4(\text{g})$ since this gives acceptable agreement between the calculated ($184.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) and experimental ($178.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) entropies of sublimation at 960 K (see below). A third-law treatment of the 54 acceptable data points from Chudinov and Choporov [70CHU/CHO2] then gives, with our selected thermal functions for the crystal and gas:

$$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(\text{PuF}_4, \text{cr}, 298.15 \text{ K}) = (301.8 \pm 3.6) \text{ kJ}\cdot\text{mol}^{-1}$$

and thus, when rounded

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuF}_4, \text{g}, 298.15 \text{ K}) = -(1548 \pm 22) \text{ kJ}\cdot\text{mol}^{-1}$$

where the increased uncertainty includes that associated with the molecular parameters of the vapour. A plot of the experimental and calculated vapour pressures data for PuF_3 and PuF_4 is given by Rand and Fuger [2000RAN/FUG]. This enthalpy of sublimation of $301.8 \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K is somewhat smaller than those for NpF_4 ($315.5 \text{ kJ}\cdot\text{mol}^{-1}$) and UF_4 ($313.0 \text{ kJ}\cdot\text{mol}^{-1}$).

18.1.2.5.b Standard entropy and heat capacity

Following the work of Konings *et al.* [96KON/BOO], which has demonstrated that the $\text{UF}_4(\text{g})$ molecule almost certainly has tetrahedral symmetry (*cf.* Section 9.1.2.5),

we have adopted their molecular parameters of $\text{UF}_4(\text{g})$ for the $\text{PuF}_4(\text{g})$ molecule, except for a small decrease in the M-F distance from 2.059×10^{-10} m for UF_4 to 2.05×10^{-10} m for $\text{PuF}_4(\text{g})$. The ground-state energy level was assumed to have a statistical weight of 3, as for $\text{UF}_4(\text{g})$. Since acceptable agreement with the measured entropy of sublimation was achieved without any higher electronic levels, none were included. Clearly other combinations of molecular parameters and electronic contributions could provide as good agreement, but the current relatively simple set should be acceptable until detailed electronic spectra are measured. The calculated values for the entropy and heat capacity of $\text{PuF}_4(\text{g})$ at 298.15 K are

$$\begin{aligned} S_{\text{m}}^{\circ}(\text{PuF}_4, \text{g}, 298.15 \text{ K}) &= (359.0 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{PuF}_4, \text{g}, 298.15 \text{ K}) &= (92.4 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

and these are the selected values. The input data used and a complete table of thermal functions up to 2000 K are given by Rand and Fuger [2000RAN/FUG]. The input data are very similar to those suggested by Konings and Hildenbrand [98KON/HIL], which appeared after the current assessment was completed.

18.1.2.6 Intermediate fluorides and PuF_5 (g)

No solid fluorides between $\text{PuF}_4(\text{cr})$ and $\text{PuF}_6(\text{cr})$, analogous to the well-established uranium compounds U_4F_{17} , U_2F_9 and UF_5 have been found, despite numerous attempts to identify them.

Jouniaux *et al.* inferred the formation of $\text{PuF}_5(\text{g})$ in their tracer thermochromatographic study [79JOU/LEG], and Kleinschmidt [86KLE/WAR] also interpreted his results when $\text{PuF}_6(\text{g})$ was leaked into the ion source of a quadrupole mass spectrometer in the presence of alumina in terms of this molecule. Kleinschmidt's suggested uncertainties in the bond energy values (246 and $595 \text{ kJ}\cdot\text{mol}^{-1}$) from 19 to $145 \text{ kJ}\cdot\text{mol}^{-1}$, so these measurements are not suitable for defining thermodynamic data of any precision.

18.1.2.7 $\text{PuF}_6(\text{cr})$

18.1.2.7.a Enthalpy of formation

This has been calculated from $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuF}_6, \text{g})$ and the enthalpy of sublimation, calculated from vapour pressure. There are three consistent studies of the vapour pressure, by Florin *et al.* [56FLO/TAN] from 273 to 336 K, Mandleberg *et al.* [56MAN/RAE], from 243 to 294 K, and Weinstock *et al.* [59WEI/WEA] from 273 to 350 K. There is good agreement between these three studies, and since the last [59WEI/WEA] is the most complete description, we have based our analysis on their data.

However Weinstock *et al.* [59WEI/WEA] fit their experimental points to a three-term function of T which implies $\Delta_{\text{sub}}C_{p,\text{m}}^{\circ} = +29.09 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This value seems very unlikely, when compared to the experimental values of $-37.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $\text{UF}_6(\text{cr})$ [92GRE/FUG] and $-38.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $\text{NpF}_6(\text{cr})$ (see this review) at 298.15 K. The average value of $\Delta_{\text{sub}}C_{p,\text{m}}$ from 273 to 324 K from the selected $C_{p,\text{m}}$ data for the crystal and gas discussed below is $-38.93 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and a refit of

their experimental data [59WEI/WEA] to an expression implying this value gives only slightly greater deviations, but of course with a small trend. Fortunately, the mid temperature of the measurements of Weinstock *et al.* is very close to 298.15 K, so that the derived value of $\Delta_{\text{sub}}S_{\text{m}}^{\circ}$ at this temperature is not very sensitive to the value of $\Delta_{\text{sub}}C_{p,\text{m}}^{\circ}$ assumed, as shown in [2000RAN/FUG], in which fits of the vapour pressure to the expression

$$\log_{10}(p/\text{bar}) = a + b/T + c \log_{10} T$$

are compared.

Combining the suggested value for $\Delta_{\text{sub}}S_{\text{m}}^{\circ}(298.15 \text{ K}) = (147.1 \pm 0.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ with $\Delta_{\text{sub}}G_{\text{m}}^{\circ}(324.7 \text{ K})$ at the triple point and the selected thermal functions of $\text{PuF}_6(\text{cr})$ and $\text{PuF}_6(\text{g})$ (see below) gives finally

$$\begin{aligned}\Delta_{\text{sub}}H_{\text{m}}^{\circ}(\text{PuF}_6, 298.15 \text{ K}) &= (48.65 \pm 1.00) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuF}_6, \text{cr}, 298.15 \text{ K}) &= -(1861.35 \pm 20.17) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

where the additional significant figures are retained to reproduce the correct vapour pressure from thermodynamic calculations.

18.1.2.7.b Standard entropy and heat capacity

Combination of the selected $\Delta_{\text{sub}}S_{\text{m}}^{\circ}(298.15 \text{ K})$ and $S_{\text{m}}^{\circ}(\text{PuF}_6, \text{g}, 298.15 \text{ K})$ gives

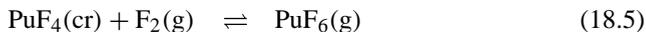
$$S_{\text{m}}^{\circ}(\text{PuF}_6, \text{cr}, 298.15 \text{ K}) = (221.8 \pm 1.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The heat capacities of $\text{PuF}_6(\text{cr})$ and l) have been estimated by Rand and Fuger [2000RAN/FUG]; the value for the solid at 298.15 K is $(168.1 \pm 2.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

18.1.2.8 $\text{PuF}_6(\text{g})$

18.1.2.8.a Enthalpy of formation

The equilibrium constants for the reaction



have been measured by Florin *et al.* [56FLO/TAN], from 440 to 873 K, Weinstock and Malm [56WEI/MAL], from 298 and 493 K, and by Trevorrow *et al.* [61TRE/SHI], from 423 to 668 K. The results are rather disparate, which is not surprising in view of the high reactivity of $\text{PuF}_6(\text{g})$ and the fact that it decomposes slowly due to self-radiation damage. However, the results of the first and third studies are in reasonable agreement, and our analysis is based on the most complete and precise investigation, by Trevorrow *et al.* [61TRE/SHI].

The calculated entropy of reaction from the estimated thermal functions is somewhat different from that derived from the least square fit to these data. A third law calculation gives

$$\Delta_{\text{r}}H_{\text{m}}^{\circ}(18.5, 298.15 \text{ K}) = (37.3 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$$

With our selected value for the enthalpy of formation of PuF₄(cr), we have

$$\Delta_f H_m^\circ(\text{PuF}_6, \text{g}, 298.15 \text{ K}) = -(1812.7 \pm 20.1) \text{ kJ}\cdot\text{mol}^{-1}$$

where the uncertainty is dominated by that in $\Delta_f H_m^\circ(\text{PuF}_4, \text{cr}, 298.15 \text{ K})$.

18.1.2.8.b Standard entropy and heat capacity

The thermal functions of PuF₆(g) ideal gas were calculated assuming the molecular parameters given by Rand and Fuger [2000RAN/FUG], using the rigid-rotator, harmonic oscillator approximation. The molecule is taken to be octahedral with O_h symmetry. Thus,

$$\begin{aligned} S_m^\circ(\text{PuF}_6, \text{g}, 298.15 \text{ K}) &= (368.90 \pm 1.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{PuF}_6, \text{g}, 298.15 \text{ K}) &= (129.32 \pm 1.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

The heat capacities have been fitted to the expression

$$\begin{aligned} C_{p,m}^\circ(\text{PuF}_6, \text{g}, T) &= (143.988 + 2.32109 \times 10^{-2} T \\ &\quad - 1.076413 \times 10^{-5} T^2 - 1.83427 \times 10^6 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

from 298.15 to 1000 K.

18.1.2.9 PuOF(cr)

Plutonium (III) oxyfluoride is not well characterised, but it was apparently formed during the attempted reduction of PuF₃(cr) by atomic hydrogen (quoted by Cunningham and Hindman [54CUN/HIN]); its thermodynamic properties can however be estimated reasonably reliably. Following Fuger [83FUG], the difference ($\Delta_f H_m^\circ(\text{PuOF}, \text{cr}, 298.15 \text{ K}) - \Delta_f H_m^\circ(\text{PuF}_3, \text{cr}, 298.15 \text{ K})/3$) is estimated to be $-(609 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$, from the corresponding values for the chloride $-(611.1) \text{ kJ}\cdot\text{mol}^{-1}$ and bromide $-(605.8 \text{ kJ}\cdot\text{mol}^{-1})$. The selected enthalpy of formation of PuOF(cr) is thus calculated to be

$$\Delta_f H_m^\circ(\text{PuOF}, \text{cr}, 298.15 \text{ K}) = -(1140 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$$

The standard entropy is estimated from the values for the other trihalides and oxyhalides:

$$S_m^\circ(\text{PuOF}, \text{cr}, 298.15 \text{ K}) = (96 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The heat capacity is estimated to be close to the sum of (1/3PuF₃ + 1/3Pu₂O₃):

$$\begin{aligned} C_{p,m}^\circ(\text{PuOF}, \text{cr}, T) &= (72.0 + 1.6 \times 10^{-2} T \\ &\quad - 3.3 \times 10^{-6} T^2 - 6.2 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ &\quad (298.15 \text{ K to } 1500 \text{ K}) \end{aligned}$$

and thus

$$C_{p,m}^\circ(\text{PuOF}, \text{cr}, 298.15 \text{ K}) = (69.4 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.3 Plutonium chloride compounds

18.1.3.1 PuCl₃ (cr)

18.1.3.1.a Enthalpy of formation

Westrum and Robinson [49ROB/WES] measured the enthalpy of solution of PuCl₃(cr) in 6 M HCl to be $-(92.67 \pm 0.42)$ kJ·mol⁻¹. From the data in Table 2.5, 6 M HCl is calculated to correspond to a molality of 6.8508, slightly larger than that used in the assessment by [83FUG/PAR]. The value of the partial molar enthalpy of formation of HCl in this solution, interpolated from fits of the enthalpy of solution data given by Parker [65PAR] is correspondingly more positive by 0.031 kJ·mol⁻¹ at $-(153.400 \pm 0.11)$ kJ·mol⁻¹ [2000RAN/FUG].

With the additional data of the enthalpy of solution of Pu(cr, α) in the same solution $-(592.04 \pm 1.67)$ kJ·mol⁻¹ (assessed by Fuger and Oetting [76FUG/OET]), the final value for the enthalpy of formation of PuCl₃(cr) becomes

$$\Delta_f H_m^\circ(\text{PuCl}_3, \text{cr}, 298.15 \text{ K}) = -(959.6 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

18.1.3.1.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of PuCl₃(cr), and the standard entropy is derived from four consistent estimates: Latimer's method, the spin-only contributions, and by comparison with similar compounds [2000RAN/FUG]. From these four, not entirely independent, estimates of 162.1, 161.5, 162.4, and 160.8 J·K⁻¹·mol⁻¹, the selected value is

$$S_m^\circ(\text{PuCl}_3, \text{cr}, 298.15 \text{ K}) = (161.7 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.3.1.c High temperature heat capacity

Lacking experimental data, the heat capacity of PuCl₃(cr) is assumed to be close to that of UCl₃(cr) ([92GRE/FUG], corrected)¹. The suggested values for PuCl₃(cr) are:

$$C_{p,m}^\circ(\text{PuCl}_3, \text{cr}, T) = (91.35 + 24.0 \times 10^{-3}T + 2.4 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 to 1041 K, and hence

$$C_{p,m}^\circ(\text{PuCl}_3, \text{cr}, 298.15 \text{ K}) = (101.2 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

¹It should be noted that the coefficient of T in the equation for $C_{p,m}^\circ(\text{UCl}_3)$ given by Grenthe *et al.* [92GRE/FUG] is too small by a factor of 4.

18.1.3.1.d Fusion data

The melting point is taken to be (1041 ± 2) K from Bjorklund *et al.* [59BJO/REA], corrected to the 1990 Temperature scale. The enthalpy of fusion is calculated from the vapourisation data for the solid and liquid by Phipps *et al.* [50PHI/SEA], corrected to $T_{\text{fus}} = 1041$ K (see Section 18.1.3.2 for further details).

$$\Delta_{\text{fus}}H_{\text{m}}^{\circ}(\text{PuCl}_3, \text{cr}, 1041 \text{ K}) = (55.0 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$$

The heat capacity of the liquid has been estimated by Rand and Fuger [2000RAN/FUG], based on that estimated for $\text{UF}_3(\text{l})$ by Glushko *et al.* [82GLU/GUR] and comparison with lanthanide chlorides [63DWO/BRE, 71DWO/BRE], to be $C_{p,\text{m}}(\text{PuCl}_3, \text{l}) = (145 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

18.1.3.2 PuCl₃ (g)

18.1.3.2.a Enthalpy of formation

The Knudsen effusion measurements of vapour pressure in tantalum from 879 to 1224 K by Phipps *et al.* [50PHI/SEA], which have very little scatter, have been corrected to the 1990 Temperature scale and the 1986 set of Fundamental constants. These authors interpreted their data to give a melting point of 1008 K, appreciably lower than the value of (1041 ± 2) K directly measured by Bjorklund *et al.* [59BJO/REA] (see Section 18.1.3.1.d). However, if the two relevant points are moved to refer to sublimation of the solid rather than vaporisation of the liquid, the least square fit for the sublimation pressures becomes

$$\log_{10}(p/\text{bar}) = 9.3677 - 15472.6/T$$

from 879 to 1034 K.

Third law treatment of the data for the sublimation using the thermal functions for $\text{PuCl}_3(\text{g})$ estimated below gives

$$\Delta_{\text{sub}}H_{\text{m}}^{\circ}(298.15 \text{ K}) = (312.2 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$$

and hence,

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuCl}_3, \text{g}, 298.15 \text{ K}) = -(647.4 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$$

The least-square fit for the vapour pressure of the liquid from 1051 to 1136 K, subject to the constraint that the vapour pressures of the solid and liquid be equal at the melting point, defines the enthalpy of fusion given above.

18.1.3.2.b Standard entropy and heat capacity

The thermal functions of $\text{PuCl}_3(\text{g})$ were calculated assuming the molecular parameters given by Rand and Fuger [2000RAN/FUG], using the rigid-rotator, harmonic oscillator approximation. These molecular parameters give

$$\begin{aligned} S_{\text{m}}^{\circ}(\text{PuCl}_3, \text{g}, 298.15 \text{ K}) &= (368.62 \pm 10.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{PuCl}_3, \text{g}, 298.15 \text{ K}) &= (78.47 \pm 5.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

18.1.3.3 PuCl₃·6H₂O(cr)

18.1.3.3.a Enthalpy of formation

The enthalpy of solution in water to give an approximately 0.001 molal solution was measured by Hinchey and Cobble [70HIN/COB] to be $-(33.70 \pm 0.63)$ kJ·mol⁻¹; the further enthalpy of dilution to infinite dilution is estimated to be $-(0.9 \pm 0.1)$ kJ·mol⁻¹ from the similar enthalpies of dilution of LnCl₃·50000H₂O(cr) to infinite solution (Ln = Sm, Nd, Pr, Ce, La) from the assessments of Wagman *et al.* [82WAG/EVA].

Hence $\Delta_{\text{sln}}H^\circ(\text{PuCl}_3 \cdot 6\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$ at infinite dilution = $-(34.60 \pm 0.64)$ kJ·mol⁻¹, which with CODATA values (Table 5.1) for Cl⁻(aq) and H₂O(l), gives,

$$\Delta_f H_m^\circ(\text{PuCl}_3 \cdot 6\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(2773.4 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$$

18.1.3.3.b Standard entropy and heat capacity

The standard entropy is estimated from that of the iso-structural and isoelectronic samarium compound $S_m^\circ(\text{SmCl}_3 \cdot 6\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (414.0 \pm 3.0)$ J·K⁻¹·mol⁻¹ [82WAG/EVA] by addition of $1.5R \ln(\text{AM}(\text{Pu})/\text{AM}(\text{Sm}))$ to allow for the difference in atomic masses (AM). The selected value is

$$S_m^\circ(\text{PuCl}_3 \cdot 6\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (420 \pm 5) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Hinchey and Cobble [70HIN/COB] also measured the solubility of this salt in water. The average of their three measurements (4.47 mol·kg⁻¹), leads (with estimates of the activity coefficients ($\gamma_{\pm} = 9.30$, $a(\text{H}_2\text{O}) = 0.365$, [70HIN/COB] corrected) based on the data for SmCl₃ aqueous solutions) to the standard Gibbs energy of the dissolution reaction $\Delta_{\text{sln}}G^\circ(\text{PuCl}_3 \cdot 6\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(30.125 \pm 0.840)$ kJ·mol⁻¹.² This value is a key component in the derivation of the standard entropy of Pu³⁺(aq), see Section 16.5.

²The uncertainty in $\Delta_{\text{sln}}G^\circ(\text{PuCl}_3 \cdot 6\text{H}_2\text{O})$ is the same as the uncertainty assigned in [76FUG/OET], and mainly reflects the scatter in the original solubility measurements. A case could be made for increasing this value to allow for the uncertainties in the water activities and activity coefficients, but the effects of doing so would have only a marginal effect on the uncertainties assigned to values for other species

18.1.3.4 PuCl₄ (cr)

The gaseous tetrachloride PuCl₄(g) is well established, but the condensed phase is not stable with respect to decomposition to PuCl₃ and Cl₂(g) at normal pressures, Abraham *et al.* [49ABR/BRO]; however reliable estimates of the thermodynamic data for the solid can be made, particularly as enthalpy data for the Pu(IV) complex, Cs₂PuCl₆(cr), are available. Thermodynamic functions have been estimated and they are given in [2000RAN/FUG]. The estimated values are:

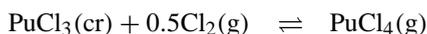
$$\begin{aligned}\Delta_f H_m^\circ(\text{PuCl}_4, \text{cr}, 298.15 \text{ K}) &= -(968.7 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1} \\ S_m^\circ(\text{PuCl}_4, \text{cr}, 298.15 \text{ K}) &= (201 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{PuCl}_4, \text{cr}, 298.15 \text{ K}) &= (121.4 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\end{aligned}$$

High temperature heat capacity values, the melting point, enthalpy of fusion and liquid heat capacity are estimated and they are also given by Rand and Fuger [2000RAN/FUG]. The calculated pressure of chlorine gas required to give condensed phase PuCl₄ from PuCl₃(cr) is about 1200 kbar at 800 K for PuCl₄(cr) and about 130 kbar at 1200 K for PuCl₄(l).

18.1.3.5 PuCl₄ (g)

18.1.3.5.a Enthalpy of formation

This has been calculated from a third-law analysis of data for the Gibbs energy change from 674 to 1024 K for the reaction



given by Benz [62BEN], using the thermal functions for PuCl₃(cr) and PuCl₄(g) estimated here. As noted below, the electronic levels in PuCl₄(g) are designated semi-arbitrarily so as to reproduce the correct entropy of this reaction, thus ensuring agreement of the second and third law enthalpies. This gives for the above reaction,

$$\Delta_r H_m^\circ(298.15 \text{ K}) = (167.6 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$$

from which the selected value is calculated

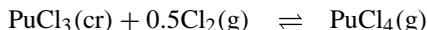
$$\Delta_f H_m^\circ(\text{PuCl}_4, \text{g}, 298.15 \text{ K}) = -(792.0 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$$

The uncertainty has been increased substantially to include that from arising from the molecular parameters.

Gruen and DeKock [67GRU/DEK] made similar measurements for the reaction involving $\text{PuCl}_3(\text{l})$ from 1052 to 1187 K, using the optical density of the principal band in the spectrum of $\text{PuCl}_4(\text{g})$ as a monitor of the pressure. There is some confusion in the reporting of the equilibrium constants for the reaction in both the table and figure, but the tabulated values, when divided by 100, (as required to correspond to the given Gibbs energy of the reaction) agree excellently with the extrapolation of the data of Benz [62BEN], using the selected fusion data for PuCl_3 . A comparison of the experimental and calculated equilibrium constants is given in the report by Rand and Fuger [2000RAN/FUG]. The values for the stabilities of $\text{PuCl}_4(\text{cr})$ and $\text{PuCl}_4(\text{g})$ give a hypothetical enthalpy of sublimation of $176.7 \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K, somewhat smaller than those for NpCl_4 and UCl_4 , which are both close to $200 \text{ kJ}\cdot\text{mol}^{-1}$.

18.1.3.5.b Standard entropy and heat capacity

The thermal functions of $\text{PuCl}_4(\text{g})$ were calculated using the rigid-rotator, harmonic oscillator approximation. Following the work of Haaland *et al.* [95HAA/MAR] on the electron diffraction and infrared spectroscopy of $\text{UCl}_4(\text{g})$, the molecule was assumed to be an undistorted tetrahedron, with a Pu-Cl distance of $2.50 \times 10^{-10} \text{ m}$, *cf.* $r(\text{U-Cl}) = 2.503 \times 10^{-10} \text{ m}$ in $\text{UCl}_4(\text{g})$ [95HAA/MAR]. The vibration frequencies were taken to be very similar to those determined for $\text{UCl}_4(\text{g})$ by these authors [95HAA/MAR]. The electronic contribution to the entropy was adjusted to reproduce fairly closely the experimental entropy of the reaction



derived from the measurements of the equilibrium constant from 674 to 1024 K by Benz [62BEN]. In fact with the first five electronic levels of $\text{UCl}_4(\text{g})$ suggested by Hildebrand *et al.* (which are a simplified version of those suggested by [73GRU/HEC] from their the spectral measurements), the calculated entropy of reaction ($120.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) is very close to the experimental value, $118.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and these electronic states were used. The full data used are given in the report by Rand and Fuger [2000RAN/FUG]. They are very similar to those suggested by Konings and Hildenbrand [98KON/HIL], which appeared after the current assessment was completed. Clearly other combinations of molecular parameters and electronic contributions could provide as good agreement, but the current set has the merit of being consistent with the broad corpus of other data adopted for the gaseous actinide halide species.

The selected data give

$$\begin{aligned} S_{\text{m}}^{\circ}(\text{PuCl}_4, \text{g}, 298.15 \text{ K}) &= (409.0 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,\text{m}}^{\circ}(\text{PuCl}_4, \text{g}, 298.15 \text{ K}) &= (103.4 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

where the uncertainties include that arising from the molecular parameters.

18.1.3.6 PuOCl(cr)

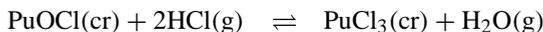
18.1.3.6.a Enthalpy of formation

Westrum and Robinson [49WES/ROB] have studied the dissolution in 6 M HCl. Their enthalpy of dissolution $-(101.13 \pm 0.42)$ kJ·mol⁻¹ gives with auxiliary data (see PuCl₃(cr) section), the following selected value

$$\Delta_f H_m^\circ(\text{PuOCl, cr, 298.15 K}) = -(931.0 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$$

18.1.3.6.b Standard entropy and heat capacity

The standard entropy has been calculated from the equilibrium constants for the reaction



measured by Sheft and Davidson [49SHE/DAV] from 816 to 969 K and Weigel *et al.* [77WEI/WIS] from 736 to 885 K, with excellent agreement. With the above enthalpy of formation and estimated heat capacities for PuOCl(cr), the Gibbs energies measured in these studies require

$$\Delta_r S_m^\circ(298.15 \text{ K}) = -(128.90 \pm 1.95) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from [49SHE/DAV], and

$$\Delta_r S_m^\circ(298.15 \text{ K}) = -(128.70 \pm 0.50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from [77WEI/WIS].

The weighted mean is $-(128.71 \pm 0.49)$ J·K⁻¹·mol⁻¹, which gives

$$S_m^\circ(\text{PuOCl, cr, 298.15 K}) = (105.6 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

where the uncertainty is dominated by that in the (estimated) standard entropy of PuCl₃(cr).

This value is slightly greater than that for UOCl (102.5 ± 8.4) J·K⁻¹·mol⁻¹ [92GRE/FUG] and that estimated from the revised Latimer method 103.9 J·K⁻¹·mol⁻¹ [93KUB/ALC].

18.1.3.6.c High temperature heat capacity

These have been estimated from those for UOCl(cr) [92GRE/FUG] and from the sum of $C_{p,m}^\circ(\text{Pu}_2\text{O}_3 + \text{UCl}_3)/3$ [82GLU/GUR, 47GIN/COR]

$$C_{p,m}^\circ(\text{PuOCl, cr, } T) = (73.03 + 17.1 \times 10^{-3}T - 5.83 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 to 1100 K, and hence,

$$C_{p,m}^\circ(\text{PuOCl, cr, 298.15 K}) = (71.6 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.3.7 Cs₂NaPuCl₆ (cr)

18.1.3.7.a Enthalpy of formation

Morss [71MOR] has measured the enthalpy of dissolution of this complex salt in 0.001 M HCl (final molality of Pu³⁺ = 0.004) to be $-54.06 \text{ kJ}\cdot\text{mol}^{-1}$, with an unknown uncertainty. This has been corrected to infinite dilution by considering two effects.

The enthalpy of dilution of PuCl₃ solution from 0.004 molal to infinite dilution has been estimated by comparison with enthalpy of dilution of lanthanide trihalides from MCl₃·13875H₂O (M = Gd, Sm, Nd, Pr, Ce, La) [82WAG/EVA],

$$\Delta_{\text{dil}}H = -(1.6 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$$

There is an additional enthalpy term to be included, namely that resulting from the change in complexing resulting from additional Cl⁻ ions; this will increase the concentration of PuCl₂⁺ ions in a solution of Cs₂NaPuCl₆ over that in a solution of PuCl₃ with the same concentration of Pu³⁺. From the data in Section 18.2.2.1, the equilibrium constant of the aqueous reaction



at the relevant ionic strengths of 0.024 and 0.032 mol·kg⁻¹ are calculated to be 6.2 and 5.2 respectively. The fractions of PuCl₂⁺ formed will thus be 0.068 and 0.11 respectively. Since the enthalpy of the complexing reaction is $(19 \pm 10) \text{ kJ}\cdot\text{mol}^{-1}$ (Section 18.2.2.1), the additional complexing will give an additional enthalpy of dilution amounting to $-(0.8 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$. The total enthalpy of dilution from 0.004 molal to infinite dilution is thus taken to be $-(2.4 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$, giving $\Delta_{\text{sln}}H(\text{Cs}_2\text{NaPuCl}_6, \text{infinite dilution}) = -(56.4 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$, and with the accepted values for the aqueous ions, [this review, 89COX/WAG]

$$\Delta_f H_m^\circ(\text{Cs}_2\text{NaPuCl}_6, \text{cr}, 298.15 \text{ K}) = -(2294.2 \pm 2.6) \text{ kJ}\cdot\text{mol}^{-1}$$

This corresponds to an enthalpy of formation of $-38.7 \text{ kJ}\cdot\text{mol}^{-1}$ from the constituent chlorides.

18.1.3.7.b Standard entropy

The standard entropy has been estimated by two independent methods [2000RAN/FUG]. From the two estimates of 436.2 and 444 J·K⁻¹·mol⁻¹, the selected value is

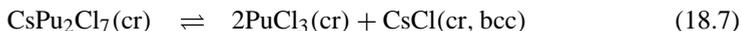
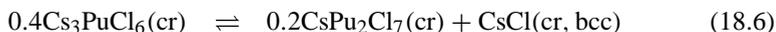
$$S_m^\circ(\text{Cs}_2\text{NaPuCl}_6, \text{cr}, 298.15 \text{ K}) = (440 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.3.8 Cs₃PuCl₆ (cr) and CsPu₂Cl₇ (cr)

18.1.3.8.a Enthalpy of formation and standard entropy

Williamson and Kleinschmidt [93WIL/KLE] have studied the Cs⁺ intensities (I) (as a monitor of the CsCl(g) pressures) over the three diphasic regions: i) CsCl(cr,bcc) +

Cs₃PuCl₆(cr), from 603 to 735 K; ii) Cs₃PuCl₆(cr) + CsPu₂Cl₇(cr), from 667 to 769 K; and iii) CsPu₂Cl₇(cr) + PuCl₃(cr), from 722 to 846 K, using a platinum effusion cell attached to a mass-spectrometer. Since the absolute pressures of CsCl(g) were not determined, but the experiments were all carried out successively in the same Knudsen cell, the best way to treat these data is to consider the totally condensed phase reactions



The Gibbs energies of these reactions can be derived by subtracting the log(IT) values given by [93WIL/KLE] for region i) from those for regions ii) and iii) respectively:

$$\Delta_r G_m^\circ(18.6, T) = ((23586 \pm 2950) - (4.00 \pm 4.13)T) \text{ J}\cdot\text{mol}^{-1}$$

from 667 to 769 K, and

$$\Delta_r G_m^\circ(18.7, T) = ((37869 \pm 3160) - (0.57 \pm 4.12)T) \text{ J}\cdot\text{mol}^{-1}$$

from 722 to 846 K.

The small differences in the temperature ranges in three series have been ignored, since the small error introduced is very much within the uncertainty of the Gibbs energies. These have then been reduced to give the enthalpies and entropies of these reactions at 298.15 K, using the heat capacities of the ternary halides estimated below. In fact, since these estimates are based on $\Delta_r C_{p,m}^\circ \sim 0$ for the formation from CsCl and PuCl₃, the corrections from the mean temperature of the measurements to 298.15 K are essentially zero and we have

$$\Delta_r H_m^\circ(18.6, 298.15 \text{ K}) = (23.58 \pm 2.95) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r S_m^\circ(18.6, 298.15 \text{ K}) = (4.00 \pm 4.13) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m^\circ(18.7, 298.15 \text{ K}) = (37.87 \pm 3.16) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r S_m^\circ(18.7, 298.15 \text{ K}) = (0.57 \pm 4.12) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

For reaction (18.6), we have also ignored the transition in Cs₃PuCl₆(cr) at 683 K noted by Benz and Douglass [61BEN/DOU]. Since the crystal structure is not known for either the low- or high-temperature phases, it is difficult to estimate the enthalpy of this transition. A correction should therefore be applied to this treatment when the relevant data become available.

The above values give, after rounding, the selected values

$$\Delta_f H_m^\circ(\text{Cs}_3\text{PuCl}_6, \text{cr}, 298.15 \text{ K}) = -(2364 \pm 8) \text{ kJ}\cdot\text{mol}^{-1}$$

$$S_m^\circ(\text{Cs}_3\text{PuCl}_6, \text{cr}, 298.15 \text{ K}) = (455 \pm 11) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{CsPu}_2\text{Cl}_7, \text{cr}, 298.15 \text{ K}) = -(2399 \pm 6) \text{ kJ}\cdot\text{mol}^{-1}$$

$$S_m^\circ(\text{CsPu}_2\text{Cl}_7, \text{cr}, 298.15 \text{ K}) = (424 \pm 7) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

where the data for CsCl(cr,bcc) have been taken from the assessment by Glushko *et al.* [82GLU/GUR].

18.1.3.8.b Heat capacity

The heat capacities of these ternary halides have been estimated by assuming there is no change in heat capacity in the formation reaction from the binary halides. The resulting values are represented closely by the expressions

$$\begin{aligned} C_{p,m}^{\circ}(\text{Cs}_3\text{PuCl}_6, \text{cr}, T) &= (256.6 + 3.46 \times 10^{-2}T - 7.40 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^{\circ}(\text{CsPu}_2\text{Cl}_7, \text{cr}, T) &= (237.8 + 5.15 \times 10^{-2}T + 1.55 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ &(T = 298.15 - 900 \text{ K}) \end{aligned}$$

and thus the values

$$\begin{aligned} C_{p,m}^{\circ}(\text{Cs}_3\text{PuCl}_6, \text{cr}, 298.15 \text{ K}) &= (258.6 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ C_{p,m}^{\circ}(\text{CsPu}_2\text{Cl}_7, \text{cr}, 298.15 \text{ K}) &= (254.9 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

18.1.3.9 Cs₂PuCl₆ (cr)

18.1.3.9.a Enthalpy of formation

Fuger *et al.* [83FUG/PAR] have analysed the results of the calorimetric study by Fuger and Brown [71FUG/BRO], who reported a value of $-(74.22 \pm 0.21) \text{ kJ}\cdot\text{mol}^{-1}$ for the dissolution of this complex salt in 1 M HClO₄. We have reworked this analysis, with the following enthalpy values:

$$\begin{aligned} \Delta_f H_m^{\circ}(\text{CsCl}, \text{cr}) &= -(442.31 \pm 0.16) \text{ kJ}\cdot\text{mol}^{-1} \text{ [82GLU/GUR]} \\ &\text{compatible with [89COX/WAG]} \\ \Delta_{\text{sln}} H_m(\text{CsCl}, \text{cr}, 1 \text{ M HCl or HClO}_4) &= (16.69 \pm 0.08) \text{ kJ}\cdot\text{mol}^{-1} \text{ (see Section 9.1.3.9)} \\ \Delta_f H_m^{\circ}(\text{PuCl}_3, \text{cr}) &= -(959.6 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1} \text{ (see Section 18.1.3.1)} \\ \Delta_{\text{sln}} H_m(\text{PuCl}_3, \text{cr}, 1 \text{ M HClO}_4) &= -(126.8 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1} \text{ [83FUG/PAR]} \\ \Delta_f H_m(\text{Pu}^{3+}, 1 \text{ M HClO}_4) - \Delta_f H_m(\text{Pu}^{4+}, 1 \text{ M HClO}_4) &= -(51.9 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1} \\ &\text{assumed to be the same as in standard conditions (see Section 16.4) and} \\ \Delta_f H_m(\text{Cl}^-, 1 \text{ M HClO}_4, \text{partial}) &= -(164.37 \pm 0.10) \text{ kJ}\cdot\text{mol}^{-1} \\ &\text{assumed to be the same as in HCl of the same molality [2000RAN/FUG]} \end{aligned}$$

The calculated value for the enthalpy of formation of the complex salt thus becomes

$$\Delta_f H_m^{\circ}(\text{Cs}_2\text{PuCl}_6, \text{cr}, 298.15 \text{ K}) \text{ from } 1 \text{ M HClO}_4 = -(1975.9 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$$

Fuger and Brown also reported measurements of the enthalpies of dissolution of the salt in 1 M and 6 M HCl, as $-(57.20 \pm 0.79) \text{ kJ}\cdot\text{mol}^{-1}$ and $-(0.75 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$, respectively, and calculations similar to the above can be made using the values of $\Delta_f H_m(\text{Pu}^{4+}, \text{in HCl})$ and $\Delta_f H_m(\text{Cl}^-, \text{in HCl, partial})$

[2000RAN/FUG], and $\Delta_{\text{sln}}H_{\text{m}}(\text{CsCl, cr, 6 M HCl}) = (11.88 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_{\text{sln}}H_{\text{m}}(\text{CsCl, cr, 1 M HCl})$ given above. The results are:

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Cs}_2\text{PuCl}_6, \text{ cr, 298.15 K}) \text{ from 1 M HCl} = -(1986.8 \pm 3.8) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Cs}_2\text{PuCl}_6, \text{ cr, 298.15 K}) \text{ from 6 M HCl} = -(1986.8 \pm 4.5) \text{ kJ}\cdot\text{mol}^{-1}$$

The weighted mean of the three measurements is, $-(1982.0 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$, which, with an increased uncertainty, is the selected value

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{Cs}_2\text{PuCl}_6, \text{ cr, 298.15 K}) = -(1982.0 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$$

This corresponds to an enthalpy of formation of $-128.7 \text{ kJ}\cdot\text{mol}^{-1}$ from $\text{CsCl}(\text{cr})$ and the unstable $\text{PuCl}_4(\text{cr})$, so that, unlike the latter, $\text{Cs}_2\text{PuCl}_6(\text{cr})$ is easily precipitated from $\text{Pu}(\text{IV})$ solutions.

18.1.3.9.b Standard entropy

The standard entropy has been taken to be the mean of two estimates (407.3 and $417.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) given by Rand and Fuger [2000RAN/FUG]. The selected value is

$$S_{\text{m}}^{\circ}(\text{Cs}_2\text{PuCl}_6, \text{ cr, 298.15 K}) = (412 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.4 Plutonium bromide compounds

18.1.4.1 PuBr₃ (cr)

18.1.4.1.a Enthalpy of formation

Westrum [49WES] has measured the enthalpy of solution of $\text{PuBr}_3(\text{cr})$ to be $-(129.08 \pm 0.42) \text{ kJ}\cdot\text{mol}^{-1}$ in 6.0 M HCl and Brown *et al.* [77BRO/HUR] reported measurements of $-(163.59 \pm 0.59) \text{ kJ}\cdot\text{mol}^{-1}$ in 0.1 M HCl and $-(157.61 \pm 0.59) \text{ kJ}\cdot\text{mol}^{-1}$ in 1.0 M HCl . The partial molar enthalpy of formation of HBr in HCl solutions is assumed to be the same as in HBr solutions of the same molality, which have been recalculated from the enthalpy of dilution data given by Parker [65PAR], and are -109.554 , -120.713 , $-119.395 \text{ kJ}\cdot\text{mol}^{-1}$ [2000RAN/FUG]. These, with the corresponding values for Cl^{-} ion [2000RAN/FUG], the enthalpies of solution of $\text{PuCl}_3(\text{cr})$ in the same solutions [49ROB/WES] and the currently assessed value for $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuCl}_3, \text{ cr, 298.15 K}) = -(959.6 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$, give values of $-(791.7 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$, $-(792.2 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ and $-(793.8 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ for the $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuBr}_3, \text{ cr, 298.15 K})$ from these solutions. The selected value is the weighted mean

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuBr}_3, \text{ cr, 298.15 K}) = -(792.6 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$$

18.1.4.1.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of PuBr₃(cr), and the standard entropy is derived from two reasonably consistent estimates: Latimer's method and the spin-only contribution [2000RAN/FUG]. From these two estimates of 205.3 and 196.4 J·K⁻¹·mol⁻¹, the selected value is

$$S_{\text{m}}^{\circ}(\text{PuBr}_3, \text{cr}, 298.15 \text{ K}) = (198 \pm 6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.4.1.c High temperature heat capacity

Lacking experimental data, the heat capacity of PuBr₃(cr) is assumed to be similar to UBr₃(cr). The suggested values for PuBr₃(cr) are:

$$C_{p,\text{m}}^{\circ}(\text{PuBr}_3, \text{cr}, T) = (104.5 + 15.0 \times 10^{-3}T - 6.38 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.1 to 935 K, and hence

$$C_{p,\text{m}}^{\circ}(\text{PuBr}_3, \text{cr}, 298.15 \text{ K}) = (101.8 \pm 6.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.4.1.d Fusion data

The melting point is taken to be (935 ± 10) K from the analysis of the vaporisation data for the solid and liquid measured by Phipps *et al.* [50PHI/SEA], as discussed in Section 18.1.4.2. As noted there, this and the derived enthalpy of fusion have been given quite large uncertainties because of the unexplained differences in the vaporisation data for PuF₃, PuCl₃ and PuBr₃. The selected values are:

$$\begin{aligned} T_{\text{fus}} &= (935 \pm 10) \text{ K} \\ \Delta_{\text{fus}}H_{\text{m}}^{\circ}(\text{PuBr}_3, \text{cr}, 935 \text{ K}) &= (47.1 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

The heat capacity of the liquid has been taken to be (150 ± 15) J·K⁻¹·mol⁻¹, based on the values for lanthanide trichlorides and tribromides.

18.1.4.2 PuBr₃(g)**18.1.4.2.a Enthalpy of formation and standard entropy**

Phipps *et al.* (50PHI/SEA) have measured the vapour pressure of PuBr₃ crystal and liquid from 795 to 1084 K, using a tantalum effusion cell. As with their studies of PuCl₃ and PuF₃, these data are precise enough to warrant correction to the 1990 Temperature scale and the latest values of the Fundamental Constants and half-lives of the plutonium isotopes. The least-square fits to the corrected data are:

$$\log_{10}(p/\text{bar}) = -15062.2/T + 10.256$$

from 795 to 928 K, and

$$\log_{10}(p/\text{bar}) = -12203.7/T + 7.914$$

from 943 to 1084 K, for the solid and liquid respectively.

The resulting entropy of sublimation $\Delta_{\text{sub}}S$ at the mean temperature of 868 K is $196.35 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which is appreciably higher than the corresponding values for PuF_3 and PuCl_3 , which are 176.3 and $179.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ respectively. The value of $\Delta_{\text{sub}}S(868 \text{ K})$ calculated from the estimated thermal functions of $\text{PuBr}_3(\text{cr})$ and $\text{PuBr}_3(\text{g})$, assuming the latter molecule has molecular parameters similar to those estimated for $\text{UBr}_3(\text{g})$ by Hildenbrand *et al.* [85HIL/GUR], is also about $180 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The reason for this sizeable difference between PuF_3 and PuCl_3 on the one hand and PuBr_3 on the other is not clear. Possible reasons could include:

- Substantial error in $S_{\text{m}}^{\circ}(\text{PuBr}_3, \text{cr})$.
- Substantial error in the data by Phipps *et al.* [50PHI/SEA].
- Reaction with the tantalum container.
- Decomposition of $\text{PuBr}_3(\text{g})$.
- Symmetry of $\text{PuBr}_3(\text{g})$ different from C_{3v} (pyramidal).
- Substantial error in $S_{\text{m}}^{\circ}(\text{PuBr}_3, \text{g})$ due perhaps to lower bending frequencies or an unexpectedly large electronic contribution.

None of these appears very plausible (except perhaps the last), and further work is required to resolve this situation. Meanwhile, we accept the very careful work of Phipps *et al.* [50PHI/SEA] and process their data with a second-law analysis, accepting that the derived values of $S_{\text{m}}^{\circ}(\text{PuBr}_3, \text{g})$ will be substantially higher than those calculated from the molecular parameters (see below).

The sublimation data give $\Delta_{\text{sub}}H(868 \text{ K}) = 288.36 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{sub}}S(868 \text{ K}) = 196.35 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and correction to 298.15 K using the thermal functions of $\text{PuBr}_3(\text{g})$ discussed below gives $\Delta_{\text{sub}}H(298.15 \text{ K}) = 304.4 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{sub}}S(298.15 \text{ K}) = 225.2 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. These in turn give the selected values

$$\begin{aligned}\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuBr}_3, \text{g}, 298.15 \text{ K}) &= -(488 \pm 15) \text{ kJ}\cdot\text{mol}^{-1} \\ S_{\text{m}}^{\circ}(\text{PuBr}_3, \text{g}, 298.15 \text{ K}) &= (423 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\end{aligned}$$

where the substantial uncertainties arise from the unexpectedly large entropy of sublimation, rather than the imprecision in the vaporisation data. A comparison between the experimental vapour pressure data and those calculated from the selected data is given in the report by Rand and Fuger [2000RAN/FUG].

The data for the vaporisation of the liquid imply $\Delta_{\text{vap}}H(1014 \text{ K}) = 233.64 \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_{\text{vap}}S(1014 \text{ K}) = 137.73 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, and the best agreement with the data for the sublimation is obtained with a melting point of $(935 \pm 10) \text{ K}$, $\Delta_{\text{fus}}H(935 \text{ K}) = (47.1 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$. This melting point is appreciably lower

than the direct measurement of (954 ± 5) K by Robinson [49ROB] on a sublimed sample of PuBr_3 . However, this value, even with a substantially different enthalpy of fusion, leads to much poorer agreement with the vapour pressures of the liquid given by Phipps *et al.* [50PHI/SEA]. Moreover, Robinson's similar measurement of the melting point of PuCl_3 was (1033 ± 5) K, compared to the more recent uncorrected values of (1040 ± 2) K [59BJO/REA] and 1042 K [61BEN/DOU], so his uncertainties were probably appreciably too low. The values of $T_{\text{fus}} = (935 \pm 10)$ K and $\Delta_{\text{fus}}H(935 \text{ K}) = (47.1 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$ are the selected values.

Clearly further work on the vaporisation of PuBr_3 is desirable, preferably with a mass spectrometer to identify the gaseous species involved.

18.1.4.2.b Heat capacity

The heat capacity of $\text{PuBr}_3(\text{g})$ was calculated using the rigid-rotator, harmonic oscillator approximation, using molecular parameters similar to those suggested for $\text{UBr}_3(\text{g})$ by Hildenbrand *et al.* [85HIL/GUR], but with somewhat smaller vibration frequencies following the work on $\text{UCl}_4(\text{g})$ by Haaland *et al.* [95HAA/MAR]. As noted in the previous section, such a model gives entropies which are appreciably smaller than those required by the vaporisation data, so the electronic contribution to the thermal functions was neglected until this discrepancy is resolved. The heat capacities up to 1500 K have been fitted to the expression

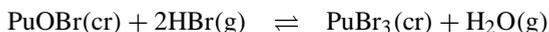
$$C_{p,m}^{\circ}(\text{PuBr}_3, \text{g}, T) = (83.135 + 3.900 \times 10^{-6}T - 1.3832 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The full data used are given in the report by Rand and Fuger [2000RAN/FUG], together with the calculated thermal functions and a plot of the vapour pressure data.

18.1.4.3 PuOBr(cr)

18.1.4.3.a Enthalpy of formation

The enthalpy and entropy of $\text{PuOBr}(\text{cr})$ have been calculated by a second-law analysis from the equilibrium constants of the reaction



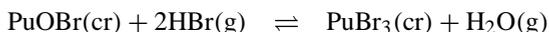
measured by Sheft and Davidson [49SHE/DAV2] from 816 to 911 K and Weigel *et al.* [82WEI/WIS] from 728 to 877 K, with good agreement; the latter are more precise and have been given a higher weight. With estimated heat capacities for $\text{PuBr}_3(\text{cr})$ and $\text{PuOBr}(\text{cr})$ (see below), the derived second-law value for $\Delta_{\text{f}}H_{\text{m}}^{\circ}(298.15 \text{ K})$ for this reaction is $-(91.7 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$, giving finally

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuOBr}, \text{cr}, 298.15 \text{ K}) = -(870.0 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$$

where the uncertainty includes that of the enthalpy of formation of $\text{PuBr}_3(\text{cr})$.

18.1.4.3.b Standard entropy and heat capacity

The entropy has been calculated from the equilibrium constants of the reaction



as noted for the enthalpy of formation above. The derived second-law value for $\Delta_r S_m^\circ(298.15 \text{ K})$ for this reaction is $-(137.3 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, giving finally

$$S_m^\circ(\text{PuOBr}, \text{cr}, 298.15 \text{ K}) = (127.0 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

where the uncertainty includes those in the properties of $\text{PuBr}_3(\text{cr})$. This value is close to that from two estimates, 118.3 and 120.3 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, [2000RAN/FUG]. This supports the value estimated for $S_m^\circ(\text{PuBr}_3, \text{cr}, 298.15 \text{ K})$ which is relevant to the discussion of the vaporisation data for PuBr_3 .

18.1.4.3.c High temperature heat capacity

These have been estimated to be consistent with those used for $\text{PuOCl}(\text{cr})$ and from $(\text{Pu}_2\text{O}_3 + \text{PuBr}_3)/3$ ([82GLU/GUR] and this review).

$$C_{p,m}^\circ(\text{PuOBr}, \text{cr}, T) = (73.7 + 17.0 \times 10^{-3}T - 5.15 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 K to 1100 K, and hence

$$C_{p,m}^\circ(\text{PuOBr}, \text{cr}, 298.15 \text{ K}) = (73.0 \pm 8.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.4.4 Cs_2PuBr_6 (cr)

18.1.4.4.a Enthalpy of formation

Fuger *et al.* [83FUG/PAR] have analysed the results of an unpublished calorimetric study by Niffle and Fuger cited in [79FUG] of the dissolution of this complex salt in 1 M HCl, which gave $\Delta_{\text{sln}}H(\text{Cs}_2\text{PuBr}_6, 298.15 \text{ K}) = -(75.55 \pm 0.22) \text{ kJ}\cdot\text{mol}^{-1}$. We have reworked this analysis, with the following different enthalpy values: $\Delta_f H_m^\circ(\text{CsBr}, \text{cr}, 298.15 \text{ K}) = -(405.60 \pm 0.25) \text{ kJ}\cdot\text{mol}^{-1}$ from [82GLU/GUR], compatible with [89COX/WAG]; $\Delta_f H_m^\circ(\text{Br}^-, 1 \text{ M HCl}, \text{partial}) = -(119.40 \pm 0.16) \text{ kJ}\cdot\text{mol}^{-1}$ [2000RAN/FUG].

The final calculated value for the enthalpy of formation of the complex salt becomes

$$\Delta_f H_m^\circ(\text{Cs}_2\text{PuBr}_6, \text{cr}, 298.15 \text{ K}) = -(1697.4 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$$

18.1.4.4.b Standard entropy

The standard entropy has been estimated to be $(470 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ by Rand and Fuger [2000RAN/FUG]. The selected value is thus

$$S_m^\circ(\text{Cs}_2\text{PuBr}_6, \text{cr}, 298.15 \text{ K}) = (470 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.5 Plutonium iodide compounds

18.1.5.1 PuI₃(cr)

18.1.5.1.a Enthalpy of formation

Brown *et al.* [77BRO/HUR] have measured the enthalpy of solution of PuI₃(cr) in oxygen free 1 M HCl to be $-(180.2 \pm 2.0)$ kJ·mol⁻¹. With the currently selected $\Delta_f H_m^\circ(\text{PuCl}_3, \text{cr}, 298.15 \text{ K})$ and the auxiliary values $\Delta_f H_m^\circ(\text{Cl}^-, 1 \text{ M HCl, partial}) = (-164.37 \pm 0.10)$ kJ·mol⁻¹, $\Delta_f H_m^\circ(\text{I}^-, 1 \text{ M HCl, partial}) = -(55.38 \pm 0.10)$ kJ·mol⁻¹ [2000RAN/FUG], the standard enthalpy of formation becomes

$$\Delta_f H_m^\circ(\text{PuI}_3, \text{cr}, 298.15 \text{ K}) = -(579.2 \pm 2.8) \text{ kJ}\cdot\text{mol}^{-1}$$

18.1.5.1.b Standard entropy and heat capacity

There are no low-temperature measurements of the heat capacity of PuI₃(cr), and the standard entropy is derived from three reasonably consistent estimates: Latimer's method, the spin-only contribution, and by comparison with similar compounds [2000RAN/FUG]. From these three estimates of 235.6, 226.2, and 226.1 J·K⁻¹·mol⁻¹, the selected value is

$$S_m^\circ(\text{PuI}_3, \text{cr}, 298.15 \text{ K}) = (228 \pm 12) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.5.1.c High temperature heat capacity

This has been estimated to be consistent with current estimates for PuCl₃(cr) and PuBr₃(cr) and uranium trihalides [92GRE/FUG], (with minor corrections).

$$C_{p,m}^\circ(\text{PuI}_3, \text{cr}, T) = (104.0 + 20.0 \times 10^{-3} T) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15K to 900 K, and hence

$$C_{p,m}^\circ(\text{PuI}_3, \text{cr}, 298.15 \text{ K}) = (110.0 \pm 8.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.5.1.d Fusion data

The melting point, enthalpy of fusion and heat capacity of the liquid are estimated from the values for the lanthanide tri-iodides and PuBr₃:

$$\begin{aligned} T_{\text{fus}} &= (930 \pm 50) \text{ K} \\ \Delta_{\text{fus}} H &= (50 \pm 8) \text{ kJ}\cdot\text{mol}^{-1} \\ C_{p,m}^\circ(\text{PuI}_3, \text{l}) &= (150 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

18.1.5.2 PuI₃(g)

18.1.5.2.a Enthalpy of formation and entropy

There are no experimental data on the volatility of PuI₃ but the stability of PuI₃(g) has been estimated by a comparison with the lanthanide trihalides. Myers and Graves [77MYE/GRA] have summarised the vapour pressures of these compounds. The vapour pressure of PuBr₃ is about twice that of NdBr₃ and Pr₃, and the data for PuI₃(g) have been chosen to give a vapour pressure about twice that of NdI₃ and PrI₃. Given the uncertainty in the entropy of PuBr₃ (see Section 18.1.4.2), conversion of the estimated vapour pressure to provide the enthalpy and entropy of sublimation will be subject to considerable uncertainty, but the selected values are:

$$\begin{aligned}\Delta_f H_m^\circ(\text{PuI}_3, \text{g}, 298.15 \text{ K}) &= -(305 \pm 15) \text{ kJ}\cdot\text{mol}^{-1} \\ S_m^\circ(\text{PuI}_3, \text{g}, 298.15 \text{ K}) &= (435 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\end{aligned}$$

18.1.5.2.b Heat capacity

The heat capacity function for PuI₃(g) was estimated to be that suggested for UI₃(g) by Hildenbrand *et al.* [85HIL/GUR]

$$C_{p,m}^\circ(\text{PuI}_3, \text{g}, T) = (83.15 + 1.4 \times 10^{-6}T - 1.0 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

from 298.15 to 1500 K and thus

$$C_{p,m}^\circ(\text{PuI}_3, \text{g}, 298.15 \text{ K}) = (82.0 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.1.5.3 PuOI(cr)

Hagemann *et al.* first obtained this oxyiodide as a by-product in the preparation of PuI₃, [49HAG/ABR]. It can be prepared more readily by the reaction of Sb₂O₃ and PuI₃, Brown *et al.* [77BRO/HUR].

Following Fuger [83FUG], the difference ($\Delta_f H_m^\circ(\text{PuOI}, \text{cr}, 298.15 \text{ K}) - \Delta_f H_m^\circ(\text{PuI}_3, \text{cr}, 298.15 \text{ K})/3$) is estimated to be $-(609 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$, from the corresponding values for the chloride $-611.1 \text{ kJ}\cdot\text{mol}^{-1}$ and bromide $-605.8 \text{ kJ}\cdot\text{mol}^{-1}$. The selected enthalpy of formation of PuOI(cr) is thus calculated to be

$$\Delta_f H_m^\circ(\text{PuOI}, \text{cr}, 298.15 \text{ K}) = -(802 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$$

The standard entropy is estimated from the values for the other trihalides and oxyhalides:

$$S_m^\circ(\text{PuOI}, \text{cr}, 298.15 \text{ K}) = (130 \pm 15) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The heat capacity is estimated to be close to the sum of $\{C_p(\text{PuI}_3, \text{cr}) + C_p(\text{Pu}_2\text{O}_3, \text{cr})\}/3$:

$$\begin{aligned}C_{p,m}^\circ(\text{PuOI}, \text{cr}, T) &= (67.0 + 3.57 \times 10^{-2}T \\ &\quad - 1.2 \times 10^{-5}T^2 - 9.0 \times 10^4 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ &(298.15 - 1000 \text{ K})\end{aligned}$$

and thus

$$C_{p,m}^{\circ}(\text{PuOI, cr, 298.15 K}) = (75.6 \pm 10.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

18.2 Aqueous plutonium group 17 (halogen) complexes

18.2.1 Aqueous plutonium fluoride complexes

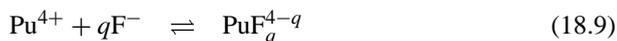
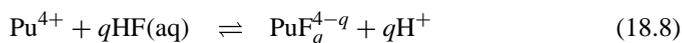
18.2.1.1 Aqueous Pu(III) fluorides

In two studies from the same group [86MAH/SAW, 93SAW/MAH], data were reported on fluoride complexation of Pu^{3+} obtained by potentiometry using a fluoride ion selective electrode. In the later study [93SAW/MAH], the credibility of the earlier result was questioned due to the evaluation method used then, which was unsuitable if higher complexes were present. The results of the recent study, however, are very surprising as they suggest that the 1:3 complex, $\text{PuF}_3(\text{aq})$, and other $\text{MF}_3(\text{aq})$ complexes are by far more stable than the 1:1 and the 1:2 complexes. This is contrary to the behaviour of Am(III) [92FUG/KHO, 95SIL/BID], and independent verification of the results of Sawant *et al.* [93SAW/MAH] is required. Appendix A contains a more detailed discussion of this paper. No data are selected for the Pu(III) fluoride system.

It is worth mentioning that the trivalent actinide ions exhibit a very similar complexation behaviour, see for example [92FUG/KHO], which resembles that of the trivalent lanthanide ions, e.g. [86CHO, 92MIL]. Hence, the stability constants of the Pu(III) fluoride complexes are expected to be of magnitudes similar to those of other actinide(III) and lanthanide(III) fluoride complexes.

18.2.1.2 Aqueous Pu(IV) fluorides

Experimental equilibrium data have been published for the following reactions



Most experiments were carried out in strongly acidic solutions, and the relevant equilibrium is thus Reaction (18.8). The data reported in [90SAW/CHA2] are converted to refer to Reaction (18.8) by taking the authors' protonation constant of F^- (*cf.* Appendix A). All reported constants are listed in Table 18.1.

The values for $\log_{10} {}^*\beta_1$ are in good agreement, but an extrapolation to $I = 0$ by linear regression is not reasonable, because the available data refer to only two different ionic strength values. We use $\Delta\varepsilon(9.4, q = 1) = -(0.12 \pm 0.09) \text{ kg}\cdot\text{mol}^{-1}$ from the corresponding Np(IV) system (the uncertainty increased by 0.05), *cf.* Section 9.2.1.2,

Table 18.1: Experimental equilibrium data for the plutonium(IV) fluoride system.

Method	Ionic medium	t (°C)	$\log_{10} {}^*\beta_q^{(a)}$	$\log_{10} {}^*\beta_q^{\circ(a)}$	Reference
$\text{Pu}^{4+} + \text{HF}(\text{aq}) \rightleftharpoons \text{PuF}_3^+ + \text{H}^+$					
cix	2 M HClO ₄	25	(4.45±0.30) ^(b)	(5.59±0.36)	[69KRY/KOM2]
	1 M HClO ₄	25	(4.20±0.30) ^(b)	(5.31±0.31)	
cix	2 M HNO ₃	25	(4.64±0.40) ^(b,c)	(5.78±0.45)	[69KRY/KOM4]
	1 M HNO ₃	25	(4.66±0.40) ^(b,c)	(5.77±0.41)	
dis	2 M HClO ₄	25	(4.64±0.15) ^(b)	(5.78±0.25)	[76BAG/RAM]
dis	2 M HClO ₄	25	(4.64±0.20) ^(b)	(5.78±0.28)	[76BAG/RAM2]
dis	2 M HClO ₄	10	4.70		[77BAG/RAM]
cou	1 M HClO ₄	25	(4.66±0.20) ^(b)	(5.77±0.22)	[79CHI/TAL]
dis	2 M HClO ₄	25	(4.47±0.20) ^(b)	(5.61±0.28)	[84NAS/CLE]
	2 M HClO ₄	15	4.50		
	2 M HClO ₄	7.5	4.51		
	2 M HClO ₄	1	4.52		
ise-F ⁻	2 M (Na,H)ClO ₄	25	(4.36±0.20) ^(b)	(5.50±0.28)	[90SAW/CHA2]
	1 M (Na,H)ClO ₄	23	4.66 ^(d)	5.76	
$\text{Pu}^{4+} + 2\text{HF}(\text{aq}) \rightleftharpoons \text{PuF}_2^{2+} + 2\text{H}^+$					
dis	2 M HClO ₄	25	(7.62±0.30) ^(b)	(9.56±0.46)	[76BAG/RAM]
dis	2 M HClO ₄	25	(7.61±0.40) ^(b)	(9.57±0.52)	[76BAG/RAM2]
dis	2 M HClO ₄	10	7.65		[77BAG/RAM]
cou	1 M HClO ₄	25	(7.32±0.40) ^(b)	(9.19±0.43)	[79CHI/TAL]
dis	2 M HClO ₄	25	(7.46±0.20) ^(b)	(9.41±0.39)	[84NAS/CLE]
	2 M HClO ₄	15	7.54		
	2 M HClO ₄	7.5	7.58		
	2 M HClO ₄	1	7.69		
ise-F ⁻	2 M (Na,H)ClO ₄	25	(7.35±0.20) ^(b)	(9.30±0.39)	[90SAW/CHA2]
	1 M (Na,H)ClO ₄	25	8.87 ^(d)	9.90	
$\text{Pu}^{4+} + 3\text{HF}(\text{aq}) \rightleftharpoons \text{PuF}_3^+ + 3\text{H}^+$					
ise-F ⁻	1 M HClO ₄	23	11.26 ^(d)	13.4	[90SAW/CHA2]
$\text{Pu}^{4+} + 4\text{HF}(\text{aq}) \rightleftharpoons \text{PuF}_4(\text{aq}) + 4\text{H}^+$					
ise-F ⁻	1 M HClO ₄	23	14.27 ^(d)	16.4	[90SAW/CHA2]

(a) Refers to the reactions indicated, the ionic strength and temperature given in the table. $\log_{10} {}^*\beta_q^{\circ}$ is in molal units, at $I = 0$ and 298.15 K.

(b) Uncertainty estimated in this review (*cf.* Appendix A).

(c) Corrected for the formation of NpNO_3^{3+} , *cf.* Appendix A.

(d) The published values refer to Reaction (18.9) and have been converted to conform to the reactions of this table (*cf.* Appendix A).

to correct the constants to $I = 0$. For the selection procedure, we use the values published by [69KRY/KOM2], [69KRY/KOM4] (after correction for the formation of PuNO_3^{3+} , see Appendix A), [76BAG/RAM], [76BAG/RAM2], and [79CHI/TAL]. From the study of Nash and Cleveland [84NAS/CLE] we use the value determined at 25°C in 2 M HClO_4 and the average of the three determinations in 1 M $\text{HClO}_4 + 1$ M NaClO_4 solution, *cf.* Table 18.1. On the other hand, we do not use the constant published in [90SAW/CHA2] (*cf.* Appendix A). The weighted average of the values listed in Table 18.1 results in $\log_{10} {}^*\beta_1^\circ$ (18.8, $q = 1$) = (5.66 ± 0.10). We convert this value to conform to Eq. (18.9) using our selected protonation constant of fluoride [92GRE/FUG]. The resulting selected value is

$$\log_{10} \beta_1^\circ (18.9, q = 1, 298.15 \text{ K}) = (8.84 \pm 0.10)$$

For the formation of the 1:2 complex, PuF_2^{2+} , constants have been reported in [76BAG/RAM, 76BAG/RAM2, 77BAG/RAM, 79CHI/TAL, 84NAS/CLE, 90SAW/CHA2]. Except for the constant of Sawant, Chaudhuri and Patil [90SAW/CHA2], the values agree well. Again, the value of [90SAW/CHA2] (*cf.* Appendix A) is not included in the selection procedure; from the study of Nash and Cleveland [84NAS/CLE] we use one value in each of the two electrolyte media at 25°C. The values of $\log_{10} {}^*\beta_2^\circ$ listed in Table 18.1 are obtained by correcting the reported constants to $I = 0$ by using $\Delta\varepsilon$ (18.8, $q = 2$) = -(0.18 ± 0.15) $\text{kg}\cdot\text{mol}^{-1}$ from the corresponding U(IV) fluoride system [92GRE/FUG], after increasing the uncertainty by 0.05. The weighted average of the four values is $\log_{10} {}^*\beta_2^\circ$ (18.8, $q = 2$) = (9.38 ± 0.19). We convert this value to conform to Equation (18.9) using our selected protonation constant of fluoride [92GRE/FUG]. The resulting selected value is

$$\log_{10} \beta_2^\circ (18.9, q = 2, 298.15 \text{ K}) = (15.7 \pm 0.2)$$

Data for the 1:3 and 1:4 complexes were published by Sawant, Chaudhuri and Patil [90SAW/CHA2]. Due to the problems with this paper (*cf.* Appendix A) and the lack of independent investigations at high fluoride concentrations, we cannot make any selection for the formation constants of PuF_3^+ and $\text{PuF}_4(\text{aq})$.

The Gibbs energies of formation of PuF_3^{3+} and PuF_2^{2+} are calculated using the selected values for Pu^{4+} and F^- .

$$\begin{aligned} \Delta_f G_m^\circ(\text{PuF}_3^{3+}, \text{aq}, 298.15 \text{ K}) &= -(810.0 \pm 2.9) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{PuF}_2^{2+}, \text{aq}, 298.15 \text{ K}) &= -(1130.7 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

From the equilibrium constants of Nash and Cleveland [84NAS/CLE] at 1, 7.5, 15 and 25°C (*cf.* Table 18.1), the authors extracted enthalpies of reaction, see Appendix A. We prefer this determination to the one of Bagawde, Ramakrishna and Patil [76BAG/RAM2, 77BAG/RAM] who had measurements at only two temperatures (10 and 25°C). However, the temperature dependencies follow the same trend in both studies. Reanalysis of the data of Nash and Cleveland [84NAS/CLE], *cf.*

Appendix A, and combination with the enthalpy of protonation of the fluoride ion, $\Delta_f H_m^\circ = (12.2 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$, results in the following selected values:

$$\Delta_r H_m^\circ(18.9, q = 1, 298.15 \text{ K}) = (9.1 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m^\circ(18.9, q = 2, 298.15 \text{ K}) = (11 \pm 5) \text{ kJ}\cdot\text{mol}^{-1}$$

From this value, we derive the enthalpies of formation and the entropies of PuF^{3+} and PuF_2^{2+} :

$$\Delta_f H_m^\circ(\text{PuF}^{3+}, \text{aq}, 298.15 \text{ K}) = -(866.1 \pm 3.9) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ(\text{PuF}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(1199.6 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1}$$

$$S_m^\circ(\text{PuF}^{3+}, \text{aq}, 298.15 \text{ K}) = -(229 \pm 13) \text{ kJ}\cdot\text{mol}^{-1}$$

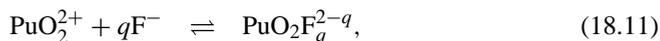
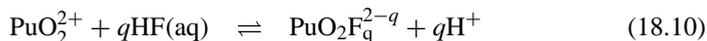
$$S_m^\circ(\text{PuF}_2^{2+}, \text{aq}, 298.15 \text{ K}) = -(105 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$$

18.2.1.3 Aqueous Pu(V) fluorides

No fluoride complexes of PuO_2^+ have been identified. Values for the NpO_2^+ complexes may be used as a guideline.

18.2.1.4 Aqueous Pu(VI) fluorides

As in the case of neptunium(VI), the investigation of fluoride complexation of plutonium(VI) is complicated by the fact that reduction of PuO_2^{2+} to Pu(IV) is favoured in acidic medium and in the presence of fluoride ion. The constants reported in the literature refer to either of the following reaction types,



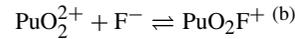
depending whether the fluoride ion was protonated or deprotonated under the experimental conditions. The constants are listed in Table 18.2. As in the case of Np(VI), the study published by Krylov, Komarov and Pushlenkov [68KRY/KOM2] yields constants that are unrealistically high, probably again due to reduction of Pu(VI) during the experiment (*cf.* Appendix A). The study of Savage [74SAV] is a rather approximate one reporting an even higher formation constant of PuO_2F^+ , calculated via the formation of a hydroxide complex, and must be discarded as well. Since the results of Patil and Ramakrishna [76PAT/RAM] are also discarded (*cf.* Appendix A), due to a very strong trend in the results, the only remaining data are those of Choppin and Rao [84CHO/RAO] and Sawant *et al.* [85SAW/CHA] referring to Reaction (18.11). Correction of these constants to $I = 0$ by using $\Delta\varepsilon(18.11, q = 1) = -(0.19 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$, as was done for the corresponding neptunium system above, yields values that are not incompatible (*cf.* Table 18.2). We select the weighted average of these constants, but we increase the resulting uncertainty of ± 0.10 to ± 0.20 to reflect

the fact that no reliable studies are available in acidic media, in which noticeably lower constants were obtained in the case of Np(VI).

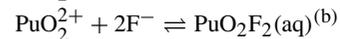
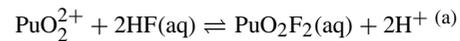
$$\log_{10} \beta_1^\circ (18.11, q = 1, 298.15 \text{ K}) = 4.56 \pm 0.20$$

The only credible study reporting constants for the formation of the 1:2 complex is by Sawant *et al.* [85SAW/CHA] in 0.1 and 1 M NaClO₄ media (*cf.* Appendix A). The constants are corrected to $I = 0$ by using $\Delta\varepsilon(18.11, q = 2) = -(0.50 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ from the corresponding Np(VI) system. The resulting values of $\log_{10} \beta_2^\circ$ are not in agreement (*cf.* Table 18.2). Agreement could be reached by using $\Delta\varepsilon(18.11, q = 2) = 0 \text{ kg}\cdot\text{mol}^{-1}$ instead of $-0.5 \text{ kg}\cdot\text{mol}^{-1}$. However, this does not correspond to the specific ion interaction coefficients commonly observed in such systems (*cf.* Appendix B). More experiments are required to examine the ionic strength dependence of this equilibrium. At this time, the unweighted average of the two values is selected, with an uncertainty that covers the range of expectancy of the two values:

$$\log_{10} \beta_2^\circ (18.11, q = 2, 298.15 \text{ K}) = 7.25 \pm 0.45$$

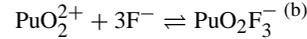


cix	1 M HClO ₄	25	(2.11±0.04)			[68KRY/KOM2]
	2 M HClO ₄	25	(2.00±0.04)			
pot	2.1 M (Na,H)ClO ₄	25	3.0			[74SAV]
dis	2 M HClO ₄	25	1.08			[76PAT/RAM]
ise-F ⁻	1 M NaClO ₄	23		(4.22±0.20) ^(d)	(4.82±0.23)	[84CHO/RAO]
ise-F ⁻	0.1 M NaClO ₄	21		(4.11±0.15) ^(d)	(4.53±0.15)	[85SAW/CHA]
	1 M NaClO ₄	21		(3.84±0.15) ^(d)	(4.44±0.18)	



cix	1 M HClO ₄	25	(4.15±0.06)			[68KRY/KOM2]
	2 M HClO ₄	25	(3.82±0.06)			
ise-F ⁻	0.1 M NaClO ₄	21		(6.92±0.15) ^(d)	(7.52±0.15)	[85SAW/CHA]
	1 M NaClO ₄	21		(6.31±0.15) ^(d)	(6.98±0.18)	

(Continued on next page)



cix	1 M HClO ₄	25	(6.08±0.07)	[68KRY/KOM2]
	2 M HClO ₄	25	(5.52±0.12)	
ise-F ⁻	0.1 M NaClO ₄	21	9.01	[85SAW/CHA]
	1 M NaClO ₄	21	7.73	

(a) $\log_{10} {}^*\beta_q$ refers to Reaction (18.10) and results from measurements in acidic solutions.

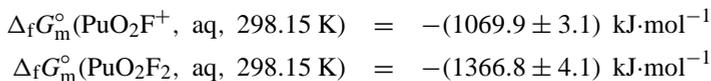
(b) $\log_{10} \beta_q$ refers to Reaction (18.11) and results from measurements in mildly acidic or neutral solutions.

(c) $\log_{10} \beta_q^\circ$ refers to Reaction (18.11). The experimental data have been corrected to $I = 0$ in the present review and, when necessary, converted to refer to Reaction (18.11) by using the selected protonation constant of fluoride ion.

(d) Uncertainty estimated in this review.

Sawant *et al.* [85SAW/CHA] also reported formation constants for the 1:3 complex, NpO_2F_3^- . Again, these constants reported for $I = 0.1$ M and $I = 1$ M are not compatible with the specific ion interaction coefficients in Appendix B. For the corresponding U(VI) system we have $\Delta\varepsilon(18.11, q = 3) = -0.52 \text{ kg}\cdot\text{mol}^{-1}$ [92GRE/FUG], and by using this value to correct the data of [85SAW/CHA] to $I = 0$ we obtain $\log_{10} \beta_3^\circ(18.11, q = 3) = 9.6$ and 8.4 for the experiments carried out at $I = 0.1$ M and $I = 1$ M, respectively. In order to obtain consistent $\log_{10} \beta_3^\circ$ values from the two determinations, we would have to use $\Delta\varepsilon = +0.8 \text{ kg}\cdot\text{mol}^{-1}$, and this would be incompatible with the commonly observed ionic strength dependence of comparable equilibria. The formation of NpO_2F_3^- needs closer examination, and no selection is made at this time.

The Gibbs energy of formation values are derived from the above selected constants using the selected $\Delta_f G_m^\circ$ values for PuO_2^{2+} and F^- .



18.2.2 Aqueous plutonium chlorine complexes

18.2.2.1 Aqueous plutonium chlorides

18.2.2.1.a Aqueous Pu(III) chlorides

Quantitative information on chloride complexation of Pu^{3+} according to the equilibria



has been published by Ward and Welch [56WAR/WEL], Martin and White [58MAR/WHI] and Shiloh and Marcus [64SHI/MAR], and is summarised in Table 18.3. The study of Ward and Welch [56WAR/WEL] was carried out at ionic strengths of 0.207, 0.5 and 1.0 M, respectively (*cf.* Appendix A). The formation constant reported by Martin and White [58MAR/WHI] is not the result of an independent measurement, but rather the result of an extrapolation of Ward and Welch's [56WAR/WEL] value at $I = 0.207$ M (HCl) using the Davies equation.

This value was used to derive the enthalpy of Reaction (18.12, $q = 1$) (see Appendix A and discussion below). The data of Ward and Welch [56WAR/WEL] reported at "room temperature", which Martin and White [58MAR/WHI] reported as 21°C , are thus corrected to $t = 25^\circ\text{C}$ (*cf.* Appendix A), using the enthalpy of reaction selected below. Shiloh and Marcus [64SHI/MAR] used very high and variable ionic strengths in their spectrophotometry experiments. These values cannot be used to select a formation constant at $I = 0$. Giffaut [94GIF] noted that spectrophotometry is not a suitable method to study chloride complexation of Pu^{3+} , due to the very small changes in the absorption spectrum up to a chloride concentration of 4 M. It is probable that this complexation could equally well be described as activity effects. The number of available formation constants is insufficient for a linear extrapolation to $I = 0$. We adopt

Table 18.3: Experimental equilibrium data for the plutonium(III) chloride system.

Method	Ionic medium	t (°C)	$\log_{10} \beta_q^{(a)}$	$\log_{10} \beta_q^{\circ(a)}$	Reference
$\text{Pu}^{3+} + \text{Cl}^- \rightleftharpoons \text{PuCl}^{2+}$					
cix	0.207 M HCl	21	$(0.35 \pm 0.20)^{(b)}$	(1.13 ± 0.20)	[56WAR/WEL]
	0.5 M HCl	21	$(0.24 \pm 0.20)^{(b)}$	(1.17 ± 0.21)	
	0.5 M H(Cl,ClO ₄)	21	$(0.25 \pm 0.20)^{(b)(c)}$	(1.19 ± 0.21)	
	1.0 M HCl	21	$-(0.04 \pm 0.50)^{(b)}$	(0.95 ± 0.52)	
recalc ^(d)	0.1 M HCl	25	$0.57^{(d)}$		[58MAR/WHI]
sp	1-13 M LiCl	25	$-(2.43 \pm 0.08)$		[64SHI/MAR]
$\text{Pu}^{3+} + 2\text{Cl}^- \rightleftharpoons \text{PuCl}_2^+$					
sp	1-13 M LiCl	25	$-(5.00 \pm 0.06)$		[64SHI/MAR]

(a) Refers to the reactions indicated, the ionic strength and temperature given in the table. $\log_{10} \beta_q^{\circ}$ is in molal units, at $I = 0$ and 298.15 K.

(b) The uncertainties are estimated in this review, (cf. Appendix A).

(c) This value was measured at $[\text{Cl}]_t = 0.2$ M.

(d) This value is the result of a recalculation of the data in [56WAR/WEL] by using the Davies equation.

a value of $\Delta \varepsilon = -(0.22 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$ from the corresponding Am(III) system [95SIL/BID] and we correct the single $\log_{10} \beta_1$ values of [56WAR/WEL] to $I = 0$ (cf. Table 18.3). The agreement is good, and the weighted average of the four values of Ward and Welch [56WAR/WEL] is $\log_{10} \beta_1^{\circ} = (1.19 \pm 0.12)$. This value is selected, but we prefer to increase its uncertainty to ± 0.2 to reflect the fact that the value is based on a single paper:

$$\log_{10} \beta_1^{\circ}(18.12, q = 1, 298.15 \text{ K}) = 1.2 \pm 0.2.$$

This value is in agreement with the selected value of the IAEA review, $\log_{10} \beta_1^{\circ} = (1.3 \pm 0.1)$ [92FUG/KHO].

Martin and White [58MAR/WHI] reported $\Delta_r H_m(18.12, q = 1, 298.15 \text{ K}) = 19 \text{ kJ}\cdot\text{mol}^{-1}$ from the difference between the enthalpy of solution of $\text{PuCl}_3(\text{s})$ in 0.1 M HClO_4 [58MAR/WHI] and in 0.1 M HCl [49ROB/WES] (cf. Appendix A). However, Fuger and Cunningham [63FUG/CUN] obtained a heat of solution value in 0.001 M $\text{HClO}_4/0.099 \text{ M NH}_4\text{ClO}_4$ which is virtually the same as the one in 0.1 M HCl and would thus indicate that the enthalpy change of Reaction (18.12, $q = 1$) is close to zero. The reason for this discrepancy is unclear. Rather than due to a medium effect, this discrepancy could be due to an effect of the acid concentration. Martin and White's [58MAR/WHI] experiments at $I = 2.0 \text{ M}$ ($\text{HClO}_4/\text{LiClO}_4$) with H^+ concentrations of 0.1, 0.5, 1.0, 1.5 and 2.0 M showed a significant change in the heat of solution of $\text{PuCl}_3(\text{s})$ between $-132.5 \text{ kJ}\cdot\text{mol}^{-1}$ (0.1 M H^+) and $-118.4 \text{ kJ}\cdot\text{mol}^{-1}$ (2.0 M H^+). On the basis of the available experimental information, we cannot recommend any reliable enthalpy value. However, the weakness of the complex PuCl^{2+} suggests that the

complexation enthalpy should be much closer to zero than the value of [58MAR/WHI].

The formation value is calculated using the selected values for Pu^{3+} and Cl^- :

$$\Delta_f G_m^\circ(\text{PuCl}^{2+}, \text{aq}, 298.15 \text{ K}) = -(717.1 \pm 2.9) \text{ kJ}\cdot\text{mol}^{-1}$$

18.2.2.1.b Aqueous Pu(IV) chlorides

The experimental equilibrium data available on the reactions



are listed in Table 18.4. Early studies [51RAB/LEM, 55RAB/COW] used emf measurements to determine the influence of increasing chloride concentrations on the redox potential of the Pu(IV)-Pu(III) couple. These evaluations did not take chloride complexation of Pu^{3+} into account, which is not negligible at the chloride concentrations used. This review makes the corresponding corrections to the formation constants reported by Rabideau and co-workers [51RAB/LEM, 55RAB/COW] (*cf.* Appendix A). The values reported in [51RAB/LEM, 55RAB/COW] both refer to the same experimental determination, and only one of the two values is considered in the selection procedure (see below). Three of the reported constants refer to $I = 4 \text{ M}$ [60GRE/NOR, 66DAN/ORL, 94GIF]. The data reported in a recent study [92MAR/ESS] and presented also in [92BIS/KRA] cannot be included in the selection of a standard state value due to the very high ionic strength used in the experiment. Using $\Delta\varepsilon(18.13, q = 1) = -0.29 \text{ kg}\cdot\text{mol}^{-1}$ from the corresponding uranium(IV) equilibrium (*cf.* [92GRE/FUG]), would lead to inconsistent $\log_{10} \beta_1^\circ$ values ranging from 0.68 to 1.64. On the other hand, a linear extrapolation to $I = 0$ is questionable because of the small number of available data points in the ionic strength range for which the parameter Ba_j in the specific ion interaction equation was optimised ($I_m < 3.5 \text{ m}$, *cf.* Appendix B). However, among the few possibilities to select a standard formation constant for the complex PuCl^{3+} , the linear regression is the one that best represents the trend in the experimental values. The uncertainties assigned to the single values take account of this difficulty, *cf.* Table 18.4. We include the values measured at $I = 4 \text{ M}$ (*i.e.*, $I_m = 4.87 \text{ m}$) in the linear regression analysis [60GRE/NOR, 66DAN/ORL, 94GIF]. Figure 18.1 shows the result of this extrapolation, and the resulting selected constant is

$$\log_{10} \beta_1^\circ(18.13, q = 1, 298.15 \text{ K}) = (1.8 \pm 0.3)$$

This value is in agreement with the one selected by the IAEA review [92FUG/KHO], $\log_{10} \beta_1^\circ = (2.0 \pm 0.5)$, and identical to the value obtained by Giffaut [94GIF] by extrapolation to $I = 0$. The resulting $\Delta\varepsilon$ value is $-(0.09 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$. The formation value is calculated using the selected values for Pu^{4+} and Cl^- .

$$\Delta_f G_m^\circ(\text{PuCl}^{3+}, \text{aq}, 298.15 \text{ K}) = -(619.5 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}$$

Rabideau and Cowan [55RAB/COW] also reported an enthalpy of Reaction (18.13, $q = 1$) from redox potential measurements at different temperatures between 6°C and

Table 18.4: Experimental equilibrium data for the plutonium(IV) chloride system.

Method	Ionic medium	t (°C)	$\log_{10} \beta_q^{(a)}$	Reference
$\text{Pu}^{4+} + \text{Cl}^- \rightleftharpoons \text{PuCl}^{3+}$				
emf	1 M H(Cl,ClO ₄)	25	0.32 ^(c)	[51RAB/LEM]
emf	1 M H(Cl,ClO ₄)	25	(0.31±0.30) ^(b,c)	[55RAB/COW]
	2 M H(Cl,ClO ₄)	25	-0.23	
cix	4 M H(Cl,ClO ₄)	20	(0.15±0.30) ^(b)	[60GRE/NOR]
dis	4 M H(Cl,ClO ₄)	25	(0.30±0.20) ^(b)	[66DAN/ORL]
dis	2 M H(Cl,ClO ₄)	25	(0.15±0.20) ^(b)	[76BAG/RAM2]
pol	5.4 M (H,Na)(Cl,ClO ₄)	25	(0.13 ± 0.02)	[92MAR/ESS] ^(d)
sp	3 M H(Cl,ClO ₄)	25	(0.20±0.20) ^(b)	[94GIF]
	4 M H(Cl,ClO ₄)	25	(0.25±0.20) ^(b)	
$\text{Pu}^{4+} + 2\text{Cl}^- \rightleftharpoons \text{PuCl}_2^+$				
cix	4 M H(Cl,ClO ₄)	20	(0.08 ± 0.07)	[60GRE/NOR]
dis	4 M H(Cl,ClO ₄)	25	-(0.80 ± 0.08)	[66DAN/ORL]
dis	2 M H(Cl,ClO ₄)	25	-(0.64 ± 0.11)	[76BAG/RAM2]
pol	5.4 M (H,Na)(Cl,ClO ₄)	25	-(1.5 ± 0.2)	[92MAR/ESS] ^(d)
sp	3 M H(Cl,ClO ₄)	25	-(0.36±0.18) ^(e)	[94GIF]
	4 M H(Cl,ClO ₄)	25	-(0.36±0.20) ^(e)	
$\text{Pu}^{4+} + 3\text{Cl}^- \rightleftharpoons \text{PuCl}_3^+$				
cix	4 M H(Cl,ClO ₄)	20	-(1.0 ± 0.4)	[60GRE/NOR]
pol	5.4 M (H,Na)(Cl,ClO ₄)	25	-(1.7 ± 0.3)	[92MAR/ESS] ^(d)

(a) Refers to the value reported for the reactions indicated, the ionic strength and temperature given in the table.

(b) The uncertainties are estimated in this review, *cf.* Appendix A.

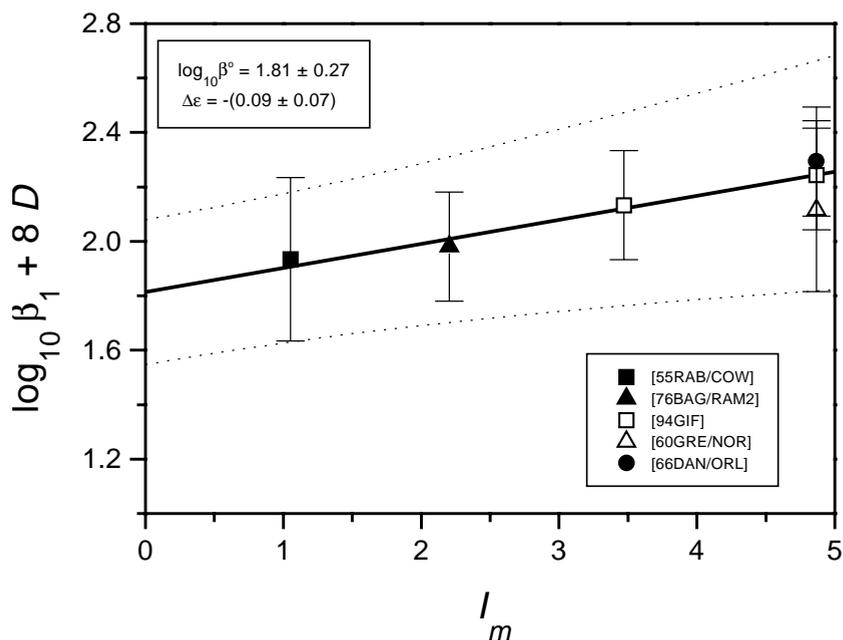
(c) These values were reported as -0.24 [51RAB/LEM] and -0.25 [55RAB/COW], respectively, and are corrected in this review for the formation of PuCl_2^+ , *cf.* the [55RAB/COW] entry in Appendix A.

(d) The same values of the same study were published in the same year in a summary paper by Bischoff *et al.* [92BIS/KRA].

(e) Reported as stepwise constants: $\log_{10} K_2(I = 3 \text{ M}) = -(0.56 \pm 0.16)$ and $\log_{10} K_2(I = 4 \text{ M}) = -(0.61 \pm 0.18)$ (*cf.* Appendix A).

Figure 18.1: Extrapolation to $I = 0$ of experimental data for the formation of PuCl^{3+} using the specific ion interaction equation. The data refer to mixed perchlorate/chloride media and are taken from [55RAB/COW], [60GRE/NOR], [66DAN/ORL], [76BAG/RAM2] and [94GIF]. The dotted lines are the limits of the uncertainty range obtained by propagating the resulting uncertainties at $I = 0$ back to $I = 5$ m.

Equilibrium: $\text{Pu}^{4+} + \text{Cl}^- \rightleftharpoons \text{PuCl}^{3+}$



45°C in perchloric and hydrochloric acid solutions, respectively. In that paper, the formation of PuCl^{2+} was not taken into account, and a corresponding correction cannot be performed due to the uncertainty in the enthalpy of PuCl^{2+} , see the discussion above. No enthalpy of formation value can thus be selected for PuCl^{3+} .

The data for the 1:2 complex (*cf.* Table 18.4), are obtained exclusively at high ionic strengths and cannot be reliably extrapolated to $I = 0$. In addition, there are large variations among the values published. Giffaut [94GIF] recently published, in addition to the constant for the 1:1 complex, stepwise constants for the 1:2 complex at $I = 3$ and 4 M and extrapolated them to $I = 0$ using the specific ion interaction model. He obtained $\log_{10} K_2^\circ = (0.80 \pm 0.16)$ with $\Delta\varepsilon = -(0.03 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}$. In view of the discrepant values from the different sources, we select no formation constant for PuCl_2^{2+} .

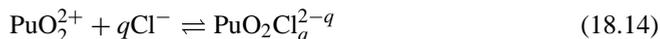
Giffaut [94GIF] has observed the formation of a 1:3 and a 1:4 complex by spectrophotometry (*cf.* Appendix A). He quantified their stability limits by estimating the stepwise constants for the formation of PuCl_3^+ and $\text{PuCl}_4(\text{aq})$ at chloride concentrations between 2 and 12 M and variable ionic strength: $-0.7 \leq \log_{10} K_3 \leq -1$ and $\log_{10} K_4 < -1$. Grenthe and Norén [60GRE/NOR] and Marx *et al.* [92MAR/ESS] have also reported formation constants for PuCl_3^+ , *cf.* Table 18.4, but an extrapolation to $I = 0$ of the available data is not considered feasible.

18.2.2.1.c Aqueous Pu(V) chlorides

No experimental identification of any complexes of the form $\text{PuO}_2\text{Cl}_q^{1-q}$ is known to us. The information given in the IAEA review [92FUG/KHO] on an unpublished value cited by Katz and Seaborg [57KAT/SEA] is, in our view, due to a printing error. A comparison with Np(V), *cf.* Section 9.2.2.3, suggests that actinide(V) chloride complexes, if they exist, are extremely weak.

18.2.2.1.d Aqueous Pu(VI) chlorides

The chloride complexes of plutonium(VI) have been studied by spectrophotometry and solvent extraction methods. A summary of published experimental results is presented in Table 18.5. The IAEA [92FUG/KHO] have reviewed the then existing data and proposed selected formation constants and reaction enthalpies for PuO_2Cl^+ and $\text{PuO}_2\text{Cl}_2(\text{aq})$ at an ionic strength of 2 M. Recently, Giffaut [94GIF] investigated the plutonium chloride system using a spectrophotometric technique (*cf.* Appendix A), and he suggested the formation of the complexes PuO_2Cl^+ , $\text{PuO}_2\text{Cl}_2(\text{aq})$ and $\text{PuO}_2\text{Cl}_3^-$ according to the equilibria



and he obtained spectroscopic evidence for the formation of $\text{PuO}_2\text{Cl}_2(\text{aq})$ (*cf.* Appendix A).

Giffaut [94GIF] derived constants for the formation of PuO_2Cl^+ at $I = 2$ M and $I = 3$ M, respectively, and extrapolated them to $I = 0$ using the specific ion interaction equation. Giffaut [94GIF] then used the resulting constant to evaluate the formation constant of $\text{PuO}_2\text{Cl}_2(\text{aq})$ from experiments at variable ionic strength, again using the

Table 18.5: Experimental equilibrium data for the plutonium(VI) chloride system.

Method	Ionic medium	$t(^{\circ}\text{C})$	$\log_{10} \beta_q^{(a)}$	Reference
$\text{PuO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{PuO}_2\text{Cl}^+$				
sp	2 M H(Cl,ClO ₄)	25	0.10	[57NEW/BAK]
sp	2 M H(Cl,ClO ₄)	2.4	-0.04	[61RAB/MAS]
	2 M H(Cl,ClO ₄)	10.2	0.00	
	2 M H(Cl,ClO ₄)	15.0	0.03	
	2 M H(Cl,ClO ₄)	20.2	0.06	
	2 M H(Cl,ClO ₄)	29.6	0.11	
dis	4 M Cl ⁻ , ClO ₄ ⁻	RT?	< -0.7	[76VOD/KOL]
prx	?	RT?	0.02	[65MAZ/SIV]
dis	2 M H(Cl,ClO ₄)	25	-(0.10 ± 0.04)	[78BED/FID]
sp	5 M NaCl	25	-(0.06 ± 0.01)	[88BÜP/KIM]
sp	2 M H(Cl,ClO ₄)	25	-(0.07 ± 0.09)	[94GIF]
	3 M H(Cl,ClO ₄)	25	-(0.06 ± 0.07)	
$\text{PuO}_2^{2+} + 2\text{Cl}^- \rightleftharpoons \text{PuO}_2\text{Cl}_2(\text{aq})$				
sp	2 M H(Cl,ClO ₄)	25	-0.46	[57NEW/BAK]
sp	2 M H(Cl,ClO ₄)	2.4	-0.68	[61RAB/MAS]
	2 M H(Cl,ClO ₄)	10.2	-0.60	
	2 M H(Cl,ClO ₄)	15.0	-0.55	
	2 M H(Cl,ClO ₄)	20.2	-0.48	
	2 M H(Cl,ClO ₄)	29.6	-0.37	
dis	4 M Cl ⁻ , ClO ₄ ⁻	RT?	-0.77	[65MAZ/SIV]
dis	2 M H(Cl,ClO ₄)	25	-(0.60 ± 0.09)	[78BED/FID]
sp	5 M NaCl	25	-(0.82 ± 0.06)	[88BÜP/KIM]
sp	0 (extrapolated) ^(c)	25	-(0.6 ± 0.2)	[94GIF]

(a) Refers to the value reported for the reactions indicated, as well as for the ionic strength and temperature given in the table.

(b) The uncertainties are estimated in this review.

(c) Extrapolated by Giffaut [94GIF] from experiments carried out at $2.1 \text{ m} < I_m < 5.9 \text{ m}$, using the specific ion interaction approach.

specific ion interaction approach which is the preferred approach in the present review (*cf.* Appendix B). This study is a very careful and comprehensive one. This review selects the values reported by Giffaut [94GIF], which are in good agreement with the other published values (*cf.* Table 18.5).

$$\begin{aligned}\log_{10} \beta_1^\circ(18.14, q = 1, 298.15 \text{ K}) &= 0.70 \pm 0.13 \\ \log_{10} \beta_2^\circ(18.14, q = 2, 298.15 \text{ K}) &= -(0.6 \pm 0.2)\end{aligned}$$

The corresponding ion interaction coefficients were evaluated by Giffaut [94GIF] for HCl media: $\Delta\varepsilon(18.14, q = 1, \text{HCl}) = -(0.08 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$ and $(18.14, q = 2, \text{HCl}) = -(0.43 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}$. The IAEA review [92FUG/KHO] selected the data from Newton and Baker [57NEW/BAK] and Rabideau and Masters [61RAB/MAS]. For the reasons outlined in Appendix A, we have doubts about the reliability of these data.

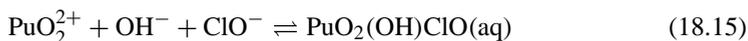
Reaction enthalpies have been extracted in the IAEA review [92FUG/KHO] from the data of Rabideau and Masters [61RAB/MAS] measured between 2.4°C and 29.6°C and at $[\text{Cl}^-]_{\text{t}} < 1.8 \text{ M}$ ($I = 2 \text{ M}$). The resulting value of $\Delta_{\text{r}}H_{\text{m}}^\circ(18.14, q = 1)$ differs from the value extracted by Rabideau and Masters [61RAB/MAS] for the 1:1 model, although only a very small proportion of $\text{PuO}_2\text{Cl}_2(\text{aq})$ is formed under these conditions. We do not consider these enthalpy data of sufficient reliability to be selected in the present review (see comments in Appendix A under [61RAB/MAS]).

The Gibbs energy of formation values are derived from the above selected constant using the selected $\Delta_{\text{r}}G_{\text{m}}^\circ$ values for PuO_2^{2+} and Cl^- .

$$\begin{aligned}\Delta_{\text{r}}G_{\text{m}}^\circ(\text{PuO}_2\text{Cl}^+, \text{aq}, 298.15\text{K}) &= -(897.6 \pm 2.9) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_{\text{r}}G_{\text{m}}^\circ(\text{PuO}_2\text{Cl}_2, \text{aq}, 298.15\text{K}) &= -(1021.4 \pm 3.1) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

18.2.2.2 Aqueous plutonium hypochlorites

In concentrated aqueous NaCl solutions plutonium radiation was reported to produce a steady state concentration of hypochlorite ion, ClO^- [88BÜP/KIM]. The oxidising character of hypochlorite stabilised the Pu(VI) oxidation state, but at the same time forms complexes with PuO_2^{2+} . Kim and Pashalidis [91KIM/PAS] and Pashalidis *et al.* [93PAS/KIM] reported the formation of $\text{PuO}_2(\text{OH})\text{ClO}(\text{aq})$ in 0.55 M NaClO solution according to the reaction



From spectrophotometric measurements at 22°C they derived $\log_{10} \beta_1 = 14.0$ at pH = 6.7 and $\log_{10} \beta_1 = 14.5$ at pH 8.4 [93PAS/KIM]. They also suggested a 1:2 complex, $\text{PuO}_2(\text{ClO})_2(\text{aq})$, with a formation constant of $\log_{10} \beta_2 = 10.3$ under the same conditions. These data cannot be selected, because they are based on questionable assumptions (*cf.* Appendix A).

18.2.3 Aqueous plutonium bromide complexes

18.2.3.1 Aqueous Pu(III) bromides

Quantitative information on bromide complexation of Pu^{3+} has only been published by Shiloh and Marcus [64SHI/MAR] in concentrated LiBr solutions of varying ionic strength up to nearly 12 M. The authors gave formation constants for PuBr^{2+} ($\log_{10} \beta_1 = -(3.45 \pm 0.08)$) and PuBr_2^+ ($\log_{10} \beta_2 = -(6.54 \pm 0.06)$). The ionic strength effects are expected to be considerable under these conditions. An extrapolation to $I = 0$ is not possible, and no standard formation value can be selected here.

18.2.3.2 Aqueous Pu(IV) bromides

The experimental equilibrium data available on the reactions



are listed in Table 18.6. The reported constants for $q = 1$ [66DAN/ORL, 75RAG/RAM] are corrected to $I = 0$, after conversion to molality units, by using the specific ion interaction equation (*cf.* Appendix B) and by adopting the ion interaction coefficient used for the corresponding uranium(IV) system [92GRE/FUG] after increasing the uncertainty by 0.05: $\Delta\varepsilon(18.16, q = 1) = -(0.29 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}$. The resulting formation constants, $\log_{10} \beta_q^\circ$, agree well (see Table 18.6), and the weighted average of these two values is selected:

$$\log_{10} \beta_1^\circ(18.16, q = 1, 298.15 \text{ K}) = (1.6 \pm 0.3)$$

Table 18.6: Experimental equilibrium data for the plutonium(IV) bromide system.

Method	Ionic medium	t ($^\circ\text{C}$)	$\log_{10} \beta_q^{(a)}$	$\log_{10} \beta_q^\circ^{(a)}$	Reference
$\text{Pu}^{4+} + \text{Br}^- \rightleftharpoons \text{PuBr}^{3+}$					
dis	4 M H(Br,Cl)	25	$(1.00 \pm 0.20)^{(b)}$	(1.76 ± 0.60)	[66DAN/ORL]
dis	2 M H(Br,ClO ₄)	25	$(0.33 \pm 0.20)^{(b)}$	(1.52 ± 0.35)	[75RAG/RAM]
$\text{Pu}^{4+} + 2\text{Br}^- \rightleftharpoons \text{PuBr}_2^{2+}$					
dis	4 M H(Br,Cl)	25	(0.64 ± 0.05)		[66DAN/ORL]

(a) Refers to the reactions indicated, the ionic strength and temperature given in the table. $\log_{10} \beta_q^\circ$ is in molal units, at $I = 0$ and 298.15 K.

(b) The uncertainties are estimated in this review (*cf.* Appendix A).

This value is in line with the stability trends of the chloride and bromide complexes in the aqueous uranium and plutonium system.

The Gibbs energy of formation is calculated using the selected values for Pu^{4+} and Br^- .

$$\Delta_f G_m^\circ(\text{PuBr}_3^+, \text{aq}, 298.15 \text{ K}) = -(591.0 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}$$

The 1:2 complex, PuBr_2^{2+} , seems to be more stable than its homologue in the Pu(IV) chloride system, *cf.* Danesi, Orlandini and Scibona [66DAN/ORL] (Appendix A). However, β_2 is small and there is no evidence for the existence of the 1:2 complex. We hence do not select any value for the formation constant of the 1:2 complex.

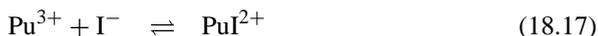
18.2.3.3 Aqueous Pu(V) and Pu(VI) bromides

No aqueous species of the form $\text{PuO}_2\text{Br}_q^{1-q}$ or $\text{PuO}_2\text{Br}_q^{2-q}$, respectively, have been identified.

18.2.4 Aqueous plutonium iodine complexes

18.2.4.1 Aqueous plutonium iodides

Studies with the purpose of investigating the stability of iodide complexes of plutonium are not available. However, in an investigation of Pu(III) thiocyanate complexes [74KHO/MAT] (*cf.* Appendix A), iodide was used as a holding reductant for plutonium, and the formation of Pu(III) iodide complexes had to be taken into account quantitatively in the evaluation of the extraction data. Hence, Khopkar and Mathur [74KHO/MAT] carried out a separate solvent extraction experiment at 30°C and $I = 1 \text{ M}$ (NH_4ClO_4) to investigate the complexation behaviour of Pu(III) with iodide. They found evidence for the formation of only one complex up to an iodide concentration of 0.7 M:



They reported an equilibrium constant of $\log_{10} \beta_1(18.17, I = 1 \text{ M}, 303.15 \text{ K}) = (0.04 \pm 0.03)$. As an attempt to extrapolate this constant to $I = 0$, we can use the same estimation for the ionic strength dependence as for the Pu(III)-SCN system, namely $\Delta\varepsilon(18.17) = -0.15 \text{ kg}\cdot\text{mol}^{-1}$. In this way we obtain $\log_{10} \beta_1^\circ(18.17, 303.15 \text{ K}) = 1.09$. This constant is of the expected order of magnitude. In spite of the paucity of data, we feel that we can recommend this value as a guideline, assuming that the temperature dependence of $\log_{10} \beta_1(18.17)$ is negligible:

$$\log_{10} \beta_1^\circ(18.17, 298.15 \text{ K}) = 1.1 \pm 0.4$$

We assign a large uncertainty to reflect that only a single determination is available and that the ionic strength extrapolation is based on estimations only.

18.2.4.2 Aqueous plutonium iodates

No aqueous complexes of iodate with any oxidation state of plutonium have been identified.

Chapter 19

Plutonium group 16 compounds and complexes

19.1 Plutonium sulphur compounds and complexes

19.1.1 Plutonium sulphates

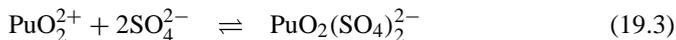
19.1.1.1 Aqueous plutonium sulphates

19.1.1.1.a Pu(VI) sulphates

There are only two experimental studies concerning the $\text{PuO}_2^{2+}\text{-SO}_4^{2-}$ system (*cf.* Table 19.1). One was performed at high total acid concentration and ionic strength [76PAT/RAM], and the authors were only able to determine the association quotient of the monosulphato-dioxoplutonium(VI) complex:



Ullman and Schreiner [86ULL/SCH] determined the enthalpy and the association quotient at lower total acid concentration and reported the association quotients for both the mono- and disulphato-dioxoplutonium(VI) complexes:



Both studies were performed at 25°C.

The value of $\Delta\varepsilon$ (19.1) is estimated from the reaction for the formation of the analogous uranium sulphate complex but with the uncertainty expanded by 0.05 ($\Delta\varepsilon$ (19.1) = $-(0.31 \pm 0.09)$ kg·mol⁻¹ [92GRE/FUG]). The result of [76PAT/RAM] is extrapolated to give $\log_{10}^*\beta_1^\circ(19.1) = (1.33 \pm 0.17)$. On the basis of the auxiliary data for the protonation constant of SO_4^{2-} , $\log_{10}^*\beta_1^\circ(19.1) = (1.47 \pm 0.11)$ was determined from $\log_{10} \beta_1^\circ(19.2)$ [86ULL/SCH]. The selected value of ($\log_{10}^*\beta_1^\circ(19.1) = (1.40 \pm 0.20)$) is based on the mean value of these results. The best estimate of $\log_{10} \beta_1^\circ(19.2)$ was calculated from the mean value of the results of [76PAT/RAM] and of [86ULL/SCH] (corrected using the auxiliary values for the protonation constant for SO_4^{2-}) and this review selects

$$\log_{10} \beta_1^\circ(19.2) = (3.38 \pm 0.20)$$

Table 19.1: Experimentally determined equilibrium constants for the Pu(VI)-SO₄²⁻ complexes.

Reference	$\log_{10} \beta^{(a)}$	I_m	t (°C)	Method
$\text{PuO}_2^{2+} + \text{HSO}_4^- \rightleftharpoons \text{PuO}_2\text{SO}_4(\text{aq}) + \text{H}^+$				
[76PAT/RAM]	(1.08±0.10)	2.2 H(ClO ₄ ⁻ , HSO ₄ ⁻)	25	ix
This review	(1.40±0.20)	0	25	
$\text{PuO}_2^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{PuO}_2\text{SO}_4(\text{aq})$				
[86ULL/SCH]	(3.45±0.1)	0 ^(b) H(ClO ₄ ⁻ , HSO ₄ ⁻)	25	cal
This review	(3.38±0.20)	0	25	
$\text{PuO}_2^{2+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{PuO}_2(\text{SO}_4)_2^{2-}$				
[86ULL/SCH]	(4.4±0.2)	0 ^(b) H(ClO ₄ ⁻ , HSO ₄ ⁻)	25	cal
This review	(4.4±0.2)	0	25	

(a) Here “ β ” refers to either β or β^* as appropriate for each reaction as written.

(b) Calorimetric measurements made between $I = 0.13 - 0.82$ m but extrapolated to $I = 0$ using PHREEQE [80PAR/THO] ion association model.

The only determination of $\log_{10} \beta_2^\circ$ (19.3) [86ULL/SCH] is selected by this review.

$$\log_{10} \beta_2^\circ (19.3) = (4.4 \pm 0.2)$$

The enthalpies determined calorimetrically by [86ULL/SCH] are accepted by this review:

$$\Delta_r H_m^\circ (19.2, 298.15 \text{ K}) = (16.1 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m^\circ (19.3, 298.15 \text{ K}) = (43 \pm 9) \text{ kJ}\cdot\text{mol}^{-1}$$

On the basis of $\Delta_r H_m^\circ$ (19.2) and the enthalpy for the SO_4^{2-} protonation reaction, $\Delta_r H_m^\circ (19.1) = -(6.3 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$. The remaining thermodynamic parameters at 25°C may be calculated from these values of $\log_{10} \beta^\circ$ and $\Delta_r H_m^\circ$.

19.1.1.1.b Pu(V) sulphates

We found no experimental evidence concerning the stability of Pu(V)- SO_4^{2-} complexes. This is disappointing given the evidence that Pu(V) is the dominant oxidised plutonium species in natural waters [80BON/TRA, 86CHO/ROB, 86ORL/PEN].

19.1.1.1.c Pu(IV) sulphates

There a number of independent evaluations of the stability of Pu(IV)- SO_4^{2-} complexes (Table 19.2). All of the measurements are made at high ionic strength and at high acidity. Although there are reports of mixed HSO_4^- - SO_4^{2-} complexes [83NAS/CLE2, 83NAS/CLE] based on indirect experimental evidence, the results of the best experiments (Table 19.3) are most consistent with the formation of two SO_4^{2-} complexes:

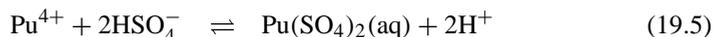
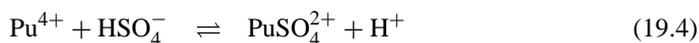


Table 19.2: Experimentally determined equilibrium constants as reported by the authors for the Pu(IV)- SO_4^{2-} complexes. All temperatures 25°C unless given.

Reference	$\log_{10} \beta^{(a)}$	I (M)	t (°C)	Method
$\text{Pu}^{4+} + \text{HSO}_4^- \rightleftharpoons \text{PuSO}_4^{2+} + \text{H}^+$				
[54SUL/AME]	2.87	2.3 Medium uncertain		sp
[61MAR/CHM]	(1.40±0.11)	2.33		ix HClO ₄
	0.98	0.5		ix HClO ₄
[64LAX/PAT]	3.19	1 HNO ₃	25	dis
	3.32	2 (Na,H) (NO ₃ ,ClO ₄)	25	dis

(Continued on next page)

Table 19.2: (continued)

Reference	$\log_{10} \beta^{(a)}$	I (M)	t ($^{\circ}\text{C}$)	Method
	3.20	2 (Na,H) (NO ₃ ,ClO ₄)	25	dis
	2.74	2.2 (Na,H) (NO ₃ ,ClO ₄)	25	dis
[73PAT/RAM]	2.80	2	10	dis HClO ₄
	2.76	2	25	dis HClO ₄
	2.68	2	40	dis HClO ₄
[73PAT/RAM2]	(2.74±0.05)	2 HClO ₄	25	dis
	2.69	2 HClO ₄	25	dis
[76BAG/RAM]	(2.82±0.02)	2 HClO ₄	25	dis
	(2.68±0.02)	2 HClO ₄	25	dis
[76BAG/RAM2]	(2.80±0.07)	2	25	dis HClO ₄
	(2.83±0.02)	2	25	dis HClO ₄
	(2.82±0.01)	2	25	dis HClO ₄
	2.84	2	25	dis HClO ₄
[77BAG/RAM]	(2.76±0.01)	2	10	dis HClO ₄
	(2.80±0.02)	2	10	dis HClO ₄
[83NAS/CLE]	(2.45±0.07)	2 (H,Na) ClO ₄	0	dis
	(2.58±0.04)	2 (H,Na) ClO ₄	10	dis
	(2.76±0.03)	2 (H,Na) ClO ₄	25	dis
	(2.85±0.05)	2 (H,Na) ClO ₄	35	dis
$\text{Pu}^{4+} + \text{SO}_4^{2-} \rightleftharpoons \text{PuSO}_4^{2+}$				
[51RAB/LEM]	(3.66±0.09)	1	(25.2 ± 0.1)	pot HClO ₄
	3.66	0.76	(25.2 ± 0.1)	pot HClO ₄
[69MOS]	2.30	0.3 Medium unknown		??
[74FAR/PEA]	3.82	2		ix HClO ₄
$\text{Pu}^{4+} + 2\text{SO}_4^{2-} \rightleftharpoons \text{Pu}(\text{SO}_4)_2(\text{aq})$				
[69MOS]	5.54	0.3		??
[74FAR/PEA]	6.58	2		ix HClO ₄

(Continued on next page)

Table 19.2: (continued)

Reference	$\log_{10} \beta^{(a)}$	I (M)	t ($^{\circ}\text{C}$)	Method
$\text{Pu}^{4+} + 2\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_2(\text{aq}) + 2\text{H}^+$				
[54SUL/AME]	4.65	2.3 Medium uncertain		sp
[61MAR/CHM]	1.30	0.5		ix HClO ₄
[64LAX/PAT]	4.71	1 HNO ₃	25	dis
	4.76	2 (Na,H) (NO ₃ ,ClO ₄)	25	dis
	4.66	2 (Na,H) (NO ₃ ,ClO ₄)	25	dis
	4.37	2.2 (Na,H) (NO ₃ ,ClO ₄)	25	dis
[73PAT/RAM]	4.36	2	10	dis
	4.37	2	25	dis
	4.41	2	40	dis
[73PAT/RAM2]	(4.34±0.05)	2 HClO ₄	25	dis
	4.50	2 HClO ₄	25	dis
[76BAG/RAM]	(4.64±0.02)	2 HClO ₄	25	dis
	(4.53±0.01)	2 HClO ₄	25	dis
$\text{Pu}^{4+} + 2\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_2(\text{aq}) + 2\text{H}^+$				
[76BAG/RAM2]	(4.66±0.01)	2	25	dis HClO ₄
	(4.69±0.01)	2	25	dis HClO ₄
	(4.51±0.01)	2	25	dis HClO ₄
	4.70	2	25	dis HClO ₄
[77BAG/RAM]	(4.60±0.01)	2	10	dis HClO ₄
	(4.43±0.01)	2	10	dis HClO ₄
$\text{PuSO}_4^{2+} + \text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_2(\text{aq}) + \text{H}^+$				
[64LUC]	(0.58±0.16)	1	(23 ± 0.5)	dis (H,Na) HNO ₃
$\text{Pu}^{4+} + 3\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_3^{2-} + 3\text{H}^+$				
[54SUL/AME]	5.35	2.3 Medium uncertain		sp
[61MAR/CHM]	2.10	0.5		ix HClO ₄

(Continued on next page)

Table 19.2: (continued)

Reference	$\log_{10} \beta^{(a)}$	I (M)	t ($^{\circ}\text{C}$)	Method
$\text{Pu}^{4+} + 2\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)(\text{HSO}_4)^+ + \text{H}^+$				
[83NAS/CLE]	(4.10 ± 0.09)	2	0	dis (H,Na) ClO_4
	(4.06 ± 0.07)	2	10	dis (H,Na) ClO_4
	(4.13 ± 0.07)	2	25	dis (H,Na) ClO_4
	(4.11 ± 0.08)	2	35	dis (H,Na) ClO_4
$\text{Pu}^{4+} + \text{NO}_3^- + \text{HSO}_4^- \rightleftharpoons \text{PuNO}_3(\text{SO}_4)^+ + \text{H}^+$				
[76BAG/RAM2]	3.03	2	25	dis HClO_4

^(a)Here “ β ” refers to either β or $^*\beta$ as appropriate for each reaction as written.

The most reliable value of $\log_{10} ^*\beta_1(I)$ (19.4) at $I = 2.2$ m is the weighted average of the results at 25°C reported in Table 19.3: (2.75 ± 0.01) . Based on the ionic interaction parameters determined for the analogous U(IV) complex ($\Delta\varepsilon$ (19.4) = $-(0.31 \pm 0.12)$ $\text{kg}\cdot\text{mol}^{-1}$ [92GRE/FUG]), this value can be extrapolated to standard conditions: $\log_{10} ^*\beta_1^{\circ}$ (19.4) = (4.91 ± 0.22) .

Table 19.3: Best values for the stability constants of the Pu(IV)-SO₄²⁻ complexes re-evaluated by the reviewers.

Reference	log ₁₀ [*] β	I _m	log ₁₀ [*] β ^o	t (°C)
$\text{Pu}^{4+} + \text{HSO}_4^- \rightleftharpoons \text{PuSO}_4^{2+} + \text{H}^+$				
[73PAT/RAM]	(2.84±0.06) ^(a)	2.2 (HClO ₄)		10
	(2.72±0.05) ^(a)	2.2 (HClO ₄)		40
[73PAT/RAM2]	(2.76±0.03)	2.2 (HClO ₄)	(4.89±0.27)	25
	(2.68±0.06)	2.2 (HClO ₄)	(4.81±0.27)	25
[74FAR/PEA]	(2.75±0.02)	2.2 (HClO ₄)	(4.88±0.26)	25
[76BAG/RAM]	(2.73±0.18)	2.2 (HClO ₄)	(4.86±0.32)	25
	(2.80±0.13)	2.2 (HClO ₄)	(4.93±0.29)	25
[76BAG/RAM2]	(3.00±0.17)	2.2 (HClO ₄)	(5.13±0.31)	25
	(2.95±0.14)	2.2 (HClO ₄)	(5.08±0.30)	25
[77BAG/RAM]	(2.71±0.03) ^(a)	2.2 (HClO ₄)		10
	(2.88±0.07) ^(a)	2.2 (HClO ₄)		10
[83NAS/CLE]	(2.45±0.07) ^(a)	2.2 (H,Na)ClO ₄		0
	(2.58±0.04) ^(a)	2.2 (H,Na)ClO ₄		10
	(2.76±0.03)	2.2 (H,Na)ClO ₄	(4.89±0.27)	25
	(2.85±0.05) ^(a)	2.2 (H,Na)ClO ₄		35
Best Value	(2.75±0.01)	2.2	(4.91±0.22)	25
$\text{Pu}^{4+} + 2\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_2(\text{aq}) + 2\text{H}^+$				
[73PAT/RAM]	(4.33±0.05) ^(a)	2.2 (HClO ₄)		10
	(4.39±0.03) ^(a)	2.2 (HClO ₄)		40
[73PAT/RAM2]	(4.35±0.02)	2.2 (HClO ₄)	(7.08±0.18)	25
	(4.51±0.02)	2.2 (HClO ₄)	(7.24±0.18)	25
[74FAR/PEA]	(4.43±0.03)	2.2 (HClO ₄)	(7.16±0.18)	25
[76BAG/RAM]	(4.66±0.07)	2.2 (HClO ₄)	(7.39±0.19)	25
	(4.47±0.08)	2.2 (HClO ₄)	(7.20±0.19)	25

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Table 19.3: (continued)

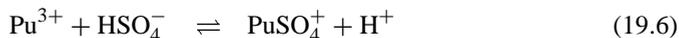
Reference	$\log_{10}^*\beta$	I_m	$\log_{10}^*\beta^\circ$	t ($^\circ\text{C}$)
[76BAG/RAM2]	(4.59±0.11)	2.2 (HClO ₄)	(7.32±0.21)	25
	(4.45±0.11)	2.2 (HClO ₄)	(7.18±0.21)	25
[77BAG/RAM]	(4.58±0.01) ^(a)	2.2 (HClO ₄)		10
	(4.38±0.05) ^(a)	2.2 (HClO ₄)		10
[83NAS/CLE]	(4.10±0.09) ^(a)	2.2 (H,Na)ClO ₄		0
	(4.06±0.07) ^(a)	2.2 (H,Na)ClO ₄		10
	(4.13±0.07)	2.2 (H,Na)ClO ₄	(6.86±0.19)	25
	(4.11±0.08) ^(a)	2.2 (H,Na)ClO ₄		35
Best Value	(4.43±0.01)	2.2	(7.18±0.32)	25

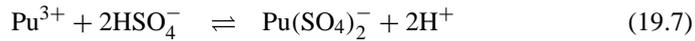
^(a)Used to calculate $\Delta_r H_m^\circ$ only.

The most reliable value of $\log_{10}^*\beta^\circ(I)$ (19.5) at $I = 2.2$ m is the weighted average of the results at 25°C reported in Table 19.3: (4.43 ± 0.01) . Based on the ionic interaction parameters determined for the analogous U(IV) complex ($\Delta\varepsilon$ (19.5) = $-(0.46 \pm 0.08)$ kg·mol⁻¹; [92GRE/FUG]), this value can be extrapolated to standard state: $\log_{10}^*\beta_2^\circ(19.5) = (7.18 \pm 0.32)$. Caution is advised in the use of $\log_{10}^*\beta_2^\circ(19.5)$ outside of the range of H⁺ concentration (1-2 M) in which it was determined. There are four independent sets of equilibrium constants determined in identical experiments over a range of temperatures from which to estimate $\Delta_r H_m^\circ$ (19.4) and $\Delta_r H_m^\circ$ (19.5): [73PAT/RAM] (including results of [76PAT/RAM]), two from [77BAG/RAM] (including the results of [76BAG/RAM] and [76BAG/RAM2]), and [83NAS/CLE]. The four determinations yield $\Delta_r H_m^\circ(19.4) = -(7.1 \pm 1.7)$, (2.4 ± 3.5) , (7.2 ± 3.0) , and (18.6 ± 1.2) kJ·mol⁻¹ and $\Delta_r H_m^\circ(19.5) = (3.1 \pm 1.8)$, (8.6 ± 1.4) , (7.5 ± 2.3) , and (1.5 ± 3.4) kJ·mol⁻¹. The unweighted average of these results is indistinguishable from 0 ($\Delta_r H_m^\circ(19.4) = (5.3 \pm 21.3)$ kJ·mol⁻¹ and $\Delta_r H_m^\circ(19.5) = (5.2 \pm 6.8)$ kJ·mol⁻¹). As we have no basis to eliminate any of these experimental results, we recommend no best value, and advise caution in the determination of fundamental thermodynamic properties from the temperature variation of $\log_{10}^*\beta_1(19.4)$ and $\log_{10}^*\beta_2(19.5)$ in this system.

19.1.1.1.d Pu(III) sulphates

There are four experimental data sets concerning the Pu(III)-sulphate system (Table 19.4). Although Pu(III)-bisulphate complexes have been postulated (Pu(HSO₄)₂⁺, and Pu(SO₄)(HSO₄)(aq); [67NAI/RAO], [83NAS/CLE2]), the results are interpreted by this review as consistent with the equilibria:





The results of [76FAR/BUC] and [78RAO/BAG] were independently extrapolated to standard state conditions. The results of [76FAR/BUC] yielded estimates of $\Delta\varepsilon(19.6) = -(0.22 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$ and $\log_{10}^*\beta_1(19.6) = (1.97 \pm 0.19)$. The results of [78RAO/BAG] yielded estimates of $\Delta\varepsilon(19.6) = -(0.17 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ and $\log_{10}^*\beta_1(19.6) = (2.26 \pm 0.10)$. The results of [67NAI/RAO] and [83NAS/CLE2] were extrapolated to $I = 0$ using the mean $\Delta\varepsilon(19.6) = -(0.20 \pm 0.09) \text{ kg}\cdot\text{mol}^{-1}$ yielding $\log_{10}^*\beta_1(19.6) = (2.17 \pm 0.12)$ ([67NAI/RAO] using the mean ionic strength 1.20 m), (1.69 ± 0.29) and (1.55 ± 0.24) [83NAS/CLE2]. The results of [67NAI/RAO] were further extrapolated to 25°C using the accepted value of

$$\Delta_r H_m^\circ(19.6) = -(5.2 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$$

calculated from the temperature variation in $\log_{10}^*\beta$ by [83NAS/CLE2]. These calculations yield an estimate of $\log_{10}^*\beta_1(19.6) = (2.17 \pm 0.12)$. An equal weighting of these five independent results yields the accepted value of

$$\log_{10}^*\beta_1^\circ(19.6) = (1.93 \pm 0.61)$$

Table 19.4: Experimentally determined equilibrium constants for the Pu(III)-SO₄²⁻ complexes.

Reference	$\log_{10} K$	I_m	t (°C)	Source of Data
$\text{Pu}^{3+} + \text{HSO}_4^- \rightleftharpoons \text{PuSO}_4^+ + \text{H}^+$				
[67NAI/RAO]	(0.72±0.02)	1.05 - 1.30	28	Ion exchange: re-evaluated by [76FAR/BUC] and [78RAO/BAG] H(ClO ₄ , HSO ₄)
[76FAR/BUC]	(0.55±0.05)	1.05	25	ix H(ClO ₄ , HSO ₄)
	(0.57±0.05)	2.2	25	ix H(ClO ₄ , HSO ₄)
[78RAO/BAG]	(0.81±0.01)	1.05	25	dis HClO ₄
	(0.81±0.02)	2.2	25	dis HClO ₄
[83NAS/CLE2]	(0.63±0.07)	2.2	2.7	ix (H,Na) HClO ₄
	(0.61±0.10)	2.2	10.0	ix (H,Na) HClO ₄
	(0.59±0.12)	2.2	16.5	ix (H,Na) HClO ₄
	(0.55±0.07)	2.2	25.0	ix (H,Na) HClO ₄
	(0.34±0.10)	2.2	25.0	ix (H,Na) HClO ₄
This Review	(0.64±0.04)	1.05 - 1.36	28	[67NAI/RAO]
	(0.80±0.05)	1.05	25	[78RAO/BAG]

(Continued on next page)

Table 19.4: (continued)

Reference	$\log_{10} K$	I_m	t (°C)	Source of Data
	(0.77±0.03)	2.2	25	[78RAO/BAG]
	(1.93±0.61)	0	25	Recommended
$\text{Pu}^{3+} + 2\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)(\text{HSO}_4)(\text{aq}) + \text{H}^+$				
[83NAS/CLE2]	(0.60±0.09)	2.2	2.7	ix
	(0.51±0.18)	2.2	10.0	ix (H, Na) HClO ₄
	(0.42±0.22)	2.2	16.5	ix (H, Na) HClO ₄
	(0.11±0.20)	2.2	25.0	ix (H, Na) HClO ₄
	-(0.05±0.25)	2.2	25.0	ix (H, Na) HClO ₄
$\text{Pu}^{3+} + 2\text{HSO}_4^- \rightleftharpoons \text{Pu}(\text{SO}_4)_2^- + 2\text{H}^+$				
[67NAI/RAO]	(0.82±0.06)	1.05 - 1.36	28	Ion exchange: re-evaluated by [76FAR/BUC] and [78RAO/BAG] H(ClO ₄ , HSO ₄)
[76FAR/BUC]	(1.03±0.05)	1.05	25	ix H(ClO ₄ , HSO ₄)
	(1.14±0.04)	2.2	25	ix H(ClO ₄ , HSO ₄)
[78RAO/BAG]	(0.68±0.05)	1.05	25	dis HClO ₄
	(0.74±0.13)	2.2	25	dis HClO ₄
This Review	(0.82±0.04)	1.05 - 1.36	28	[67NAI/RAO]
	(0.69±0.12)	1.05	25	[78RAO/BAG]
	(0.88±0.12)	2.2	25	[78RAO/BAG]
	(0.11±0.20)	2.2	25	[83NAS/CLE2]
	(0.25±0.26)	2.2	25	[83NAS/CLE2]
	(1.74±0.76)	0	25	Recommended

The results of [76FAR/BUC] yielded estimates of $\Delta\varepsilon(19.7) = -(0.29 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ and $\log_{10}^*\beta_2^{\circ}(19.7) = (2.36 \pm 0.19)$. The results of [78RAO/BAG] yielded estimates of $\Delta\varepsilon(19.7) = -(0.36 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$ and $\log_{10}^*\beta_2^{\circ}(19.7) = (1.95 \pm 0.65)$. The result of [67NAI/RAO] was extrapolated to $I = 0$ using the mean $\Delta\varepsilon(19.7) = (0.32 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}$ to yield $\log_{10}^*\beta_2^{\circ}(19.7) = (2.12 \pm 0.48)$ [67NAI/RAO]. On the basis of our reinterpretation of the results of [83NAS/CLE2] in terms of the formation of $\text{Pu}(\text{SO}_4)_2^-$ (see Appendix A), and subsequent extrapolation to $I = 0$ as above, $\log_{10}^*\beta_2^{\circ}(19.7) = (1.28 \pm 0.30)$ and (1.42 ± 0.34) . The results of [67NAI/RAO] was further corrected to the standard temperature using the accepted enthalpy

$$\Delta_r H_m^{\circ}(19.7) = -(33 \pm 16) \text{ kJ}\cdot\text{mol}^{-1}$$

calculated from the results of [83NAS/CLE2] (see Appendix A). This calculation yields a final estimate of $\log_{10}^*\beta_2^{\circ}(19.7) = (2.02 \pm 0.48)$. The results of [83NAS/CLE2]

represent a different population than the other results. The average of the means of the two populations with errors expanded to cover the range of both populations is accepted by this review:

$$\log_{10} {}^*\beta_2^\circ(19.7) = (1.74 \pm 0.76)$$

The value of $\log_{10} {}^*\beta_2^\circ(19.7)$ should be applied with caution outside of the range of H^+ concentration (1-2 M) where it has been determined.

Chapter 20

Plutonium group 15 compounds and complexes

20.1 Plutonium nitrogen compounds and complexes

20.1.1 Plutonium nitrides

The only solid phase reported in this system is plutonium mononitride, PuN (cr).

The constitutional behaviour and the thermodynamic properties of this system were reviewed in 1968 [68SPE/LEI] and the thermodynamic properties of PuN(cr) in 1987 [87MAT/OHS]. A compilation of phase equilibria and thermodynamic properties of the Pu-N system was published in 1989 [89WRI].

20.1.1.1 PuN(cr)

20.1.1.1.a Crystal structure

PuN(cr) has a face-centred cubic rock-salt structure (space group Fm3m). The lattice parameter of a sample of PuN(cr) with very low impurity content is $a_0 = 4.90476 \pm 0.00008 \times 10^{-10}$ m [71TEN/BOM]. The effects of small changes in stoichiometry and of impurities is discussed in the section on the plutonium - nitrogen phase diagram.

20.1.1.1.b Low temperature heat capacity and standard entropy

The temperature dependence of the heat capacity of PuN(cr) has been determined using an adiabatic calorimeter for the temperature range 10-300 K [78HAL/LEE]. The lowest temperature achieved was a consequence of the radioactive self heating, and is too high to allow an unambiguous determination of the value of the electronic specific heat, γ . An approximate value was, however, derived using the expression

$$C_p = \gamma T + \beta T^3$$

over the temperature range (10-15) K.

The value obtained for γ is (64 ± 4) mJ·K⁻²mol⁻¹ and the Debye characteristic temperature, (Θ_D) is (245 ± 5) K.

The thermodynamic data which are given [78HAL/LEE] are strictly applicable only to self damaged PuN(cr). The reported values for the heat capacity and entropy at

298.15 K indicate that the earlier estimates [68SPE/LEI] were sound. The experimental values with estimated uncertainties are recommended;

$$C_{p,m}^{\circ}(\text{PuN, cr, 298.15 K}) = (49.6 \pm 1.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^{\circ}(\text{PuN, cr, 298.15 K}) = (64.8 \pm 1.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

20.1.1.1.c High temperature enthalpy increments

Measurements have been made of the enthalpy increments for PuN(cr) in the temperature range 457-1562 K using a drop calorimeter [72OET/LEI]. The experimental data are represented by:

$$(H_T^{\circ} - H_{298.15}^{\circ}) = 45.002 T + (7.710 \times 10^{-3}) T^2 - (1.410 \times 10^4) \text{ J}\cdot\text{mol}^{-1}$$

$$C_p^{\circ} = 45.002 + (1.542 \times 10^{-2}) T \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

With the values of $C_{p,m}^{\circ}$ at 298.15 K [78HAL/LEE], and the data for the enthalpy increments [78OET] thermal functions for PuN(cr) were calculated up to 3000 K [87MAT/OHS].

20.1.1.1.d Enthalpy of formation

The enthalpy of formation, $\Delta_f H_m^{\circ}$ (PuN, cr, 298.15 K) has been determined by oxygen bomb calorimetry [67LAP/BUN], [69JOH/DEV]. The samples used in the earlier work contained small quantities of carbon and oxygen; the exact chemical form of the impurities was unknown, and the value given for the enthalpy of formation is $\Delta_f H_m^{\circ}$ (PuN, cr, 298.15 K) = $-(293.72 \pm 6.28) \text{ kJ}\cdot\text{mol}^{-1}$ derived using the enthalpy of formation of PuO₂(cr) [58HOL/MUL], $\Delta_f H_m^{\circ}$ (PuO₂, cr, 298.15 K) = $-(1058.01 \pm 1.59) \text{ kJ}\cdot\text{mol}^{-1}$.

The later measurements [69JOH/DEV] on a well characterised sample of PuN(cr) gave

$$\Delta_f H_m^{\circ}(\text{PuN, cr, 298.15 K}) = -(299.20 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$$

This value which is recommended here was derived with the enthalpy of formation of PuO₂(cr) [69JOH/DEV] which is the recommended value given in Section 17.2.1.2

$$\Delta_f H_m^{\circ}(\text{PuO}_2, \text{ cr, 298.15 K}) = -(1055.8 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$$

If the recommended value for $\Delta_f H_m^{\circ}$ (PuO₂, cr, 298.15 K) were used to recalculate the earlier experimental data [67LAP/BUN] the derived value for $\Delta_f H_m^{\circ}$ (PuN, cr, 298.15 K) would be even more positive than the recommended value.

20.1.1.1.e The Gibbs energy of formation

The recommended two term equation for the Gibbs energy of formation of PuN(cr) in the temperature range 298-2000 K is:

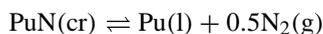
$$\Delta_f G_m^{\circ}(\text{PuN, cr}) = -((302825 \pm 221) - (97.27 \pm 0.15)T) \text{ J}\cdot\text{mol}^{-1}$$

This equation is derived using the recommended values for the enthalpy of formation [69JOH/DEV], the entropy [78HAL/LEE] at 298.15 K, and the Gibbs energy functions for PuN(cr) [78OET]. The Gibbs energy functions for elemental plutonium [76OET/RAN] and for N₂(g) [89COX/WAG] were also used in the assessment. The recommended value for the Gibbs energy of formation at 298.15 K is,

$$\Delta_f G_m^\circ(\text{PuN, cr, 298.15 K}) = -(273.7 \pm 2.6) \text{ kJ}\cdot\text{mol}^{-1}$$

There are several determinations of the Gibbs energy of formation of PuN(cr) from measurements of vapour pressure of congruently vaporizing PuN(cr). One set of data [69KEN/LEA] gives values for $\Delta_f G_m^\circ(\text{PuN, cr})$ at 1000 K within 1 kJ·mol⁻¹ and at 2000 K within 3 kJ·mol⁻¹ of the recommended values. The vaporisation behaviour of PuN(cr) has been discussed in detail [87MAT/OHS, 92SUZ/MAE].

The decomposition pressures of N₂ gas for the reaction,



have been measured [64OLS/MUL] in the temperature range 2563-3043 K.

20.1.1.1.f The phase diagram

Detailed investigations of the range of composition of the Pu mononitride phase have not been undertaken, but it is probably quite small. There is no detailed information about the solubility of nitrogen in elemental plutonium, but in the temperature range 1544-1635 K the solubility is low [69KEN/LEA]. PuN(cr) has been frequently prepared by the reaction of nitrogen with Pu hydride or with elemental plutonium in the presence of hydrogen [64OLS/MUL] at elevated temperatures; typically at *ca.* 850 K. During the preparation at relatively high temperatures, PuN(cr) can easily become contaminated with both oxygen and carbon. PuN(cr) can also be prepared by the carbothermic reduction of PuO₂(cr) in the presence of N₂ gas [83SUZ/ARA]. Because of the possibility of incorporation of both carbon and oxygen in the mononitride lattice, care must be taken in the interpretation of measurements of the variation of lattice parameters.

The lattice parameters of so-called “pure” PuN(cr), that is material with low levels of impurities, vary in the range, $a_0 = (4.9025 - 4.9075) \times 10^{-10} \text{ m}$ [68SPE/LEI]. The presence of the impurities carbon and oxygen increases the lattice parameter, for example, up to $4.9117 \times 10^{-10} \text{ m}$ [64ANS/DEA].

Pu mononitride and Pu monocarbide form a complete range of solid solutions; these compounds are isomorphous. The solubility of oxygen expressed in terms of the hypothetical Pu monoxide is (13 ± 3 mol %) [93JAI/GAN]. The relatively small variations of the lattice parameter of PuN in the presence of oxygen would indicate this. The lattice parameter and thermodynamic properties of “PuO” have been determined from studies of the Pu-C-O system, and this enabled meagre thermodynamic information to be obtained for the Pu-N-O system. An assessment of the thermodynamic properties and phase equilibria of these systems has been published [80POT/SPE].

Studies of the vaporisation of Pu mononitride in the temperature ranges, 1658-1976 K [69KEN/LEA] and 1400-2400 K [76ALE/CLA], indicated that Pu mononitride had

vaporized congruently and that single phase material was left in the Knudsen effusion cells with compositions of $\text{PuN}_{0.98}$ and $\text{PuN}_{0.975}$ respectively; the level of impurities was not given. This is evidence for the existence of some hypostoichiometry for this phase.

The lattice parameter of PuN increases due to radiation damage; this increase is *ca.* 10^{-14} m per week [62RAN/FOX]; further studies up to saturation indicated that the lattice expansion was higher by a factor of two [93OKA/MAE] due to different isotopic compositions of the samples. When the data were referred to a dose, the two sets of results are consistent. Radiation damage may be responsible for some variation in the reported lattice parameters, but the effect is small and is readily annealed out by heat treatment.

Under 1 bar of nitrogen gas, Pu mononitride decomposes on heating to give Pu(l) at (2843 ± 30) K [64OLS/MUL], [64CAR]. Even at 3043 K with a nitrogen gas pressure of 2.42 bar the melting behaviour is still incongruent [64OLS/MUL]. The estimated temperature for the congruent melting of PuN is (3103 ± 50) K at a nitrogen pressure of (4.94 ± 1.97) bar [68SPE/LEI].

20.1.1.2 PuN(g)

Evidence for the existence of the molecule PuN(g) has been obtained [78GRE/REE] from the infrared spectra of matrix isolated species sputtered from Pu metal in the presence of argon, $^{14}\text{N}_2(\text{g})$ and $^{15}\text{N}_2(\text{g})$. In addition to PuN evidence was also found for PuN_2 . The spectra of the species which condensed in the solid argon matrix are considered to be representative of the analogous gaseous molecules. PuN_2 is a linear molecule.

UN(g) has been identified as a minor species during the vaporisation of UN(cr) at temperatures above 2100 K [67GIN], and by analogy, the existence of PuN(g) has been assumed. Estimates have been made of the dissociation energy and vapour pressure above PuN(cr) for PuN(g), [75ALE/OGD, 87MAT/OHS].

More studies are required before thermodynamic quantities could be recommended for PuN(g); it certainly would not be a major species in the vaporisation of PuN(cr) at temperatures up to 2500 K.

20.1.2 Plutonium azide complexes

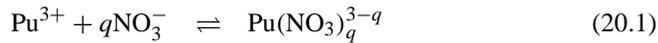
A formation constant $\beta_1 = 3$ for an azide complex of Pu(III), in 5 M perchlorate medium, has been reported [77CUI/MUS]. In a later thesis by one of the authors [81CUI] a value of $\beta_1 = 4$ was reported. The authors indicated problems were encountered with oxidation of plutonium to Pu(IV). There is some doubt as to the absence of higher complexes [83MUS/CUI], and the SIT equations (*cf.* Appendix B) cannot be properly used for extrapolation of the result to lower ionic strengths. No value for β_1 is selected in the present review. However, the value for the formation constant of $\text{PuN}_3^{2+}(\text{aq})$ would be expected to be similar to that of the corresponding americium(III) complex ($\beta_1^\circ = (47 \pm 11)$) [95SIL/BID].

20.1.3 Plutonium nitrates

20.1.3.1 Aqueous plutonium nitrates

20.1.3.1.a Aqueous Pu(III) nitrates

Only two distribution studies reporting quantitative information on nitrate complexation of Pu(III) according to the equilibria:



have been available to this review. Shevchenko, Timoshev and Volkova [59SHE/TIM] studied the system at $I = 1$ M and reported constants for nitrate complexes with $q = 1, 2$ and 3 (Table 20.1). As in other TBP extraction studies, there seem to be problems with the extraction mechanism and the treatment of data (see Appendix A). Lahr and Knoch [70LAH/KNO] worked in very high ionic strength (8 M) media, substituting all perchlorate by nitrate, and consequently causing substantial changes in the ionic medium. These changes could not be accounted for in this review, since no experimental data are reported by these authors (Appendix A). Besides these two works, there is a study by Fuks and Siekiersky [87FUK/SIE] in which no constants are reported, but which gives a comparison of the constant of the Pu(III) pentanitrate complex with the value for the corresponding lanthanum complex.

Table 20.1: Experimental equilibrium data for the Pu(III) nitrate system.

Method	Ionic medium	t (°C)	$\log_{10} \beta_q(I)^{(a)}$	Reference
$\text{Pu}^{3+} + \text{NO}_3^- \rightleftharpoons \text{PuNO}_3^{2+}$				
dis, TBP	1 M HClO ₄	20	(0.77 ± 0.04)	[59SHE/TIM]
dis, TOA	8 M HClO ₄	20	1.18	[70LAH/KNO]
$\text{Pu}^{3+} + 2\text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)_2^+$				
dis, TBP	1 M HClO ₄	20	(1.15 ± 0.02)	[59SHE/TIM]
dis, TOA	8 M HClO ₄	20	0.07	[70LAH/KNO]
$\text{Pu}^{3+} + 3\text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)_3(\text{aq})$				
dis, TBP	1 M HClO ₄	20	(1.16 ± 0.8)	[59SHE/TIM]
dis, TOA	8 M HClO ₄	20	-0.72	[70LAH/KNO]
dis, TAMAN	2 M NH ₄ NO ₃	25	(b)	[87FUK/SIE]

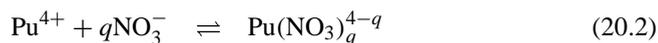
(a) Refers to the value reported for the reactions indicated, for the ionic medium and at the temperature given in the table.

(b) $\log_{10} \beta_5^\circ = \log_{10} \beta_5^\circ(\text{La}) + 0.44$

Thus, based on information in the available references, it was not possible to select any formation constants for Pu(III) nitrate complexes. The corresponding values for Am(III) [95SIL/BID] could be used as a guideline.

20.1.3.1.b Aqueous Pu(IV) nitrates

Due to the importance of Pu(IV) nitrate complexes in industrial separation processes, several investigators have studied the Pu(IV) nitrate system using spectrophotometry, distribution measurements and potentiometry. The data for the reactions



are collected in Table 20.2.

sp	2 M HClO ₄	20	(0.46 ± 0.1) (0.46 ± 0.20) ^(c)	(0.39 ± 0.07)	[49HIN]
dis, TTA	6 M (? HCl or HClO ₄)	25	0.67		[49ZEB/NEU] ^(d)
dis, TTA	6 M (? HCl or HClO ₄)	45	0.92		
pot	1.0 M HClO ₄	25	(0.54 ± 0.01)		[51RAB/LEM]
cix	4 M HClO ₄	20	(0.74 ± 0.02) (0.74 ± 0.30) ^(c)	(0.96 ± 0.10)	[60GRE/NOR]
cix	4 M HClO ₄	20	0.74		[61GOL/GOL] ^(d)
dis, TBP	1.02 M HClO ₄	?	0.72 ^{(e),(f)}		[64LAX/PAT]
dis, TBP	1.9 M (H,Na)ClO ₄	?	0.62 ^{(e),(f)}		
dis, TBP	4.7 M (H,Na)ClO ₄	?	0.72 ^(e) 0.66 ^(f)		
dis, TTA	4.0 M H(ClO ₄)	25	(0.97 ± 0.03) (0.96 ± 0.20) ^(c)	(0.96 ± 0.10)	[66DAN/ORL]
dis, TTA	6.0 M H(ClO ₄)	25	(1.00 ± 0.03)	(1.02 ± 0.10)	
pot	0.5 M HNO ₃	25	0.72		[66WAI]
pot	1 M HNO ₃	25	0.75		
dis, TOA	8 M HClO ₄	20	0.69		[70LAH/KNO]
sp	< 1 M HNO ₃ , var	?	0.38		[71MOS]
dis, TTA	2 M HClO ₄	25	(0.65 ± 0.01)	(0.78 ± 0.10)	[76BAG/RAM2]

(Continued on next page)

dis, TTA	2 M HClO ₄	10	(0.57 ± 0.01)	(0.77 ± 0.10)	[77BAG/RAM]
sp	<i>I</i> = 2.34 m	?	0.59		[94VEI/SMI]
$\text{Pu}^{4+} + 2\text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)_2^{2+}$					
dis, TTA	6 M (? HCl or HClO ₄)		0.65		[49ZEB/NEU] ^(d)
cix	4 M HClO ₄	20	(1.37 ± 0.02)		[60GRE/NOR]
cix	4 M HClO ₄	20	0.36		[61GOL/GOL] ^(d)
dis, TBP	1.02 M HClO ₄	?	0.97 ^{(e),(f)}		[64LAX/PAT]
dis, TBP	1.9 M (H,Na)ClO ₄	?	0.81 ^(e)		
			0.88 ^(f)		
dis, TBP	4.7 M (H,Na)ClO ₄	?	1.06 ^(e)		
			1.17 ^(f)		
dis, TTA	4.0 M HClO ₄	25	(1.43 ± 0.03)		[66DAN/ORL]
dis, TTA	6.0 M HClO ₄	25	(1.36 ± 0.03)		
dis, TOA	8 M HClO ₄	20	0.42		[70LAH/KNO]
sp	< 1 M HNO ₃ , var	?	0.43		[71MOS]
dis, TTA	2 M HClO ₄	25	(1.12 ± 0.01)		[76BAG/RAM2]
dis, TTA	2 M HClO ₄	10	(1.15 ± 0.01)		[77BAG/RAM]
sp	<i>I</i> = 2.34 m	?	1.08		[94VEI/SMI]

(Continued on next page)

dis, TTA	6 M (? HCl or HClO ₄)	25	0.17	[49ZEB/NEU]
cix	4 M HClO ₄	20	(1.18 ± 0.5)	[60GRE/NOR]
cix	4 M HClO ₄	20	0.18	[61GOL/GOL]
dis, TBP	1.02 M HClO ₄	?	0.65 ^(e)	[64LAX/PAT]
			0.60 ^(f)	
dis, TBP	1.9 M (H,Na)ClO ₄	?	0.67 ^(e)	
			0.60 ^(f)	
dis, TBP	4.7 M (H,Na)ClO ₄	?	1.11 ^(e)	
			1.03 ^(f)	
dis, TTA	4.0 M HClO ₄	25	-(0.39 ± 0.5)	[66DAN/ORL]
dis, TTA	6.0 M HClO ₄	25	-(0.01 ± 0.2)	
dis, TOA	8 M HClO ₄	20	0	[70LAH/KNO]
$\text{Pu}^{4+} + 4\text{NO}_3^- \rightleftharpoons \text{Pu}(\text{NO}_3)_4(\text{aq})$				
dis, TBP	1.9 M (H,Na)ClO ₄	?	0.13 ^(e)	[64LAX/PAT]
			0.08 ^(f)	
dis, TBP	4.7 M (H,Na)ClO ₄	?	0.86 ^(e)	
			0.30 ^(f)	
dis, TOA	8 M HClO ₄	20	-0.72	[70LAH/KNO]

^(a) Refers to the value reported for the reactions indicated, for the ionic medium and at the temperature given in the table.

(continued on next page)

- but does not exist as cited (there is a study by these authors concerning some organic complexes of another metal that was published in the journal at the cited pages).
- (e) Calculated with the modified Fomin Majorova method.
 - (f) Calculated with the Fronaeus method.

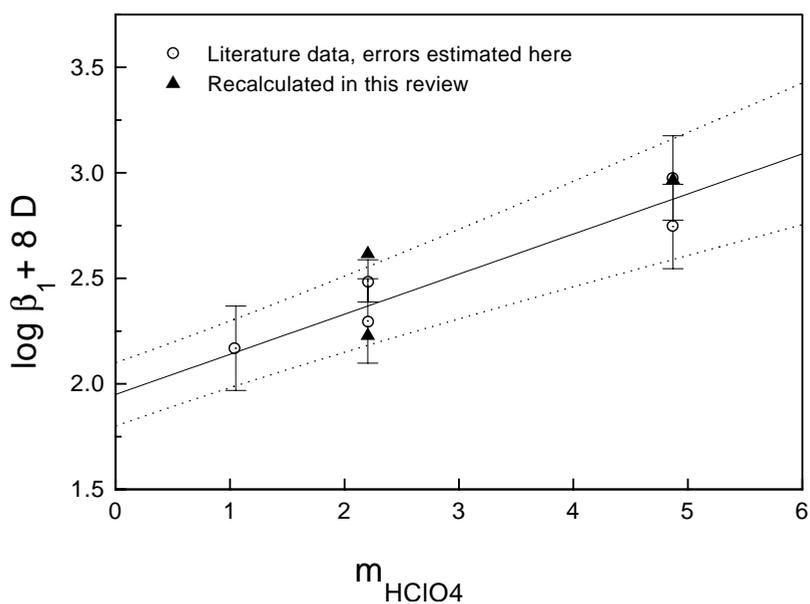
Hindman [49HIN] made one of the first spectrophotometric studies of the Pu(IV) nitrate system. He found spectral evidence for complexation and explained the experimental data with the formation of only the first complex for concentrations of nitrate ≤ 2 M. This study is considered reliable by this review and results of a recalculation of the constant at trace ligand concentration and at the given ionic medium is also reported in Appendix A. Rabideau and Lemons [51RAB/LEM] performed a careful potentiometric study of the redox potential of the Pu(III)/Pu(IV) couple at $I = 1$ M with increasing nitrate concentrations.

As explained in Appendix A, it is difficult to separate the effect of complexation of Pu(IV) from changes in activity factors, even if the possibility of Pu(III) nitrate complexation is neglected. In most of the other works, values of formation constants for two or more (as many as four) species are needed to fit the experimental data. Furthermore the overall formation constant for the third or fourth complex is, in most of the cases, lower than the second, representing unusual behaviour in complexation. As also explained in Appendix A, during preparation of this review, an attempt was also made to account for activity factor changes during the determination of the constant (*i.e.*, to obtain values of the constant at the ionic strength of the corresponding perchlorate medium at trace nitrate concentrations). In Table 20.2 values of the constant for the first complex thus calculated for data up to 2 M nitrate are presented together with the original values reported by the authors, and values with uncertainties as assigned in the present review. The recalculation of the results of distribution studies which use TBP as extractant is difficult, and the results of such studies are not used here (see Appendix A and also [64LAX/PAT]).

In Figure 20.1 the values of the constants from several studies [49HIN, 51RAB/LEM, 60GRE/NOR, 76BAG/RAM2] and the result at 4 M only from [66DAN/ORL] have been converted to the molal scale and plotted as $\log_{10} K + 8D(I)$ vs. ionic strength, which in this case corresponds to perchloric acid concentrations. Even though the available data cover an ionic strength interval which does not contain measurements at low ionic strength, an attempt to obtain the thermodynamic constant and the best fit straight line together with the 95% confidence limit interval is shown in Figure 20.1. In the same figure the constants recalculated in the present review are represented with filled symbols. As seen the changes in the value of the first constant are small, even though in the recalculation the higher complexes are neglected. Even though the end user of the database may use an ion-association approach to account for activity coefficient changes, the range of application of these approaches is well below a ionic strength of one molar and, at these concentrations, the higher complexes do not form. The higher complexes are, in most cases, impossible to separate from the activity coefficient changes in the system that occur in the course of carrying out the measurements.

There is evidence that anionic complexes form at very high nitrate concentrations in acidic solutions, and these complexes can be taken up on anion exchange resins [86WEI/KAT]. However, no data suitable for determining thermodynamic constants for these complexes are available. The corresponding values for Am(III) [95SIL/BID] could be used as a guideline.

Figure 20.1: Extrapolation to infinite dilution of the experimental data for the formation of PuNO_3^{3+} using SIT. The data refer to mixed perchlorate nitrate media and are taken from [49HIN, 51RAB/LEM, 60GRE/NOR, 66DAN/ORL, 76BAG/RAM2]; the filled triangles represent the data recalculated in the present review for the corresponding perchlorate medium and at trace nitrate concentrations.



Hence the following formation constant results from the extrapolation:

$$\log_{10} \beta_1^\circ(20.2, q = 1, 298.15 \text{ K}) = 1.95 \pm 0.15$$

and has been selected in this review. This value, and the value of $\Delta\varepsilon = -(0.19 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$, obtained simultaneously, compare well with those for the corresponding values for the neptunium complex (Section 11.1.4.1) and with $\log_{10} \beta_1^\circ = 1.47 \pm 0.13$ and $\Delta\varepsilon = -(0.21 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ reported for the uranium complex [92GRE/FUG].

20.1.3.1.c Aqueous Pu(V) nitrates

No nitrate complexes of dioxoplutonium(V) have been identified.

20.1.3.1.d Aqueous Pu(VI) nitrates

Quantitative information on the formation of nitrate complexes of plutonium(VI) according to the reaction



(Table 20.3) has been reported by Heisig and Hicke [52HEI/HIC], Lahr and Knoch [70LAH/KNO] and Mazumdar and Sivamakrishnan [65MAZ/SIV] using distribution measurements, while Krevinskaya *et al.* [59KRE/NIK] and Vasiliev, Andeichuk and Ryukov [75VAS/AND2] have used spectrophotometric measurements. As noted in Appendix A, the data from several groups [59KRE/NIK, 70LAH/KNO, 75VAS/AND2] have been rejected due to experimental shortcomings. The apparently high value of the constant reported in [75VAS/AND2] has to do with the fact that it does not refer to Equation (20.3) ($q = 2$) but to a reaction involving water substitution (see Appendix A for details).

The dioxoplutonium(VI) nitrate complexes are weak as is also the case for the other actinides [92GRE/FUG] (also see Section 11.1.4.1). This makes it difficult to distinguish between complex formation and changes in the activity factors of the species studied, caused by the large changes in the composition of the ionic medium when substituting the inert anion (often perchlorate) by the ligand ion (nitrate). As discussed in Appendix A for both studies considered here ([65MAZ/SIV] and [52HEI/HIC]), the experimental data can be explained at least equally well by accounting for these activity factor changes and assuming no formation of nitrate complexes. However, even assuming that the end user of the database requires an ion association approach for use in a calculation code, it is not reasonable to attempt to correct the values to $I = 0$ from the high ionic strengths (higher than 4.5 molal) pertinent to these two works. If a value of β_1 for formation of $\text{PuO}_2\text{NO}_3^+$ is required, use of the first association constant recommended for the analogous uranium system [92GRE/FUG] will probably not cause too large an error.

20.1.3.2 Solid plutonium nitrates

There is a limited amount of information on the solid nitrate compounds of plutonium.

Table 20.3: Experimental equilibrium data for the dioxoplutonium(VI) nitrate system.

Method	Ionic medium	t (°C)	$\log_{10}\beta(I)^{(a)}$	$\log_{10}\beta(I)^{(b)}$	Reference
$\text{PuO}_2^{2+} + \text{NO}_3^- \rightleftharpoons \text{PuO}_2\text{NO}_3^+$					
dis, TTA	4.6 M (Li,H)ClO ₄	?	-0.60	0	[52HEI/HIC]
sp	var. PuO ₂ (NO ₃) ₂	?	1.86		[59KRE/NIK]
dis, TTA	4.1 M (Na,H)ClO ₄	?	-0.04	0	[65MAZ/SIV]
dis, TOA	8 M HClO ₄	20	-0.57		[70LAH/KNO2]
$\text{PuO}_2^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{PuO}_2(\text{NO}_3)_2(\text{aq})$					
sp	var. PuO ₂ (NO ₃) ₂	?	3.41		[59KRE/NIK]
dis, TTA	4.1 M (Na,H)ClO ₄	?	~ -0.7	0	[65MAZ/SIV]
dis, TOA	8 M HClO ₄	20	-0.55		[70LAH/KNO]
sp	0.1-20 M HNO ₃	?	(4.65±0.05) ^(c)		[75VAS/AND2]
			< -2.1 ^(a)		

(a) Refers to the value reported for the reactions indicated, for the ionic medium and at the temperature given in the table.

(b) Recalculated in this review by assuming only the first complex forms for nitrate concentrations ≤ 2 M and accounting for activity factor changes on substituting perchlorate ions with nitrate.

(c) Refers to the reported constant for the reaction which includes water molecules, that is: $\text{PuO}_2(\text{H}_2\text{O})_6^{2+} + 2\text{NO}_3^- \rightleftharpoons \text{PuO}_2(\text{NO}_3)_2(\text{H}_2\text{O})_{6-x} + x\text{H}_2\text{O}$. The value for the constant corresponding to Eq. (20.3), $q=2$, has been calculated in this review.

20.1.3.2.a Pu(IV)

Drummond and Welch [56DRU/WEL] and Staritsky [56STA] reported preparation of $\text{Pu}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}(\text{s})$ and the latter also provided crystallographic data (powder diffraction pattern, space group Fdd2; $a = (1.114 \pm 0.002)$ nm; $b = (2.258 \pm 0.003)$ nm; and $c = (1.051 \pm 0.003)$ nm). The compound is isomorphous with the corresponding salts of thorium and cerium. No chemical thermodynamic data are available for this compound.

20.1.3.2.b Pu(VI)

The preparation and properties of a series of related hydrates of dioxoplutonium(VI) nitrate were described by Krevinskaia *et al.* [59KRE/NIK2]. A different precipitate, $\text{PuO}_2(\text{NO}_3)_2 \cdot \text{HNO}_3 \cdot n\text{H}_2\text{O}(\text{s})$, was isolated from 12.9 M aqueous nitric acid, [59KRE/NIK]. The solubilities of $\text{Pu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ in aqueous nitric acid solutions were reported. The solubility in the lowest nitric acid concentration used (2 M) was reported as 271.8 g Pu (probably ²³⁹Pu) per kilogram of saturated solution (*i.e.*, approximately 1.65 m HNO₃, 2.34 m PuO₂(NO₃)₂). From this, activity coefficients estimated using the SIT, and water activities approximated from the experimental

work on the corresponding uranium system [65DAV/LAW], the value

$$\Delta_f G_m^\circ(\text{PuO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}, \text{s}, 298.15 \text{ K}) = -(2393.3 \pm 3.2) \text{ kJ} \cdot \text{mol}^{-1}$$

is calculated.

Krevinskaia *et al.* [59KRE/NIK2] also dehydrated the hexahydrate by storing it over desiccants and by heating. Several lower hydrates including a trihydrate and a dihydrate were proposed, but it was not proven that these are equilibrium phases. The dihydrate was also reported by DeSando [67DES]. Lattice parameters based on unpublished X-ray diffraction data have been reported [86WEI/KAT] for both the hexahydrate and the trihydrate.

20.2 Plutonium phosphorus compounds and complexes

20.2.1 Aqueous plutonium phosphorus compounds and complexes

20.2.1.1 Aqueous plutonium phosphates

20.2.1.1.a Aqueous Pu(III) phosphates

There is only one quantitative study on the Pu(III) phosphate system known to us, performed by Moskvina [71MOS4]. Solubility measurements of $\text{PuPO}_4 \cdot x\text{H}_2\text{O}(\text{s})$ as function of the acidity of the solutions, as well as a cation exchange technique, were used to study the phosphate complexation of Pu(III). The same author has published in another compilatory work values of these constants extrapolated to infinite dilution with the aid of the Davies' equation [69MOS]. As discussed in Appendix A, the very stable $\text{PuPO}_4(\text{aq})$ complex proposed to explain the solubility data in slightly acidic to neutral solutions is not accepted in the present review because of possible experimental shortcomings with the solubility measurements in this acidity range. The solubility data at pH values < 4 were recalculated in the present review to obtain the solubility product of $\text{PuPO}_4 \cdot x\text{H}_2\text{O}(\text{s})$. The value $\log_{10} K_{s,0}(20.4, 0.5 \text{ M NaClO}_4) = -(21.5 \pm 0.5)$ obtained for the reaction:



was recalculated to $I = 0$ resulting in

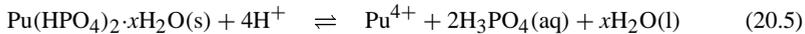
$$\log_{10} K_{s,0}^\circ(20.4, 298.15 \text{ K}) = -(24.6 \pm 0.8)$$

in reasonable agreement with the corresponding value $-(24.79 \pm 0.60)$ for the analogous americium solid [95SIL/BID].

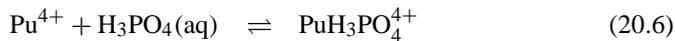
The cation exchange technique does not seem well-suited to the study of complexes of a highly charged cation with several possible ligands to produce potential cationic complexes. The constants for the complexes of the general formula $\text{Pu}(\text{H}_2\text{PO}_4)_n^{3-n}$ ($n = 1 - 4$) reported by Moskvina [71MOS4] and obtained from the cation exchange data are not accepted by this review because of possible experimental shortcomings (*cf.* Appendix A).

20.2.1.1.b Aqueous Pu(IV) phosphates

The system Pu(IV) phosphate has been studied mainly by solubility methods. There are three studies in which quantitative information on Pu(IV) phosphate complexation is reported [49KIN, 60DEN/MOS2, 60DEN/MOS]. All three are based on solubility measurements of the gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s})$ (Table 20.4). King [49KIN] has carried out a precise and well documented solubility study, but the data treatment is complicated at low ligand concentrations. The calculated contribution to the ligand concentration from the dissolution of the solid depends on the model used, and at high ligand concentrations, interactions with the neutral ligand may cause activity coefficient changes. Measurements at two acidity levels at constant ionic strength have been used to obtain conditional equilibrium constants valid at the acidity level used for complexes of the general composition $\text{PuH}_p(\text{PO}_4)_q^{4+p-3q}$ (see Appendix A). From this study, only the solubility product corresponding to the reaction:



and the constant corresponding to the complex with one phosphate group, for which both p and q values are uniquely determined, have been selected. From the proton concentration dependent constants reported in [49KIN] this review calculates $\log_{10} {}^*K_{s,0}(\text{20.5}, 2.08 \text{ M (H, Na)NO}_3) = -(8.79 \pm 0.18)$ and $\log_{10} \beta_1(\text{20.6}, 2.08 \text{ M (H, Na)NO}_3) = (2.3 \pm 0.2)$.



Practically the same values have been obtained from the recalculation of the data obtained by Denotkina, Moskvina and Shevchenko [60DEN/MOS] in 2.0 M HNO_3 .

Recalculation of these constants for $I = 0$ using the SIT equations and interaction coefficients selected in this review (Appendix B) results in

$$\begin{aligned} \log_{10} {}^*K_{s,0}(\text{20.5}, 298.15 \text{ K}) &= -(11.8 \pm 0.5) \\ \log_{10} \beta_1(\text{20.6}, 298.15 \text{ K}) &= 2.4 \pm 0.3 \end{aligned}$$

The Gibbs energy of formation of the complex $\text{PuH}_3\text{PO}_4^{4+}$ is calculated using the selected values for Pu^{4+} and $\text{H}_3\text{PO}_4(\text{aq})$ as:

$$\Delta_f G_m^\circ(\text{PuH}_3\text{PO}_4^{4+}, \text{aq}, 298.15 \text{ K}) = -(1641.1 \pm 3.6) \text{ kJ} \cdot \text{mol}^{-1}$$

By using the phosphoric acid dissociation constants selected in this review, the constant

$$\log_{10} K_{s,0}(\text{20.7}, 298.15 \text{ K}) = -(30.45 \pm 0.51)$$

was obtained.

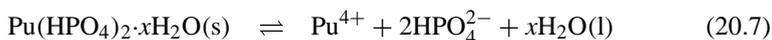


Table 20.4: Experimental equilibrium data for the Pu(IV) phosphate system.

Method Reaction	Ionic medium	t (°C)	$\log_{10} K$	Reference
$\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s}) + 4\text{H}^+ \rightleftharpoons \text{Pu}^{4+} + 2\text{H}_3\text{PO}_4(\text{aq}) + x\text{H}_2\text{O}(\text{l})$				
sol	2.08 M (H,Na)NO ₃	25	$-(8.79 \pm 0.15)^{\text{(a)}}$	[49KIN]
$\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s}) + 4\text{H}^+ \rightleftharpoons \text{PuH}_3\text{PO}_4^{4+} + \text{H}_3\text{PO}_4(\text{aq})$				
sol	2.08 M HNO ₃	25	$-(6.52 \pm 0.15)^{\text{(a)}}$	[49KIN]
$\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s}) + (p-2)\text{H}^+ \rightleftharpoons \text{PuH}_p(\text{PO}_4)_2^{p+}$				
sol	2.08 M (H,Na)NO ₃	25	$(-5.16, p = 4.2)^{\text{(b)}}$	[49KIN]
$\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s}) + 2\text{H}_3\text{PO}_4(\text{aq}) \rightleftharpoons \text{PuH}_p(\text{PO}_4)_4^{p-8} + (p-8)\text{H}^+$				
sol	2.08 M (H,Na)NO ₃	25	$(-3.72, p = 9.3)^{\text{(b)}}$	[49KIN]
$\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s}) + \text{H}_3\text{PO}_4(\text{aq}) \rightleftharpoons \text{PuH}_p(\text{PO}_4)_3^{p-5} + (p-5)\text{H}^+$				
sol	2.08 M (H,Na)NO ₃	25	$(-4.12, p = 6.6)^{\text{(c)}}$	[49KIN]
$\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s}) + 3\text{H}_3\text{PO}_4(\text{aq}) \rightleftharpoons \text{PuH}_p(\text{PO}_4)_5^{p-11} + (p-11)\text{H}^+$				
sol	2.08 M (H,Na)NO ₃	25	$(-3.88, p = 12.1)^{\text{(c)}}$	[49KIN]
$\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{Pu}^{4+} + 2\text{HPO}_4^{-2} + x\text{H}_2\text{O}(\text{l})$				
sol	2 M HNO ₃	?	$-(27.7 \pm 0.04)$	[60DEN/MOS2]
sol	$I \longrightarrow 0$	25	$-(30.45 \pm 0.5)$	This review
$\text{Pu}^{4+} + \text{H}_3\text{PO}_4(\text{aq}) \rightleftharpoons \text{PuH}_3\text{PO}_4^{4+}$				
sol	$I \longrightarrow 0$?	(2.4 ± 0.3)	This review

(a) Estimated in the present review from proton concentration dependent constants in [49KIN].

(b) Conditional constants obtained with fractional p values.

(c) These constants are an equally good alternative to the constants denoted by (b).

This value is in very good agreement with the value for the corresponding uranium species [92GRE/FUG]. As the actual extent of hydration of this solid is unknown, it is treated here simply as “Pu(HPO₄)₂(am)”. The corresponding value of $\Delta_f G_m^\circ$ for Pu(HPO₄)₂(am) is calculated as

$$\Delta_f G_m^\circ(\text{Pu}(\text{HPO}_4)_2, \text{am, hyd, 298.15 K}) = -(2843.8 \pm 5.1) \text{ kJ}\cdot\text{mol}^{-1}$$

20.2.1.1.c Aqueous Pu(V) phosphates

The only quantitative information on Pu(V) phosphate system available in the literature is a study by Moskvin and Poznyakov [79MOS/POZ] using the sorption-precipitation of Pu(V) on Fe(III) hydroxide. For the reaction



the authors report $\log_{10} \beta_1(20.8, 1 \text{ M NH}_4\text{Cl}) = (2.39 \pm 0.04)$. A recalculation in the present review of these data (see Appendix A) results in $\log_{10} \beta_1(20.8, 1 \text{ M NH}_4\text{Cl}) = (2.35 \pm 0.05)$. Even though the data for Pu(V) in this work seem better than those for the corresponding Np(V) system, this value is not selected since no confirmation from other more conventional experimental methods is available.

20.2.1.1.d Aqueous Pu(VI) phosphates

The Pu(VI) phosphate system has been studied experimentally mainly through solubility measurements [65DEN/SHE, 67DEN/SHE] (*cf.* Table 20.5). Moskvin [69MOS] reported formation constants at $I = 0.5 \text{ M}$ in an unspecified medium and temperature, obtained through distribution measurements.

In the study of the solubility of $\text{NH}_4\text{PuO}_2\text{PO}_4(\text{s})$ in dilute nitric and perchloric acid solutions [65DEN/SHE], it is evident that a phase transformation of the solid occurred at low pH values (see Appendix A). The dissolution mechanism assumed by the authors is not supported by experimental evidence. The recalculation of the data is complicated by the uncertainties about the composition of the solid phase in equilibrium. Thus, the constants reported in this study are not accepted in the present review. In another study by the same group [67DEN/SHE], solubility measurements for $\text{PuO}_2\text{HPO}_4\cdot 4\text{H}_2\text{O}(\text{s})$ were carried out using aqueous $\text{H}_3\text{PO}_4(\text{aq})$ solutions of variable ionic strength. Furthermore, the formation constant for the complex $\text{PuO}_2\text{H}_2\text{PO}_4^+$ was obtained using the solubility product and the constant for the complex $\text{PuO}_2\text{HPO}_4(\text{aq})$ reported in [65DEN/SHE], which is also not accepted in the present review for the reasons mentioned above. In a review paper Moskvin [69MOS] reported the formation constant for the complex $\text{PuO}_2\text{H}_2\text{PO}_4^+$ as measured by solvent extraction at $I = 0.5 \text{ M}$, and also an estimate of this constant at zero ionic strength (see Appendix A). The details of this experimental study have not been available for the present review, hence these data have not been considered further. Even more inconclusive is the study of Weger *et al.* [93WEG/OKA], in which weak qualitative spectrophotometric evidence was presented for the formation of Pu(VI) complexes with each of the three anions

Table 20.5: Literature equilibrium constants for the Pu(VI) phosphate system.

Method Reaction	Ionic medium	<i>t</i> (°C)	log ₁₀ <i>K</i>	Reference
$\text{PuO}_2^{2+} + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{PuO}_2\text{H}_2\text{PO}_4^-$				
sol	0.02-0.2 M H ₃ PO ₄ (aq)	25	(3.93 ± 0.13)	[67DEN/SHE]
$\text{PuO}_2^{2+} + \text{HPO}_4^{2-} \rightleftharpoons \text{PuO}_2\text{HPO}_4(\text{aq})$				
sol	0-0.1 M HNO ₃	?	8.17	[65DEN/SHE]
sol	0.02-0.2 M H ₃ PO ₄	25	8.17	[67DEN/SHE]
est	<i>I</i> → 0	?	8.19	[69MOS]
$\text{NH}_4^+ + \text{PuO}_2^{2+} + \text{PO}_4^{3-} \rightleftharpoons \text{NH}_4\text{PuO}_2\text{PO}_4(\text{aq})$				
sol	0-0.1 M HNO ₃	?	21.43	[65DEN/SHE]
$\text{PuO}_2\text{HPO}_4(\text{s}) \rightleftharpoons \text{PuO}_2^{2+} + \text{HPO}_4^{2-}$				
sol	0-0.1 M HNO ₃	?	-(12.55 ± 0.3)	[65DEN/SHE]
sol	0.02-0.2 M H ₃ PO ₄	25	-12.51	[67DEN/SHE]
$\text{NH}_4\text{PuO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{NH}_4^+ + \text{PuO}_2^{2+} + \text{H}_2\text{PO}_4^-$				
sol	0-0.1 M HNO ₃	?	-(26.64 ± 0.3)	[65DEN/SHE]

of phosphoric acid. Therefore, no data have been selected for the Pu(VI) phosphate system.

20.3 Solid plutonium phosphorus compounds

The only compound which has been identified in this system is Pu monophosphide, PuP(cr).

20.3.1 PuP(cr)

20.3.1.a Crystal Structure

PuP has a face-centred cubic rock-salt structure (space group Fm3m). The reported lattice parameters vary; $a_0 = 5.644 - 5.664 \times 10^{-10}$ m [57GOR, 64BAS, 66KRU/MOS, 67KRU/MOS, 85HAL/JEF]. It is suggested that the lattice parameter of this compound decreases with increase in phosphorus concentration [72DEL/BRJ].

Low temperature X-ray diffraction experiments indicated that PuP(cr) distorts to a tetragonal lattice [79MUE/LAN] at 5 K. The ferromagnetic ordering temperature is (125.5 ± 0.5) K [69LAM/FRA].

20.3.1.b Heat capacity

The heat capacity of PuP(cr) was measured using a transient technique for temperatures up to 18 K and an adiabatic method above this temperature [85HAL/JEF]. The measurements show a large magnetic transition at (125.5 ± 0.5) K, the Curie temperature. There is also a small unexplained anomaly at 17.5 K. The quantities from the analyses of these measurements are:

- Coefficient of electronic specific heat (γ) = (12.8 ± 2) $\text{mJ}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$.
- Debye temperature (Θ_{D}) = (187 ± 4) K.
- Einstein temperature (Θ_{E}) = (320 ± 10) K.
- Magnetic entropy (S_{mag}^0) = (3.0 ± 0.2) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.
- The standard entropy was calculated from the measurements of heat capacity:

$$C_{p,m}^{\circ}(\text{PuP, cr, 298.15 K}) = (50.20 \pm 4.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_{\text{m}}^{\circ}(\text{PuP, cr, 298.15 K}) = (81.32 \pm 6.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The heat capacity was also measured using a thermal pulse technique [66KRU/MOS, 68MOS/KRU] but the values are some 24% higher than the measurements recommended above. This pulse technique has given high values of the heat capacity for both UP(cr) and US(cr). The heat capacity measured with a thermal pulse technique from near room temperature to 923 K showed an increase of *ca.* 2% in this temperature range.

20.3.1.c Enthalpy of formation

An estimation has been made in this review based on selected values of the enthalpies of formation for UP(cr), UN(cr) and PuN(cr).

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuP, cr, 298.15 K}) = -(318 \pm 21) \text{ kJ}\cdot\text{mol}^{-1}$$

20.3.1.d Melting point

There is no published phase diagram of the PuP system. PuP(cr) melts with much vapourisation and decomposition in argon at 2873 ± 30 K [66KRU/MOS].

20.4 Plutonium arsenic compounds

20.4.1 Solid plutonium arsenic compounds

20.4.1.1 Plutonium arsenides

The only compound which has been identified in this system is Pu monoarsenide.

20.4.1.2 PuAs (cr)

20.4.1.2.a Crystal Structure

PuAs has a Fm3m, face-centred cubic rock-salt structure (space group Fm3m) [67KRU/MOS] with lattice parameter, $a_0 = 5.859 \pm 0.001 \times 10^{-10}$ m. in agreement with an earlier measurement [57GOR], $a_0 = 5.855 \times 10^{-10}$ m.

20.4.1.2.b Heat capacity

The heat capacity of PuAs(cr) has been measured from below 20 K using a transient technique and from 13 to 300 K using an adiabatic method [90HAL/MOR, 90HAL/JEF]. The data quoted here are for a sample annealed at 1273 K for 2 h in order to remove any radiation damage.

- The electronic component of the heat capacity $\gamma = 8.5 \text{ J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$.
- The Curie temperature was 125 K which agreed well with that determined from magnetic measurements.
- The Debye temperature (Θ_D) = 193 K.
- The entropy was calculated from the measurements of heat capacity:

$$C_{p,m}^{\circ}(\text{PuAs, cr, 298.15 K}) = (51.6 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^{\circ}(\text{PuAs, cr, 298.15 K}) = (94.3 \pm 7.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

20.4.1.2.c Enthalpy of formation

There are no measurements of the enthalpy of formation of PuAs(cr) but an estimate has been made here from analogous data for UAs(cr) and the systematic trends for the actinide pnictides.

$$\Delta_f H_m^{\circ}(\text{PuAs, cr, 298.15 K}) = -(240 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$$

Another estimated value [76MIE] falls within this band.

20.4.1.2.d Phase diagram

There are no published data for the phase diagram but PuAs(cr) melts in argon with rapid vaporisation at $(2693 \pm 30) \text{ K}$ [67KRU/MOS].

20.5 The plutonium-antimony system

Two compounds are reported for this system, Pu monoantimonide (PuSb, cr) and Pu diantimonide (PuSb₂, cr)

20.5.1 PuSb(cr)

20.5.1.a Crystal structure

PuSb has a face-centred cubic rock-salt structure (space group Fm3m) with reported lattice parameters, $a_0 = 6.2405 \pm 0.0005 \times 10^{-10}$ m [67KRU/MOS], and $a_0 = 6.2397 \pm 0.0001 \times 10^{-10}$ m [95ARA/OHM]. The face-centred cubic structure transforms to the cubic CsCl structure at pressures above 17 GPa and at 42 GPa to a tetragonal structure with space group P4/mmm [90DAB/BEN].

20.5.1.b Heat capacity

The heat capacity of PuSb has been measured from below 20 K using a transient technique and from 13 to 300 K using an adiabatic method [90HAL/MOR]. The sample was annealed at 1273 K for 2 h in argon in order to remove the radiation damage. Transitions were found at 75 K and 87 K and the values of the entropy associated with these transitions are 1.51 kJ·mol⁻¹ and, 0.76 kJ·mol⁻¹ respectively.

A decrease in transition temperatures with irradiation damage has been reported [88BLA/HAL], [86HAL/JEF].

The electronic component of the heat capacity (γ) is 5 ± 5 J·K⁻²·mol⁻¹.

The standard entropy was calculated from the measurement of heat capacity [90HAL/MOR] as:

$$C_{p,m}^{\circ}(\text{PuSb, cr, 298.15 K}) = (52.8 \pm 3.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_{\text{m}}^{\circ}(\text{PuSb, cr, 298.15 K}) = (106.9 \pm 7.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

20.5.1.c Enthalpy of formation

There are no measurements of the enthalpy of formation of PuSb(cr), but an estimate can be made from the data for USb(cr) and other systematic trends for the actinide pnictides. The estimated value is,

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{PuSb, cr, 298.15 K}) = -(150 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$$

Another estimated value [76MIE] lies within the above uncertainty band.

20.5.2 Plutonium diantimonide, PuSb₂(cr)

There is no structural information for this compound and the thermodynamic information is sparse.

20.5.2.a Thermodynamic quantities

There are measurements of the partial Gibbs energies of plutonium in the two-phase alloys.

$\text{PuSb}_2(\text{cr}) + \text{Sb}(\text{cr or l})$ [84LEB/KOB]. These data were obtained using an emf cell with a molten salt electrolyte of the type,



in the temperature range 808-950 K. For the composition range 5-11 at. % Pu, the E was independent of the Pu concentration.

From these measurements for the reaction, $\varepsilon - \text{Pu}(\text{cr}) + 2\text{Sb}(\text{cr}) \rightarrow \text{PuSb}_2(\text{cr})$,

$$\Delta_f G_m^\circ(\text{PuSb}_2, \text{cr}) = -(279225 - 72.75T) \text{ J}\cdot\text{mol}^{-1}$$

These data imply a very high stability for this compound as do the measurements of the same group for $\text{PuBi}_2(\text{cr})$ [69LEB/BAB]. These values of high stability are not consistent with the trends of the thermodynamic data for the actinide pnictides.

20.5.2.b Phase diagram

There is no published phase diagram for the plutonium-antimony system. $\text{PuSb}(\text{cr})$ melts at $(2253 \pm 30) \text{ K}$ [67KRU/MOS], and there are estimates of plutonium solubility in $\text{Sb}(\text{l})$ [84LEB/KOB]; 0.05 at.% at 1000 K and 0.11 at.% at 1100 K.

20.6 The plutonium-bismuth system

The phases reported for this system are plutonium monobismuthide (PuBi , cr) and plutonium dibismuthide (PuBi_2 , cr). The existence of diplutonium bismuthide (Pu_2Bi , cr) is uncertain.

20.6.1 Pu monobismuthide (PuBi, cr)

20.6.1.a Crystal structure

$\text{PuBi}(\text{cr})$ has a face-centred cubic rock-salt structure (space group $\text{Fm}\bar{3}\text{m}$). The reported measurements of lattice parameter are; $a_0 = 6.348 \times 10^{-10} \text{ m}$ [58BOC/KON] and $6.350 \times 10^{-10} \text{ m}$ [61ELL].

20.6.1.b Entropy

The entropy of $\text{PuBi}(\text{cr})$ has been estimated by adopting a scheme [62GRØ/WES] in which contributions for the lattice entropy of the appropriate elements are taken. The scheme was developed such the estimated values are consistent with the known experimental data the values and trends within the actinide pnictides and chalcogenides [62WES/GRØ].

The assessed value is

$$S_m^\circ(\text{PuBi}, \text{cr}, 298.15 \text{ K}) = (120 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

20.6.1.c Enthalpy of formation

There are no experimental determinations of the enthalpy of formation of PuBi(cr), however there is an estimated value [76MIE],

$$\Delta_f H_m^\circ (\text{PuBi, cr, 298.15 K}) = -(117 \pm 20) \text{ kJ}\cdot\text{mol}^{-1}$$

20.6.2 Pu dibismuthide (PuBi₂, cr)

20.6.2.a Crystal Structure

There is no information on the crystal structure of this compound.

20.6.2.b Entropy

The entropy was estimated in an analogous manner to that of PuBi(cr). The estimated value is,

$$S_m^\circ (\text{PuBi}_2, \text{cr, 298.15 K}) = (163 \pm 14) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

20.6.2.c Enthalpy of formation

There are no direct determinations of the enthalpy of formation of PuBi₂(cr). There are measurements of the partial Gibbs energy of Pu in the two phase field, PuBi₂(cr) + Bi(cr or l) using an EMF cell [69LEB/BAB] from which the Gibbs energy of formation in the temperature range 700-900 K can be calculated. The implied value of the enthalpy of formation at these temperatures would imply that the compound has a higher stability than would be expected from the trends within the actinide pnictides [81CHI/AKH].

There is also an estimate of the enthalpy of formation [76MIE]:

$$\Delta_f H_m^\circ (\text{PuBi}_2, \text{cr}) = -(126 \pm 22) \text{ kJ}\cdot\text{mol}^{-1}$$

20.6.2.d The Gibbs energy of formation

The Gibbs energy of formation of PuBi₂(cr) has been evaluated [81CHI/AKH] from measurements [69LEB/BAB] using a molten salt EMF cell to measure the thermodynamic activities in Pu unsaturated and saturated solution. With these data and the solubility of Pu in liquid Bi the estimated value of this quantity for the temperature range 700-900 K is

$$\Delta_f G_m^\circ (\text{PuBi}_2, \text{cr}) = -(216438 - 64.48T) \text{ J}\cdot\text{mol}^{-1}$$

All the experimental data described above for this system require confirmation.

20.6.2.e The phase diagram

There are several studies of some of the phase relationships in this system. PuBi(cr) melts congruently at *ca.* 1573 K [68ELL/MIN]. PuBi₂(cr) decomposes peritectically and there is a considerable discrepancy between the reported values for this temperature, 1103 K [68ELL/MIN] and 801 K [58BOC/KON].

There are also determinations of the solubility of plutonium in liquid bismuth [61ELL/CRA, 56FRO]; the solubility was also derived from measurements of plutonium activities in this region of the phase diagram [69LEB/BAB]. At 1073 K the solubility of plutonium in liquid bismuth is *ca.* 14 at. % [56FRO].

A preliminary phase diagram for this system has been published [68ELL/MIN] based on published partial phase diagrams [61SCH, 58BOC/KON].

Chapter 21

Plutonium group 14 compounds and complexes

21.1 Plutonium carbon compounds and complexes

21.1.1 Plutonium carbides

Holley, Rand and Storms [84HOL/RAN] reviewed the chemical thermodynamics of plutonium carbides in the early 1980s, and little significant information has been published in the interim. Thermodynamic quantities for these compounds are included here for information, but only minor additional assessment has been carried out. Compounds in the Pu-C system include a sub-stoichiometric monocarbide PuC_x ($x = 0.8-0.9$), a sesquicarbide a tri-plutonium dicarbide (with a region of stability below 848 K) and above 1933 K, a dicarbide. Although there is a substantial amount of thermodynamic data for this system, there is an unexplained discrepancy between the stabilities indicated from the enthalpy of combustion data (at 298.15 K) and from the Gibbs energy measurements, predominantly from measurements of the Pu(g) pressures over diphasic regions from 1450-2470 K. Although there are several inconsistencies between the text, tables and figures in their review, we accept the (calorie unit) values as assessed by Holley, Rand and Storms, with minor corrections; these are a reasonable compromise between the discrepant data.

21.1.1.1 Plutonium monocarbides

The low temperature heat capacities of at least sixteen samples have been measured, with reasonable, but not complete consistency. The most complete set of results is that by Hall *et al.* [79HAL/HAI] (a few of whose results were published by Haines *et al.* [80HAI/HAL]). Except for the samples near the upper phase boundary, all of these gave heat capacities which increased monotonically with temperature. The results, though somewhat scattered, suggest that both $C_{p,m}^\circ(298.15 \text{ K})$ and $S_m^\circ(298.15 \text{ K}) - S_m^\circ(0 \text{ K})$ are close to a linear functions of C/Pu (see Figures 6.21 and 6.22 of [84HOL/RAN]). From the latter curve, we take for $\text{PuC}_{0.84}$, $S_m^\circ(298.15 \text{ K}) - S_m^\circ(0 \text{ K}) = (71.1 \pm 2.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ (Holley *et al.* quote a value of $16.84 \text{ cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 70.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ in their text, but actually used the higher value in subsequent calculations). As for neptunium monocarbide we take the zero-point entropy to correspond to the fully randomized

state, $S_m^\circ(0\text{ K}) = (3.7 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and thus

$$S_m^\circ(\text{PuC}_{0.84}, \text{cr}, 298.15\text{ K}) = (74.8 \pm 2.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The heat capacity is

$$C_{p,m}^\circ(\text{PuC}_{0.84}, \text{cr}, 298.15\text{ K}) = (47.1 \pm 1.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

These are the selected values.

The heat capacities derived from the two enthalpy drop studies on $\text{PuC}_{0.82}$ and $\text{PuC}_{0.87}$ merge well with the low-temperature data - see Holley *et al.* [84HOL/RAN] for details. However, the equation they give does not reproduce the heat capacities in their Table A.6.11, and we prefer the simpler equation

$$C_{p,m}^\circ(\text{PuC}_{0.84}, \text{cr}, T) = 71.5910 - 5.95042 \cdot 10^{-2}T + 4.94346 \cdot 10^{-5}T^2 \\ - 9.9320 \cdot 10^5 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \quad (298.15 \text{ to } 1875\text{ K})$$

as the appropriate data for $\text{PuC}_{0.84}$.

As noted above, the enthalpy and Gibbs energy data for the monocarbide are not very consistent, and we adopt the compromise suggested by the thorough analysis of Holley *et al.*, and select

$$\Delta_f H_m^\circ(\text{PuC}_{0.84}, \text{cr}, 298.15\text{ K}) = -(45.2 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$$

from which

$$\Delta_f G_m^\circ(\text{PuC}_{0.84}, \text{cr}, 298.15\text{ K}) = -(49.8 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$$

21.1.1.2 Plutonium sesquicarbide

In addition to their studies on various plutonium monocarbides, Hall *et al.* [79HAL/HAI] measured the low temperature heat capacities of three well-characterised samples containing predominantly Pu_2C_3 , the most carbon rich being $\text{PuC}_{1.44}$, and three further samples containing PuC_{1-x} or graphite as well as Pu_2C_3 . Linear extrapolation of all these results (see Figures 6.21 and 6.22 of Holley *et al.* [84HOL/RAN]) gave the following selected values

$$C_{p,m}^\circ(\text{Pu}_2\text{C}_3, \text{cr}, 298.15\text{ K}) = (114.0 \pm 0.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ S_m^\circ(\text{Pu}_2\text{C}_3, \text{cr}, 298.15\text{ K}) = (150.0 \pm 2.9) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The enthalpy drop measurements by Oetting [80OET] merge smoothly with the low temperature data, and Holley *et al.* fitted these data to the equation

$$C_{p,m}^\circ(\text{Pu}_2\text{C}_3, \text{cr}, T) = 156.000 - 7.98726 \cdot 10^{-2}T + 7.04170 \cdot 10^{-5}T^2 \\ - 2.1757 \cdot 10^6 T^{-2} \quad (298.15 \text{ to } 2285\text{ K})$$

Holley *et al.* [84HOL/RAN] discuss in detail the many measurements of the stability of $\text{Pu}_2\text{C}_3(\text{cr})$, including two measurements of the enthalpy of combustion. As noted earlier, the many studies of the Gibbs energy of formation at temperatures from 900 to 1933 K consistently give more positive values than those calculated from the enthalpy of formation and the thermal functions. As for the monocarbide, we have accepted the values from the thorough analysis by Holley *et al.* [84HOL/RAN] (from their Table A.6.12), which lead finally to the selected values.

$$\begin{aligned}\Delta_f H_m^\circ(\text{Pu}_2\text{C}_3, \text{cr}, 298.15 \text{ K}) &= -(149.4 \pm 16.7) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{Pu}_2\text{C}_3, \text{cr}, 298.15 \text{ K}) &= -(156.5 \pm 16.7) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

21.1.1.3 Triplutonium dicarbide

This phase, whose structure is unknown, but is related to the fcc monocarbide, is found in Pu-rich alloys below 848 K, where it decomposes into PuC_{1-x} and $\text{Pu}(\text{cr}, \text{bcc})$. In their study of plutonium carbides, Hall *et al.* [79HAL/HAI] measured the low temperature heat capacity of two samples with compositions $\text{PuC}_{0.64}$ and $\text{PuC}_{0.68}$; the results are again shown on Figures 6.21 and 6.22 of Holley *et al.* [84HOL/RAN]. From these data, the entropy increment for the $\text{Pu}_3\text{C}_2(\text{cr})$ is interpolated to be

$$S_m^\circ(298.15 \text{ K}) - S_m^\circ(0 \text{ K}) = (194.1 \pm 4.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Holley *et al.* [84HOL/RAN] derive limits for the stability of this phase from the reliable phase diagram information from 300 to 850 K, which suggest fairly strongly that this phase is completely disordered, giving the selected values

$$\begin{aligned}S_m^\circ(\text{Pu}_3\text{C}_2, \text{cr}, 298.15 \text{ K}) &= (210.0 \pm 5.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ \Delta_f H_m^\circ(\text{Pu}_3\text{C}_2, \text{cr}, 298.15 \text{ K}) &= -(113 \pm 30) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f G_m^\circ(\text{Pu}_3\text{C}_2, \text{cr}, 298.15 \text{ K}) &= -(123.5 \pm 30.0) \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

where the uncertainties in the enthalpy and Gibbs energies of formation include those of the mono- and sesquicarbides.

For these calculations, the heat capacity was estimated to be

$$C_{p,m}^\circ(\text{Pu}_3\text{C}_2, \text{cr}, T) = 120.67 + 4.686 \cdot 10^{-2}T + 1.9456 \cdot 10^5 T^{-2} \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ (298.15 \text{ to } 850 \text{ K})$$

extrapolated from the values from Hall *et al.* [79HAL/HAI]; the value at 298.15 K is

$$C_{p,m}^\circ(\text{Pu}_3\text{C}_2, \text{cr}, 298.15 \text{ K}) = (136.8 \pm 2.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

21.1.1.4 Plutonium dicarbide

The invariancy involving $\text{Pu}_2\text{C}_3(\text{cr})$, $\text{PuC}_2(\text{cr})$ and graphite at $(1933 \pm 5) \text{ K}$ gives, with the current data

$$\Delta_f G_m^\circ(\text{PuC}_2, \text{cr}, 1933 \text{ K}) = -(87.2 \pm 10.0) \text{ kJ}\cdot\text{mol}^{-1}$$

Since there are no experimental heat capacity data for this phase, which is stable only above 1933 K, no further analysis of its thermodynamic properties is warranted.

21.1.2 Plutonium carbonates

21.1.2.1 The aqueous plutonium carbonates

The problems associated with attempts to define rigorously the composition and stability of Pu carbonate complexes in aqueous solution are based on the difficulties attendant upon the identification and maintenance of the oxidation state of Pu, the possible precipitation of sparingly soluble compounds in the course of an experiment, the difficulty in the identification of complex species in solutions containing both OH^- and $\text{CO}_3^{2-}/\text{HCO}_3^-$ ions and the necessary covariance of OH^- , CO_3^{2-} and HCO_3^- in aqueous solution. As a result of these difficulties the analysis of experiments in this system are rarely straightforward and commonly no unique model of complexation can be developed to explain experimental results.

The maintenance of oxidation state in Pu stock solutions is a matter of utmost importance in the description of the experimental constraints for these studies. The oxidation, reduction and/or disproportionation of the aquo ions or complexes or the precipitation of Pu-containing phases in the course of preparation, transfer or during an experiment can all lead to systematic errors. As a result, it is difficult to properly assign uncertainties unless Pu oxidation state and total Pu content of an experimental solution is verified in the course of the experiment.

A second source of experimental uncertainty is the radiolysis of the basic carbonate solutions (a result of the α decay of the Pu). The reaction of nuclear decay products with molecules of water can result in the production of reducing materials and $\text{H}_2\text{O}_2(\text{aq})$ with the resulting redox reactions noted above. In particular radiolysis can lead to ambiguities in the characterisation of the oxidation states of the Pu species in any long-term experiments and, therefore, verification of Pu oxidation state and concentration is particularly important in these experiments. Radiation effects may also affect the stability of solid phases and are of crucial importance in solubility studies. The changes noted in the X-ray powder pattern of $\text{PuO}_2\text{CO}_3(\text{s})$ by Robouch and Vitorge [87ROB/VIT] documents such variations.

The quantitative description of the interaction between Pu ions and the species present in carbonate solutions requires the use of well documented values of the equilibrium constants that determine the concentrations of H_2CO_3 , HCO_3^- , CO_3^{2-} , $\text{CO}_2(\text{g})$ and OH^- in solution. Because of the interrelationship between the concentrations of these species and the magnitude of the dissociation constant of HCO_3^- , it is not feasible to vary the ratio of $\text{CO}_3^{2-}/\text{OH}^-$ over more than a small range. In many cases, this covariance prevents an accurate determination of the number of OH^- groups that are associated with a specific Pu or Pu-carbonate species.

It is, therefore, usually not possible to demonstrate the existence of a unique aqueous model that describes the experimental results and this leads to a great deal of undocumented uncertainty in the results of this review. Where more than one model appeared to be compatible with experimental results, the model with the minimum number of complexes that contain the minimum number of ligands was chosen as most likely. We have been guided in a number of cases by the previous review of the uranium carbonate systems [92GRE/FUG] and, as in previous reviews of plutonium

complexation, the much more extensive studies of uranium complexation. Where differences between the uranium and plutonium systems were found, these are clearly documented in the following discussion. In the absence of better experimental data on the stoichiometries of the plutonium carbonate complexes, however, we are forced to use those determined for the analogous uranium complexes.

In the following discussion, we outline the evidence for the existence of Pu-carbonate complexes, the evidence for mixed hydroxide-carbonate complexes, if any, and the justification for the selection of results used to calculate the values of stability constants recommended in this review.

21.1.2.1.1 Pu(VI) carbonate complexes

The large number of compilations that review equilibria in the Pu(VI) carbonate system [70CLE, 71KEL, 79SAL/AVO, 80LEM/TRE, 80BEN/TEA, 82ALL, 82JEN, 83ALL, 85NEW/SUL, 87BRO/WAN] are based on a small set of experimental studies [62GEL/MOS, 67GEL/MOS, 78WOO/MIT, 82SUL/WOO, 86GRE/RIG, 86GRE/ROB, 87ROB/VIT, 88ULL/SCH] which are summarised in Table 21.1. A recent paper by Pashalidis *et al.* [97PAS/CZE] arrived too late for critical evaluation and for the results to be included in this review (*cf.* Appendix A).

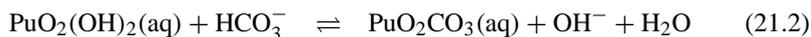
In the following discussion we outline the evidence for the existence of the carbonate complexes cited in Table 21.2, the evidence for mixed hydroxide-carbonate complexes, if any, and the justification for the selection of the results used to calculate the values tabulated in Table 21.2.

21.1.2.1.1.a The monocarbonato complex

The spectrophotometric and calorimetric study of Sullivan and Woods [82SUL/WOO] and the solubility study of Robouch and Vitorge [87ROB/VIT] are consistent with the existence of a monocarbonato species. Both of these studies were undertaken at near neutral pH. Sullivan and Woods [82SUL/WOO] interpreted their results, on the basis of a limited change in experimental pH in the course of HCO_3^- additions, as referring to the formation of an hydroxy-monocarbonato complex:



A reanalysis of their results (see Appendix A), however, suggests that an equally likely interpretation would involve the formation of the monocarbonato complex:



This latter result is more consistent with the interpretation from the analogous U(VI) and Np(VI) (see [92GRE/FUG] and Section 12.1.2.1.2) and is accepted by this review. The equilibrium constant determined by Sullivan and Woods [82SUL/WOO] is assumed to refer to Reaction (21.2): $\log_{10} {}^*K(21.2, 0.1 \text{ M NaClO}_4) = (2.67 \pm 0.60)$. The SIT correction is very small, and $\log_{10} {}^*K^\circ(21.2) = (2.67 \pm 0.60)$. On the basis of a thermodynamic cycle using the recommended values for the stability of $\text{PuO}_2(\text{OH})_2(\text{aq})$

Table 21.1: Summary of experimental results concerning PuO_2^{2+} - CO_3^{2-} complexes.

Method	I	t ($^{\circ}\text{C}$)	$\log_{10} K$	Reference
$\text{PuO}_2^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2\text{CO}_3(\text{aq})$				
sp	0.1 M	25	13.8 ^(a)	[82SUL/WOO]
sol	3.0 M	(20±1)	8.6	[87ROB/VIT]
sol	0	(20±1)	9.3 ^(b)	
$\text{PuO}_2^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2(\text{CO}_3)_2^{2-}$				
sol	0.175-0.438 M to	(20±1)	13.84 ^(c)	[62GEL/MOS]
sol	0	(20±1)	15.05 ^(d)	
sol	0	(20±1)	15.0 ^(e)	[67GEL/MOS]
sp	0.1 M	25	13.2 ^(a,f)	[82SUL/WOO]
sol	3 M	(20±1)	13.6	[87ROB/VIT]
sol	0	(20±1)	14.4 ^(b)	
cal	var.	25	15.1 ^(d)	[88ULL/SCH]
$\text{PuO}_2^{2+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2(\text{CO}_3)_3^{4-}$				
sp	0.15 M	25	3.24 ^(g)	[78WOO/MIT]
sol	3 M	(20±1)	18.2	[87ROB/VIT]
sol	0	(20±1)	17.0 ^(b)	
cal	var.	25	18.5 ^(d)	[88ULL/SCH]
$\text{PuO}_2^{2+} + 6\text{CO}_3^{2-} \rightleftharpoons (\text{PuO}_2)_3(\text{CO}_3)_6^{6-}$				
sp, emf	3 M	(22±1)	48.1 ^(h)	[86GRE/RIG] [86GRE/ROB]

(a) Based on experiments from a $\text{PuO}_2(\text{OH})_2$ starting material. This datum derived from experiment and compiled association constants for intermediates.

(b) SIT extrapolation.

(c) $(\text{NH}_4)_2\text{Pu}_2\text{O}_7$ (?) solid.

(d) Using Davies equation extrapolation.

(e) $(\text{NH}_4)_4\text{PuO}_2(\text{CO}_3)_3$ (?) solid.

(f) Correction using $\text{PuO}_2(\text{OH})_2$ formation constants.

(g) Formed at pH=11.4 from an unidentified hydrolysis product.

(h) No clear identity of the trimer.

Table 21.2: Recommended values for the equilibrium constants and enthalpies in the Pu(VI) carbonate system.

Reaction	$\log_{10} K^\circ$	$\Delta_r H_m^\circ$ (kJ·mol ⁻¹)
$\text{PuO}_2^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2\text{CO}_3(\text{aq})$	(11.6±3)	-(3.9±4.8)
$\text{PuO}_2^{2+} + 2\text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2(\text{CO}_3)_2^{2-}$	(14.5±2.6)	-(27±4)
$\text{PuO}_2^{2+} + 3\text{CO}_3^{2-} \rightleftharpoons \text{PuO}_2(\text{CO}_3)_3^{4-}$	(17.7±0.9)	-(38.6±2.0)
$3\text{PuO}_2^{2+} + 6\text{CO}_3^{2-} \rightleftharpoons (\text{PuO}_2)_3(\text{CO}_3)_6^{6-}$ (in 3 M NaClO ₄)	(50.1±2.5)	
$\text{PuO}_2\text{CO}_3(\text{s}) \rightleftharpoons \text{PuO}_2^{2+} + \text{CO}_3^{2-}$		-(14.2±0.3)

(see Section 17.1.1) and the auxiliary data for the stability of water and dissociation of bicarbonate, the equilibrium constant for the reaction



was found to be $\log_{10} \beta^\circ(21.3) = 13.8_{(-1.6)}^{(+0.8)}$ with the asymmetry in errors due to the error asymmetry assigned to the formation of $\text{PuO}_2(\text{OH})_2(\text{aq})$ (see Section 17.1.1). Robouch and Vitorge [87ROB/VIT] also determined the value of $\log_{10} \beta(21.3, 3.5 \text{ m NaClO}_4, 20^\circ\text{C}) = (8.6 \pm 0.6)$ from a solubility study (see Appendix A). Using the value of $\varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)} = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ as an estimate of $\varepsilon_{(\text{PuO}_2^{2+}, \text{ClO}_4^-)}$ but with the errors expanded to ± 0.08 , $\log_{10} \beta_1^\circ(21.3) = (9.3 \pm 0.5)$ was found. This result is assumed to apply to 25°C. The discrepancy between the reported values is large and therefore the mean is taken as the recommended value with an appropriately large uncertainty:

$$\log_{10} \beta_1^\circ(21.3, 298.15 \text{ K}) = 11.6 \pm 3.0$$

Sullivan and Woods [82SUL/WOO] give two estimates of the enthalpy of a reaction that we interpret to be (21.2). Based on spectrophotometric data, they assign $\Delta_r H_m(21.2, 0.1 \text{ m}) = -(6.3 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$; based on calorimetry, they assign $\Delta_r H_m(21.2, 0.1 \text{ m}) = -(1.5 \pm 1) \text{ kJ}\cdot\text{mol}^{-1}$. The mean value with errors expanded to encompass the errors in the two measurement is taken as the recommended value

$$\Delta_r H_m(21.2, 0.1 \text{ M}) = -(3.9 \pm 4.8) \text{ kJ}\cdot\text{mol}^{-1}$$

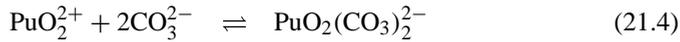
In the absence of a reliable estimate of the enthalpy of formation of $\text{PuO}_2(\text{OH})_2(\text{aq})$, there is no basis for the assignment of $\Delta_f H_m^\circ(21.3)$ and no value is recommended.

21.1.2.1.1.b The dicarbonato complex

The evidence for the existence of the dicarbonato complex is based on the fitting of a model curve to solubility data [87ROB/VIT] and enthalpy titration data [88ULL/SCH]. In both cases the stability range of this complex is small.

Neither study provides evidence for the existence of a mixed hydroxide-carbonate species over the narrow range of pH in which measurements were reported.

The association constant for the reaction



was estimated from solubility experiments in 3 M NaClO₄ solutions at (20 ± 1)°C by Robouch and Vitorge [87ROB/VIT] ($\log_{10} \beta_2 = (13.6 \pm 1.4)$). Using the interaction coefficients for the analogous UO₂²⁺ species and ClO₄⁻ (with the uncertainties expanded by 0.05) and the tabulated value of $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})}$ to calculate $\Delta\varepsilon(21.4) = -(0.26 \pm 0.17) \text{ kg}\cdot\text{mol}^{-1}$, the measured value can be extrapolated to I = 0, $\log_{10} \beta_2(21.4, 20^\circ\text{C}) = (14.7 \pm 1.4)$. Ullman and Schreiner [88ULL/SCH] determined $\log_{10} \beta_2^\circ(21.4, 298.15 \text{ K}) = (15.1 \pm 1.2)$ using a procedure inconsistent with the procedures adopted by this review (*cf.* Appendix A). For the purposes of this review, the uncertainty in this result is expanded to $\log_{10} \beta_2^\circ(21.4, 298.15 \text{ K}) = (15.1 \pm 2.2)$ to account for this inconsistency. The enthalpy of reaction determined by [88ULL/SCH], however,

$$\Delta_r H_m^\circ(21.4) = -(27 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$$

is accepted by this review as measured.

The determination of $\log_{10} \beta_2(21.4, 20^\circ\text{C})$ of Robouch and Vitorge [87ROB/VIT] can be corrected to 25°C using the enthalpy determined in [88ULL/SCH]. The result of this correction yields a second estimate, $\log_{10} \beta_2^\circ(21.4) = (13.9 \pm 1.4)$. An average of the two available experimental results yields

$$\log_{10} \beta_2^\circ(21.4, 298.15 \text{ K}) = (14.5 \pm 2.6)$$

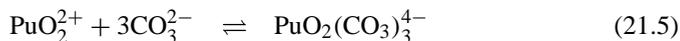
which is accepted by this review.

On the basis of these parameters, the remaining thermodynamic parameters, as listed in Table 4.2, can be calculated: $\Delta_r G_m^\circ(21.4, 298.15 \text{ K}) = -(82.767 \pm 14.841) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S_m^\circ(21.4, 298.15 \text{ K}) = (187.042 \pm 51.553) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

21.1.2.1.1.c The tricarbonato complex

A spectrophotometric study [78WOO/MIT] demonstrated that the principal carbonate complex in 0.15 M Na(ClO₄⁻, OH⁻) at pH = 11.4 is a tricarbonato species. The shape of the calorimetric titration curve of PuO₂²⁺ with Na₂CO₃ indicates that the tricarbonato complex is the dominant and limiting species at [CO₃²⁻]_T : [PuO₂²⁺]_T ratios of 3 or greater in strongly basic solution [88ULL/SCH]. The existence of the tricarbonato complex is also consistent with the curve fitting procedure in the solubility experiments [87ROB/VIT].

Newton and Sullivan [85NEW/SUL] reviewed the data of Woods, Mitchell and Sullivan [78WOO/MIT] and calculated an association constant for the reaction



assuming that the initial Pu(VI) species at pH = 11.4 is $\text{PuO}_2(\text{OH})_3^-$. Their estimate, $\log_{10} \beta_3(21.5) = (20 \pm 2)$, is not considered reliable due to the number of assumptions necessary for its calculation including the stoichiometry of the PuO_2^{2+} hydrolysis species and its stability (see Section 17.1.1).

The enthalpy titrations [88ULL/SCH] yield an estimate of $\log_{10} \beta_3^{\circ}(21.5) = (18.5 \pm 1.2)$ and

$$\Delta_r H_m^{\circ}(21.5) = -(38.6 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$$

(errors expanded to take into account the calculation procedure used in [88ULL/SCH] which is inconsistent with the procedure of this review, see Appendix A).

The solubility experiments at 20°C [87ROB/VIT] gave $\log_{10} \beta_3(21.5) = (18.2 \pm 0.8)$ in 3 M NaClO₄. This value can be extrapolated to $I = 0$ using $\varepsilon_{(\text{PuO}_2^{2+}, \text{ClO}_4^-)} = (0.46 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ (from the analogous interaction coefficient from UO_2^{2+} with the uncertainty expanded) and $\varepsilon_{(\text{PuO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+)} = -(0.2 \pm 0.3) \text{ kg}\cdot\text{mol}^{-1}$ (from the mean and range of the analogous interaction coefficients for $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{NpO}_2(\text{CO}_3)_3^{4-}$). Using these values, $\Delta\varepsilon(21.5) = -(0.42 \pm 0.31)$ and this value is used to convert the experimental value of [87ROB/VIT] to $\log_{10} \beta_3^{\circ}(21.5, 293.15 \text{ K}) = (16.7 \pm 1.4)$. This value is further corrected using the accepted enthalpy for Reaction 21.5 from [88ULL/SCH] to $\log_{10} \beta_3^{\circ}(21.5) = 16.6 \pm 1.4$. The weighted average of this value and that of [88ULL/SCH] is accepted by this review for the stability constant of $\text{PuO}_2(\text{CO}_3)_3^{4-}$

$$\log_{10} \beta_3^{\circ}(21.5, 298.15 \text{ K}) = (17.7 \pm 0.9)$$

The remaining thermodynamic parameters, as listed in Table 4.2, can be calculated from this value and $\Delta_r H_m^{\circ}(21.5)$: $\Delta_r G_m^{\circ}(21.5, 298.15 \text{ K}) = -(101.032 \pm 5.137) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S_m^{\circ}(21.5, 298.15 \text{ K}) = (209.399 \pm 18.490) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

21.1.2.1.1.d The dicarbonato trimer

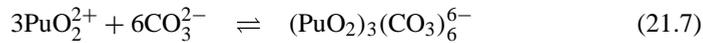
Grenthe and coworkers, [86GRE/RIG] and [86GRE/ROB] have interpreted spectrophotometric and emf data in terms of the formation of a biscarbonato-dioxoplutonium(VI) trimeric species:



with $\log_{10} K(21.6, I = 3 \text{ M NaClO}_4, 22^\circ\text{C}) = -(7.5 \pm 0.5)$. These experiments were performed at high total Pu(VI) concentrations, high ionic strength and near neutral pH, conditions which appear to stabilize this and similar polymeric species. In contrast,

evidence of this species was not found in either the calorimetric experiments of Ullman and Schreiner [88ULL/SCH] or the spectrophotometric experiments of Woods, Mitchell and Sullivan [78WOO/MIT]. No evidence of this species was found in the solubility experiments of Robouch and Vitorge [87ROB/VIT] at high ionic strength and moderate total Pu(VI) concentrations. This value is accepted for the conditions at which it was measured, but because of the large variation in the estimated interaction coefficients for the analogous U(VI) and Np(VI) species (see Section 12.1.2.1.2.c and [92GRE/FUG]), this value cannot be reliably extrapolated to the standard state. Given the evidence that the stability of this complex is limited to high Pu(VI) concentration and high ionic strength, the extrapolation, if possible, would require caution.

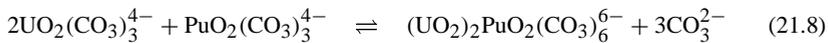
Together with the enthalpy and $\Delta\varepsilon$ of Reaction (21.5), $\log_{10} \beta_3^\circ(21.5, 298.15\text{K})$ can be extrapolated to the ionic strength and temperature of the [86GRE/RIG] experiment: $\log_{10} \beta_3(21.5, I = 3 \text{ M NaClO}_4, 22^\circ\text{C}) = (19.2 \pm 1.4)$. This permits the expression of the stability of the trimer in standard form:



At $I = 3 \text{ M}$ the accepted value for $\log_{10} \beta_{6,3}(21.7, 3 \text{ M}) = (50.1 \pm 2.5)$.

21.1.2.1.1.e Mixed U(VI) carbonate complex

Grenthe, Riglet and Vitorge [86GRE/RIG] noted that a mixed $\text{PuO}_2^{2+}\text{-UO}_2^{2+}$ trimer also forms in high-ionic-strength solutions. They reported the stability constant for the reaction:



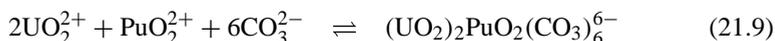
in 3 M NaClO_4 and at $(22 \pm 1)^\circ\text{C}$ as $\log_{10} K(21.8) = -8.8$, with no uncertainty assigned. Grenthe *et al.* [92GRE/FUG] re-evaluated the uncertainties in the reported stability constant, assumed that the experimental value could be applied to 25°C , and extrapolated the reported value to $I = 0$ to give $\log_{10} K^\circ(21.8) = -(8.8 \pm 0.2)$. In a later correction [95GRE/PUI] to the TDB uranium volume, revised interaction coefficients for the U(VI) system were proposed, and it was assumed that the interaction coefficients of the U(VI) system could be applied, by analogy, to the Pu(VI) system to re-evaluate the extrapolation to $I = 0$ ($\Delta\varepsilon = (0.16 \pm 0.36) \text{ kg}\cdot\text{mol}^{-1}$). This revised value is accepted:

$$\log_{10} K^\circ(21.8) = -(8.2 \pm 1.3)$$

Hence

$$\Delta_f G_m^\circ((\text{UO}_2)_2\text{PuO}_2(\text{CO}_3)_6^{6-}, 298.15 \text{ K}) = -(6135.7 \pm 10.5)$$

Using this selected value and the selected stability constants for $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{PuO}_2(\text{CO}_3)_3^{4-}$ the formation constant for the reaction:



is calculated to be $\log_{10} K^\circ(21.9, 298.15 \text{ K}) = (52.7 \pm 1.6)$. Because of the uncertainty in the assignment of interaction coefficients in the Pu(VI) system, however, this value should be used with caution at any ionic strengths much different from that of the original experiment.

21.1.2.1.2 The Pu(V) carbonate complexes

A stability constant for the reaction



was determined by laser photoacoustic spectrometry by [90BEN] and [92BEN/HOF]: $\log_{10} \beta_1(21.10, I = 0.5 \text{ M NaClO}_4, 296.15 \text{ K}) = (4.60 \pm 0.03)$. Using the recommended value of $\varepsilon_{(\text{NpO}_2\text{CO}_3^-, \text{Na}^+)}$ as an estimate of $\varepsilon_{(\text{PuO}_2\text{CO}_3^-, \text{Na}^+)}$ = $-(0.18 \pm 0.18)$ (with the uncertainty expanded), $\Delta\varepsilon(21.10) = -(0.34 \pm 0.19) \text{ kg}\cdot\text{mol}^{-1}$. Using this value of $\Delta\varepsilon$ and assuming that the measurements at 296.15 K can be used at 298.15 K:

$$\begin{aligned} \log_{10} \beta_1^\circ(21.10, 296 \text{ K}) &= (5.12 \pm 0.14) \\ \Delta_r G_m^\circ(21.10, 298.15 \text{ K}) &= -(29.2 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

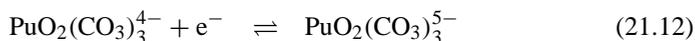
which, in the absence of an enthalpy determination for correction to standard state conditions, are accepted as the recommended values at 25°C. Although no such analogous species has been reported in the U system, in the Np system $\log_{10} \beta^\circ(\text{NpO}_2\text{CO}_3^-) = (4.96 \pm 0.06)$ in fairly good agreement with the reported result. There is no experimental basis for the assignment of an entropy or enthalpy to reaction 21.10.

The stability of the limiting Pu(V) carbonate complex at high carbonate concentration and 25°C was determined from measurements of the formal potential of the Pu(VI)/Pu(V) couple in 0.3-1.5 M (Na_2CO_3) medium by Capdevila [92CAP]. On the basis of the reversibility of the couple (determined by cyclic voltammetry) and the stoichiometry of the limiting $\text{PuO}_2(\text{CO}_3)_3^{4-}$ complex, the limiting Pu(V) complex was assumed to have the form $\text{PuO}_2(\text{CO}_3)_3^{5-}$ and be formed by a single electron transfer. It was recognised that the $\text{PuO}_2(\text{CO}_3)_3^{5-}$ complex could lose a CO_3^{2-} subsequent to reduction. It is possible that the reaction at the electrode involves both electron and carbonate ion exchange:



where $n = 1, 2$. Given the high concentrations of CO_3^{2-} in solution this reaction might continue to be reversible at the voltametric electrode. Although there is no independent evidence of the stoichiometry of the stable limiting Pu(V) carbonate complex in solution, the tricarbonato stoichiometry of the limiting complex ($n = 0$ in Eq. (21.11)) is accepted by analogy to the Np(V) species (see Section 12.1.2.1.3). Capdevila [92CAP] gave the reversible potential of the Pu(VI)/Pu(V) couple in 1 M Na_2CO_3 as $(339 \pm 7) \text{ mV vs. SHE}$ at 25°C and reported the results of similar experiments at temperatures between 5 and 65°C and in solutions ranging from 0.3

to 1.5 M Na₂CO₃. Wester and Sullivan [83WES/SUL] reported a half-wave potential of 110 mV vs. the SCE in 1 M Na₂CO₃ which is equivalent to (352 ± 10) mV (using the 241.5 mV for the potential of the SCE [92GRE/FUG] and our estimate of error); [84VAR/BEG] found the same value in 2 M Na₂CO₃ (110 mV vs. SCE and (352 ± 10) mV vs. SHE) and [74SIM/VOL] found slightly lower values for this couple (300 ± 10) and (320 ± 10) mV in 0.1 and 1 M K₂CO₃ at 20°C, respectively. On the basis of the experiments of [92CAP] the value of the electrode potential found by [74SIM/VOL] in 1 M K₂CO₃ can be adjusted to 25°C and gives (315 ± 10) mV vs. SHE. [86LIE/KIM] found a halfwave potential of -(80 ± 10) mV vs. the Ag/AgCl electrode at (25 ± 0.2)°C which is equivalent to (300 ± 10) mV vs. SHE. Based on the analogy to the U(VI)/U(V) couple, the potentials reported are assumed to be those describing the reaction



Insufficient detail is given in [74SIM/VOL, 83WES/SUL, 84VAR/BEG, 86LIE/KIM] to fully evaluate the potentials of the reference electrodes and possible effects of non-negligible junction potentials under the experimental conditions used and therefore the assignment of uncertainty by individual authors and by us probably overestimates the true precision of the reports. Given the extensive data set of [92CAP], a study in which all possible analytical precautions were made to eliminate possible junction potentials and in which the necessary corrections for the composition of the bridging solution on the potential of the reference electrode were done, this review accepts the formal potential of [92CAP] as the basis of the assignment of a stability for the limiting Pu(V) complex in carbonate solution.

On the basis of experiments in solutions of Na₂CO₃ ranging in concentration from 0.3 to 1.5 M [92CAP], the potential of the one electron transfer described by Equation (21.12), can be extrapolated to $I = 0$. Capdevila [92CAP] gives this value at 25°C as (186 ± 10) mV or equivalently $\Delta_r G_m^\circ$ (21.12, 298.15 K) = -(17.95 ± 0.96) kJ·mol⁻¹ with $\Delta\varepsilon$ (21.12, 298.15 K) = 0.25 ± 0.1 kg·mol⁻¹ (note that Capdevila [92CAP] found $\Delta\varepsilon = 0.305 - 0.0015t$ (°C) on the basis of experiments at a number of temperatures).

The value of the formation constant of PuO₂(CO₃)₃⁵⁻



can be calculated from the recommended stability of PuO₂(CO₃)₃⁴⁻, $\Delta_r G_m^\circ$ (21.5, 298.15 K) = -(101.03 ± 5.14) kJ·mol⁻¹, the recommended potential of the Pu(VI)/Pu(V) couple in acid solution, extrapolated to $I = 0$ (Reaction 16.7, 936 ± 5 mV, see Section 16.3) or equivalently, $\Delta_r G_m^\circ$ (16.8, 298.15 K) = -(90.29 ± 0.52) kJ·mol⁻¹. On the basis of these calculations,

$$\begin{aligned} \Delta_r G_m^\circ(21.13, 298.15 \text{ K}) &= -(28.68 \pm 5.25) \text{ kJ}\cdot\text{mol}^{-1} \\ \log_{10} \beta_3^\circ(21.13, 298.15 \text{ K}) &= (5.03 \pm 0.92) \end{aligned}$$

which are the values recommended by this review. In the U and Np systems, the analogous complexes have stabilities given by $\log_{10} \beta_3^\circ(\text{UO}_2(\text{CO}_3)_3^{5-}) = (7.41 \pm 0.27)$ [92GRE/FUG] and $\log_{10} \beta_3^\circ(\text{NpO}_2(\text{CO}_3)_3^{5-}) = (5.50 \pm 0.15)$ (see Section 12.1.2.1.3).

Capdevila [92CAP] also estimated the entropy of Reaction (21.12) at infinite dilution ($\Delta_r S_m^\circ$ (21.12) = $(170 \pm 48) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) based on the temperature dependence of the reduction potential at each of four ionic strengths. The enthalpy of the reduction can then be calculated from the Gibbs energy to give $\Delta_r H_m^\circ$ (21.12, 298.15 K) = $-(68.6 \pm 5.5) \text{ kJ}\cdot\text{mol}^{-1}$. Using the recommended enthalpies of the $\text{PuO}_2^{2+}/\text{PuO}_2^+$ aquo ion couple ($\Delta_r H_m^\circ$ (16.8, 298.15 K) = $-(88.09 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1}$) and for the enthalpy of reaction for the formation of $\text{PuO}_2(\text{CO}_3)_3^{4-}$ from PuO_2^{2+} and CO_3^{2-} ($\Delta_r H_m^\circ$ (21.5, 298.15 K) = $-(38.6 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$), the remaining thermodynamic parameters describing Reaction (21.13) can be calculated:

$$\begin{aligned}\Delta_r H_m^\circ(21.13, 298.15 \text{ K}) &= -(19.11 \pm 8.50) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_r S_m^\circ(21.13, 298.15 \text{ K}) &= (32.1 \pm 33.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}\end{aligned}$$

There is no experimental evidence of the stability or existence of the $\text{PuO}_2(\text{CO}_3)_2^{3-}$ complex in aqueous solution. In Section 12.1.2.1.3 the value $\log_{10} \beta_2^\circ(\text{NpO}_2(\text{CO}_3)_2^{3-}) = (6.53 \pm 0.10)$ is selected. The absence of evidence may result from disproportionation [90RIG] of $\text{PuO}_2(\text{CO}_3)_2^{3-}$, and indicates that the field of stability for this species is small.

21.1.2.1.3 The Pu(IV) carbonate complexes

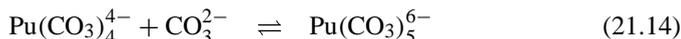
Solubility experiments with Pu(IV) solids in basic carbonate and bicarbonate media show that plutonium solubility increases dramatically over that expected in basic carbonate-free media [83KIM/LIE, 86LIE/KIM, 94YAM/SAK]. Although there are some reservations concerning the final oxidation state of the dissolved plutonium and the effects of radiolysis in experiments described in [83KIM/LIE] and in [86LIE/KIM] (see Appendix A and [87DEL]), these results clearly indicate that one or more highly co-ordinated carbonate complexes are formed under these conditions. Spectrophotometric experiments indicate that at least two complexes are formed, a limiting complex at high CO_3^{2-} concentrations with a strong absorbance at 486 nm and a second complex found in near-neutral bicarbonate medium having an additional absorbance peak at 492 nm [58MOS/GEL, 83WES/SUL, 85EIS/KIM, 86LIE/KIM, 92CAP, 94CLA/EKB, 94HOB/PAL, 96CAP/VIT, 96NIT/SIL]. Kim and co-workers [83KIM/LIE, 86LIE/KIM] have suggested a range of possible complexes of the form $\text{Pu}(\text{OH})_x(\text{CO}_3)_y^{4-x-2y}$. Their calculations and those of [85EIS/KIM], however, indicate that at most three carbonate-containing species are sufficient to describe the observed solubility data and systematic variations in Pu(IV) solubility with pH in laser-induced photoacoustic spectra.

There have been some differences in opinion as to whether mixed hydroxide-carbonate complexes are important in basic Pu(IV)-containing carbonate media. A review of the papers reporting such complexes [58MOS/GEL, 83KIM/LIE, 94HOB/PAL, 94YAM/SAK] is not compelling, as OH^- and CO_3^{2-} covaried in the experimental solutions. The best currently available experiments indicate that such species, if found, are not dominant in solution [83KIM/LIE]. The results of solubility

experiments that lead to the assignment of a mixed hydroxide-carbonate stoichiometry can, in most cases, be explained by the simultaneous and independent formation of hydrolysis products and carbonate complexes (see also Section 12.1.2.1.4)

In a conventional spectrophotometric study starting with the limiting complex in concentrated $\text{CO}_3^{2-}/\text{HCO}_3^-/\text{CO}_2(\text{aq})$ media, Capdevila and Vitorge [92CAP, 96CAP/VIT] found that only two carbonate-containing species were necessary to describe their observations. Consistent with the constraints imposed by the solubility experiments of [83KIM/LIE] and [86LIE/KIM] and by analogy to the U(IV)-H₂O-CO₂ system [92GRE/FUG], Capdevila and Vitorge identified these species as $\text{Pu}(\text{CO}_3)_4^{4-}$ and $\text{Pu}(\text{CO}_3)_5^{6-}$. A recent X-ray and spectroscopic study by Clark *et al.* [98CLA/CON] has confirmed the identity of the limiting complex proposed by Capdevila and Vitorge [92CAP, 96CAP/VIT]. Attempts to identify a carbonate-containing precursor complex to $\text{Pu}(\text{CO}_3)_4^{4-}$ were prevented by precipitation of the Pu(IV), presumably as the amorphous $\text{Pu}(\text{OH})_4$ (this presumption is consistent with the observations of Yamaguchi, Sakamoto and Ohnuki [94YAM/SAK]), in near-neutral bicarbonate solutions.

The equilibrium constant, K_5° for the reaction

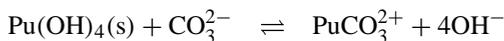


was found to be independent of pH between pH = 8 to 11, indicating that there is no OH⁻ exchange in the course of formation of the limiting pentacarbonato complex [92CAP, 96CAP/VIT]. A re-evaluation of the results of [85EIS/KIM] (see Appendix A) is consistent with this interpretation and the existence of only two carbonate-containing Pu(IV) complexes in these solutions.

Capdevila and Vitorge [96CAP/VIT] reanalysed the results reported in [92CAP] to determine the stability constant of Reaction (21.14) at $I = 0$ from experiments performed between $I = 0.2$ to 4.5 m at $t = (22 \pm 1)^\circ\text{C}$. This value is accepted as the best estimate for $\log_{10} K_5^\circ(21.14)$ at 25°C

$$\log_{10} K_5^\circ(21.14, 298.15 \text{ K}) = -(1.36 \pm 0.09)$$

The value of $\Delta\varepsilon(21.14)$ was found to be $(0.11 \pm 0.08 \text{ kg}\cdot\text{mol}^{-1})$. There is no direct basis for assigning a value to $\log_{10} \beta_5^\circ$ for $\text{Pu}(\text{CO}_3)_5^{6-}$. However, using the additional results of [92CAP] and [96CAP/VIT] concerning the disproportionation of Pu(V), a value of $\log_{10} \beta_5(3 \text{ M NaClO}_4) = (35.8 \pm 1.3)$ can be assigned. Other possible carbonate complexes have been proposed. Moskvina and Gel'man [58MOS/GEL] interpreted short-term solubility experiments in concentrated K₂CO₃ media that showed a linear increase in solubility with increasing carbonate concentration to reflect the following equilibrium:



A re-evaluation of these results (see Appendix A) suggests, however, that the solid controlling plutonium solubility in these experiments may have been a hydrated form of $\text{K}_4\text{Pu}(\text{CO}_3)_4(\text{s})$, a solid that was subsequently identified by this same group

[58GEL/ZAI]. If this reinterpretation of the Moskvin and Gel'man [58MOS/GEL] experiment is correct, then their observations are consistent with those of Capdevila [92CAP] and indicate that $\text{Pu}(\text{CO}_3)_5^{6-}$ is the important limiting complex in such carbonate rich solutions:



Unfortunately, due to the uncertain nature of the solutions and the high ionic strengths used by Moskvin and Gel'man [58MOS/GEL], it is not possible to rigorously evaluate the equilibrium constant for the above reaction.

The presently available results are insufficient to independently assign thermodynamic parameters at infinite dilution to Pu(IV) carbonate species. More work is needed to apply the accepted method of calculating thermodynamic parameters for Pu(IV) carbonate complexes in solution.

21.1.2.1.4 The Pu(III) carbonate complexes

Due to the facility with which Pu(III) oxidises to Pu(IV) in basic aqueous solution, there are no experimental studies to determine the identity of carbonate complexes and on which to base estimates of their stability. Based on an analogy between the trivalent actinides and the trivalent lanthanides and using an empirical correction for the effective ionic radius of the metals, Cantrell [88CAN] estimated the stability constants at $I = 0$ and 25°C for PuCO_3^+ ($\log \beta_1^\circ = 7.5$) and $\text{Pu}(\text{CO}_3)_2^-$ ($\log \beta_2^\circ = 12.4$). In the absence of experimental verification of the existence of these species and confirmation of their stabilities, no values are recommended.

21.1.2.2 Solid plutonium carbonates

21.1.2.2.1 Solid plutonium(VI) carbonates

The only characterised solid phase in the Pu(VI) carbonate system is $\text{PuO}_2\text{CO}_3(\text{s})$ [86GRE/ROB, 87ROB/VIT]. Lattice parameters are given in [86GRE/ROB], $a = 4.803(7) \text{ \AA}$; $b = 9.31(2) \text{ \AA}$; $c = 4.23(1) \text{ \AA}$. This phase is isostructural with the analogous U(VI) and Np(VI) phases.

The solubility product of $\text{PuO}_2\text{CO}_3(\text{s})$ in 3 M NaClO_4 at $(20 \pm 1)^\circ\text{C}$ has been determined by Robouch and Vitorge [87ROB/VIT]: $\log_{10} K_{\text{s},0}(\text{21.15}) = -(13.5 \pm 0.6)$. At infinite dilution ($\Delta\varepsilon(\text{21.15}) = 0.38 \pm 0.09 \text{ kg}\cdot\text{mol}^{-1}$) this leads to a value of $\log_{10} K_{\text{s},0}(\text{21.15}) = -(14.2 \pm 0.3)$. In the absence of an estimate of the enthalpy of the reaction



the value of $\log_{10} K_{\text{s},0}(\text{21.15})$ at 20°C is accepted as the best estimate of the solubility product at 25°C .

$$\log_{10} K_{\text{s},0}^\circ(\text{21.15}, 298.15 \text{ K}) = -(14.2 \pm 0.3)$$

Gel'man *et al.* [62GEL/MOS, 67GEL/MOS] described additional solid phases of composition $\text{K}_4\text{PuO}_2(\text{CO}_3)_3(\text{s})$, $(\text{NH}_4)_4\text{PuO}_2(\text{CO}_3)_3(\text{s})$, $\text{Ni}_2\text{PuO}_2(\text{CO}_3)_3(\text{s})$, $(\text{NH}_4)_2\text{PuO}_2(\text{CO}_3)_2(\text{s})$ and $\text{HgPuO}_2(\text{CO}_3)_2 \cdot x\text{H}_2\text{O}(\text{s})$. No crystallographic or thermodynamic studies of these phases have been reported and therefore no further discussion is warranted.

21.1.2.2.2 Solid plutonium(V) carbonates

Formation of the hydrated compounds $\text{M}_3\text{PuO}_2(\text{CO}_3)_2(\text{s})$ for $\text{M}^+ = \text{Na}^+$ and Rb^+ [81VOL/VIS] has been reported, and a somewhat less convincing case has been made for formation of hydrated $\text{Na}_4\text{PuO}_2(\text{CO}_3)_{2.5}(\text{s})$ [81VOL/VIS]. No thermodynamic data can be derived from the information available for these compounds.

21.1.3 Plutonium thiocyanate complexes

21.1.3.1 Aqueous Pu(III) thiocyanate complexes

Four experimental studies have been published reporting formation constants of Pu(III) thiocyanate complexes. Three of them are extraction studies [65CHO/KET, 74KHO/MAT, 78RAO/BAG2], and in one paper [66CAS/MAG] the Pu(III) thiocyanate system was studied with electrophoresis, chromatography, as well as anion and cation exchange. The reported constants in that study [66CAS/MAG] were derived from the cation exchange data (*cf.* Appendix A). While Khopkar and Mathur [74KHO/MAT] used iodide as a holding reductant to maintain plutonium in the +III oxidation state, Rao *et al.* [78RAO/BAG2] stated that such measures are not necessary due to the reducing properties of SCN^- . The data are presented in Table 21.3 and refer to the reactions:



The results of these investigations show that the Pu(III) thiocyanate complexes are weak. The constants reported for the 1:2 complex differ strongly, possibly due to activity factor changes or differences in the fitting procedures. In the present review, we do not select any data for higher Pu(III) thiocyanate complexes. In contrast, the data for the 1:1 complex are in fair agreement (*cf.* Table 21.3). For their extrapolation to $I = 0$, we assume that the $\Delta\varepsilon$ value that was estimated for the corresponding Am(III) system can be used for the Pu(III) system as well, $\Delta\varepsilon(21.16, q = 1) = -0.15 \text{ kg}\cdot\text{mol}^{-1}$ [95SIL/BID]. The resulting values at $I = 0$ are listed in Table 21.3. The value of [66CAS/MAG] is rather small compared with those of the other three studies, but there is no technical reason to discard this value. The uncertainties given by the authors reflect only the goodness of fit. We estimate that the uncertainties of the zero ionic strength values, taking systematic and extrapolation errors into account, are between ± 0.2 and ± 0.4 logarithmic units. In the light of these uncertainties, the four values do not appear inconsistent. We select the unweighted average of these values and assign an uncertainty that covers all four values:

$$\log_{10} \beta_1^\circ(21.16, q = 1, 298.15 \text{ K}) = (1.3 \pm 0.4)$$

Table 21.3: Experimental equilibrium data for the plutonium(III) thiocyanate system.

Method	Ionic medium	pH	t (°C)	$\log_{10} \beta_q^{(a)}$	$\log_{10} \beta_q^{\circ(b)}$	Reference
$\text{Pu}^{3+} + \text{SCN}^- \rightleftharpoons \text{PuSCN}^{2+}$						
dis	1 M NaClO ₄	2.0	25	(0.46±0.05)	1.51 ^(c)	[65CHO/KET]
cix	3 M NaClO ₄	2.0	25	0.04	0.95 ^(c)	[66CAS/MAG]
dis	1 M NH ₄ ClO ₄	2.8	30	(0.34±0.03)	1.39 ^(c)	[74KHO/MAT]
dis	2 M NaClO ₄	0.0	25	(0.33±0.03)	1.36 ^(c)	[78RAO/BAG2]
$\text{Pu}^{3+} + 2 \text{SCN}^- \rightleftharpoons \text{Pu}(\text{SCN})_2^+$						
dis	1 M NaClO ₄	2.0	25	(0.75±0.08)		[65CHO/KET]
cix	3 M NaClO ₄	2.0	25	-0.1		[66CAS/MAG]
dis	1 M NH ₄ ClO ₄	2.8	30	(0.95±0.04)		[74KHO/MAT]
dis	2 M NaClO ₄	0.0	25	-(0.30±0.26)		[78RAO/BAG2]
$\text{Pu}^{3+} + 3 \text{SCN}^- \rightleftharpoons \text{Pu}(\text{SCN})_3(\text{aq})$						
cix	3 M NaClO ₄	2.0	25	-0.7		[66CAS/MAG]

(a) $\log_{10} \beta_q$ refers to the equilibrium and the ionic strength given in the table.

(b) $\log_{10} \beta_q^{\circ}$ is the corresponding value corrected to $I = 0$ at 298.15 K.

(c) The uncertainties given by the authors do not include systematic errors and have therefore not been propagated to zero ionic strength.

The measurements of Khopkar and Mathur ([74KHO/MAT], Figure 3) at 15, 30, 37 and 45°C show that $\log_{10} \beta_1$ is virtually temperature independent in this range. They derived an enthalpy for the formation of PuSCN^{2+} of $\Delta_r H_m$ (1 M, 303.15 K) = (0.25 ± 0.75) kJ·mol⁻¹. We assume $\Delta_r H_m$ of this reaction to be independent of ionic strength and assign an uncertainty that is meant to reflect this assumption as well as the variation of the experimental data. The rounded enthalpy value is then:

$$\Delta_r H_m^\circ(21.16, q = 1, 298.15 \text{ K}) = (0 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$$

The thermodynamic formation data are derived from these constants and the selected data for Pu^{3+} and SCN^- :

$$\begin{aligned} \Delta_f G_m^\circ(\text{PuSCN}^{2+}, \text{aq}, 298.15 \text{ K}) &= -(493.7 \pm 5.3) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f H_m^\circ(\text{PuSCN}^{2+}, \text{aq}, 298.15 \text{ K}) &= -(515.4 \pm 6.0) \text{ kJ}\cdot\text{mol}^{-1} \\ S_m^\circ(\text{PuSCN}^{2+}, \text{aq}, 298.15 \text{ K}) &= -(15.4 \pm 25.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned}$$

21.1.3.2 Aqueous Pu(IV), Pu(V) and Pu(VI) thiocyanate complexes

No experimental studies are available on the formation of SCN^- complexes of Pu(IV), Pu(V) and Pu(VI). Rao *et al.* [78RAO/BAG2] have tried to investigate the complexation behaviour of Pu(IV) with thiocyanate, but they observed fast reduction to Pu(III); $(\text{SCN})_2(\text{aq}) + 2e^- \rightleftharpoons 2\text{SCN}^-$, $E^\circ = 0.77 \text{ V}$ [78RAO/BAG2]. Hence, the Pu(IV) state is not stable in the presence of thiocyanate, and the same can be expected for Pu(V) and Pu(VI), although the redox kinetics are unknown.

21.2 Plutonium silicides

A number of plutonium silicides are known: Pu_5Si_3 , Pu_3Si_2 , PuSi , Pu_3Si_5 , PuSi_2 [86BUR]. Krikorian and Hagerty [90KRI/HAG] have determined a value of $\Delta_f H_m^\circ(\text{Pu}_5\text{Si}_3, 298.15 \text{ K}) = -(417 \pm 105)$ kJ·mol⁻¹ for the enthalpy of formation of Pu_5Si_3 based on exchange reactions of plutonium with various silicides and the approximations $\Delta_f S_m^\circ(\text{Pu}_5\text{Si}_3, 298.15 \text{ K}) = (0 \pm 16)$ J·K⁻¹·mol⁻¹ and $\Delta_f C_p = 0$ J·K⁻¹·mol⁻¹. Values of the enthalpies of formation for other plutonium silicides were also estimated. Because of the approximations required in estimating $\Delta_f H_m^\circ$ at 298.15 K from the results of the arc-melting experiments at an ill-defined temperature near 2000 K, this value of $\Delta_f H_m^\circ(\text{Pu}_5\text{Si}_3, 298.15 \text{ K})$ is not selected in the present review.

Chapter 22

Plutonium group 2 (alkaline-earth) compounds

Several ternary oxides of alkaline earth elements with plutonium have been reported, and general synthesis and X-ray diffraction data for these compounds have been summarised by Weigel, Katz and Seaborg [86WEI/KAT] and references therein. However, chemical thermodynamic data for these compounds are relatively limited.

The thermodynamic quantities calculable from the available experimental data are exclusively enthalpies of formation. Gibbs energies would, of course, be more useful for thermodynamic modelling. However, in this review no entropy (or Gibbs energy) values are estimated for these mixed oxides. Entropies determined experimentally for uranium solids (*e.g.* γ - $\text{UO}_3(\text{cr})$) give a clear indication that entropies for M(VI) oxides are likely to be greater than those predicted based on “Latimer type” contributions derived from entropies of M(III) or M(IV) solids ([92GRE/FUG], especially Appendix D). However, $\text{PuO}_3(\text{cr})$ does not exist, and no information is available from direct measurements on the hydrated Pu(VI) oxides. Furthermore, the entropies reported for $\text{PuO}_2(\text{cr})$ and $\text{PuF}_4(\text{cr})$ are anomalously low compared to entropies for analogous solids of lower actinides, and this leaves little confidence that a reliable estimate could be made for the entropy contribution of Pu(IV) in BaPuO_3 .

22.1 Plutonium strontium compounds

22.1.1 $\text{Sr}_3\text{PuO}_6(\text{cr})$

The value of the heat of solution of $\text{Sr}_3\text{PuO}_6(\text{cr})$ in 1 M HCl was reported by Gens *et al.* [85GEN/FUG] from eight replicate measurements on two well-characterised samples. From this and auxiliary data in Appendix A, the recommended value

$$\Delta_f H_m^\circ(\text{Sr}_3\text{PuO}_6, \text{cr}, 298.15 \text{ K}) = -(3042.1 \pm 7.9) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated.

22.1.2 $\text{SrPuO}_3(\text{cr})$

As this review was nearing completion, Nakajima *et al.* [97NAK/ARA2] reported results of a Knudsen cell investigation of the vaporization of SrPuO_3 at 1433-1913 K. From the study the authors derived values for $\Delta_f H_m^\circ(\text{SrPuO}_3, 298.15 \text{ K})$ using both

second- and third-law treatments. The reported values from the two calculations differ by $24 \text{ kJ}\cdot\text{mol}^{-1}$, and the values from this work are not selected in the present review.

22.2 Plutonium barium compounds

22.2.1 Ba_3PuO_6 (cr)

The value of the heat of solution of $\text{Ba}_3\text{PuO}_6(\text{cr})$ in 1 M HCl was reported by Gens *et al.* [85GEN/FUG] from sixteen replicate measurements on four well-characterised samples. From this and auxiliary data in Appendix A, the recommended value

$$\Delta_f H_m^\circ(\text{Ba}_3\text{PuO}_6, \text{cr}, 298.15 \text{ K}) = -(2997 \pm 10) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated.

22.2.2 BaPuO_3 (cr)

Morss and Eller [89MOR/ELL] reported the enthalpy of formation of $\text{BaPuO}_3(\text{cr})$. The value as recalculated in the present review (*cf.* Appendix A), is:

$$\Delta_f H_m^\circ(\text{BaPuO}_3(\text{cr})) = -(1654.2 \pm 8.3) \text{ kJ}\cdot\text{mol}^{-1}$$

No entropy or Gibbs energy values are available for this compound.

22.2.3 Barium alkaline-earth compounds

Enthalpy of formation data have been reported for three barium alkaline-earth compounds, the perovskite-type oxides of the form $\text{Ba}_2\text{MPuO}_6(\text{cr})$ with $M = \text{Mg}, \text{Ca}$ and Sr .

No entropy or Gibbs energy values are available for these compounds.

22.2.3.1 $\text{Ba}_2\text{MgPuO}_6(\text{cr})$

The value of the heat of solution of $\text{Ba}_2\text{MgPuO}_6(\text{cr})$ in 1 M HCl was reported by Gens *et al.* [85GEN/FUG] from twelve replicate measurements on three well-characterised samples. From this and auxiliary data in Appendix A, the recommended value

$$\Delta_f H_m^\circ(\text{Ba}_2\text{MgPuO}_6, \text{cr}, 298.15 \text{ K}) = -(2995.8 \pm 8.8) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated.

22.2.3.2 $\text{Ba}_2\text{CaPuO}_6(\text{cr})$

The value of the heat of solution of $\text{Ba}_2\text{CaPuO}_6(\text{cr})$ in 1 M HCl was reported by Gens *et al.* [85GEN/FUG] from twelve replicate measurements on three well-characterised samples. From this and auxiliary data in Appendix A, the recommended value

$$\Delta_f H_m^\circ(\text{Ba}_2\text{CaPuO}_6, \text{cr}, 298.15 \text{ K}) = -(3067.5 \pm 8.9) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated.

22.2.3.3 Ba₂SrPuO₆(cr)

The value of the heat of solution of Ba₂SrPuO₆(cr) in 1 M HCl was reported by Gens *et al.* [85GEN/FUG] from eight replicate measurements on two well-characterised samples. From this and auxiliary data in Appendix A, the recommended value

$$\Delta_f H_m^\circ(\text{Ba}_2\text{SrPuO}_6, \text{cr}, 298.15 \text{ K}) = -(3023.3 \pm 9.0) \text{ kJ}\cdot\text{mol}^{-1}$$

is calculated.

Chapter 23

Plutonium group 1 (alkali) compounds

No experimental chemical thermodynamic data appear to have been reported for compounds of the type $(M_2O)_x \cdot PuO_y$, although several have been synthesized [[85FUG](#), [86WEI/KAT](#)].

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List of cited authors

This chapter contains an alphabetical list of the authors of the references cited in this book. 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 variations in spelling between different publications. These inconsistencies are not corrected in this volume.

Table 23.1: Authors list

Author	References
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Brothers, J. A.	[58BRO/HAR]
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Fedorov, I. A.	[64POZ/FED]
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Felmy, A. R.	[89FEL/RAI], [90RAI/FEL], [92RAI/FEL], [95RAI/FEL], [97FEL/RAI], [98RAI/FEL], [99RAI/HES], [99RAI/HES2]
Fernelius, W. C. (chairman)	[77FER]
Ferri, D.	[81CIA/FER], [83FER/GRE], [85FER/GRE]
Fidelis, I.	[78BED/FID]
Fink, J. K.	[82FIN]
Firestone, R. B.	[86BRO/FIR]
Fischer, J.	[61JOH/FIS]
Fitzgibbon, G. C.	[71FIT/PAV]
Florin, A. E.	[56FLO/TAN]
Flotow, H. E.	[74OSB/FLO], [75OSB/FLO], [76FLO/OSB], [81FLO/TET]
Flowers, G. C.	[81HEL/KIR]
Foltyn, E. M.	[90FOL]
Fomin, V. V.	[60LIP/POZ]
Forchioni, A.	[83MUS/CUI]
Fox, A. C.	[62RAN/FOX]
Fradin, F. Y.	[69LAM/FRA]
Francis, K. E.	[56MAN/RAE]
de Franco, M.	[77CHE/DEA]
Fred, M.	[75FRE], [83FRE/BLA], [86BLA/FRE]
Freeman, R. D.	[84FRE]
Fried, S.	[69COH/FRI], [69FRI/SCH], [70COH/FRI], [52FRI/DAV]
Fried, S. M.	[74OSB/FLO], [75OSB/FLO], [76FLO/OSB], [76GRU/MCB]
Friedman, A. M.	[85SCH/FRI]
Frlec, B.	[67FRL/CLA]
Frolova, L. M.	[76FRO/CHI], [76FRO/CHI2]
Frolova, U. K.	[66FRO/KUM]
Fronæus, S.	[51FRO]
Frost, B. R. T.	[56FRO]
Fruvip, D. J.	[85CHA/DAV]
Fry, A. J.	[61STO/FRY]

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Author	References
Fuger, J.	[63FUG/CUN], [69FUG/BRO], [71FUG/BRO], [73FUG/BRO], [76FUG/OET], [77BRO/HUR], [77MAG/FUG], [79FUG], [82MOR/FUG], [83FUG], [83FUG/PAR], [83MOR/WIL], [85FUG], [85GEN/FUG], [85MAR/FUG], [89SCH/GEN], [91GOU/JEM], [92FUG/KHO], [92GRE/FUG], [94MER/FUG], [2000RAN/FUG]
Fuks, L.	[87FUK/SIE]
Fulton, R. W.	[85KRU/RAI], [92RAI/FEL]
Gainar, I.	[64GAI/SYK]
Gal'chenko, G. L.	[59POP/GAL]
Gallegos, C. F.	[81ROL/GAL]
Gallo, L. S.	[61PAU/GAL]
Gandhe, S. P.	[79KUS/GAN]
Gardner, E. R.	[64MAR/BON], [65GAR/MAR]
Garisto, F.	[89LEM/GAR]
Garvin, D.	[87GAR/PAR]
Gatti, R.	[94SIL/NIT]
Gaumann, T.	[61BER/GAU]
Gel'man, A. D.	[58GEL/ZAI], [58GEL/ZAI2], [58MOS/GEL], [59GEL/ZAI], [62GEL/MOS], [64GEL/ZAI], [67GEL/MOS], [68KRO/MEF], [68ZAI/ALE], [68ZAI/ALE2], [70KRO/GEL], [72BLO/BUK], [72BLO/BUK2], [72MEF/KRO], [72MEF/KRO2], [72PER/KRO], [74MEF/KRO]
Gens, R.	[83MOR/WIL], [85GEN/FUG], [89SCH/GEN]
Gerdanian, P.	[77CHE/DEA]
Gerding, T. J.	[68TRE/GER]
Gibney, R. B.	[73SAN/GIB]
Giffaut, E.	[92CAP/VIT], [93GIF/VIT], [93GIF/VIT2], [94GIF], [94GIF/VIT], [96CAP/VIT]
Gingerich, K. A.	[67GIN]
Ginnings, D. C.	[47GIN/COR]
Girichev, G. V.	[96KON/BOO]
Giricheva, N. I.	[96KON/BOO]
Gleiser, M.	[73HUL/DES]
Glushko, V. P.	[82GLU/GUR]
Golodets, G. I.	[61GOL/GOL]
Golub, A. M.	[61GOL/GOL]
Goodman, G. L.	[65WEI/GOO]
Gorbenko-Germanov, D. S.	[65IAK/GOR], [66GOR/KLI], [66GOR/ZEN]
Gordon, J. E.	[76GOR/HAL]
Gordon, S.	[80SCH/GOR], [83SCH/GOR], [84MUL/GOR]
Gore, S. J. M.	[85EWA/GOR]
Gorum, A. E.	[57GOR]
Goudiakas, J.	[91GOU/JEM]
Grass, F.	[71SHE/GRA]
Graves, D. T.	[77MYE/GRA]
Green, D. W.	[78GRE/REE]

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Author	References
Grenthe, I.	[60GRE/NOR], [81CIA/FER], [83FER/GRE], [85FER/GRE], [86BRU/GRE], [86GRE/RIG], [86GRE/ROB], [87RIG/VIT], [89BRU/GRE], [92GRE/FUG], [92GRE/WAN], [94OST/BRU], [95GRE/PUJ], [95PAS/KIM], [97GRE/PLY], [97PUJ/RAR], [2000GRE/WAN]
Grigor'ev, M. S.	[89BUD/FED], [94GRI/CHA]
Gruber, J. B.	[73GRU/HEC]
Gruen, D. M.	[67GRU/DEK], [76GRU/MCB]
Grønvold, F.	[62GRØ/WES], [62WES/GRØ]
Gudi, N. M.	[79KUS/GAN], [79RAO/GUD], [81PAT/RAM]
Guggenheim, E. A.	[35GUG], [66GUG]
Guillaume, B.	[83BOU/GUI]
Guillaumont, R.	[69MET/GUI], [72MET/GUI], [75HUB/HUS], [76HUB/HUS], [76MET/GUI], [77DUP/GUI]
Gurvich, L. V.	[82GLU/GUR], [85HIL/GUR]
Gutina, E. A.	[74ARK/GUT]
Gutmacher, R. G.	[86BLA/FRE]
Güldner, R.	[82WEI/WIS]
Gélétseanu, I.	[63MOS/GÉL]
Haaland, A.	[95HAA/MAR]
Hagemann, F.	[49ABR/BRO], [49HAG/ABR]
Hagerty, D. C.	[90KRI/HAG]
Hahn, R. L.	[84MAD/BEG]
Haines, H. E.	[79HAL/HAI]
Haines, H. R.	[80HAI/HAL]
Haire, R. G.	[78LLO/HAI]
Hall, R. A. O.	[85HAL/JEF]
Hall, R. O. A.	[59LEE/MAR], [76GOR/HAL], [78HAL/LEE], [79HAL/HAI], [80HAI/HAL], [86HAL/JEF], [88BLA/HAL], [90HAL/JEF], [90HAL/MOR]
Halow, I.	[82WAG/EVA]
Halperin, J.	[83HAL/OLI]
Hamann, S. D.	[82HAM]
Hart, R. G.	[58BRO/HAR]
Haschke, J. M.	[92HAS], [93STA/LAR]
Hatcher, J. B.	[53WES/HAT]
Hauske, H.	[77WEI/WIS]
Hawkins, D. T.	[73HUL/DES]
Head, E. L.	[58HOL/MUL]
Heathman, S.	[90DAB/BEN]
Hecht, H. G.	[73GRU/HEC]
Hedlund, T.	[88HED]
Heisig, D. L.	[52HEI/HIC]
Helgeson, H. C.	[74HEL/KIR], [81HEL/KIR], [88SHO/HEL], [88TAN/HEL], [89SHO/HEL], [89SHO/HEL2], [90OEL/HEL], [92SHO/OEL]
Hellmann, H.	[83HEL], [86WEI/HEL]

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Author	References
Heppner, P. M.	[92BIS/KRA]
Herpin, P.	[73DER/FAU3]
Herrick, C. C.	[65FEB/HER]
Herrmann, G.	[89KIM/KAN2]
Hess, N. J.	[96CLA/CON], [96CLA/CON2], [97FEL/RAI], [98RAI/FEL], [99RAI/HES], [99RAI/HES2]
Heumann, F. K.	[51ZEB/ALT]
Hicke, T. E.	[52HEI/HIC]
Hietanen, S.	[85FER/GRE]
Higashi, K.	[88NAK/ARI], [89MOR/PRA], [89PRA/MOR], [90PRA/MOR], [91PRA/YAM], [91YAM/PRA], [93PRA/MOR], [93PRA/YAM], [95MOR/PRA]
Hildenbrand, D. L.	[85HIL/GUR], [92KLE/LAU], [92KLE/LAU2], [98KON/HIL]
Hinchey, R. J.	[70HIN/COB]
Hindman, J. C.	[49HIN], [49HIN2], [49HIN/AME], [49HIN/MAG], [49HIN/MAG2], [49MAG/LAC], [50HIN/KRI], [52COH/HIN], [52COH/HIN2], [54CUN/HIN], [54HIN], [54SUL/AME], [54SUL/HIN], [55COH/SUL], [59SUL/HIN], [61SUL/HIN]
Hirsch, V.	[88HIR/LIE]
Hobart, D. E.	[83BOU/GUI], [84MAD/BEG], [84VAR/BEG], [84VAR/HOB], [94HOB/PAL], [95CLA/HOB], [96ROB/SIL]
Hoff, H. A.	[79MUE/LAN]
Hoffman, D. C.	[87BEN/HOF], [92BEN/HOF], [94NEU/HOF]
Hoffmann, G.	[83MAR/HOF]
Holley, Jr., C. E.	[58HOL/MUL], [68HUB/HOL], [71FIT/PAV], [72HUB/HOL], [73SAN/GIB], [84HOL/RAN]
Holloway, J. H.	[70COH/FRI], [82BRO/WHI]
Homann, K.	[88MIL/CVI]
Hoshi, M.	[70UEN/HOS]
Hostettler, J. D.	[84HOS]
Hovey, J. K.	[89HOV/NGU]
Howse, R. M.	[86EWA/HOW]
Hubbard, W. N.	[69JOH/DEV], [73JOH/SMI], [83FUG/PAR]
Huber, Jr., E. J.	[58HOL/MUL], [68HUB/HOL], [72HUB/HOL]
Hubert, S.	[75HUB/HUS], [76HUB/HUS]
Hulet, E. K.	[81LUN/HUL]
Hultgren, R.	[73HUL/DES]
Hung, T. K.	[87RÖS/MIL], [90RÖS/HUN]
Hurst, R.	[54DAW/ELL], [56MAN/RAE]
Hurtgen, C.	[77BRO/HUR], [78HUR]
Hussonnois, M.	[75HUB/HUS], [76HUB/HUS]
Iakolev, G. N.	[65IAK/GOR]
Ichas, V.	[94AMA/BRA]
Ihle, H.	[59AXE/IHL]
Ihle, H. R.	[60IHL/AXE]
Il'inskaya, T. A.	[75BEL/IL']

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Author	References
Inoue, Y.	[85INO/TOC], [85INO/TOC2]
Iorga, E. V.	[75IOR/SHC]
Itagaki, H.	[89TAN/NAG], [91ITA/TAN], [92ITA/NAK]
Iuliano, M.	[87CIA/TUL]
Ivanov, M. I.	[57POP/IVA]
Ivantsov, A. I.	[67SOL/TSV]
Janecky, D. R.	[96CLA/CON]
Jeffery, A. J.	[85HAL/JEF], [86HAL/JEF], [90HAL/JEF]
Jemine, X.	[91GOU/JEM]
Jenkins, H. D. B.	[82MOR/FUG]
Jensen, B. S.	[82JEN]
Jensen, K. A. (chairman)	[71JEN]
Jette, E. R.	[55JET]
Johns, I. B.	[45JOH]
Johnson, C. E.	[61JOH/FIS]
Johnson, G. K.	[69JOH/DEV], [73JOH/SMI], [88TAS/O'H]
Johnson, J. W.	[92SHO/OEL]
Johnson, K. A.	[65MUL/ELL]
Johnson, K. S.	[79JOH/PYT]
Jones, B. F.	[90NOR/PLU]
Jones, M. M.	[53JON]
Joshi, A. R.	[84KAS/JOS]
Joshi, J. K.	[82NAI/CHA]
Jouniaux, B.	[79JOU/LEG]
Jove, J.	[86THE/JOV]
Kallay, N.	[88MIL/CVI]
Kanellakopoulos, B.	[89KIM/KAN], [89KIM/KAN2], [91KIM/KLE], [92NEC/KIM], [94NEC/KIM], [94NEC/RUN]
Kapshukov, I. I.	[73SUD/SOL], [74SIM/VOL], [74VIS/VOL], [74VOL/KAP], [74VOL/KAP2], [76VOL/VIS], [77VOL/VIS], [79VOL/TOM], [79VOL/VIS], [79VOL/VIS2], [81VOL/VIS], [81VOL/VIS2], [81VOL/VIS3], [81VOL/VIS4], [84VOL/KAP]
Karle, I.	[49ABR/BRO]
Kasar, U. M.	[84KAS/JOS]
Kasha, M.	[49KAS]
Kato, Y.	[93LI/KAT], [96KAT/KIM]
Katz, J. J.	[49ABR/BRO], [49HAG/ABR], [51KAT/RAB], [57KAT/SEA], [86WEI/KAT]
Kawamura, Y.	[95YAJ/KAW]
Kay, A. E.	[64KAY/LOA]
Kazantsev, G. N.	[84LEB/KOB]
Keenan, T. K.	[54NIG/PEN], [64KEE/KRU], [65KEE]
Keller, C.	[71KEL]
von Keller, C.	[69KEL/FAN]
Kelley, K. K.	[73HUL/DES]
Kent, R. A.	[68KEN], [69KEN], [69KEN/LEA]

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Author	References
Ketels, J.	[65CHO/KET]
Khachkuruzov, G. A.	[82GLU/GUR]
Khalkin, V. A.	[87RÖS/MIL], [89RÖS/DIT], [90RÖS/HUN]
Khalturin, G. V.	[76SEV/KHA]
Kharitonov, Y. Y.	[73KHA/MOS]
Khodakovskii, I. L.	[95PAR/KHO]
Khodakovsky, I. L.	[72NIK/SER], [92FUG/KHO]
Khopkar, P. K.	[74KHO/MAT]
Kim, J. I.	[83KIM/LIE], [84KIM/BER], [84LIE/KIM], [85EIS/KIM], [85KIM], [85LIE/TRE], [86LIE/KIM], [88BÜP/KIM], [88KLE/KIM], [89KIM/KAN], [89KIM/KAN2], [91KIM/KLE], [91KIM/PAS], [92NEC/KIM], [92RUN/MEI], [93PAS/KIM], [93PAS/KIM2], [93PAS/RUN], [94KIM], [94NEC/KIM], [94NEC/RUN], [94RUN/KIM], [95FAN/NEC], [95NEC/FAN], [95NEC/RUN], [95PAS/KIM], [96FAN/NEC], [96MOR/KIM], [97NEC/FAN], [97PAS/CZE]
Kim, J. J.	[74PIT/KIM]
Kimura, M.	[68KIM/SCH]
Kimura, T.	[96KAT/KIM]
King, E. L.	[49KIN]
Kipatsi, H.	[80ALL/KIP]
Kirkham, D. H.	[74HEL/KIR], [81HEL/KIR]
Kleinschmidt, P. D.	[86KLE/WAR], [86WAR/KLE], [92KLE/LAU], [92KLE/LAU2], [93WIL/KLE]
Klenze, R.	[88KLE/KIM], [91KIM/KLE]
Klimov, V. C.	[66GOR/KLI]
Kline, R. J.	[60RAB/KLI]
Knoch, W.	[70LAH/KNO]
Knott, H. W.	[79MUE/LAN]
Kober, V. I.	[84LEB/KOB]
Koehly, G.	[83BOU/GUI]
Kok-Scheele, A.	[96KOV/BOO]
Kolokoltsov, V. B.	[76VOD/KOL]
Komarov, E. V.	[68KRY/KOM], [68KRY/KOM2], [69KRY/KOM], [69KRY/KOM2], [69KRY/KOM3], [69KRY/KOM4]
Konings, R. J. M.	[90COR/KON], [90COR/KON2], [92GRE/FUG], [95HAA/MAR], [96KON/BOO], [96KOV/BOO], [98KON/HIL]
Konobeevskii, S. T.	[58BOC/KON]
Koppold, F.	[84KIM/BER]
Kovaleva, T. V.	[76VOD/KOL]
Kovács, A.	[96KON/BOO], [96KOV/BOO]
Kramer-Schnabel, U.	[92BIS/KRA]
Krasnova, O. G.	[96KON/BOO]
Kraus, K. A.	[45DAM/KRA], [46KRA/DAM], [46KRA/DAM2], [48KRA/NEL], [48KRA/NEL2], [49KRA/DAM], [49KRA/DAM2], [49KRA/DAM3], [50KRA/NEL], [56KRA]
Kremers, H. E.	[45MOE/KRE]

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Author	References
Krevinskaia, M. E.	[59KRE/NIK]
Krevinskaia, M. Y.	[59KRE/NIK2]
Krikorian, O. H.	[90KRI/HAG]
Kritchevsky, E. S.	[50HIN/KRI]
Krot, N. N.	[68KRO/MEF], [70KRO/GEL], [72BLO/BUK], [72BLO/BUK2], [72MEF/KRO], [72MEF/KRO2], [72PER/KRO], [74MEF/KRO], [76SHI/STE], [77ERM/PER], [79FED/PER], [89BUD/FED], [91SHI/TAN], [94GRI/CHA], [94NIK/BES]
Kruger, O. L.	[66KRU/MOS], [67KRU/MOS], [68KRU/SAV], [68MOS/KRU], [69JOH/DEV], [69LAM/FRA], [76ALE/CLA]
Krupka, K. M.	[85KRU/RAI]
Kruse, F. H.	[64KEE/KRU]
Krylov, V. N.	[68KRY/KOM], [68KRY/KOM2], [69KRY/KOM], [69KRY/KOM2], [69KRY/KOM3], [69KRY/KOM4]
Kubaschewski, O.	[63RAN/KUB], [93KUB/ALC]
Kuchitsu, K.	[88MIL/CVI]
Kudryavtsev, A. N.	[75BEL/IL']
Kudryavtsev, E. G.	[90PAZ/KUD]
Kumok, V. N.	[66PRO/KUM]
Kusumakumari, K. M.	[79KUS/GAN]
Kutaitsev, V. I.	[58BOC/KON]
LaChapelle, T. J.	[49HIN/MAG], [49HIN/MAG2], [49MAG/LAC]
Laffitte, M. (chairman)	[82LAF]
Lahr, H.	[70LAH/KNO]
Laidler, J. B.	[64BAG/LAI], [66LAI]
Lam, D. J.	[69LAM/FRA]
Lander, G. H.	[79MUE/LAN], [85HAL/JEF]
Langmuir, D.	[90NOR/PLU]
Lapage, R.	[67LAP/BUN]
Lapitskii, A. V.	[63MOS/GÉL]
Larson, D. T.	[93STA/LAR]
Latimer, W. M.	[52LAT]
Lau, K. H.	[92KLE/LAU], [92KLE/LAU2]
Lawson, P. S.	[65DAV/LAW]
Laxminarayanan, T. S.	[64LAX/PAT]
LeBlanc, J. C.	[93LEM/CAM]
Leary, J. A.	[59BJO/REA], [69KEN/LEA]
Lebedev, V. A.	[69LEB/BAB], [84LEB/KOB]
Lederer, C. M.	[79SHI/LED]
Lee, J. A.	[59LEE/MAR], [70LEE/MEN], [76GOR/HAL], [78HAL/LEE], [79HAL/HAI], [80HAI/HAL], [85HAL/JEF], [88BLA/HAL]
Lee, J. H.	[91BYR/LEE]
Legoux, Y.	[79JOU/LEG]
Leigh, G. J.	[90LEI]
Leikina, E. V.	[72CHA/LEI], [75CHA/MAT]
Leitnaker, J. M.	[68SPE/LEI], [72OET/LEI]

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Author	References
Lemire, R. J.	[80LEM/TRE], [81PAQ/LEM], [84LEM], [89LEM/GAR], [92GRE/FUG], [93LEM/BOY], [93LEM/CAM], [93TAY/LEM], [94CAM/LEM], [96LEM/CAM], [96LEM/CAM2]
Lemons, J. F.	[51RAB/LEM], [56FLO/TAN]
Lewis, B. M.	[88TAS/O'H]
Lewis, G. N.	[61LEW/RAN]
Li, Y.	[93LI/KAT]
Licht, T. S.	[59DEB/LIC]
Lierse, C.	[83KIM/LIE], [84KIM/BER], [84LIE/KIM], [85EIS/KIM], [85LIE/TRE], [86LIE/KIM], [88BÜP/KIM], [93PAS/KIM], [93PAS/KIM2]
Lieser, K. H.	[88HIR/LIE]
Liljenzin, J. O.	[80ALL/KIP]
Lim, C. K.	[51ROB/LIM]
Lindemer, T. B.	[83BES/LIN]
Lipis, L. V.	[60LIP/POZ]
Livet, J.	[83MUS/CUI]
Lloyd, M. H.	[78LLO/HAI]
Loasby, R. G.	[64KAY/LOA]
Long, G.	[56MAN/RAE]
Lorenzelli, R.	[64ANS/DEA]
Lucas, M.	[64LUC]
Ludwig, R.	[87RÖS/MIL], [90RÖS/HUN]
Lundqvist, R.	[81LUN], [81LUN/HUL]
Lyon, W. L.	[67LYO/BAI]
Madic, C.	[84BLA/MAD], [84MAD/BEG], [86THE/JOV]
Maeda, A.	[92SUZ/MAE], [93OKA/MAE]
Magette, M.	[77MAG/FUG]
Magnusson, L. B.	[49HIN/MAG], [49HIN/MAG2], [49MAG/LAC]
Magon, L.	[66CAS/MAG], [72CAS/MAG], [72CAS/MAG2]
Mahajan, M. A.	[86MAH/SAW], [93SAW/MAH]
Malinin, G. V.	[77MAL]
Malm, J. G.	[56WEI/MAL], [57MAL], [59WEI/WEA], [74OSB/FLO], [75OSB/FLO], [76FLO/OSB], [93MAL/WIL]
Mandleberg, C. J.	[56MAN/RAE], [61MAN/DAV]
Mang, M.	[89KIM/KAN2]
Mangin, J. P.	[91VIT/OLI]
Marcus, Y.	[64SHI/MAR]
Mardon, P. G.	[59EVA/MAR], [59LEE/MAR]
Markin, T. L.	[64MAR/BON], [65GAR/MAR], [66MAR/RAN]
Markov, V. K.	[64MAR/VER]
Marov, I. N.	[61MAR/CHM]
Marquart, R.	[83MAR/HOF]
Marsh, S. F.	[94VEI/SMI], [96ALL/VEI]
Marshall, W. L.	[84MAR/MES]

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Author	References
Marteau, M.	[74MUS/COU], [77CUI/MUS], [77MUS/MAR], [78MUS/MAR], [78MUS/MAR2]
Martell, E. A.	[64SIL/MAR], [71SIL/MAR]
Martin, D. J.	[78HAL/LEE]
Martin, P. E.	[58MAR/WHI]
Martinot, L.	[85MAR/FUG]
Martinsen, K.-G.	[95HAA/MAR]
Marx, G.	[92BIS/KRA], [92MAR/ESS]
Mashirov, L. G.	[76VOD/KOL]
Maslennikov, A.	[94PER/DAV]
Mason, M. J.	[97FEL/RAI], [95RAI/FEL]
Masters, B. J.	[61RAB/MAS]
Mathers, W. G.	[58BRO/HAR]
Mathur, J. N.	[74KHO/MAT], [91CHO/MAT], [94MAT/CHO]
Matsui, T.	[87MAT/OHS]
Matuzenko, M. Y.	[74CHA/MAT], [75CHA/MAT]
Matyashchuk, I. V.	[73SIM/MAT]
May, H. M.	[90NOR/PLU]
Maya, L.	[83MAY], [84MAY]
Mayorga, G.	[73PIT/MAY], [74PIT/MAY]
Mazer, J. J.	[90OKA/REE]
Mazumdar, A. S. G.	[65MAZ/SIV]
McBeth, R. L.	[76GRU/MCB]
McDonald, R. A.	[85CHA/DAV]
McElroy, D.	[79HAL/HAI], [80HAI/HAL]
McKay, H. A. C.	[70AL-/WAI], [70AL-/WAI2]
McNeilly, C. E.	[64CHI/MCN]
McVey, W. H.	[51CON/MCV], [53CON/MCV]
Medvedev, V. A.	[82GLU/GUR], [89COX/WAG], [92FUG/KHO]
Mefod'eva, M. P.	[65MOS/MEF], [67GEL/MOS], [68KRO/MEF], [70KRO/GEL], [72MEF/KRO], [72MEF/KRO2], [74MEF/KRO]
Meinrath, G.	[91MEI], [92RUN/MEI], [94MEI]
Mendelssohn, K.	[70LEE/MEN]
Men'shikova, T. S.	[58BOC/KON]
Merinis, J.	[79JOU/LEG]
Merli, L.	[94MER/FUG]
Mesmer, R. E.	[76BAE/MES], [84MAR/MES], [91AND/CAS]
Messier, D. R.	[68MES]
Metivier, H.	[69MET/GUI], [72MET/GUI], [73MET], [76MET/GUI]
Meyer, N. J.	[62BAE/MEY]
Miedema, A. R.	[76MIE]
Milanov, M.	[87RÖS/MIL], [89RÖS/DIT]
Millero, F. J.	[79MIL], [92MIL]
Mills, I.	[88MIL/CVI]
Miner, W. N.	[68ELL/MIN]
Mitchell, M. L.	[78WOO/MIT]

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Author	References
Moeller, T.	[45MOE/KRE]
Monnin, C.	[90MON]
Moore, D. A.	[80RAI/SER], [95RAI/FEL], [98RAI/FEL], [99RAI/HES], [99RAI/HES2]
Morgan, J. J.	[81STU/MOR]
Morgenstern, A.	[96MOR/KIM]
Moriyama, H.	[88NAK/ARI], [89MOR/PRA], [89PRA/MOR], [90PRA/MOR], [91PRA/YAM], [91YAM/PRA], [93PRA/MOR], [93PRA/YAM], [95MOR/PRA]
Morris, D. E.	[94CLA/EKB]
Morse, J. W.	[86CHO/ROB]
Morss, L. R.	[71MOR], [82MOR/FUG], [83MOR/WIL], [85GEN/FUG], [86MOR], [89MOR/ELL], [89SCH/GEN], [93MAL/WIL]
Mortimer, M. J.	[76GOR/HAL], [78HAL/LEE], [79HAL/HAI], [80HAI/HAL], [85HAL/JEF], [86HAL/JEF], [88BLA/HAL], [90HAL/JEF], [90HAL/MOR]
Moser, J. B.	[66KRU/MOS], [67KRU/MOS], [68MOS/KRU]
Moskvin, A. I.	[58MOS/GEL], [60DEN/MOS], [60DEN/MOS2], [62GEL/MOS], [62MOS/ZAI], [63MOS/GÉL], [64MOS/PER], [65DEN/SHE], [65MOS/MEF], [67GEL/MOS], [67MOS/ESS], [69MOS], [70MOS], [71MOS], [71MOS2], [71MOS3], [71MOS4], [73KHA/MOS], [75MOS], [78MOS/POZ], [79MOS/POZ]
Mrochek, J.	[65DAV/LAW]
Mueller, M. H.	[79MUE/LAN]
Mulac, W. A.	[83SCH/GOR], [84MUL/GOR]
Mulak, J.	[82WES/MUL]
Mulford, R. N. R.	[58HOL/MUL], [64EIC/MUL], [64OLS/MUL], [65MUL/ELL], [66MUL], [66OLS/MUL]
Muller, A. B.	[85MUL], [92GRE/FUG]
Munoz, J. L.	[86NOR/MUN]
Muñoz, M.	[86BRU/GRE]
Murav'eva, L. P.	[72BAR/MUR], [73BAR/MUR]
Murray, J. W.	[85SAN/MUR]
Musante, Y.	[73MUS/POR], [75MUS]
Musikas, C.	[63MUS], [68SON/MUS], [74MUS/COU], [77CUI/MUS], [77MUS/MAR], [78MUS], [78MUS/MAR], [83MUS/CUI]
Musikas, G.	[78MUS/MAR2]
Myers, C. E.	[77MYE/GRA]
Nagasaki, S.	[88NAG/TAN], [89TAN/NAG]
Nair, G. M.	[67NAI/RAO], [82NAI/CHA]
Nakajima, K.	[97NAK/ARA], [97NAK/ARA2]
Nakayama, S.	[88NAK/ARI], [92ITA/NAK], [96NAK/YAM]
Nash, K. L.	[83NAS/CLE], [83NAS/CLE2], [84NAS/CLE], [85THO/NAS]
Naumov, G. B.	[72NIK/SER]
Navratil, J. D.	[92FUG/KHO]
Nazarov, V. K.	[66SHI/NAZ]
Ndalamba, P.	[93ERI/NDA]

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Author	References
Nebel, D.	[62SCH/NEB]
Neck, V.	[91KIM/KLE], [92NEC/KIM], [94NEC/KIM], [94NEC/RUN], [95FAN/NEC], [95NEC/FAN], [95NEC/RUN], [96FAN/NEC], [97NEC/FAN], [99NEC/FAN]
Néher-Neumann, E.	[85FER/GRE]
Nelson, D. M.	[86ORL/PEN]
Nelson, F.	[48KRA/NEL], [48KRA/NEL2], [50KRA/NEL]
Neu, M. P.	[94NEU/HOF], [95CLA/HOB], [96CLA/CON], [96CLA/CON2], [96RUN/NEU]
Neumann, F. K.	[49ZEB/NEU]
Newton, T. W.	[57NEW/BAK], [75NEW], [85NEW/SUL], [94HOB/PAL]
Nguyen-Trung, C.	[89HOV/NGU], [92GRE/FUG], [95PAL/NGU]
Nichkov, I. F.	[69LEB/BAB], [84LEB/KOB]
Nigon, J. P.	[54NIG/PEN]
Nikitin, A. A.	[72NIK/SER]
Nikol'ski, V. D.	[59KRE/NIK], [59KRE/NIK2]
Nikonov, M. V.	[94NIK/BES]
Nitani, N.	[96KAT/KIM]
Nitsche, H.	[87BEN/HOF], [87NIT], [88TUC/STA], [90NIT/STA], [91NIT], [92BEN/HOF], [94NEU/HOF], [94SIL/NIT], [96NIT/SIL], [97NIT/SIL]
Nordstrom, D. K.	[86NOR/MUN], [90NOR/PLU]
Norén, B.	[60GRE/NOR]
Novak, C. F.	[95NOV/ROB], [96ROB/SIL]
Novotný, P.	[85SÖH/NOV]
Nuttall, R. L.	[82WAG/EVA]
O'Boyle, D. R.	[68ELL/MIN]
O'Connor, P.	[44O'C]
O'Hare, P. A. G.	[88TAS/O'H]
Oelkers, E. H.	[90OEL/HEL], [92SHO/OEL]
Oetting, F. L.	[72OET/LEI], [76FUG/OET], [76OET/RAN], [78OET], [80OET], [82OET], [83FUG/PAR], [83OET/ADA]
Offerlé, S.	[95OFF/CAP]
Ogard, A. E.	[70OGA]
Ogden, J. S.	[75ALE/OGD]
Ohmichi, T.	[92SUZ/MAE], [95ARA/OHM]
Ohnuki, T.	[94YAM/SAK]
Ohse, R. W.	[68OHS/CIA], [79BRA/OHS], [87MAT/OHS]
Okajima, S.	[90OKA/REE], [91OKA/REE], [93OKA/REE], [93WEG/OKA]
Okamoto, Y.	[93OKA/MAE], [94ARA/OKA]
Oliver, J.	[91VIT/OLI]
Oliver, J. H.	[83HAL/OLI]
Olson, W. M.	[64OLS/MUL], [66OLS/MUL]
Orlandini, F.	[66DAN/ORL], [70CAS/ORL]
Orlandini, K. A.	[86ORL/PEN]

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Author	References
Osborne, D. W.	[53WES/HAT], [70OSB/WEI], [74OSB/FLO], [75OSB/FLO], [76FLO/OSB]
Osthols, E.	[94OST/BRU]
Ouweltjes, W.	[90COR/KON]
Pages, M.	[86BEN/DAB], [90DAB/BEN]
Palmer, C. E. A.	[92BEN/HOF]
Palmer, D. A.	[95PAL/NGU]
Palmer, P. D.	[94CLA/EKB], [94HOB/PAL], [96CLA/CON], [96CLA/CON2], [98CLA/CON]
Pan, P.	[95PAN/CAM], [96LEM/CAM2], [96PAN], [98PAN/CAM]
Paquette, J.	[81PAQ/LEM]
Parker, V. B.	[65PAR], [76PAR], [82WAG/EVA], [83FUG/PAR], [84BUS/PLU], [87GAR/PAR], [95PAR/KHO]
Parkhurst, D. L.	[80PAR/THO], [90NOR/PLU]
Parsons, R.	[74PAR]
Pascard, R.	[64ANS/DEA]
Pashalidis, I.	[91KIM/PAS], [93PAS/KIM], [93PAS/KIM2], [93PAS/RUN], [95PAS/KIM], [97PAS/CZE]
Patil, S. K.	[64LAX/PAT], [72PAT], [73PAT/RAM], [73PAT/RAM2], [75PAT/RAM], [75RAG/RAM], [76BAG/RAM], [76BAG/RAM2], [76PAT/RAM], [77BAG/RAM], [78PAT/RAM], [78RAO/BAG], [78RAO/BAG2], [78RAO/PAT], [79CHI/TAL], [79KUS/GAN], [79RAO/GUD], [81PAT/RAM], [84KAS/JOS], [85SAW/CHA], [85SAW/RIZ], [86MAH/SAW], [90SAW/CHA2], [93SAW/MAH]
Paul, A. D.	[61PAU/GAL]
Paul, M. T.	[70PAU]
Pavone, D.	[71FIT/PAV]
Pazukhin, E. M.	[90PAZ/KUD]
Pearce, J. H.	[59LEE/MAR]
Pearson, J. M.	[74FAR/PEA]
Peekema, R. M.	[58STR/PEE]
Penneman, R. A.	[54NIG/PEN]
Penrose, W. R.	[86ORL/PEN]
Peretrukhin, V. F.	[64MOS/PER], [72PER/KRO], [74PER/ALE], [77ERM/PER], [79FED/PER], [82PER/SPI], [94PER/DAV], [95PER/SHI]
Perez-Bustamante, J. A.	[65PER]
Perminov, V. P.	[94NIK/BES]
Pershin, A. S.	[84PER/SAP]
Peterson, D. E.	[86WAR/KLE]
Peterson, J. R.	[78PIT/PET], [83BOU/GUI], [84VAR/HOB]
Phipps, T. E.	[50PHI/SEA], [56PHI/SEA]
Pikaev, A. K.	[95PER/SHI]
Pitzer, K. S.	[73PIT], [73PIT/MAY], [74PIT/KIM], [74PIT/MAY], [75PIT], [76PIT/SIL], [78PIT/PET], [79BRA/PIT], [79PIT]
Plummer, L. N.	[80PAR/THO], [84BUS/PLU], [90NOR/PLU]
Plyasunov, A.	[97GRE/PLY]
Plyasunov, A. V.	[97PUI/RAR]

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Author	References
Popov, M. M.	[57POP/IVA], [59POP/GAL]
Portanova, R.	[72CAS/MAG], [72CAS/MAG2]
Porthault, M.	[73MUS/POR]
Porto, R.	[87CIA/TUL]
Posokhov, A. K.	[91POS/ROV]
Potemkina, T. I.	[89BUD/FED]
Potter, P. E.	[80POT/SPE], [90COR/KON2]
Pozharskii, B. G.	[59KRE/NIK], [59KRE/NIK2], [60LIP/POZ], [64POZ/FED]
Poznyakov, A. N.	[78MOS/POZ], [79MOS/POZ]
Pratopo, M. I.	[89MOR/PRA], [89PRA/MOR], [90PRA/MOR], [91PRA/YAM], [91YAM/PRA], [93PRA], [93PRA/MOR], [93PRA/YAM], [95MOR/PRA]
Prins, G.	[90COR/KON2]
Prussin, T.	[96ROB/SIL]
Pryke, D. C.	[86PRY/REE]
Puigdomènech, I.	[95GRE/PUI], [95SIL/BID], [97PUI/RAR], [98SPA/PUI]
Pushlenkov, M. F.	[68KRY/KOM], [68KRY/KOM2], [69KRY/KOM3], [69KRY/KOM4]
Pytkowicz, R. M.	[79JOH/PYT], [79PYT]
Rabideau, S. W.	[51RAB/LEM], [53RAB], [55RAB/COW], [56RAB], [57RAB], [60RAB/KLI], [61RAB/MAS]
Rabinowitch, E.	[51KAT/RAB]
Rae, H. K.	[56MAN/RAE]
Raghavan, R.	[75RAG/RAM]
Rai, D.	[80RAI/SER], [80RAI/SER2], [81RAI/SWA], [82RAI/RYA], [84RAI], [85KRU/RAI], [85RAI/RYA], [87RAI/SWA], [87RYA/RAI], [89FEL/RAI], [90RAI/FEL], [92RAI/FEL], [95RAI/FEL], [97FEL/RAI], [98RAI/FEL], [99RAI/HES], [99RAI/HES2]
Ramakrishna, V. V.	[73PAT/RAM], [73PAT/RAM2], [75PAT/RAM], [75RAG/RAM], [76BAG/RAM], [76BAG/RAM2], [76PAT/RAM], [77BAG/RAM], [78PAT/RAM], [78RAO/BAG], [78RAO/BAG2], [79KUS/GAN], [81PAT/RAM]
Ramanujam, A.	[79KUS/GAN]
Rananiah, M. V.	[78PAT/RAM]
Rand, M. H.	[62RAN/FOX], [63RAN/KUB], [66MAR/RAN], [66RAN], [76OET/RAN], [80RAN], [81CHI/AKH], [84HOL/RAN], [90COR/KON2], [95GRE/PUI], [95SIL/BID], [99RAR/RAN], [2000RAN/FUG]
Randall, M.	[61LEW/RAN]
Rao, C. L.	[67NAI/RAO]
Rao, L. F.	[84CHO/RAO], [91SUL/CHO], [94RIZ/RAO]
Rao, P. R. V.	[78RAO/BAG], [78RAO/BAG2], [78RAO/PAT], [79KUS/GAN], [79RAO/GUD]
Rard, J. A.	[97PUI/RAR], [99RAR/RAN]
Raspopin, S. P.	[69LEB/BAB], [84LEB/KOB]
Rauh, E. G.	[66ACK/FAI], [75ACK/RAU]

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Author	References
Rausch, M. P.	[75ALE/OGD]
Reavis, J. G.	[59BJO/REA]
Rebizant, J.	[88BLA/HAL], [94AMA/BRA]
Reddy, J. F.	[79MUE/LAN]
Reed, D. T.	[90OKA/REE], [91OKA/REE], [93OKA/REE], [93WEG/OKA]
Reedy, G. T.	[78GRE/REE]
Rees, J. H.	[86PRY/REE]
Rees, T. F.	[84REE/DAN]
Richards, R. R.	[85SCH/FRI]
Richter, K.	[87RIC/SAR]
Riglet, C.	[86GRE/RIG], [87RIG/VIT], [89RIG/ROB], [90RIG]
Riley, B. F.	[70RIL]
Rizkalla, E. N.	[94RIZ/RAO]
Rizvi, G. H.	[85SAW/CHA], [85SAW/RIZ]
Robbins, J. L.	[76ALE/CLA]
Roberts, K. E.	[94NEU/HOF], [95NOV/ROB], [96ROB/SIL]
Roberts, L. E. J.	[63ROB/WAL]
Roberts, M. M.	[82ALC/ROB]
Roberts, R. A.	[86CHO/ROB]
Robinson, H. P.	[49ROB], [49ROB/WES], [49WES/ROB]
Robinson, R. A.	[51ROB/LIM], [59ROB/STO]
Robouch, P.	[86GRE/ROB], [87ROB/VIT], [89BRU/GRE], [89RIG/ROB], [89ROB]
Robouch, P. B.	[95SIL/BID]
Rolon, C. E.	[81ROL/GAL]
Rossotti, H.	[69ROS]
Roulet, G.	[71ROU]
Rovnyi, S. I.	[91POS/ROV]
Rudolph, G.	[95NEC/FAN]
Rukov, A. G.	[81VOL/VIS], [81VOL/VIS2]
Runde, W.	[92RUN/MEI], [93PAS/RUN], [94NEC/RUN], [94RUN/KIM], [95NEC/RUN], [96CLA/CON2], [96RUN/NEU]
Russo, R. E.	[92BEN/HOF]
Ryan, J. L.	[82RAI/RYA], [85RAI/RYA], [87RAI/SWA], [87RYA/RAI], [89FEL/RAI], [90RAI/FEL]
Rykov, A. G.	[66RYK/YAK], [71RYK/BLO], [73RYK/BLO], [76FRO/CHI], [76FRO/CHI2], [79VOL/VIS], [79VOL/VIS2], [81VOL/VIS3], [81VOL/VIS4]
Ryukov, A. G.	[75VAS/AND], [75VAS/AND2]
Rösch, F.	[87RÖS/MIL], [89RÖS/DIT], [90RÖS/HUN]
Sabau, C. A.	[90OKA/REE], [91OKA/REE]
Saito, A.	[75UEN/SAI], [77SAI/UEN], [78SAI/UEN]
Sakamoto, Y.	[94YAM/SAK]
Saltelli, A.	[79SAL/AVO]
Saluja, P. P. S.	[93LEM/CAM]
Salvatore, F.	[81CIA/FER], [83FER/GRE], [85FER/GRE]

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Author	References
Sanchez, A. L.	[85SAN/MUR]
Sandenaw, T. A.	[65SAN], [73SAN/GIB]
Sandino, M. C. A.	[95GRE/PUJ]
Sapozhnikova, T. V.	[84PER/SAP]
Sari, C.	[68SAR/BEN], [87RIC/SAR]
Sasayama, T.	[83SUZ/ARA]
Savage, D. J.	[74SAV]
Savage, H.	[68KRU/SAV]
Sawant, R. M.	[85SAW/CHA], [85SAW/RIZ], [86MAH/SAW], [89SAW/CHA], [90SAW/CHA], [90SAW/CHA2], [93SAW/MAH]
Scatchard, G.	[36SCA], [76SCA]
Schedin, U.	[71SCH], [75SCH]
Schlehman, G. J.	[66ATL/SCH]
Schlyter, K.	[68ARN/SCH]
Schmidt, K. H.	[80SCH/GOR], [83SCH/GOR], [84MUL/GOR]
Schoebrechts, J. P.	[89SCH/GEN]
Schomaker, V.	[68KIM/SCH]
Schonfeld, F. W.	[61SCH], [68ELL/MIN]
Schott, J.	[91AND/CAS]
Schramke, J. A.	[89FEL/RAI]
Schreiner, F.	[69FRI/SCH], [85SCH/FRI], [86ULL/SCH], [88ULL/SCH]
Schumm, R. H.	[82WAG/EVA]
Schwabe, K.	[62SCH/NEB]
Scibona, G.	[66DAN/ORL], [71DAN/CHI], [74DAN/CHI]
Scott, B. L.	[98CLA/CON]
Scott, F. A.	[58STR/PEE]
Seaborg, G. T.	[57KAT/SEA], [86WEI/KAT]
Sears, G. W.	[50PHI/SEA], [56PHI/SEA]
Seifert, R. L.	[50PHI/SEA], [56PHI/SEA]
Sekine, K.	[96NAK/YAM]
Sekine, T.	[91KIM/KLE]
Selig, H.	[70COH/FRI]
Senin, M. D.	[59POP/GAL]
Serebrennikov, V. V.	[66FRO/KUM]
Sergeyeva, E. I.	[72NIK/SER], [92FUG/KHO]
Serik, V. F.	[75DRO/SER], [78DRO/SER]
Serne, R. J.	[80RAI/SER], [80RAI/SER2]
Sevost'yanova, E. P.	[76SEV/KHA]
Shabana, R.	[76SOU/SHA]
Shannon, R. D.	[76SHA]
Sharma, H. D.	[64LAX/PAT]
Shcherbakov, V. A.	[75IOR/SHC]
Sheft, I.	[49HAG/ABR], [49SHE/DAV], [49SHE/DAV2]
Sherief, M. K.	[71SHE/GRA]
Shevchenko, V. B.	[59SHE/TIM], [60DEN/MOS], [60DEN/MOS2], [64POZ/FED], [65DEN/SHE], [67DEN/SHE], [67DEN/SHE2]

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Author	References
Shilin, I. V.	[66SHI/NAZ]
Shiloh, M.	[64SHI/MAR]
Shilov, V. P.	[76SHI/STE], [91SHI/TAN], [95PER/SHI]
Shin, C.	[79SHI/CR1]
Shinn, W. A.	[61TRE/SHI]
Shirley, V. S.	[79SHI/LED]
Shock, E. L.	[88SHO/HEL], [89SHO/HEL], [89SHO/HEL2], [92SHO/OEL]
Sibley, T. H.	[85SAN/MUR]
Siekierski, S.	[83SOK/SIE], [87FUK/SIE]
Silber, H. B.	[94SIL/NIT], [96ROB/SIL]
Sillén, L. G.	[64SIL/MAR], [71SIL/MAR]
Silva, R. J.	[87BEN/HOF], [88TUC/STA], [90NIT/STA], [92BEN/HOF], [94NEU/HOF], [95SIL/BID], [96NIT/SIL], [97NIT/SIL]
Silver, G. L.	[83SIL]
Silvester, L. F.	[76PIT/SIL], [78PIT/PET]
Simakin, G. A.	[73SIM/MAT], [74SIM/VOL], [74VIS/VOL], [75SIM], [76VOL/VIS], [77SIM]
Simpson, O. C.	[50PHI/SEA], [56PHI/SEA]
Sivaramakrishnan, C. K.	[65MAZ/SIV]
Skavdahl, R. E.	[64CHI/MCN]
Skiba, O. V.	[69LEB/BAB], [84LEB/KOB]
Sles, V. G.	[76VOD/KOL]
Smirnov, N. L.	[75BEL/IL'], [79BEL/SMI]
Smith, C. A.	[94VEI/SMI], [96ALL/VEI]
Smith, D. W.	[68KIM/SCH]
Smith, P. N.	[73JOH/SMI]
Smith-Briggs, J. L.	[92EWA/SMI]
Soderholm, L.	[93MAL/WIL]
Sokolov, V. B.	[75DRO/SER], [78DRO/SER]
Sokolowska, A.	[83SOK/SIE]
Solntsev, V. M.	[73SUD/SOL]
Solovkin, A. S.	[67SOL/TSV], [74SOL], [80SOL/ZAK]
Sontag, R.	[68SON/MUS]
Souka, N.	[76SOU/SHA]
Spahiu, K.	[83SPA], [93ERI/NDA], [98SPA/PUI]
Spear, K. E.	[68SPE/LEI], [80POT/SPE]
Spencer, P. J.	[93KUB/ALC]
Spirlet, J. C.	[86HAL/JEF], [88BLA/HAL], [90DAB/BEN], [90HAL/MOR], [94AMA/BRA], [86BEN/DAB], [90HAL/JEF]
Spiryakov, V. I.	[79VOL/VIS2]
Spitsyn, V. I.	[82PER/SPI]
Stakebake, J. L.	[93STA/LAR]
Standifer, E. M.	[88TUC/STA], [90NIT/STA]
Staritzky, E.	[54NIG/PEN], [56STA]
Stary, A. E.	[67ERM/STA]
Steindler, M. J.	[61JOH/FIS], [68TRE/GER]

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Table 23.1: (continued)

Author	References
Stepanova, E. S.	[76SHI/STE]
Stephens, D. R.	[66STE]
Sterner, S. R.	[97FEL/RAI]
Steunenberg, R. K.	[61TRE/SHI]
Stokes, R. H.	[59ROB/STO]
Storms, E. K.	[84HOL/RAN]
Stoughton, R. W.	[61STO/FRY]
Street, R. S.	[62RAN/FOX], [65GAR/MAR]
Strickert, R. G.	[85KRU/RAI]
Stromatt, R. W.	[58STR/PEE]
Struchkov, Y. T.	[94GRI/CHA]
Stumm, W.	[81STU/MOR]
Sturtevant, J. M.	[59STU]
Sudakov, L. V.	[73SUD/SOL]
Suglobov, D. N.	[76VOD/KOL]
Sullivan, J.	[54SUL/AME]
Sullivan, J. C.	[54SUL/HIN], [55COH/SUL], [59SUL/HIN], [61SUL/HIN], [69SUL/ZIE], [78WOO/MIT], [80SCH/GOR], [81WES/SUL], [82SUL/WOO], [83SCH/GOR], [83WES/SUL], [84MUL/GOR], [85NEW/SUL], [85SCH/FRI], [85THO/NAS], [91SUL/CHO], [93PAS/KIM], [93PAS/KIM2], [94RIZ/RAO]
Sutcliffe, P. W.	[70LEE/MEN], [78HAL/LEE]
Suzuki, Y.	[83SUZ/ARA], [92SUZ/MAE], [93OKA/MAE], [94ARA/OKA], [97NAK/ARA], [97NAK/ARA2]
Sverjensky, D. A.	[89SHO/HEL2], [92SHO/OEL]
Swang, O.	[95HAA/MAR]
Swanson, J. L.	[80RAI/SER2], [81RAI/SWA], [87RAI/SWA]
Swendeman, N.	[59DEB/LIC]
Sykes, K. W.	[62SYK/TAY], [64GAI/SYK]
Sylva, R. N.	[83BRO/ELL]
Syverud, A. N.	[85CHA/DAV]
Söhnel, O.	[85SÖH/NOV]
Tran The, P.	[91VIT/TRA]
Tait, D. C.	[96CLA/CON], [96CLA/CON2]
Takahashi, Y.	[88NAG/TAN]
Talnikar, S. G.	[79CHI/TAL]
Tanaka, S.	[88NAG/TAN], [89TAN/NAG], [91ITA/TAN], [92ITA/NAK]
Tananaev, I. G.	[89TAN], [90TAN], [91SHI/TAN], [94TAN]
Tanet, G.	[85BID/TAN]
Tanger, IV, J. C.	[88TAN/HEL]
Tannenbaum, I. R.	[56FLO/TAN]
Taranov, A. P.	[79BEL/SMI]
Tasker, I. R.	[88TAS/O'H]
Taylor, B. L.	[62SYK/TAY]
Taylor, J. R.	[82TAY]
Taylor, P.	[93TAY/LEM]

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Table 23.1: (continued)

Author	References
Teague, L. S.	[80BEN/TEA]
Tennery, V. J.	[71TEN/BOM]
Tetenbaum, M.	[81FLO/TET], [83TET]
Thevenin, T.	[86THE/JOV]
Thomason, H. P.	[86EWA/HOW], [92EWA/SMI]
Thompson, M. C.	[83SCH/GOR]
Thompson, M. E.	[85THO/NAS]
Thompson, R. C.	[80SCH/GOR]
Thorn, R. J.	[66ACK/FAI]
Thorstenson, D. C.	[80PAR/THO]
Timoshev, V. G.	[59SHE/TIM]
Tochiyama, O.	[85INO/TOC], [85INO/TOC2]
Tolmachev, Y. M.	[75BEL/IL']
Tomat, G.	[72CAS/MAG2]
Tomilin, S. V.	[79VOL/TOM], [79VOL/VIS], [79VOL/VIS2], [81VOL/VIS], [81VOL/VIS2], [81VOL/VIS3], [81VOL/VIS4]
Tondello, E.	[72CAS/MAG]
Torres, R. A.	[92BEN/HOF]
Torretto, P. C.	[96ROB/SIL]
Trabalka, J. R.	[80BON/TRA]
Trautmann, N.	[89KIM/KAN2]
Treiber, W.	[85LIE/TRE]
Tremaine, P. R.	[80LEM/TRE], [89HOV/NGU]
Trevorow, L. E.	[61TRE/SHI], [68TRE/GER]
Truswell, A. E.	[54DAW/ELL]
Tsvetkova, Z. N.	[67SOL/TSV]
Tucker, D. B.	[88TUC/STA]
Tul'skii, M. N.	[78DRO/SER]
Turcotte, R. P.	[76FAH/TUR]
Ueno, K.	[70UEN/HOS], [75UEN/SAI], [77SAI/UEN], [78SAI/UEN]
Ueta, S.	[95YAJ/KAW]
Ullman, W. J.	[86ULL/SCH], [88ULL/SCH]
Unrein, P. J.	[76CHO/UNR]
Ustinov, V. A.	[74ARK/GUT], [79BEL/DOB]
VanCamp, J. B.	[61PAU/GAL]
Varlashkin, P. G.	[84VAR/BEG], [84VAR/HOB]
Vasil'ev, V. P.	[62VAS]
Vasil'ev, V. Y.	[73RYK/BLO], [75VAS/AND], [75VAS/AND2]
Vaughn, G. A.	[70WIT/VAU]
Vavilov, S. K.	[69LEB/BAB]
Veirs, D. K.	[94VEI/SMI], [96ALL/VEI]
Veits, I. V.	[82GLU/GUR]
Vernyi, E. A.	[64MAR/VER]
Vinogradov, A. V.	[64MAR/VER]

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Table 23.1: (continued)

Author	References
Visyashcheva, G. I.	[74SIM/VOL], [74VIS/VOL], [74VOL/KAP], [74VOL/KAP2], [76VOL/VIS], [77VOL/VIS], [79VOL/TOM], [79VOL/VIS], [79VOL/VIS2], [81VOL/VIS], [81VOL/VIS2], [81VOL/VIS3], [81VOL/VIS4]
Vitorge, P.	[84VIT], [86GRE/RIG], [86GRE/ROB], [87RIG/VIT], [87ROB/VIT], [89RIG/ROB], [90CAP/VIT], [91VIT/OLI], [91VIT/TRA], [92CAP/VIT], [93GIF/VIT], [93GIF/VIT2], [94CAP/VIT], [94GIF/VIT], [95CAP/VIT], [95OFF/CAP], [95VIT], [96CAP/VIT], [96DEL/VIT], [97CAP/VIT], [98CAP/VIT], [98VIT/CAP], [99RAI/HES2]
Vladimirova, N. A.	[73SIM/MAT]
Vodovatov, V. A.	[76VOD/KOL]
Volden, H. V.	[95HAA/MAR]
Voliotis, S.	[73DER/FAU3]
Volkov, Y. F.	[74SIM/VOL], [74VIS/VOL], [74VOL/KAP], [74VOL/KAP2], [76VOL/VIS], [77VOL/VIS], [79VOL/TOM], [79VOL/VIS], [79VOL/VIS2], [81VOL/VIS], [81VOL/VIS2], [81VOL/VIS3], [81VOL/VIS4]
Volkov, Y. V.	[84VOL/KAP]
Volkova, A. A.	[59SHE/TIM]
Webster Keogh, D.	[98CLA/CON]
Wagman, D. D.	[73HUL/DES], [82WAG/EVA], [89COX/WAG]
Wain, A. G.	[66WAI], [70AL-/WAI], [70AL-/WAI2]
Wallmann, J. C.	[51WES/WAL]
Walsh, K. A.	[59BJO/REA]
Walter, A. J.	[63ROB/WAL], [64COH/WAL]
Wang, P.	[90ARC/WAN]
Wanner, H.	[87BRO/WAN], [88WAN], [91WAN], [92GRE/FUG], [92GRE/WAN], [95SIL/BID], [99RAR/RAN], [99WAN], [99WAN/ÖST], [2000GRE/WAN], [2000ÖST/WAN], [2000WAN/ÖST]
Ward, J. W.	[86KLE/WAR], [86WAR/KLE]
Ward, M.	[56WAR/WEL]
Weaver, E. E.	[59WEI/WEA]
Weger, H. T.	[93WEG/OKA]
Weigel, F.	[77WEI/WIS], [82WEI/WIS], [83MAR/HOF], [86WEI/HEL], [86WEI/KAT]
Weinstock, B.	[56WEI/MAL], [59WEI/WEA], [68KIM/SCH], [70OSB/WEI]
Weinstock, G.	[65WEI/GOO]
Welch, G. A.	[56DRU/WEL], [56WAR/WEL], [67NAI/RAO]
Wester, D.	[84MUL/GOR]
Wester, D. W.	[81WES/SUL], [82WES/MUL], [83WES/SUL]
Westrum, Jr., E. F.	[49ROB/WES], [49WES], [49WES/EYR], [49WES/ROB], [50EYR/WES], [51WES/EYR], [51WES/WAL], [53WES/HAT], [62GRØ/WES], [62WES/GRØ]
Whiffen, D. H. (chairman)	[79WHI]
White, A. G.	[58MAR/WHI]
White, Jr., H. J.	[87GAR/PAR]

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Table 23.1: (continued)

Author	References
Whitfield, M.	[79WHI2]
Whittaker, B.	[82BRO/WHI]
Williams, C. W.	[83MOR/WIL], [85GEN/FUG], [93MAL/WIL]
Williams, S. J.	[85EWA/GOR], [86EWA/HOW], [92EWA/SMI]
Williamson, M. A.	[93WIL/KLE]
Wishnevsky, V.	[77WEI/WIS], [82WEI/WIS]
Wittenberg, L. J.	[70WIT/VAU]
Wolf, M. J.	[49ABR/BRO]
Wood, D. D.	[93TAY/LEM]
Woodley, R. E.	[81WOO]
Woods, M.	[78WOO/MIT], [82SUL/WOO]
Wriedt, H. A.	[89WRI]
Wyart, J.-F.	[92BLA/WYA]
Xi, R. H.	[92BIS/KRA], [92MAR/ESS]
Yajima, T.	[95YAJ/KAW]
Yakovlev, G. N.	[66RYK/YAK], [74SIM/VOL], [74VIS/VOL], [74VOL/KAP], [74VOL/KAP2], [76VOL/VIS]
Yamada, N.	[88NAK/ARI]
Yamaguchi, T.	[91PRA/YAM], [91YAM/PRA], [93PRA/YAM], [94YAM/SAK], [96NAK/YAM]
Yamawaki, M.	[89TAN/NAG], [91ITA/TAN], [92ITA/NAK], [97NAK/ARA2]
Yanovskii, A. I.	[94GRI/CHA]
Yeh, S.	[80BAL/YEH]
Yoshida, Z.	[93LI/KAT], [96KAT/KIM]
Yui, M.	[98RAI/FEL], [99RAI/HES], [99RAI/HES2]
Yungman, V. S.	[82GLU/GUR], [85HIL/GUR]
Zachariassen, W. H.	[52ZAC], [63ZAC/ELL]
Zaitsev, L. M.	[58GEL/ZAI], [58GEL/ZAI2], [59GEL/ZAI], [67GEL/MOS]
Zaitseva, V. P.	[62GEL/MOS], [62MOS/ZAI], [64GEL/ZAI], [68ZAI/ALE], [68ZAI/ALE2]
Zakharenkov, V. F.	[84PER/SAP]
Zakharov, Y. N.	[80SOL/ZAK]
Zastenker, Y. Y.	[59KRE/NIK], [59KRE/NIK2]
Zebroski, E. L.	[49ZEB/NEU], [51ZEB/ALT]
Zenkova, R. A.	[66GOR/ZEN]
Zielen, A. J.	[59ZIE], [61SUL/HIN], [69SUL/ZIE], [70ZIE/COH]
Zwick, B. D.	[94VEI/SMI]
deBruin, H. J.	[65DAV/LAW]
Östho, E.	[99WAN/ÖST], [2000GRE/WAN], [2000ÖST/WAN], [2000WAN/ÖST]

Part V

Appendices

Appendix A

Discussion of selected references

This appendix is comprised of discussions relating to a number of key publications which contain experimental information cited in this review. These discussions are fundamental in explaining the accuracy of the data concerned and the interpretation of the experiments, but they are too lengthy or are related to too many different sections to be included in the main text. The notation used in this appendix is consistent with that used in the present book, and not necessarily consistent with that used in the publication under discussion.

[44O'C]

This is a preliminary study. The results on Pu(VI) hydrolysis agree qualitatively with later potentiometric and spectroscopic studies. Although Schedin [75SCH] cited a value of $\log_{10}^*\beta_1 = 5.3$ from this report, no hydrolysis constants calculated by O'Connor could be found in [44O'C].

[45DAM/KRA]

See entries for [46KRA/DAM2] and [49KRA/DAM3].

[46KRA/DAM]

This report, describing a potentiometric study of the hydrolysis of Pu(V), is the same as [49KRA/DAM] except for minor editorial changes.

[46KRA/DAM2]

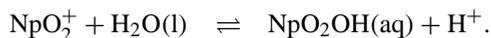
This report was not available for review. It is probably the same as another unavailable 1945 report CL-P-427 [45DAM/KRA] by the same authors and essentially the same work as described in [49KRA/DAM3]; it is likely the first report on actinide(III) hydrolysis. It has not been available to the reviewer, but a reference states that the first hydrolysis constant $^*\beta_1$ of Pu(III) obtained from potentiometric titration is 7.5×10^{-8} . Thus $-\log_{10}^*\beta_1 = 7.12$.

[48KRA/NEL]**a) Neptunium**

The discussion on neptunium(V) hydrolysis and the solubility of $\text{NpO}_2\text{OH}(\text{am})$ used the same experimental data as [56KRA], and the same values for $\log_{10} K_{s,0}$ and $\log_{10} \beta_1$ were reported. The values from this report have been incorrectly cited elsewhere [85LIE/TRE, 88NAK/ARI].

Values for $\log_{10} K_{s,0}$ are reported for 15 different solutions. The solubilities for $\text{NpO}_2\text{OH}(\text{s})$ were back calculated from values for $\log_{10} K_{s,0}$ in Table 3 (see also [56KRA]). It was assumed that Debye-Hückel values had been used to estimate the activity coefficients. There are no details provided as to the temperature of the measurements (assumed in this review to have been 25°C) or electrode calibration. The reported values apparently are for freshly precipitated solids, and are likely to be greater than the solubilities for aged material. Considering the lack of detail, solubility product values based on this work are in reasonable agreement with later work [76SEV/KHA, 85LIE/TRE, 88TUC/STA].

The sparse titration measurements described in the report were analysed by assuming the only hydrolysis reaction is



$\text{Np}(\text{V})$ was titrated with NaOH and back titrated in a carbon dioxide free atmosphere. It is not clear how the electrodes were calibrated in the rather low (constant) ionic strength medium, and the hydrolysis constants reported are probably mixed constants. Insufficient details are available to re-evaluate the data.

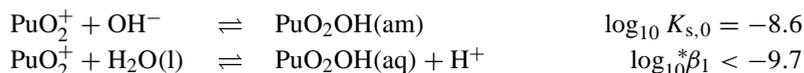
When $[\text{Np}]_{\text{total}} = 0.32$ or 0.89 mM, the pH was buffered at around $\text{pH} = 8.8$, while for $[\text{Np}]_{\text{total}} = 2.0$ and 9.0 mM, the solution was buffered at lower pH values, $\text{pH} = 8.0$ and 7.3 respectively. The titration curves show a distinct break for a neptunium to hydroxide ratio of 1:1 only for the experiment at the highest $[\text{Np}]_{\text{total}}$. As the pH buffering during the titrations appears to be primarily the result of precipitation of the solid, it is unlikely the derived values for the first hydrolysis constant are accurate. The titration curves may have been influenced by local precipitation, even below pH values of 9.

b) Plutonium

The results on plutonium(V) hydrolysis are based on data in [46KRA/DAM], used also in [49KRA/DAM] and [56KRA]. However, not only are there minor inconsistencies in the lower plutonium concentrations, but values for the solubility product of $\text{PuO}_2\text{OH}(\text{am})$ are calculated even for a OH^- :Pu ratio of 0.1 for the most dilute solution. This was done despite the comments in a paper by Kraus and Dam [49KRA/DAM] that plutonium(V) hydroxide is probably at least moderately soluble, because in the more dilute solutions precipitation does not start until approximately 50 per cent of the plutonium(V) has been hydrolysed. Only the data for the precipitation of $\text{Pu}(\text{V})$ from chloride solutions (using 0.55 M KOH) were used for calculating the solubility product. The pH values for the most concentrated solution (used for calculations in Table 3) appear

to be higher than those shown on the curve in [49KRA/DAM], especially for $\text{OH}^-:\text{Pu}$ ratios near 0.5. The reported values for $\log_{10} K_{s,0}$ vary from -8.3 to -9.5 , with the values being most negative for solutions having lower initial concentrations of Pu(V) , and at low ratios of $\text{OH}^-:\text{Pu(V)}$. It is not clear how the disproportionation during the precipitation [49KRA/DAM] was addressed.

The hydrolysis constant was based on the data from a titration of an aqueous perchlorate solution of Pu(V) with 0.58 M NaOH . The following (logarithmic) values were recommended for the solubility product and the hydrolysis constant



i.e., $\log_{10}^* K_{s,0} = 5.4$, for solutions having ionic strengths between 2.60×10^{-3} and 4.43×10^{-2} , and assuming $\log_{10} K_w = -14.0$. Ionic strength effects on $^* \beta_1$ are expected to be small.

The results on plutonium(VI) hydrolysis are based on data also discussed in [49KRA/DAM2] and [56KRA].

[48KRA/NEL2]

This report is mainly a description of a spectrophotometric investigation of actinide (IV) species in 0.5 M NaCl or NaClO_4 . Little difference was found between the spectra in perchlorate medium and those for $< 0.5 \text{ M Cl}^-$. Polymerization of Pu(IV) was found to be rapid compared to depolymerization for $< 0.1 \text{ M H}^+$. A more complete analysis of these results was reported in a later paper [50KRA/NEL]. Results of titration of Pu(III) with NaOH (from Kraus and Dam [46KRA/DAM2]) are reported. In perchlorate medium ($I = 0.069 \text{ M}$) $\log_{10}^* \beta_1 = -7.1$. The titration study was later reported in detail in [49KRA/DAM3], and is discussed further in the Appendix A entry for that reference.

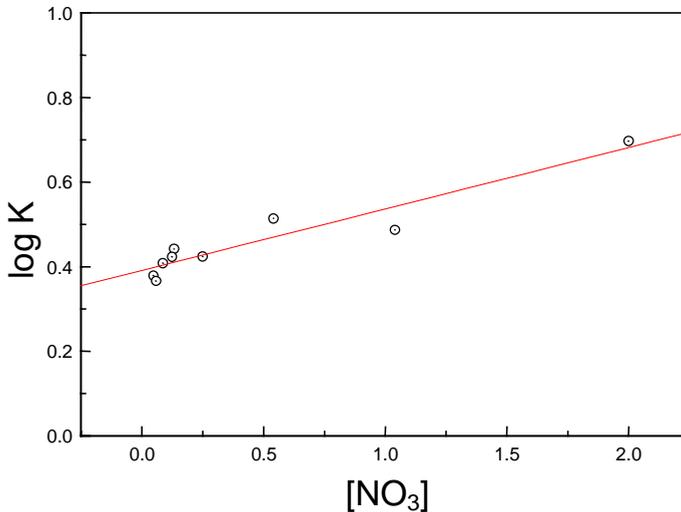
[49HIN]

This is a careful spectrophotometric study performed at 25°C and $2 \text{ M H}(\text{NO}_3, \text{ClO}_4)$. Measurements in solutions $0.5\text{--}14.6 \text{ M HNO}_3$ with variable ionic strength have also been carried out to study the higher complexes. Here the data at constant ionic strength are discussed first, while for the variable and high ionic strength data only some qualitative comments can be made. The author defines the constant:

$$K = \frac{[\text{PuNO}_3^{3+}]}{[\text{Pu}^{4+}] \cdot [\text{NO}_3^-]} = K^\circ \cdot \frac{f_{\text{Pu}^{4+}} f_{\text{NO}_3^-}}{f_{\text{PuNO}_3^{3+}}} \quad (\text{A.1})$$

where the symbol f_i represents activity coefficients in molar scale. The experimental data are then explained in terms of the formation of one complex with constant $\log K(\text{A.1}, I = 2 \text{ M}) = (0.46 \pm 0.10)$.

Figure A.1: Calculated $\log_{10} K$ for average data with the adjustment of E by the author. The line is $\log_{10} K = 0.39 + 0.145 [\text{NO}_3^-]$



Since in a spectrophotometric study the properties of the complex are measured, its existence is established. Hence the speciation proposed by the author together with the value calculated for the constant at $I = 2 \text{ M}$ are accepted in the present review. Properly, in order that the value can be converted to the molal scale and used in the standard SIT procedure (see Appendix B), the constant should be extrapolated so as to apply to trace nitrate concentrations at $I = 2 \text{ M}$ (HClO_4). For this reason the value estimated by the author using the assumption that the activity coefficients, and also the constant K (A.1, $I = 2 \text{ M}$), do not change while the medium is changed from 2 M HClO_4 to 2 M HNO_3 , is accepted. However, for this reason (and because the study was carried out at 20°C rather than 25°C) the estimated uncertainty is increased to 0.20. If an attempt is made to take account of the variation in the ionic medium at constant ionic strength using the SIT, a linear dependence of the constant on the concentration of nitrate is predicted. As can be seen from Figure A.1, this seems to be the case, and from the intercept of the line at zero nitrate, a value of $\log_{10} K(\text{A.1}, 2 \text{ M HClO}_4) = 0.39 \pm 0.1$ is estimated. The results for the mixtures ($9.1 \text{ M NH}_4\text{NO}_3 + 1 \text{ M HNO}_3$) and ($9.1 \text{ M Ca}(\text{NO}_3)_2 + 0.1 \text{ M HNO}_3$) are further complicated by the interaction of the negatively charged hexanitrate complex ion with NH_4^+ and Ca^{2+} . The results from the measurements at high ionic strength from the work of Hindman [49HIN] are unlikely to provide thermodynamic data that can be used for the purposes of the present review, and are not considered further here.

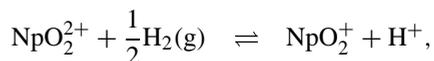
[49HIN2]

In this paper there are some data on hydrolysis of Pu(IV) from spectrophotometric measurements for 0.1 to 1.1 M HCl solutions at constant total Cl⁻ concentration (1.1 M). A value of $\log_{10} K = 1.5$ to 1.6 was found. The values are comparable to others for this system in similar media.

[49HIN/MAG2]

The authors studied the $\text{NpO}_2^{2+}/\text{NpO}_2^+$ couple by emf measurements. Potentials were measured after addition of aliquots of tin(II) chloride to a NpO_2^+ solution in 1 M HCl. The investigators believed that the reaction is reversible, but note that the precision of their measurements was affected a) by the slow reduction of Np(VI) by chloride in the presence of the platinum electrode and b) by the kinetically slow reduction of Np(VI) by Sn(II).

They reported for the reaction in 1 M HCl at 25°C,



the formal potential $E^{o'}$ = (1.14 ± 0.02) V.

Because no correction was made for the possible complexation of the metal ions by chloride, the value is not used in this review.

[49KAS]

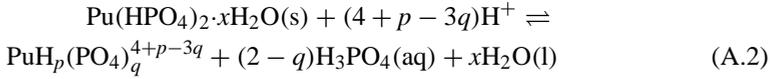
Values of 7.9×10^{-56} and 6.3×10^{-56} were reported for $\log_{10} K_{s,0}$ of plutonium(IV) hydroxide for solutions 0.0615 M in HCl and (0.0520 M HClO₄ + 0.95 M NaClO₄) respectively. Equilibrium with colloidal plutonium(IV) hydroxide (detected spectrophotometrically) was assumed, but only 6.2% and 3.0% of the plutonium solution species were Pu(IV). It was assumed (incorrectly) that no hydrolysis of the Pu(IV) had occurred.

A value of 3×10^{-56} from calculations based on the work of Kraus (as described in: Metallurgical Project Report, CN-2289, Nov. 1, 1944, p.17) was also reported.

[49KIN]

This is a careful solubility study performed at (25.00 ± 0.07)°C, at relatively high and constant concentrations of HNO₃ (0.35 M, 0.832 M and 2.08 M), while varying the phosphoric acid concentration over a wide range (0-1.2 M). The composition of the solid phase was determined chemically. A crystalline Pu(IV) phosphate was shown by X-ray analysis to be isomorphous with the corresponding Th(IV) and Ce(IV) phosphates, having the formula $\text{Pu}_2\text{H}(\text{PO}_4)_3 \cdot y\text{H}_2\text{O}(\text{s})$. Solubility measurements on this crystalline phase have shown that in solution it transforms to a more compact form of the gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s})$. Hence the solubility measurements have been performed with gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s})$ as analysed chemically. Care was taken to assure a constant ionic strength, especially at the lowest concentration of HNO₃.

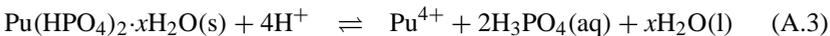
The attainment of equilibrium was tested both from undersaturation and supersaturation. The solubility data for gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s})$ have been explained as the result of formation of complexes of the general composition $\text{PuH}_p(\text{PO}_4)_q^{4+p-3q}$:



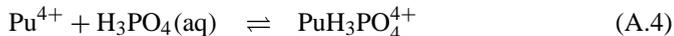
The data analysis to determine the number of phosphate groups per plutonium resulted in two possible combinations of species. Species with $q = 1, 2$ and 4 or $q = 1, 3$ and 5 phosphate groups explain the data equally well. The author reported hydrogen-ion dependent constants of the type:

$$\begin{aligned} K'_q(\text{A.2}, 2.08 \text{ M NO}_3^-) &= K_q(\text{A.2}, 2.08 \text{ M NO}_3^-) \cdot [\text{H}^+]^{4+p-3q} \\ &= [\text{PuH}_p(\text{PO}_4)_q^{4+p-3q}][\text{H}_3\text{PO}_4(\text{aq})]^{2-q} \end{aligned}$$

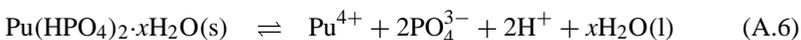
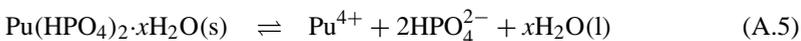
The values of the proton dependent constants K'_0 and K'_1 are not unique since at low added phosphoric acid concentrations the total phosphate concentration is affected by the choice of species formed when the solid dissolves. Since all sets of constants lead to a hydrogen ion dependence of greater than 4 for K'_0 , (probably due to interactions of Pu^{4+} with H^+ and Na^+), the sets giving dependence nearest to four have been chosen. Then from the values of the constants obtained at the same nitrate level (2.08 M), but two different proton concentrations, the p values for the different species were calculated. A value of $p = 3$ results for the species with $q = 1$, while fractional values in the range 2.1-2.4 result for the other complexes. This indicates that the first complex is $\text{Pu}(\text{H}_3\text{PO}_4)^{4+}$, while the higher complexes are probably mixed ligand species, containing both $\text{H}_3\text{PO}_4(\text{aq})$ and H_2PO_4^- ligands. Thus, since the analysis of the number of phosphate groups and proton content in the higher complexes is not conclusive because of the limited number (two) of determinations of constants at different acidities, and the uncertainties in the changes of the activity coefficients, only the values of the solubility product referring to the reaction:



and the constant corresponding to the formation of the first complex:



are considered further. At an ionic strength of 2.08 M the present review calculates $\log_{10} {}^*K_{s,0}(\text{A.3}, I = 2.08 \text{ M}) = -(8.79 \pm 0.15)$ and $\log_{10} \beta(\text{A.4}, I = 2.08 \text{ M}) = (2.27 \pm 0.30)$. Extrapolation of these values to $I = 0$ yields $\log_{10} {}^*K_{s,0}(\text{A.3}) = -(11.75 \pm 0.50)$ and $\log_{10} \beta(\text{A.4}) = (2.40 \pm 0.40)$, where the increased uncertainties should compensate for uncertainties in the estimated values of interaction coefficients. By using the phosphoric acid dissociation constants selected in this review, the constants $\log_{10} K_{s,0}^\circ(\text{A.5}) = -(30.45 \pm 0.51)$ and $\log_{10} {}^*K_{s,0}^\circ(\text{A.6}) = -(55.15 \pm 0.52)$ are obtained.



[49KRA/DAM]

This paper, describing a potentiometric study of the hydrolysis of Pu(V), is the same as [46KRA/DAM] except for minor editorial changes. It also appears to have been written based on the same data used in another report [48KRA/NEL] and a later review paper [56KRA]. Despite the later publication date for [49KRA/DAM], perusal of the bibliography in the two references suggests [48KRA/NEL] was written after [49KRA/DAM]. There are some inconsistencies in the reported stock plutonium concentrations - particularly for the lowest solution concentration in perchlorate medium.

No explicit discussion of the solubility product of $\text{PuO}_2\text{OH}(\text{am})$ is provided, but a limiting solubility of $50 \text{ mg}\cdot\text{dm}^{-3}$ is proposed as a lower limit based on the pH of initial precipitation ($\log_{10} K_{s,0}$ of the order of -8 to -9). Values are extracted from the same data in the report [48KRA/NEL] and the later review [56KRA]. See also the discussion of [48KRA/NEL].

[49KRA/DAM2]

This describes a potentiometric study of the hydrolysis of Pu(VI). Solution concentrations of total plutonium ranged from 0.7 to $1.3 \times 10^{-3} \text{ M}$ in 1 M NaClO_4 . The authors report that the results did not indicate the primary hydrolysis species was polymeric. However, the range in total plutonium(VI) concentration was small, and the solutions were relatively dilute. The authors report a “molarity constant” $\log_{10} {}^*K_{11m} = 5.71$, and that ${}^*K_{21m}$ is approximately equal to ${}^*K_{11m}$. These are concentration (not mixed) quotients for the noted medium. Only a portion of the data was published, and no attempt has been made to reanalyse that data in the present report.

Figure 1 is incorrect [56KRA], but is shown properly as Figure 1 of [48KRA/NEL].

[49KRA/DAM3]

This paper is based on potentiometric titrations supposedly done in the absence of carbonate (although some carbonate seems to have been present) and oxygen. Near pH 6.5 it becomes thermodynamically possible to oxidise Pu(III) to Pu(IV) with water. Thus stable titration values can only be obtained at lower pH values, where ≤ 0.5 moles of OH^- has been added per mole Pu(III). The end point of titration was found to occur after addition of about 2.4 moles of OH^- , not after 3 moles of OH^- as would be expected. This suggests possible formation of a basic salt (perhaps a hydroxocarbonate). Complexation by ClO_4^- and Cl^- was neglected. Calculations are based on the assumption that Pu^{3+} and PuOH^{2+} were the only plutonium species in the region of stability of Pu(III), *i.e.*, at pH < 6.5 for ClO_4^- , and < 7 for Cl^- . The reported results are:

Ionic medium	0.069 M ClO_4^-	0.024 M Cl^-
$-\log_{10} {}^*K_1(\text{at } I)$	7.22	7.37

With activity factor corrections of 0.35 and 0.33, respectively, the average value reported by the authors was 6.95 at ($I = 0$).

If the SIT is applied, the hydrolysis constants ($I = 0$) are -6.83 and -7.06 from the values from the perchlorate and chloride titrations, respectively.

[49MAG/LAC]

Redox titrations and spectrophotometric experiments were done for Np(III)-Np(IV) in 1 M HCl. No hydrolysis values are given.

[49ZEB/NEU]

The reference (which reported results of a study of complexation of Pu(IV) with nitrate in aqueous solution) was not available to the reviewers. Hindman [54HIN] cited results from this extraction study for “ $I = 6.0$ ” (units, probably $\text{mol}\cdot\text{dm}^{-3}$, were not stated and the medium was not described) as “ $K_1 = 8.3$ ” at 45°C , and “ $K_1 = 4.7$ ”, “ $K_2 = 0.96$ ” and “ $K_3 = 0.33$ ” at an unstated temperature (presumably a room temperature near 25°C). The reported value of “ $5.3 \text{ kJ}\cdot\text{mol}^{-1}$ ” for the enthalpy of reaction for the first complexation step is consistent with the K_1 value of $4.7 \text{ dm}\cdot\text{mol}^{-1}$ having been determined at $25\text{-}26^\circ\text{C}$, and presumably K_2 and K_3 were also determined at the same temperature. The information from this study was not used in determining selected values in the present review.

[50BUS/COW]

Potentiometric titrations of Pu(III) solutions provide information on the hydrolysis of Pu(III) and the solubility of Pu(III) hydroxide at $I = 0.04$. The titration curve indicates extensive hydrolysis of Pu(III) occurred before precipitation. No account was taken of hydrolysis in the calculation of the solubility product, and the final solid had a stoichiometry close to $\text{Pu}(\text{OH})_{2.5}\text{Cl}_{0.5}$. The “solubility product” for this chlorohydroxide, seemingly described as $a_{\text{OH}^-}^{2.5} m_{\text{Cl}^-}^{0.5} (0.5 m_{\text{Pu}_{\text{tot}}})$ was then reported as 9.1×10^{21} . Recalculation suggests 8.4×10^{-21} , whereas in later sources referring to this paper, *e.g.* [56KRA], a value of 2×10^{-20} ($a_{\text{OH}^-}^{2.5} m_{\text{Cl}^-}^{0.5} m_{\text{Pu}_{\text{tot}}} (?)$) is noted. None of these values is actually ${}^*K_{s,0}$, nor is there adequate information to calculate the value. The quantitative results from this paper are not used in the present review. This work indicates the value of the first hydrolysis constant for Pu(III) near room temperature is $\log_{10} {}^*K_1(I = 0.04 \text{ M}(\text{chloride})) = -(7.25 \pm 0.4)$.

[50KRA/NEL]

Spectrophotometric measurements (470 nm) were done in combination with pH measurements to measure the hydrolysis of Pu^{4+} in 0.5 M chloride and perchlorate solutions. The uncertainties in the logarithm (base 10) of the equilibrium constants are estimated in the present review to be about 0.2 (0.3 for the solution of lowest acidity). The molar absorbance of the hydrolysed species was assumed to be zero at 470 nm, however, Rabideau and Kline [60RAB/KLI] reanalysed the data for the perchlorate solutions and deduced a value of (10 ± 3) for the molar absorbance of PuOH^{3+} (and hence, $\log_{10} {}^*\beta_1 = -(1.72 \pm 0.05)$). Considerable difficulty was reported with polymerization and disproportionation of the Pu(IV) solutions ($7.2 \times 10^{-4} \text{ M}$ in aqueous plutonium species). Somewhat larger values for ${}^*\beta_1$ were found from the measurements in the chloride solutions, and this was attributed to chloride complexation.

When the data were reanalysed assuming the molar absorbances for Pu^{4+} and PuOH^{3+} were unchanged regardless of whether the medium was perchlorate or chloride, similar values were calculated for the hydrolysis constants $-\log_{10}^*\beta_1 = -1.81$ in 0.5 M perchlorate, -1.83 in 0.5 M chloride. The values changed by more than 0.1 in $\log_{10}^*\beta_1$ if the measurements in the most basic solutions were excluded. In the present review these newly recalculated values are used, and the uncertainties in the $\log_{10}^*\beta_1$ values are estimated as ± 0.2 .

Note: in the Appendix A note for this reference in the uranium review [92GRE/FUG], the species mentioned in the last sentence should have been UCl^{3+} not UO_2Cl^+ .

[51CON/MCV]

Connick and McVey measured the potential of the cell



In two independent sets of experiments, they determined the cell potential (a) at 25°C and (b) as a function of temperature between 9.4 and 35°C in steps of 5°C . The authors corrected their experimental values to standard hydrogen pressure and also introduced a correction for the Pu^{4+} reduction by alpha auto-radiolysis. An additional correction to unit concentrations gave $E^{\circ'} = (0.982 \pm 0.002) \text{ V}$. The following values are given:

$$\begin{aligned} \Delta_r G &= -(94.7 \pm 0.2) \text{ kJ}\cdot\text{mol}^{-1}, \\ \Delta_r H &= -(55.6 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}, \text{ and} \\ \Delta_r S &= (127.8 \pm 5.7) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}. \end{aligned}$$

Fuger and Oetting [76FUG/OET] corrected $\Delta_r H$ for Pu^{4+} hydrolysis. Their correction of $-0.8 \text{ kJ}\cdot\text{mol}^{-1}$ lies within the uncertainty of the uncorrected value.

From Connick and McVey's data, we calculate:

$$(\partial E / \partial T)_{\text{isotherm}} = (0.00125 \pm 0.00004) \text{ V}\cdot\text{K}^{-1}.$$

From this temperature coefficient of the potential, we derive $\Delta_r S = (120.6 \pm 3.9) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ which agrees with the value derived directly from $\Delta_r G$ and $\Delta_r H$.

[51RAB/LEM]

By measuring the potential of the cell



at 25.1°C , for various $\text{Pu}(\text{III})/\text{Pu}(\text{IV})$ ratios at an ionic strength of 1 M, Rabideau and Lemons determined the potential of the $\text{Pu}(\text{IV})/\text{Pu}(\text{III})$ couple. The authors corrected their experimental values to standard hydrogen pressure and to unit concentration of hydrogen ion. They obtained the formal potential $E^{\circ'} = (0.9821 \pm 0.0005) \text{ V}$. This

value is in excellent agreement with the value $E^{\circ} = (0.982 \pm 0.002)$ V determined by Connick and McVey [51CON/MCV].

Also, from measurements of the redox potential as a function of the acid concentration at an ionic strength of 1 M, the first hydrolysis constant for Pu^{4+} , β_1 , was determined. No time dependence of the results was mentioned, although this might have been expected, particularly in the less acidic mixtures. Therefore, the uncertainty in $\log_{10} \beta_1$ was estimated in the present review as ± 0.2 .

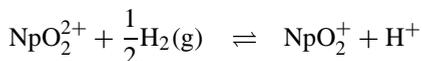
Comments on the use of this work to determine formation constants for chloro complexes of Pu(IV) (and for correction for Pu(III) chloride complexes) are provided below in the discussion of the paper by Rabideau and Cowan [55RAB/COW].

The authors explained the shift of the redox potential in nitrate media to more positive values (as compared to the value in perchlorate media) as evidence for the formation of PuNO_3^{3+} , and calculated the overall formation constant $\log_{10} \beta_1 = (0.54 \pm 0.01)$. The possible formation of nitrate complexes of Pu(III) and activity coefficient changes while substituting perchlorate ions for nitrate were neglected. Even though the changes in the medium are small, so are the changes in the potential. In the course of the present review an attempt was made to account for the measured potential changes considering only activity coefficient changes. The potential differences can be expressed as a linear function of the nitrate concentration with slope $59.2 \Delta \varepsilon \text{ mV} \cdot \text{mol}^{-1}$. In spite of a very good fit, a very large interaction coefficient difference ($\Delta \varepsilon = 1.39 \text{ kg} \cdot \text{mol}^{-1}$) was obtained. This may partly be the result of the contribution of mixing terms in the $\Delta \varepsilon$ value in addition to contributions from complexation. More data would be needed to separate the two effects, and no recalculated value of the constant could be obtained from these data.

[52COH/HIN]

a) $\text{NpO}_2^{2+}/\text{NpO}_2^+$ system

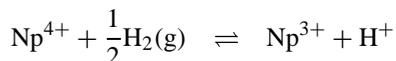
Cohen and Hindman determined the potential in 1.027 molal HClO_4 at 25°C for the reaction



as $E^{\circ} = (1.1373 \pm 0.0008)$ V (for comments see [61SUL/HIN]). From potential measurements as a function of the neptunium concentration, they estimated the junction potential of their cell to 0.0002 V. The investigators did, however, not consider this in further correction because it was relatively small compared to the uncertainty in the redox potential. From potential measurements at 15°C and at 35°C , two isothermal temperature coefficients $(dE/dT)_{\text{isotherm}} = -0.00030$ and $-0.00023 \text{ V} \cdot \text{K}^{-1}$ were determined. This yields an average value $(dE/dT) = -(0.00027 \pm 0.00005) \text{ V} \cdot \text{K}^{-1}$. Using E° and this value, this review determines $\Delta_r S_m = -(26.1 \pm 4.8) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, $\Delta_r G_m = -(109.73 \pm 0.08) \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_r H_m = -(117.5 \pm 1.4) \text{ kJ} \cdot \text{mol}^{-1}$ for the above noted reaction at standard temperature.

b) Np⁴⁺/Np³⁺ system

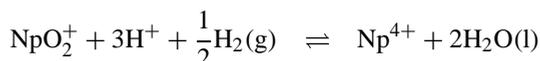
The authors also determined the potential in 1.027 m HClO₄ at 25°C for the reaction



as $E^{\circ} = (0.1551 \pm 0.0010)$ V. From additional measurements at 15°C, and at 35°C, two isothermal temperature coefficients $(dE/dT)_{\text{isotherm}} = 0.00132$ and $0.00139 \text{ V}\cdot\text{K}^{-1}$ were determined. This review calculated the average value $(dE/dT) = (0.00136 \pm 0.00005) \text{ V}\cdot\text{K}^{-1}$. From these values, this review determines $\Delta_r S_m = (131.2 \pm 4.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, $\Delta_r G_m = -(14.7 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_r H_m = (24.4 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$.

[52COH/HIN2]

Cohen and Hindman measured the emf of the NpO₂⁺/Np⁴⁺ couple in molal HClO₄ using a platinum electrode and a SHE. For the cell reaction



the formal potential $E^{\circ} = (0.7391 \pm 0.0010)$ V. Using $1 \text{ m} \hat{=} 0.9581 \text{ M}$, we correct this potential to the molar scale and 1 bar pressure:

$$E^{\circ} = (0.7431 \pm 0.0010) \text{ V}$$

The authors also determined

$$(dE/dT)_{\text{isotherm}} = -(0.00269 \pm 0.00006) \text{ V}\cdot\text{K}^{-1}$$

by measuring the cell also at 37 and 47°C. Using the corrected E° value and this temperature dependence of the cell potential, this review determines

$$\begin{aligned} \Delta_r S &= -(259.5 \pm 5.8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \\ \Delta_r G &= -n \cdot F \cdot E^{\circ} = -(71.7 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}, \text{ and} \\ \Delta_r H &= \Delta_r G + T \Delta_r S = -(149.1 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

for the above noted reduction reaction at standard temperature.

[52HEI/HIC]

The authors studied the formation of a nitrate complex of Pu(VI) by determining the distribution of Pu(VI) between aqueous phases consisting of (a) 1 M LiNO₃ and 3.5 M LiClO₄, or (b) 4.5 M LiNO₃, and an organic phase containing the extractant TTA. From the two measurements and the value of D_0 at 4.5 M LiClO₄, a value of 0.19 was estimated for the formation constant of PuO₂NO₃⁺. The complex is quite weak, and the results could be equally well explained as resulting from activity coefficient

changes. These sparse results for high ionic strength are not used in the present review. The authors also made a substantial effort to determine the distribution of Pu(III) in the same system, but found that Pu(III) oxidised to Pu(IV) during the measurements, even in the presence of a holding reductant.

[53WES/HAT]

This paper describes heat capacity measurements for a sample of $\text{NpO}_2(\text{cr})$ for the temperature range 10.8 to 312.7 K. From their data, the authors derived a value of $S_{\text{m}}^{\circ}(\text{NpO}_2, \text{cr}, 298.15 \text{ K}) = (80.3 \pm 0.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ that is accepted in the present review. Based on a least squares fit of the equally weighted heat capacities reported for temperatures between 228.55 K and 312.69 K,

$$C_{p,\text{m}}^{\circ}(\text{NpO}_2, \text{cr}, T) = (67.511 + 26.599 \times 10^{-3}T - 8.190 \times 10^5 T^{-2}) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

and $C_{p,\text{m}}^{\circ}(\text{NpO}_2, \text{cr}, 298.15 \text{ K}) = (66.2 \pm 0.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The estimated uncertainty for the value at 298.15 K is based on the agreement of the fitted values with the experimental data, and is somewhat greater than the 0.5% estimated by the authors [53WES/HAT].

[54CON]

The bulk of this reference is a review of redox equilibria and disproportionation reactions involving the (IV), (V) and (VI) states of plutonium in aqueous solutions. The value for the solubility product for $\text{Pu}(\text{OH})_3$, $K_{\text{s},0}$, ($[\text{Pu}^{3+}][\text{OH}^{-}]^3$) was estimated by analogy with the corresponding lanthanum compound.

[54CUN/HIN]

Oxidation potentials, heats and Gibbs energy of formation values are reported from emf and spectrophotometry experiments in HCl and HClO_4 , mostly at 1 M. There is little information provided on Np(III), but the paper reports Np(III) is rapidly oxidised in air to Np(IV), especially in presence of OH^{-} .

[54HIN]

Although this is a survey paper, it contains some attempts to predict complexation constants using an electrostatic model. The model was applied to calculating the first hydrolysis constants for actinide(III), lanthanide(III) and actinide(IV) ions, see Table A.1.

The experimental lanthanide values are from Moeller and Kremers [45MOE/KRE]; the calculated values are based on a coordination number of 8 for the M^{3+} ions.

A value for the solubility product of $\text{Pu}(\text{OH})_3(\text{s})$, $K_{\text{s},0} = 2 \times 10^{-20}$, is also estimated. This value appears to have originated (or first appeared) in Latimer's book [52LAT] – “calculated by assuming that the solubility product is similar to that of the rare-earth element with the same ionic radius” – and has often been cited in later reviews (*e.g.*, [56KRA], [70CLE]).

Table A.1: Calculated and observed values for the first hydrolysis constants of several tripositive ions (from [54HIN]).

Ion	Radius nm	Observed $-\log_{10}^*\beta_1$	Calc. $-\log_{10}^*\beta_1$
U ³⁺	0.106	> 4	9.2
Np ³⁺	0.105		9.2
Pu ³⁺	0.103	7.0	9.0
La ³⁺	0.106	10.0	9.2
Ce ³⁺	0.104	9.6	9.1
Pr ³⁺	0.102	9.7	8.9

[54NIG/PEN]

Np(V) was precipitated in 0.1 M K₂CO₃ solution. The solid phase was assumed to be KNpO₂CO₃(s), but later work [66GOR/ZEN, 74VIS/VOL] showed several different (probably hydrated) crystallographically distinct phases may form in these conditions. Analogous Na⁺, K⁺ and NH₄⁺ Pu(V) salts were precipitated from carbonate solutions. No thermodynamic data are available.

[54SUL/HIN]

This is a thorough study using TTA in benzene as the extraction system. It was confirmed that the same apparent distribution ratio was attained between the aqueous phase and organic (chelated) phase either when the Np(IV) was introduced to the aqueous phase or initially (as the chelate) to the organic phase. The stability of the Np(IV) oxidation state in solution was experimentally verified. The experiment was performed in strong acid to avoid hydrolysis of Np(IV). Polynuclear Np species were not observed. All sulphate is assumed to be in the form of HSO₄⁻ in 2 M HClO₄. The measurements were made at (10.2 ± 0.2)°C and (35.3 ± 0.2)°C. Two Np(IV)-SO₄²⁻ complexes were observed. Sufficient data are available for recalculation of association quotients and errors. In the recalculation procedure, the results at low SO₄²⁻/ΣNp ratios (where the first complex dominates) are used to estimate the association quotient for the first complex. This value is then used with the remaining points to calculate the stability of the second complex. This procedure has the effect of reducing the total errors of the estimates and to distribute the errors more evenly between the two association quotients.

[55COH/SUL]

The authors measured the rate of isotopic exchange between Np(V) and Np(VI) at $I = 3$ M (HClO₄) as a function of chloride and nitrate concentration, respectively. The concentration of chloride and nitrate, respectively, was varied between 0 and 2.7 M (replacing ClO₄⁻ to maintain $I = 3$ M). No significant effect on the reaction rate was observed for the nitrate solutions, giving no evidence for the formation of NpO₂NO₃⁺.

In agreement with other work, especially spectroscopic evidence, changes in activity coefficient values alone can be used to explain these results.

However, the chloride concentration had a marked effect on the reaction rate. Since no evidence has been obtained for complex formation between Np(V) and chloride, Cohen, Sullivan and Hindman [55COH/SUL] analysed the kinetic data only in terms of Np(VI) chloride complex formation. Two different paths were examined: The formation of NpO_2Cl^+ only, and the formation of both NpO_2Cl^+ and $\text{NpO}_2\text{Cl}_2(\text{aq})$. The experiments were carried out at three temperatures: 0.0, 4.78 and 9.84°C.

The data fit equally well up to a concentration of 1.5 M chloride by assuming either one or two complexes. Despite the large experimental uncertainties at high chloride concentrations, the data were best represented in this region by the mechanism involving two chloride complexes. The authors, however, mention that the data could probably also be interpreted by an activity change as was observed with the corresponding nitrate system, rather than by the formation of a second chloride complex. For $\log_{10} \beta_1$ and $\log_{10} \beta_2$, respectively, Cohen, Sullivan and Hindman [55COH/SUL] reported 0.10 and -0.80 at 0.0°C, 0.00 and -0.74 at 4.78°C, and -0.09 and -0.70 at 9.84°C. We assume that the enthalpies of the two complexation reactions are constant within this temperature range and up to 25°C, and we obtain from these data $\Delta_r H_m = -29.0 \text{ kJ}\cdot\text{mol}^{-1}$ for the formation reaction of NpO_2Cl^+ , and $\Delta_r H_m = +15.3 \text{ kJ}\cdot\text{mol}^{-1}$ for the overall formation reaction of $\text{NpO}_2\text{Cl}_2(\text{aq})$. Using these enthalpies to calculate the equilibrium constants at 25°C yields $\log_{10} \beta_1(298.15 \text{ K}) = -0.37$ and $\log_{10} \beta_2(298.15 \text{ K}) = -0.56$. We use only the first value in our evaluation and assign it an uncertainty of ± 0.20 . The second value is probably due to a medium effect. It should be noted that the IAEA review [92FUG/KHO] obtained approximately the same value for $\log_{10} \beta_1(298.15 \text{ K})$ but -0.94 for $\log_{10} \beta_2(298.15 \text{ K})$ probably due to a transcription error (interchanging the $\log_{10} \beta_2$ values at 0.0 and 9.84°C). Also, it seems that the two enthalpy and the two entropy values given in the table of [92FUG/KHO, p.81] all carry the wrong sign.

[55RAB/COW]

Rabideau and co-workers [51RAB/LEM, 55RAB/COW] studied chloride complexation and disproportionation of plutonium(IV) in aqueous solutions of $I = 1 \text{ M}$ and $I = 2 \text{ M}$, respectively, containing HCl/NaCl and HClO_4 . From the difference of the formal potentials in chloride and perchlorate media, the authors calculated the complex formation constant of PuCl^{3+} , assuming that no plutonium(III) chloride complexes were formed. However, the formation of PuCl^{2+} may have a significant influence on the redox equilibrium measured. The discrepancy between the formation constant of PuCl^{3+} of $\log_{10} \beta_1 = -0.23$ measured here [55RAB/COW] and, for example, the value of 0.15 obtained in [76BAG/RAM2] in the same medium ($I = 2 \text{ M}$) may be explained by the formation of PuCl^{2+} in the study of Rabideau and Cowan [55RAB/COW]. In this review, we correct the formation constant of PuCl^{3+} obtained at $I = 1 \text{ M}$ and $[\text{Cl}]_f = 1 \text{ M}$ for the formation of PuCl^{2+} . For the formation constant of PuCl^{2+} we use the value of Ward and Welch [56WAR/WEL] at $I = 1 \text{ M}$ (HCl): $\log_{10} \beta_1 = -(0.04 \pm 0.10)$, cf. Table 18.3. The fact that this value may include the ef-

fect of the presence of a certain proportion of PuCl_2^+ is not relevant for this correction. Rabideau and co-workers measured the potential of the following redox equilibrium:



Under the experimental conditions used, Pu(IV) is present as a mixture of Pu^{4+} and PuCl^{3+} , and Pu(III) as a mixture of Pu^{3+} and PuCl^{2+} . The difference of the redox potentials in perchloric and hydrochloric acid can be described as follows:

$$E^\circ(\text{HClO}_4) - E^\circ(\text{HCl}) = 0.05916 \times \log_{10} \left(\frac{1 + [\text{Cl}^-] \times \beta_1(\text{PuCl}^{3+}, I=1, 298.15 \text{ K})}{1 + [\text{Cl}^-] \times \beta_1(\text{PuCl}^{2+}, I=1, 298.15 \text{ K})} \right) \quad (\text{A.8})$$

The potential difference measured at 1 M HCl at 25°C is $E^\circ(\text{HClO}_4) - E^\circ(\text{HCl}) = 0.0118 \text{ V}$. The resulting constant is $\log_{10} \beta_1(\text{PuCl}^{3+}, I = 1 \text{ M}, 298.15 \text{ K}) = 0.31$, to which we assign an uncertainty of ± 0.30 .

The authors also reported a value for the formation of PuCl^{3+} at $I = 2 \text{ M}$ (HCl). It is not possible to correct this value for the formation of PuCl^{2+} , because the formation constant of PuCl^{2+} has not been determined experimentally at $I = 2 \text{ M}$ (HCl), and the possibility of the formation of PuCl^{2+} , for which the formation constant is unknown, cannot be ruled out.

The paper of Rabideau and Cowan [55RAB/COW] also presents a value for the enthalpy of the formation reaction of PuCl^{3+} , derived from the reaction enthalpies of Reaction (A.7) in 1 M HClO_4 and 1 M HCl, respectively. The problem is the same as with the formation constant, namely that the formation of PuCl^{2+} is a significant side reaction that has to be taken into account for the evaluation of the enthalpy of the formation reaction of PuCl^{3+} . Since no enthalpy of formation value is selected for PuCl^{2+} in this review, the necessary correction cannot be made, and the enthalpy of formation of PuCl^{3+} reported in this paper also must be discarded.

[56KRA]

This is a review of actinide hydrolysis. The discussion uses data and calculations from earlier reports, primarily [48KRA/NEL]. The references to the solubility products from [50BUS/COW] appear to be in error. Busey and Cowan concluded the precipitated solids in their experiments were chlorohydroxides. The value cited by Kraus as the solubility product for $\text{La(OH)}_3(\text{s})$ is identical to that reported by Busey and Cowan for the mixed solid. However, the value of 2×10^{-20} for the solubility product of $\text{Pu(OH)}_3(\text{s})$ is the calculated value from Latimer [52LAT], not the value in the report of Busey and Cowan. They reported 9.1×10^{-21} as the solubility product of the mixed solid (the details of that calculation are not clear, but the difference in the solubility products is reasonable based on the experimental curves). The solubility product for the hydroxide would presumably be even smaller than for the mixed solid.

The following list of solubility product values ($*K_{s,0}$) for $\text{M(OH)}_3(\text{s})$, $\text{M}=\text{actinide}$, La, primarily based on Latimer [52LAT], was reported:

U(III)	10^{-19}	Cm(III)	1.9×10^{-21}
Pu(III)	2×10^{-20}	La(III)	2.5×10^{-19}
Am(III)	2.7×10^{-21}		

These values are only valid for fresh precipitates.

[56RAB]

Rabideau determined the formal potential of the $\text{PuO}_2^{2+}/\text{PuO}_2^+$ couple by potentiometric titrations of PuO_2^{2+} in 1 M HClO_4 using either I^- or Pu^{3+} as a reducing titrant. He obtained $E^{\circ'} = (0.9164 \pm 0.0002)$ V. From measurements of this potential at 6.62, 15.95, and 25.00°C he determined $\Delta_r S = -24.69 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which gives the isothermal temperature coefficient $dE^{\circ'}/dT = -0.0003 \text{ V}\cdot\text{K}^{-1}$.

These measurements were done very carefully and have small reported uncertainties. However, the sources of the values required to calibrate the electrodes for use in solutions of moderate ionic strength at temperatures other than 25°C were not provided, and consequent systematic errors cannot be ruled out.

[56WAR/WEL]

This paper is also discussed in the americium book of this series [95SIL/BID]. The authors used a cation exchange method to investigate the formation of chloride complexes of trivalent actinides. They used solutions of ionic strength of 0.207, 0.5 and 1.0 M HCl. In addition, they carried out an experiment using 0.2 M HCl + 0.3 M HClO_4 , and they obtained practically the same result as in the case of 0.5 M HCl. Ward and Welch evaluated their measurements by assuming the formation of a 1:1 complex only, but they noticed a deviation from linearity of the distribution ratio at $I = 1$ M (HCl), which they took as an indication for the formation of a weak 1:2 complex with chloride and estimated a formation constant of $\beta_2 \approx 2$. The reported constants, changed to refer to the formation of the 1:1 complex, PuCl^{2+} , are $\log_{10} \beta_1 = 0.35_4$ ($I = 0.207$ M), 0.23_7 ($I = 0.5$ M, HCl), 0.25_2 ($I = 0.5$ M, HCl/ HClO_4), and -0.04_1 ($I = 1$ M). There is no indication in the paper of [56WAR/WEL] of the temperature of the experiment, but Martin and White [58MAR/WHI] referred to these experiments as having been carried out at $(21 \pm 1)^\circ\text{C}$. These values are used in this review to derive the selected formation constant for PuCl^{2+} , and we estimate the uncertainties in the first three values to be ± 0.20 and in the value at $I = 1$ M to be ± 0.50 , due to the deviation from linearity.

[57NEW/BAK]

See comments under Rabideau and Masters [61RAB/MAS].

[57RAB]

The potential of the Pu(IV)/Pu(III) couple was measured as a function of the acid concentration at constant ionic strength. From these measurements, the value of the first hydrolysis constant, β_1 , was determined at 14.9, 25.0 and 34.4°C. No time dependence of the results was mentioned, although this might have been expected, particularly in the less acidic mixtures where slow Pu(IV) disproportionation and possibly precipitation can occur. Therefore, the uncertainty in $\log_{10}^* \beta_1$ was estimated in the present

review as ± 0.2 . No marked difference was noted in the potentials when the electrolyte was changed from LiClO_4 to NaClO_4 . The value of β_1 at 25°C differs somewhat from the value determined spectrophotometrically in similar media [60RAB/KLI].

[58GEL/ZAI]

This paper reports the preparation of a number of potassium-containing Pu(IV)-carbonate solids by precipitation from alcohol-water mixtures. The stoichiometries of the solids were established from chemical analyses and the derived molar ratios of plutonium:carbonate:potassium. The following stoichiometric compounds were identified: $\text{K}_4(\text{Pu}(\text{CO}_3)_4) \cdot n\text{H}_2\text{O}$, $\text{K}_6(\text{Pu}(\text{CO}_3)_5) \cdot n\text{H}_2\text{O}$, $\text{K}_8(\text{Pu}(\text{CO}_3)_6) \cdot n\text{H}_2\text{O}$ and $\text{K}_{12}(\text{Pu}(\text{CO}_3)_8) \cdot n\text{H}_2\text{O}$. A crystal with the composition $\text{K}_6(\text{Pu}(\text{CO}_3)_5) \cdot 3\text{-}4\text{H}_2\text{O}$ was identified and characterized in terms of optical and magnetic properties. The paper contains no crystallographic details and no thermodynamic data were reported.

[58GEL/ZAI2]

Crystalline solids were prepared, and the following formulae proposed: $\text{Na}_{2n-4}\text{Pu}(\text{CO}_3)_n \cdot x\text{H}_2\text{O}(\text{s})$ with $n = 4$ and 5 .

[58MAR/WHI]

Martin and White measured the heat of solution of $\text{PuCl}_3(\text{s})$ in solutions of $\text{HClO}_4/\text{LiClO}_4$ and HClO_4 , respectively, at various concentrations. The authors reported an enthalpy value for the complex formation reaction



of $\Delta_r H_m(\text{A.9}, I = 0.1 \text{ M}, 298.15 \text{ K}) = 19 \text{ kJ}\cdot\text{mol}^{-1}$. Note that the authors used the then common procedure of defining complexation using dissociation reactions, rather than formation reactions as used in the present review. This value was obtained in the following way: The heat of solution of $\text{PuCl}_3(\text{s})$ measured in 0.1 M HClO_4 [58MAR/WHI], $-138.2 \text{ kJ}\cdot\text{mol}^{-1}$, was compared with the heat of solution measured in 0.1 M HCl by Westrum and Robinson [49ROB/WES], $-132.9 \text{ kJ}\cdot\text{mol}^{-1}$. By assuming that chloride complexation (due to the use of PuCl_3) in Martin and White's experiments in perchlorate solutions is negligible, the authors evaluated the enthalpy of Reaction (A.9) using the following equation:

$$\begin{aligned} \Delta_r H_m(\text{A.9}, I = 0.1 \text{ M}) &= (\Delta_{\text{sol}} H_m(\text{PuCl}_3, 0.1 \text{ M HCl}) - \Delta_{\text{sol}} H_m(\text{PuCl}_3, 0.1 \text{ M HClO}_4)) \\ &\times \left(\frac{1}{K(\text{A.9}, I = 0.1 \text{ M}) \times [\text{Cl}^-]} + 1 \right) \end{aligned} \quad (\text{A.10})$$

Note that the notation of Martin and White [58MAR/WHI] is transformed in this review to correspond to Reaction (A.9). The constant $K(\text{A.9}, I = 0.1 \text{ M})$ was taken from Ward and Welch [56WAR/WEL] and corrected to $I = 0.1 \text{ M}$ by using the Davies equation, resulting in $\log_{10} K(\text{A.9}, I = 0.1 \text{ M}) = 0.52$. However, it was reported by Martin and White [58MAR/WHI] that this constant

had been determined at $t = (21 \pm 1)^\circ\text{C}$ (no indication of the working temperature was given by Ward and Welch [56WAR/WEL]). Hence, Martin and White [58MAR/WHI] used the constant at 21°C in Eq. (A.10) and found the values at 25°C by iteration. They found $\log_{10} K(\text{A.9}, I = 0.1 \text{ M}, 298.15 \text{ K}) = 0.57$ and $\Delta_r H_m(\text{A.9}, I = 0.1 \text{ M}, 298.15 \text{ K}) = 19 \text{ kJ}\cdot\text{mol}^{-1}$. This enthalpy is surprisingly high considering the obvious weakness of the complex PuCl^{2+} , and it is in contradiction with other determinations [49ROB/WES, 63FUG/CUN] which suggest that the heat of solution of $\text{PuCl}_3(\text{s})$ is virtually independent of chloride concentration.

[58MOS/GEL]

The value reported for the dissociation constant of the PuCO_3^{2+} complex in sodium carbonate or potassium carbonate solutions is not considered to be reliable. The solubility of a “freshly prepared precipitate of Pu(IV)” was determined presumably by alpha counting of the supernatant solutions after equilibration times of 20-24 hours. These were stated to be of sufficient duration for equilibrium to be attained, which probably means that the counting rate became constant for a given aliquot. The absence of primary counting data makes it impossible to evaluate the precision of the measurements. The initial solid phase was not adequately characterized and there is no indication that the final solids were identical to the starting material. The reported spectra showing broad peaks at 585 nm suggest that some of the plutonium may have been in the Pu(VI) rather than the Pu(IV) form (see the discussion for [83WES/SUL]). It is possible that the solid phase that equilibrated with the K_2CO_3 solutions was of the form $\text{K}_4\text{Pu}(\text{CO}_3)_4 \cdot n\text{H}_2\text{O}(\text{s})$ (a phase proposed by Gelman and Zaitseva [58GEL/ZAI]; see Clark, Hobart and Neu [95CLA/HOB]), rather than the proposed $\text{Pu}(\text{OH})_4(\text{s})$. The potassium salt would dissolve to form the pentacarbonato complex in excess CO_3^{2-} solutions and yield the observed linear increase in solubility with CO_3^{2-} concentration. Other reviewers of this work [79SAL/AVO, 80LEM/TRE, 81PAQ/LEM] have indicated that the value for the solubility product of $\text{Pu}(\text{OH})_4(\text{s})$ given here $\sim 10^{-47}$ is unrealistically high based on analogies to other systems. If the solid phase controlling solubility was $\text{K}_4\text{Pu}(\text{CO}_3)_4 \cdot n\text{H}_2\text{O}(\text{s})$, the solubility product of the phase would be $\sim 10^{-13}$ based on the stability of the pentacarbonato complex found by Capdevila [92CAP] and poorly constrained estimates of solution compositions. In the absence of experimental identification of the solid phase, and the uncertainty concerning the experimental conditions, this solubility product is not recommended.

[58STR/PEE]

The authors carried out single redox measurements at 25°C of the couples Pu(III)/Pu(IV), Np(III)/Np(IV), and Np(V)/Np(VI), in HClO_4 , HCl , HNO_3 and H_2SO_4 solutions. In determining the values of the constants, the authors did not rely on their own measurements in perchlorate solutions; instead, the value measured by Cohen and Hindman [52COH/HIN] was used. This seems justified as the measurements of Stromatt, Peekema and Scott [58STR/PEE] in perchlorate media using a calomel reference electrode may have been affected by precipitation of KClO_4 at the liquid junc-

tion. From the potential differences, the authors estimated complexation constants for $\text{NpO}_2\text{SO}_4(\text{aq})$ ($\beta_1 \approx 13$), NpNO_3^{3+} ($\beta_1 \approx 2.4$), and NpCl^{3+} ($\beta_1 \approx 0.5$). Obviously, the investigation of the formation of complexes was not an objective of this study and these values are therefore only rather approximate.

For the Np(V)/Np(VI) couple the authors even found a shift in potential in nitric acid solutions that would correspond to stronger complexes for Np(V) than for Np(VI) . No complexation constants based on this work are accepted in the present review.

[59GEL/ZAI]

Solids were prepared, and the following formulae proposed:

$(\text{NH}_4)_{2n-4}\text{Pu}(\text{CO}_3)_n \cdot x\text{H}_2\text{O}(\text{s})$ with $n = 4, 5, 6$.

[59KRE/NIK]

This is a report of a potentiometric study of the hydrolysis of Pu(VI) (1-10 mM $\text{PuO}_2(\text{NO}_3)_2$ dissolved in 0.186 mM HNO_3 solutions). The observed changes in pH (measured against standard buffers) were interpreted in terms of mononuclear Pu(VI) hydroxo, nitrate and hydroxynitrate species. The ionic strength also changed from 3 to 30 mM during the experiments. The results suggest hydrolysis occurs at a much lower pH value than was found in many of the later potentiometric studies [72CAS/MAG, 75SCH]. Inclusion of $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ in the species set improves the overall fit of the data, but cannot make the results any more consistent with other studies. However, the results are much more compatible with those from other studies if it is assumed the plutonium(VI) nitrate hexahydrate solid, used to prepare the stock solution, had about 0.16 moles of occluded HNO_3 per mole of plutonium. The values from this paper were not used in the present assessment of hydrolysis constants for plutonium(VI).

In view of the difficulties in determining the proper hydrolysis species in this study, the results also could not be used to formulate conclusions concerning the nature and stability of the nitrate complexes.

[59SHE/TIM]

This is a solvent extraction study of Pu(III) nitrate complexes at $(20 \pm 1)^\circ\text{C}$ using TBP (tri-butylphosphate) in benzene as extractant. Hydrazine, 0.2 M, was used as a reducing agent, and in separate experiments it was proven that hydrazine is not extracted by TBP and does not complex Pu(III) . For the extraction reaction:



at constant nitric acid concentration (0.5 M) and varying TBP concentration (0.5, 1 M) the number of TBP molecules in the complex is calculated to be 2.94 (the authors reported 2.97). In HNO_3 - NH_4NO_3 mixtures the effect of H^+ ions (0.5, 0.75, 1 M) on the extraction of Pu(III) was tested, and essentially the same D values were obtained. First, a test in 1 M HClO_4 , 0.2 M $\text{N}_2\text{H}_4\text{HClO}_4$, 5.7×10^{-4} M $\text{Pu}(\text{ClO}_4)_3$ solutions was

performed to obtain $D = 0.0003$. Then solutions: 0.2 M $\text{N}_2\text{H}_4\text{HNO}_3$, 5.7×10^{-4} M $\text{Pu}(\text{NO}_3)_3$, 1 M H^+ and $[\text{NO}_3^-] = 0.25, 0.5, 0.75, 1$ M, $[\text{ClO}_4^-] = 1 - [\text{NO}_3^-]$ M were equilibrated. The data were explained in terms of the formation of three aqueous nitrate complexes of Pu(III) with constants: $\log \beta_1 = (0.73 \pm 0.04)$, $\log \beta_2 = (1.16 \pm 0.03)$, and $\log \beta_3 = (1.16 \pm 0.03)$.

There are two major drawbacks in this and other TBP studies:

- The mechanism of the extraction is not always clear and may be complicated by “side reactions”
- It is not possible to determine D_0 as in TTA studies, since only the neutral complex is extracted. Hence, the treatment of the results has a high degree of subjectivity inherent in the Fomin-Majorova and similar methods

For these reasons, no recalculation of these results was done, and the reported values are not accepted in the present review.

[59SUL/HIN]

The authors used spectrophotometry to determine the first hydrolysis constant for Np^{4+} in 2 M perchlorate medium. Only measurements for acid concentrations ≥ 0.02 M were used to calculate the reported equilibrium constant, but the raw data were not available to this review for recalculation. It was found that “there is no change in the neptunium(IV) spectrum until the acidity is decreased to approximately 0.1 molar”, but this is inconsistent with the later results of Paul [70PAU]. The reported ratio of the molar absorptivities is much smaller than was found in the present review by recalculating the data of Paul (see Appendix A discussion of [70PAU]). After conversion to molal units and correction to $I=0$, using the specific-ion interaction theory coefficients $\varepsilon_{(\text{Np}^{4+}, \text{ClO}_4^-)} = (0.84 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{NpOH}^{3+}, \text{ClO}_4^-)} = (0.50 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ (estimated), $\log_{10}^* \beta_1^\circ = -(1.25 \pm 0.16)$ is calculated in the present review. However, in view of the rather arbitrary pH limit and the lack of details regarding the evaluation of the molar absorptivities of Np^{4+} and NpOH^{3+} , the uncertainty in the value has been increased to ± 0.40 .

[60DEN/MOS]

The authors reported experimental solubility data for $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s})$ at $(25.0 \pm 0.5)^\circ\text{C}$ in 2 M HNO_3 solutions with varying concentrations of phosphoric acid (0.012–2 M $\text{H}_3\text{PO}_4(\text{aq})$). The composition of the solid was determined by chemical analysis as reported in earlier work [60DEN/MOS2]. Even though the experimental conditions are almost identical with those of King [49KIN], the authors propose a different dissolution mechanism and the formation of five plutonium-hydrogen phosphate complexes to explain the solubility data:



$$\begin{aligned}
 \log_{10} \beta_n(\text{A.11}, n = 1, 25^\circ\text{C}, 2 \text{ M HNO}_3) &= 12.9 \\
 \log_{10} \beta_n(\text{A.11}, n = 2, 25^\circ\text{C}, 2 \text{ M HNO}_3) &= 23.7 \\
 \log_{10} \beta_n(\text{A.11}, n = 3, 25^\circ\text{C}, 2 \text{ M HNO}_3) &= 33.4 \\
 \log_{10} \beta_n(\text{A.11}, n = 4, 25^\circ\text{C}, 2 \text{ M HNO}_3) &= 43.2 \\
 \log_{10} \beta_n(\text{A.11}, n = 5, 25^\circ\text{C}, 2 \text{ M HNO}_3) &= 52.0
 \end{aligned}$$

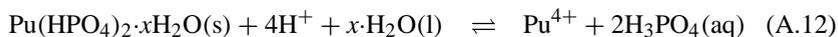
There is no experimental evidence to sustain this assumption, and it is impossible to determine the composition of the ligand at constant hydrogen ion concentration. Apparently the assumption about the formation of HPO_4^{2-} complexes originates in a previous study [60DEN/MOS2] and was used to explain solubilities at low acidities, while neglecting the hydrolysis of Pu^{4+} ion. Hence, the data from this paper have been recalculated using the same solubility scheme and practically the same constants as in the work of King [49KIN]. The following complexes and values of the formation constants are used (see Appendix A entry for [49KIN] for the definition of the constants): $\log_{10} K'_q(\text{A.2}, q = 0) = -8.72$, $\log_{10} K'_q(\text{A.2}, q = 1) = -5.16$ and the same values for $K'_2(\text{A.2})$ and $K'_4(\text{A.2})$ are used as in [49KIN].

[60DEN/MOS2]

The authors have measured the solubility of gelatinous $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ at $(25.0 \pm 0.4)^\circ\text{C}$ in 2 M (H^+, Na^+) ClO_4 and (H, Li) NO_3 solutions of varying hydrogen ion concentration up to 2 M. The composition of the solid phase was determined by chemical analysis, which showed a 1:2 metal to phosphate ratio, while the value of x was reported to be variable between 1 and 4. The solubility was measured only from undersaturation.

In the data analysis, the authors analyzed solubility data for low $[\text{H}^+]$ ($< 0.3 \text{ M}$) without considering the hydrolysis of Pu^{4+} ion, but instead assumed the complex $\text{Pu}(\text{HPO}_4)_2$. Since there is no experimental evidence for the formation of this complex, data treatment along the following lines is carried out here:

The dissolution reaction can be written:



for which the equilibrium constant is:

$$*K_{s,0}^\circ(\text{A.12}) = [\text{Pu}^{4+}] \cdot [\text{H}_3\text{PO}_4(\text{aq})]^2 \cdot [\text{H}^+]^{-4} \cdot \gamma_{\text{Pu}^{4+}} \cdot \gamma_{\text{H}_3\text{PO}_4}^2 \cdot \gamma_{\text{H}^+}^{-4} \cdot a_w^x$$

and may be considered to a good approximation invariable as the proton concentration is varied at constant ionic strength and anion concentration. By calculating $[\text{Pu}^{4+}]$ from this expression, and the total phosphate as twice the total plutonium concentration (from Eq. (A.12)), and using dissociation constants for $\text{H}_3\text{PO}_4(\text{aq})$ (calculated at this ionic strength with the SIT equations and interaction coefficients in Appendix B), the solubility was calculated by considering only one phosphate complex, namely $\text{PuH}_3\text{PO}_4^{4+}$ with the formation constant at $I = 2 \text{ M}$ from the work of King [49KIN]. Due to the low phosphate concentrations resulting from the dissolution of solid, the

higher complexes may be neglected. A maximum of 11% of the Pu(IV) is complexed at the highest acidities. The resulting calculated solubilities are compared to the experimental data and to the author's model in Figure A.2. The values of the solubility products obtained are: $\log_{10} {}^*K_{s,0}(\text{A.12}, 2 \text{ M NaClO}_4) = -(10.51 \pm 0.20)$ and $\log_{10} {}^*K_{s,0}(\text{A.12}, 2 \text{ M LiNO}_3) = -(9.32 \pm 0.30)$.

[60GRE/NOR]

Grenthe and Norén studied the formation of nitrate and chloride complexes by using a cation exchange resin in the H^+ form. The ionic strength was maintained at $I = 4 \text{ M}$ with perchloric acid, and the ligand concentration was varied up to 2.5 M (nitrate) and 3.5 M (chloride), respectively. Care was taken to avoid disproportionation and hydrolysis. The possibility of reduction of Pu(IV) by the resin was pointed out by Laxminarayanan, Patil and Sharma [64LAX/PAT] who also noted this should not have greatly affected the results, because Pu(III) should form complexes of comparable stability. The calculation of the complex formation constants was done according to a method developed by Fronæus, which is based on the introduction of special mathematical functions that allow a graphical analysis and a stepwise evaluation of the different constants. The results of this study show that the nitrate complexes of plutonium(IV) are more stable than the corresponding chloride complexes. It could be shown that three nitrate complexes exist: PuNO_3^{3+} , $\text{Pu}(\text{NO}_3)_2^{2+}$ and $\text{Pu}(\text{NO}_3)_3^+$, whereas in the case of chloride as a ligand the formation constant of the 1:3 complex is only a very approximate value, and the existence of this complex cannot be considered proven. The constants reported for the Pu(IV) nitrate complexes at 20°C and $I = 4 \text{ M}$ (HClO_4) are: $\log_{10} \beta_1 = (0.74 \pm 0.02)$, $\log_{10} \beta_2 = (1.37 \pm 0.02)$ and $\log_{10} \beta_3 = (1.2 \pm 0.3)$ (but also see the discussion below with respect to whether the values for the dinitrato and trinitrato complexes are meaningful). For the Pu(IV) chloride system, the values reported at 20°C and $I = 4 \text{ M}$ (HClO_4) are: $\log_{10} \beta_1 = (0.15 \pm 0.06)$, $\log_{10} \beta_2 = (0.08 \pm 0.07)$ and $\log_{10} \beta_3 = -(1.0 \pm 0.4)$.

In the study of Grenthe and Norén [60GRE/NOR] the complex PuCl_2^{2+} was found to be more stable than was found in other studies, *e.g.* [66DAN/URL, 76BAG/RAM2, 92MAR/ESS]. However, this review selects no value for the formation of PuCl_2^{2+} but uses the value reported by Grenthe and Norén [60GRE/NOR] for the formation of PuCl^{3+} in the selection process in Part IV, Section 18.2.2.1.b. This value does not need to be recalculated even though formation of PuCl_2^{2+} is not considered, because the evaluation procedure used by Grenthe and Norén was a stepwise one starting with the calculation of β_1 from a region where only PuCl^{3+} is formed. For the extrapolation procedure to $I = 0$, *cf.* Part IV, Section 18.2.2.1.b, we increase the uncertainties to ± 0.30 to account for the differences in the limited number of determinations, especially regarding the higher chloride complexes. Correction to 25°C using the enthalpy selected in this review, results in $\log_{10} \beta_1 = (0.12 \pm 0.30)$ which is used, after correction to molal units (resulting in $\log_{10} \beta_{1,m} = 0.03$), in the extrapolation procedure to obtain a value at $I = 0$.

In this work, for the nitrate complexes, special care was taken to avoid activity

Figure A.2: Solubility data for $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s})$ at 25°C in (a) 2 M $(\text{H},\text{Na})\text{ClO}_4$ and (b) 2 M $(\text{H},\text{Li})\text{NO}_3$ from [60DEN/MOS2]. The experimental data are compared with calculated values obtained using the solubility products estimated in this review and the constant for the complex $\text{PuH}_3\text{PO}_4^{4+}$ from [49KIN].

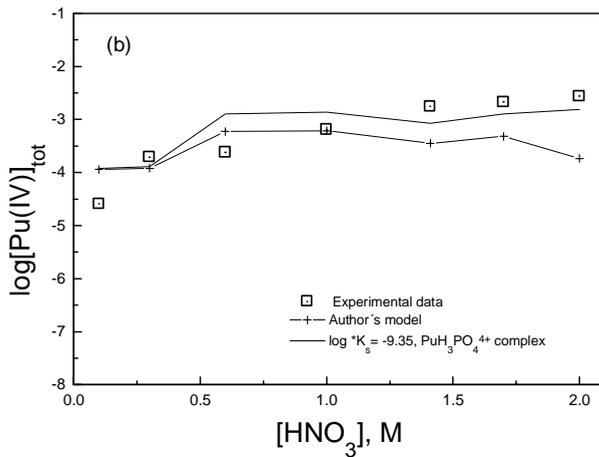
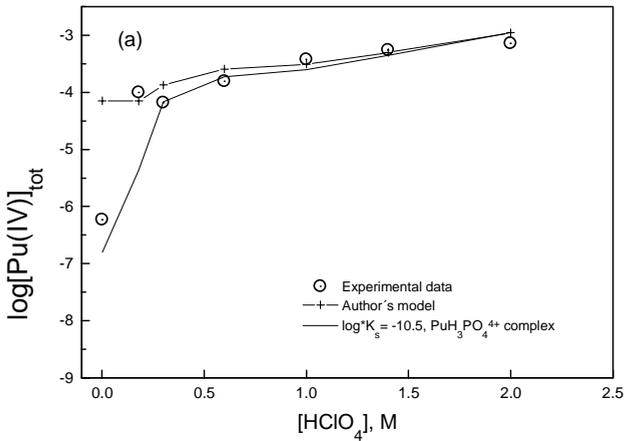
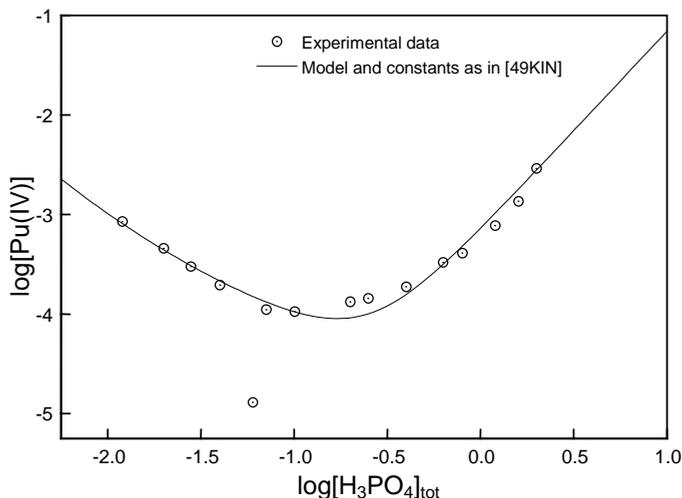


Figure A.3: Solubility of $\text{Pu}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}(\text{s})$ at 25°C in 2 M HNO_3 solutions with varying concentrations of phosphoric acid from [60DEN/MOS]. The continuous curve represents the values calculated with the model and the set of equilibrium constants from [49KIN].



coefficient changes by taking the limit of the functions for very low nitrate ion concentrations. However, for weak complexes the effect of complexation at low ligand concentrations is small, and at higher ligand concentrations activity factor changes occur. A calculation to fit the distribution data while taking into account activity effects and the distribution of only Pu^{4+} and the first complex has been attempted.

The resulting constant, $\log_{10} \beta_1 = (0.96 \pm 0.05)$, is in very good agreement with the value recalculated for similar conditions using the results from Danesi, Orlandini and Scibona [66DAN/ORL], and also the interaction coefficient differences are practically identical. In the present review, an increased uncertainty of ± 0.30 has been assigned to the authors' value, in part because the study was carried out at 20°C rather than 25°C , and the values for the higher complexes have been rejected.

[60LIP/POZ]

This is a qualitative spectrophotometric study of $\text{Pu}(\text{IV})$ nitrate complexes in 0.5-10 M HNO_3 solutions and at an unspecified temperature. On the basis of the variation of the molar absorptivity with the concentration of nitric acid at a series of wavelengths, the formation of several complexes was deduced. The conclusions are only qualitative, in that the maxima and minima (in the paper, extremes) in the variation of light absorption at various wavelengths with nitric acid concentration are assumed to show the formation of a new complex. The conclusions that at 1.5 M the complex with one ligand forms, at 1.5-2.1 M the complex with two ligands is formed, at 2.1-3.8 M the complex

with three ligands, for 3.8-5.6 M the complex with four ligands, for 5.6-7.1 M the complex with five ligands and for HNO₃ concentrations above 7.1 M the complex with six ligands is formed, are all based in the above mentioned extremes and are not quantitative. The fact that in mixtures of NH₄NO₃-HNO₃ the light absorption corresponds to a much smaller pure HNO₃ concentration is interpreted by the authors to mean H⁺ ions are as necessary as nitrate for the formation of the complexes, because they help in dehydrating Pu⁴⁺.

[60RAB/KLI]

This paper on the hydrolysis of plutonium(IV) is a report of spectrophotometric results in HClO₄-NaClO₄ mixtures for an ionic strength of 2 M. Results were obtained in H₂O(l) and D₂O(l), at 15.4 and 25.0°C, at 330 nm and 469 nm. Replicate experiments gave markedly more reproducible results using the data for 330 nm. Care was taken to extrapolate the results to the time of mixing, thus ensuring rapid hydrolysis was the only reaction under consideration. The uncertainties in the values of log₁₀*β₁ are estimated as ±0.2 in the present review.

[61MAR/CHM]

This paper reports a cation exchange study of the complexing of Pu(IV) in 0.5 and 2.33 M H⁺ (mostly HClO₄). The temperature was not specified and there is no demonstration that equilibrium was attained in the 5 hours allotted for the experiment. The Pu valence was confirmed initially but there was no verification of valence stability in the course of the experiment. There is no evaluation of HSO₄⁻/SO₄²⁻ equilibria in the determination of HSO₄⁻ concentrations. This is likely to contribute significantly to errors in the 0.5 M experiments. The 2.33 M experiment indicates that only a single 1:1 complex forms and sufficient data is given to permit re-evaluation of the experiment. A reevaluation of the 2.33 experiment using the deprotonation constant for HSO₄ of [51ZEB/ALT] at *I* = 2 M HClO₄ (0.084 ± 0.02) yields log₁₀ β(*I*) = (1.33 ± 0.09). At 0.5 M the 1:1, 1:2, 1:3, and 1:4 Pu(IV)-SO₄²⁻ complexes postulated are probably artefacts of hydrolysis and/or air oxidation. In the absence of temperature information, neither of these results can be extrapolated to standard state and are not included in the determination of best values.

[61RAB/MAS]

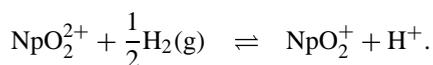
The authors were interested in the influence of chloride solutions on the kinetics of the redox reaction between PuO₂²⁺ and Sn²⁺. They investigated the redox kinetics at five different temperatures: 2.4, 10.2, 15.0, 20.2 and 29.6°C. In order to correct for the formation of the chloride complexes of PuO₂²⁺ and Sn²⁺, the authors determined their formation constants at these five temperatures by means of the spectrophotometric method used by Newton and Baker [57NEW/BAK]. The ionic strength used was *I* = 2 M H(Cl, ClO₄), and the chloride concentration was varied between 0.25 and 1.75 M. The results of Rabideau and Masters [61RAB/MAS] are in agreement

with those of Newton and Baker [57NEW/BAK]. However, while Newton and Baker [57NEW/BAK] needed to assume the formation of $\text{PuO}_2\text{Cl}_2(\text{aq})$ to explain their data, Rabideau and Masters [61RAB/MAS] obtained equally good agreement by using either only PuO_2Cl^+ or both PuO_2Cl^+ and $\text{PuO}_2\text{Cl}_2(\text{aq})$ in the evaluation of their measurements. This observation is compatible with that of Mazumdar and Sivaramakrishna [65MAZ/SIV] who observed complexes higher than PuO_2Cl^+ only above 1.75 M Cl^- . The same conclusion can be drawn from the series of visible absorption spectra measured by Giffaut [94GIF]. With our selected formation constant, we can calculate that the proportion of 1:2 complex in Rabideau and Master's experiments was between 2% and 12%. This is a rather small amount from which to determine a stability constant, and thus the constants reported here [57NEW/BAK, 61RAB/MAS] for the formation of $\text{PuO}_2\text{Cl}_2(\text{aq})$ probably have rather larger uncertainties.

From the variation of the constants over the temperature range between 2.4 and 29.6°C, Rabideau and Masters [61RAB/MAS] derived a reaction enthalpy value under the assumption that only PuO_2Cl^+ was formed. They obtained $\Delta_r H_m = 14 \text{ kJ}\cdot\text{mol}^{-1}$ for the formation reaction of PuO_2Cl^+ . The IAEA review [92FUG/KHO] used the Rabideau and Masters' values from the 1:2 model to derive $\Delta_r H_m = (8 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$ for the formation of PuO_2Cl^+ and $\Delta_r H_m = (17 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$ for the formation of $\text{PuO}_2\text{Cl}_2(\text{aq})$. In light of the above discussion (only a small proportion of 1:2 complex formed), the value of the enthalpy of reaction for the 1:1 complex should not be strongly affected, regardless of whether the formation of the 1:2 complex is taken into account. Therefore, the value $\Delta_r H_m = 14 \text{ kJ}\cdot\text{mol}^{-1}$ seems more likely to be correct, but on the other hand the value $\Delta_r H_m = 8 \text{ kJ}\cdot\text{mol}^{-1}$ selected in the IAEA review is consistent with the value for the corresponding U(VI) system [92GRE/FUG]. In view of these uncertainties, we do not select enthalpy data from this study.

[61SUL/HIN]

The authors used a cell arrangement which eliminated liquid junction potentials to determine the formal potential of the reaction



They determined $E^{\circ'} = (1.13638 \pm 0.00016) \text{ V}$ in 1 M HClO_4 at 25°C. The authors also recalculated the value of Cohen and Hindman [52COH/HIN] which was derived in 1 molal HClO_4 . Using $1 \text{ m} \hat{=} 0.9581 \text{ M HClO}_4$, the formal potential was corrected from $(1.1373 \pm 0.0008) \text{ V}$ to $(1.1361 \pm 0.0010) \text{ V}$. Cohen and Hindman, however, used 1.027 molal HClO_4 . Therefore, the corrected value determined by this review is $E^{\circ'} = (1.1366 \pm 0.0010) \text{ V}$.

[62GEL/MOS]

This paper reports four experiments on the solubility of ammonium diplutonate ($(\text{NH}_4)_2\text{PuO}_2\text{O}_7$) in distilled water and in carbonate solutions (0.175 to 0.438 M). There are four difficulties in interpreting this data: 1) From three solubility

measurements the authors assign association quotients to three different complexes ($\text{PuO}_2\text{CO}_3(\text{OH})^-$, $\text{PuO}_2(\text{CO}_3)_2$, $\text{PuO}_2(\text{CO}_3)(\text{OH})_2^{2-}$). This would appear to be an over-parameterisation of the data; 2) There is no evidence as to the nature and stability of the solid phase used in these experiments; 3) It does not seem feasible that an OH^- dependence could be determined on the basis of an experiment performed at essentially constant pH (9.5 to 9.6); and 4) It is not clear how these model complexes were chosen. Jensen [82JEN] and Newton and Sullivan [85NEW/SUL] pointed out these problems and recommended that these data be used carefully or not at all. Jensen [82JEN] and Ullman and Schreiner [88ULL/SCH] noted that the reported stability of the $\text{PuO}_2(\text{CO}_3)(\text{OH})^-$ complex is much too large to be reasonable. In spite of the difficulty in interpreting this experiment, it appears that these authors assigned a reasonable stability to the $\text{PuO}_2(\text{CO}_3)_2^{2-}$ complex ($\log_{10} \beta_2 = 13.82$; $\log_{10} \beta_2^\circ = 15.04$ using the Davies extrapolation). No reliance should be placed on these results.

[62MOS/ZA1]

The solubility product value for $\text{PuO}_2(\text{OH})_2(\text{s})$, $\log_{10} K_{s,0} = -22.7$, is apparently based on a single solubility measurement for “ammonium diplutonate” after equilibration for 4 to 6 hours at room temperature. The nature of the equilibrium solid was not established, and it is unlikely 4 to 6 hours was long enough for an equilibrium solubility to be established. The solid was assumed by the authors to convert to (hydrated) $\text{PuO}_2(\text{OH})_2(\text{s})$, an assumption in agreement with the later results of Cleveland [70CLE2]. There is no indication the oxidation state of the aqueous species was checked. However, the short equilibration period probably did limit changes caused by radiolysis to the oxidation state of plutonium in solution. Therefore, the reported solubility product is probably a valid maximum value, and is accepted as such in the present review.

Table 1 contains a large number of typographical errors that make it difficult to interpret. For example, the calculated concentrations of $(\text{PuO}_2)_2(\text{OH})_3^+$ are apparently entered one row from their correct locations in the table. If the authors' selected equilibrium constants are used, saturation concentrations of plutonium as much as an order of magnitude greater than the experimental concentrations are calculated.

[62SYK/TAY]

Measurements were done using UV-visible spectroscopy of solutions of Np(IV), Np(V), and Np(VI). The ionic strength was maintained at $I = 2$ M with NaClO_4 , and the temperature was 25°C . Formation constants were derived for NpSO_4^{2+} ($\beta_1 = 3200$), $\text{NpO}_2\text{SO}_4(\text{aq})$ ($\beta_1 = 44$), NpCl^{3+} ($\beta_1 = 0.53$), NpO_2Cl^+ ($\beta_1 = 0.62$), and NpNO_3^{3+} ($\beta_1 = 1.3$). Observations also indicated formation of a second Np(IV) sulphate complex and a Np(VI) nitrate complex, but no association constants were determined. No absorption spectra or evaluation procedures are given in the paper. The data provided are insufficient to critically review the conclusions and estimate errors.

[63MOS/GÉL]

A $\text{NpO}_2\text{HCO}_3(\text{aq})$ formation constant is reported from “unpublished” work: $\log_{10} K = -2.2$ at $I = 0.15 \text{ M}$ and -2.4 at 0 M with indication about neither the ionic strength correction procedure, nor the experimental procedure, nor the interpretation (of the experimental results), nor the definition of the equilibrium constant. High $\text{CO}_2(\text{g})$ partial pressures would be more likely to stabilise a $\text{NpO}_2\text{HCO}_3(\text{aq})$ species; but no evidence of any $\text{Np}(\text{V})$ bicarbonate complex has been found in other studies using such conditions [84VIT, 86GRE/ROB, 90RIG, 98VIT/CAP]. It is concluded the value in this publication [63MOS/GÉL] is in error. In a later paper, one of the authors [71MOS2] proposed different (incorrect) $\text{Np}(\text{V})$ carbonate complexes for other chemical conditions (*cf.* discussion of [71MOS2]).

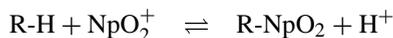
[63MUS]

This is a polarographic study of the change in the half-wave potential of the $\text{Np}^{4+}/\text{Np}^{3+}$ reduction potential in the presence of bisulphate ion. All ΣSO_4 was assumed to be HSO_4^- . Experiments were performed at 3 M ionic strength and 1.1 M acid strength. The data are provided in sufficient detail to enable recalculation of the association quotients and errors. In the recalculation, using a quadratic model, a correction was made for the presence of SO_4^{2-} .

[64GAI/SYK]

This is a cation exchange study of $\text{Np}(\text{V})$ nitrate complexes in 2 M H (ClO_4 , NO_3) mixtures at 25°C . The ligand concentration was varied from $0.2 - 1.8 \text{ M}$. It is assumed that no adsorption of the complex by the resin occurred and only the first complex formed. The authors obtained $\beta_1 = (0.56 \pm 0.06)$ as the average of 0.54 and 0.58 from two separate runs, both with 0.01 standard deviation. The disproportionation of $\text{Np}(\text{V})$ was accounted for by estimating $\log_{10} K_{\text{disprop.}} = -6.08$ at 2 M acid, (it was concluded that less than 1.5% of $\text{Np}(\text{V})$ disproportionated). The spectra in methanol showed no new bands and the same peak height was observed; only a solvation change could be observed.

The reaction with the resin, denoted R-H can be written:



assuming that no other ions are exchanged. The thermodynamic constant of the exchange reaction is:

$$K_{\text{cix}}^\circ = \frac{[\text{R-NpO}_2]_{\text{r}} \cdot [\text{H}^+]_{\text{aq}} \cdot f_{\text{cp},\text{r}} \cdot f_{\text{H}^+,\text{aq}}}{[\text{NpO}_2^+]_{\text{aq}} \cdot [\text{R-H}]_{\text{r}} \cdot f_{\text{NpO}_2^+,\text{aq}} \cdot f_{\text{R-H},\text{r}}} = C_f \frac{[\text{R-NpO}_2]_{\text{r}} \cdot f_{\text{H}^+,\text{aq}}}{[\text{NpO}_2^+]_{\text{aq}} \cdot f_{\text{NpO}_2^+,\text{aq}}}$$

where

$$C_f = \frac{[\text{H}^+]_{\text{aq}} \cdot f_{\text{cp},\text{r}}}{[\text{R-H}]_{\text{r}} \cdot f_{\text{R-H},\text{r}}}$$

is to a good approximation constant, since the composition of the resin and the concentration of protons do not change. The same can not hold for $f_{\text{H}^+, \text{aq}}$ and $f_{\text{NpO}_2^+, \text{aq}}$ while making full substitution of the perchlorate anion by nitrate. This would be true in the ionic strength interval where the interaction coefficient part of the activity coefficient expression is negligible as compared to Debye-Hückel term, *e.g.*, less than 0.3 M ionic strength. Thus the experimentally determined $K_d = [\text{Np(V)resin}]_{\text{tot}}/[\text{Np(V)}]_{\text{aq}}$ is expressed as:

$$\begin{aligned} K_d &= \frac{[\text{R-NpO}_2]_{\text{r}}}{[\text{NpO}_2^+] \cdot (1 + \beta_1^\circ \cdot [\text{NO}_3^-] \cdot f_{\text{cp}1}^{-1} \cdot f_{\text{NpO}_2^+, \text{aq}} \cdot f_{\text{NO}_3^-, \text{aq}} + \dots)} \\ &= \frac{K_{\text{cix}}^\circ}{C_f} \cdot \frac{f_{\text{NpO}_2^+, \text{mix}}}{f_{\text{H}^+, \text{mix}}} \{1 + \beta_1 \cdot [\text{NO}_3] \cdot f_{\text{NpO}_2^+, \text{aq}} \cdot f_{\text{cp}1, \text{mix}}^{-1} + \dots\}^{-1} \quad (\text{A.13}) \end{aligned}$$

The same expression is valid in measurements of K_d° in perchloric acid, but without the term in parenthesis and activity factors of the cation i denoted f_{i, ClO_4} . Then:

$$\frac{K_d^\circ}{K_d} = \frac{f_{\text{NpO}_2^+, \text{ClO}_4^-} \cdot f_{\text{H}^+, \text{mix}}}{f_{\text{NpO}_2^+, \text{mix}} \cdot f_{\text{H}^+, \text{ClO}_4^-}} \{1 + \beta_1 \cdot [\text{NO}_3] \cdot f_{\text{NpO}_2^+, \text{mix}} \cdot f_{\text{cp}1, \text{mix}} + \dots\}^{-1} \quad (\text{A.14})$$

Then by expressing the values of $\log_{10}(K_d^\circ/K_d)$ as a function of the nitrate concentration, an upper limit for the stability constant of the first complex may be estimated. In fact, according to SIT, the logarithm of the activity ratio on the right hand side may be expressed as $\Delta\varepsilon(\text{NO}_3^-)$, while the deviations from linearity may be accounted for by varying the value of the constant in the term inside parenthesis. In this particular case the linear model better represents the experimental data than the model with one complex as used by the authors. The authors themselves suggested the reported association constant “may include . . . contributions from long range medium effects represented by the variation of activity coefficients with composition”, and the reported Np(V)/nitrate association constant is not accepted in the present review.

Similar experiments were performed with chloride as an anion. The evaluation of the distribution coefficients at $I = 2 \text{ M H}(\text{Cl}, \text{ClO}_4)$ and chloride concentrations varying between 0.2 M and 1.8 M, yielded for the formation of $\text{NpO}_2\text{Cl}(\text{aq})$: $\beta_1 = (0.51 \pm 0.06)$ as an average of (0.45 ± 0.01) and (0.57 ± 0.03) obtained in two separate runs. This constant is very similar to the one reported for the nitrate system, (0.56 ± 0.06) , and it can be concluded that an equally good explanation of the results may be possible by considering activity effects rather than complex formation (see the discussion above).

[64GEL/ZAI]

A value of $K_{s,0} = 0.5 \times 10^{-9}$ was reported for the solubility product for $\text{PuO}_2\text{OH}(\text{s})$ from an experiment reported later in more detail [68ZAI/ALE].

[64KEE/KRU]

Keenan and Kruse prepared $\text{KNpO}_2\text{CO}_3(\text{s})$, and $\text{KPuO}_2\text{CO}_3(\text{s})$ hydrated compounds, by precipitation in 0.1 M KHCO_3 solution. X-ray powder diffraction patterns were

obtained, but several different hydrated phases can possibly be prepared in similar conditions. No data from this work was used by the present review.

[64LAX/PAT]

This is a solvent extraction study of nitrate and sulphate complexation with Pu(IV) using the extractant tri-*n* butyl phosphate(TBP), 20% in toluene. In the study of nitrate complexation the aqueous solutions had total ionic strengths of 1.02 M H (ClO₄, NO₃), 1.9 M (0.6 M H⁺, 1.3 M Na⁺, 1.9 M (ClO₄, NO₃)) and 4.7 M (0.7 M H⁺, 4 M Na⁺, 4.7 M (ClO₄, NO₃)). The temperature and Pu isotope were not specified. No holding oxidant or reductant was used. The authors cited the measurements of Brothers, Hart and Mathers [58BRO/HAR] where the activity coefficient of the nitrate ion remains constant in the case of addition of perchlorate in nitrate solutions, but this is not true while exchanging H⁺ for Na⁺ as done in this work. The constants do not depend only on the ionic strength, but also on the composition of the aqueous solution.

The graphical method of differentiation used by the authors with a function based on values for only 5-9 points seems highly subjective. In this review, both a polynomial fit of all the points and also a non-linear curve fit considering only the part in [HTDB]³/*D*, (differentiating 3 ln[NO₃] analytically) were carried out. Totally different results were obtained, and the estimated uncertainty is more than 0.5 log units for the first constant. With two calculation methods, one taking the limit of the derivative (modified Fomin Majorova method) and the other the limit of the integral of a function (Fronaeus method), values of the constants, especially for higher order complexes, differing by more than one logarithmic unit are obtained. The fitting of a logarithmic function gives quite erroneous results for small numbers, lending higher weight to the smallest numbers. Other attempts to recalculate the results by including activity effects explicitly were also unsuccessful. In conclusion, no reliable values for nitrate complexation constants could be found based on the results in this paper. The values reported by the authors as obtained with the modified Fomin Majorova method (with the HNO₃·TBP complex) and with the Fronaeus method are reported in Table 20.2, but are not accepted in the present review.

The paper also described determination of formation constants for Pu(IV) sulphato complexes based on TBP extractions from 2 M (Na,H) (NO₃, ClO₄) solutions. Corrections were made for the effect of 1:1, 1:2 and 1:3 nitrate complexes with Pu(IV) using formation constants based on the experiments discussed above. The paper also included results for TTA extraction, but no data or details were provided. Subsequent work by this same group [73PAT/RAM2] described the TBP work as “not reliable” and therefore these results are not included in the determination of recommended values.

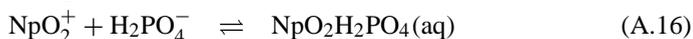
[64LUC]

An extraction study of Pu(IV)-SO₄²⁻ complexes in 1 M (H,Na)NO₃, 0.5 M H⁺ at (23 ± 0.5)°C is discussed. Only the stability of the stepwise addition of HSO₄⁻ to form the 1:2 complex was determined by the author in the absence of stability constants for the NO₃⁻ complexes. The H⁺ concentrations were low, and the valence stability was not verified

after the initiation of the experiment. Thus, the results were probably affected both by air oxidation and hydrolysis product formation. The experiment was performed rapidly in an attempt to avoid oxidation, but attainment of equilibrium was not confirmed. The result of this study is not used in the determination of a recommended value for $\log_{10} \beta$ (19.5).

[64MOS/PER]

This is a cation exchange study performed at $(20 \pm 2)^\circ\text{C}$ in a 0.2 M NH_4ClO_4 medium. The authors reported distribution coefficients of Np(V) both at constant total phosphate concentration and variable pH and also at constant pH and variable total phosphate. The distribution data were explained by the formation of the complexes $\text{NpO}_2\text{HPO}_4^-$ and $\text{NpO}_2\text{H}_2\text{PO}_4(\text{aq})$ according to:



with constants:

$$\log_{10} \beta(\text{A.15}, 20^\circ\text{C}, 0.2 \text{ M } \text{NH}_4\text{ClO}_4) = (2.85 \pm 0.15)$$

$$\log_{10} \beta(\text{A.16}, 20^\circ\text{C}, 0.2 \text{ M } \text{NH}_4\text{ClO}_4) = 0.8$$

The second complex was a minor species for the experimental conditions studied, accounting for 5-17% of the total neptunium in solution. Its constant is calculated as the difference between two large numbers from the variation of the constant $\beta_1(\text{NpO}_2\text{HPO}_4^-)$ with pH. On the other hand, the variation of the constant of the dominant complex may be partially or completely due to changes in activity factors as a singly charged ligand is replaced by one that is doubly charged (the ligand concentration represents 50% of the medium anions). The phosphoric acid constants used were not recalculated at the given ionic strength. Recalculation of the data using the appropriate protonation constants for phosphoric acid results in $\log_{10} \beta(\text{A.15}, 20^\circ\text{C}, 0.2 \text{ M } \text{NH}_4\text{ClO}_4) = (2.46 \pm 0.15)$, if this is considered to be the sole species to form in the given conditions. Extrapolation of this value to $I = 0$ with the SIT equations and interaction coefficients in Appendix B (in fact, the ionic interaction coefficient terms at these low ionic strengths is very small, since

$$\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = 0.25 \cong -\varepsilon_{(\text{NH}_4^+, \text{HPO}_4^{2-})} = 0.24$$

(the value of $\varepsilon_{(\text{NH}_4^+, \text{HPO}_4^{2-})}$ was estimated as equal to $\varepsilon_{(\text{K}^+, \text{HPO}_4^{2-})}$ (Table B.5)) and the interaction coefficient of the singly-charged complex is small) results in:

$$\log_{10} \beta^\circ(\text{A.15}, 298.15 \text{ K}, I = 0) = (2.97 \pm 0.15)$$

[64POZ/FED]

This is a qualitative spectrophotometric study performed in 2, 3 and 5.7 M HNO_3 solutions and at 20, 40, 60°C. The main result reported is that an increase in the temperature

from 20 to 60°C of a 2 M HNO₃ solution results in a spectral effect similar to that found by increasing the nitric acid concentration to about 5 M.

[64SHI/MAR]

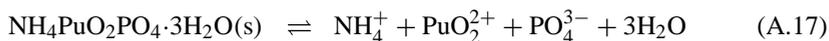
Shiloh and Marcus studied the spectra of neptunium(III), plutonium(III) and americium(III) in chloride and bromide solutions, respectively. They found evidence for the formation of NpCl²⁺, NpCl₂⁺, NpBr²⁺, NpBr₂⁺, PuCl²⁺, PuCl₂⁺, PuBr²⁺, PuBr₂⁺, AmCl²⁺, AmCl₂⁺, and AmBr²⁺. The ionic strengths used were very high and varied between 1 M and 13.7 M of LiCl and LiBr, respectively. It is not possible to correct these values to $I = 0$.

[65CHO/KET]

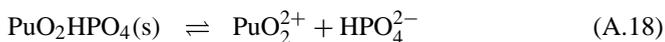
This is a solvent extraction study in which the authors determined the formation constants of the 1:1 and 1:2 thiocyanate complexes of Nd(III), Eu(III), Pu(III), Am(III), Cm(III) and Cf(III). NaClO₄ was used as inert electrolyte to adjust the ionic strength to 1 M, and the pH was adjusted to 2 with HClO₄. The following stepwise constants were reported for the Pu(III) complexes: $K_1(\text{PuSCN}^{2+}, 1 \text{ M}, 298.15 \text{ K}) = (2.90 \pm 0.31)$ and $K_2(\text{Pu}(\text{SCN})_2^+, 1 \text{ M}, 298.15 \text{ K}) = (1.95 \pm 0.29)$. These measurements were carried out in a thermostated water bath at $(25 \pm 0.1)^\circ\text{C}$. The authors evaluated the formation constant of PuSCN²⁺, K_1 , from the measurements in the concentration range $0 < [\text{SCN}^-]_f < 0.1 \text{ M}$, and the constant K_2 from data in the concentration range $0.1 < [\text{SCN}^-]_f < 1 \text{ M}$. Unfortunately, the authors presented only a few "typical graphs of the data", *i.e.*, Nd(III) and Cm(III) for the evaluation of K_1 , and Nd(III) and Pu(III) for the evaluation of K_2 . However, the study is a careful one, and we assume that the graphs of the other data are of a similar linearity as those shown in Figures 1 and 2 of [65CHO/KET].

[65DEN/SHE]

The authors studied the solubility of ammonium dioxoplutonium(VI) phosphate in dilute nitric or perchloric acid solutions of pH 1.0 to 6.4. There is no evidence that the solid phase was characterized before or after equilibration in aqueous acidic solutions. It is very probable that at low pH the ammonium dioxoplutonium(VI) phosphate was converted partially or totally to hydrated PuO₂HPO₄(s) or other solid phases. The authors report the following values of solubility products, both from measurements in the pH interval 1 to 3:



$$\log_{10} K_{s,0}(\text{A.17}, 0-0.1 \text{ M H}(\text{NO}_3, \text{ClO}_4)) = -(26.64 \pm 0.30)$$



$$\log_{10} K_{s,0}(\text{A.18}, 0-0.1 \text{ M H}(\text{NO}_3, \text{ClO}_4)) = -(12.55 \pm 0.30)$$

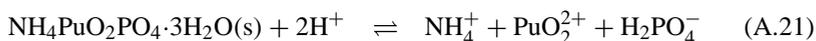
The complexes assumed to form in the whole pH range are PuO₂HPO₄(aq) and NH₄PuO₂PO₄(aq). The overall formation constants for these complexes according to

the reactions:



are also reported as $\log_{10} \beta$ (A.19, 0-0.1 M HNO₃, HClO₄) = 21.43 and $\log_{10} \beta$ (A.20, 0-0.1 M HNO₃, HClO₄) = 8.17.

A recalculation of the data was attempted assuming, at first, no phase change and the formation of $\text{PuO}_2(\text{H}_2\text{PO}_4)_n^{2-n}$ complexes in this pH range. The overall dissolution reaction considered was:



The constant $*K_{s,0}$ (A.21) = $[\text{PuO}_2^{2+}][\text{NH}_4^+][\text{H}_2\text{PO}_4^-][\text{H}^+]^{-2}$ was calculated assuming total phosphate and total ammonium equal to the total concentration of Pu(VI). Then the concentration of H_2PO_4^- was expressed through total phosphate and the constants of phosphoric acid. By combining the dioxoplutonium(VI) concentration from the solubility product with that of total dioxoplutonium(VI) as free dioxoplutonium(VI) plus H_2PO_4^- complexes, the solubility could be expressed as a function of pH. Much higher solubilities would be obtained at the low pH values if this were the solid phase in equilibrium. The ionic strength was not maintained constant, and the solubility products are influenced by ionic strength changes for values between 0 and 0.1 M, where changes in activity coefficients can be accounted for reasonably well solely by the Debye-Hückel term in the SIT equations (Appendix B). Even with ionic strength corrections of all the constants, the lower solubilities at pH 1-4 can not be explained. Thus it seems certain that at pH values lower than 3 there was a transformation of the solid phase. An attempt was made to do a calculation in the same way using the data at low pH, but assuming $\text{PuO}_2\text{HPO}_4(\text{s})$ as the stable solid phase. In the absence of dioxoplutonium(VI)-phosphate complexes the solubility *versus* pH curve should have a slope of 0.5 instead of 0.67 at equilibrium with ammonium dioxoplutonium(VI) phosphate. This is true for both sets of data and limiting values for the solubility of solids can be obtained. However, it is impossible from such a sparse set of data (5-6 points) to obtain two solubility products and at least two complex formation constants. For these reasons the solubility products and stability constants reported in this work are considered unreliable and are not accepted.

[65IAK/GOR]

The pale green solid $\text{K}_4\text{PuO}_2(\text{CO}_3)_3(\text{s})$ was prepared by oxidizing a 0.017 M Pu(IV) aqueous solution in concentrated K_2CO_3 media at 95 to 100°C over 15 to 20 minutes. The stoichiometry of the solid was determined by chemical analysis. Its X-ray diffraction pattern was found to be similar to the known pattern for $\text{K}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$. No thermodynamic data can be deduced from this work; but one of the authors later [66GOR/KLI] carried out solubility measurements for the same type of solid phases, and that work was used in the present review to deduce equilibrium constants.

[65MAZ/SIV]

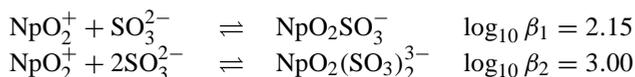
This is a solvent extraction study using TTA 0.2 M and 0.4 M in benzene as the extractant. For the nitrate complexation experiments the aqueous phase was a sodium perchlorate solution at pH = 1.15, with a total ionic strength of 4.1 M and nitrate concentrations up to 2 M. Trace (10^{-4} M) concentrations of Pu(VI) were used. The authors observed photochemical reduction of Pu(VI), which could be avoided in the absence of light. The extraction mechanism was tested.

The authors explained the extraction results in terms of two nitrate complexes of Pu(VI). Another approach would have been to allow for differences in the interactions of H^+ and PuO_2^{2+} with nitrate and perchlorate in each extraction mixture. This could be done using $\Delta\varepsilon(H) = \varepsilon_{(H^+, ClO_4^-)} - \varepsilon_{(H^+, NO_3^-)} = 0.07 \text{ kg}\cdot\text{mol}^{-1}$ and $\Delta\varepsilon(PuO_2) = \varepsilon_{(PuO_2^{2+}, ClO_4^-)} - \varepsilon_{(PuO_2^{2+}, NO_3^-)} \cong 0.46 - 0.24 = 0.22 \text{ kg}\cdot\text{mol}^{-1}$ (with the uranium(VI) values for plutonium(VI), see also: Appendix B Table B.3 and footnotes (r) and (v) to that table). The conditional constants would depend not only on the ionic strength, but also on the activity coefficient of the nitrate ion, which at the same ionic strength would vary with the concentration of the positive ions H^+ and Na^+ . The data in this paper [65MAZ/SIV] can then be equally well explained by assuming only activity changes and no complex formation.

The reported [65MAZ/SIV] nitrate complexation constants are $\beta_1 = 0.92$ and (in the authors' words, "very approximately") $\beta_2 = 0.2$. Using the ion association approach, only the value $\log_{10} \beta_1 = -(0.04 \pm 0.20)$ is accepted, where the uncertainty is assigned in the present review.

[65MOS/MEF]

Stability constants are given for two sulphite complexes of NpO_2^+ :



No experimental detail is given for these tabulated values. By analogy to the other experiments reported in this paper, it is assumed that these refer to the $I = 0$ and $t = 25^\circ\text{C}$ standard state. Insufficient experimental detail is given to permit re-evaluation according to the TDB standards. These values are not further considered in this review.

[65PER]

This is primarily a study of the solubility of $Pu(OH)_4(\text{am})$ as a function of pH (0.54 to 3.50) at $(24 \pm 2)^\circ\text{C}$. Equilibration periods were short (approximately 60 hours), and equilibrium was probably not achieved. Values of $\log_{10} K_{s,0}$ ranging from -48.0 to -58.2 were reported, and ionic strength corrections to obtain values of $K_{s,0}^\circ$ were done using an extended Debye-Hückel treatment. However, as discussed by Rai [84RAI], Perez-Bustamante assumed in these calculations that all the plutonium in solution was Pu(IV). Disproportionation and hydrolysis undoubtedly caused the concentration of Pu^{4+} to be lower than the total concentration of plutonium in solution. This would be

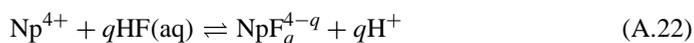
particularly true of the less acidic solutions. Thus, the values of $\log_{10} K_{s,0}$ would be more negative than those reported by Perez-Bustamante. This probably accounts for the drift in the reported $\log_{10} K_{s,0}$ values, with those from the lowest pH measurements being affected the least. Colloid formation may also have led to an overestimate of the plutonium in the filtered solutions. The short equilibration period (Figure 3 in [65PER]) probably introduced an error of -1 to -2 in the opposite direction. The heading in Table 1 should read “mg Pu·l” not “ μ g Pu·l”.

Solubility data for Pu(VI) in solutions having high hydroxide concentrations indicates amphoteric behaviour for hydrated $\text{PuO}_2(\text{OH})_2(\text{s})$. The oxidation state of the solution species at high pH was not identified, nor were ionic strength effects considered in estimating the formation constant of the “ $(\text{PuO}_2)_2(\text{OH})_5^-$ ”.

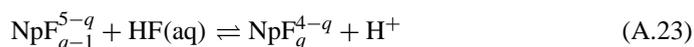
[66AHR/BRA]

The complexation of Np(IV) by sulphate was determined from a cation exchange distribution study in 4 M perchloric acid. The authors made corrections for the possible formation of Np(V) in solution and the resulting interference in their adsorption study. The authors present reasonable, but not compelling, arguments for the corrections necessary to account for this source of interference. The authors linearised their data for calculations, but gave sufficient data to enable recalculation of the association quotients and errors. In the recalculation, the data at very high $\text{SO}_4^{2-}/\Sigma\text{Np}$ ratios were not considered, as the precision of these distribution measurements is very low.

In the case of fluoride complexing of Np(IV), emf measurements were performed using a $\text{Fe}^{3+}/\text{Fe}^{2+}$ electrode in addition to the cation exchange measurements. Here, the emf method relies on the competition between Fe^{3+} and Np^{4+} for the fluoride ion – complexation of fluoride by Fe^{3+} changes the cell potential and allows the stability of the Np(IV) fluoride complexes to be determined. The measurements were done at a temperature of 20°C, and the ionic strength was maintained at $I = 4$ M with HClO_4 . The $\text{HF}(\text{aq})$ concentration was varied between 10^{-5} and 1.4×10^{-2} M in the distribution measurements, and from 10^{-3} to 2×10^{-2} M in the emf measurements. From the distribution measurements the authors reported constants for the following reactions:



$\log_{10} {}^*\beta_1(\text{A.22}, q = 1) = (4.82 \pm 0.02)$ and $\log_{10} {}^*\beta_2(\text{A.22}, q = 2) = (7.57 \pm 0.08)$, while from the emf measurements they reported stepwise constants according to the reactions



for the formation of NpF_2^{2+} , NpF_3^+ and $\text{NpF}_4(\text{aq})$: $\log_{10} {}^*K_2(\text{A.23}, q = 2) = (2.69 \pm 0.10)$, $\log_{10} {}^*K_3(\text{A.23}, q = 3) = (2.34 \pm 0.15)$, and $\log_{10} {}^*K_4(\text{A.23}, q = 4) \approx 1.3$. The authors were unable to determine a value for $\log_{10} {}^*K_1(\text{A.23}, q = 1)$ with the emf method, because they did not observe any significant potential difference at an average

complexation degree of $\bar{n} < 1$: The affinity of Np^{4+} for fluoride is so high that Fe^{3+} is not an effective competitor at $\bar{n} < 1$.

For our evaluation, we prefer the overall constants according to Reaction (A.22) to the stepwise constants. If we assume that $\log_{10} {}^*\beta_1(\text{A.22}, q = 1, 293.15 \text{ K}) = (4.82 \pm 0.02)$ is also valid for the emf measurements, because the second constant from the emf study, $\log_{10} {}^*K_2(\text{A.23}, q = 2) = (2.69 \pm 0.10)$ is nearly identical to the one from the distribution measurements, $\log_{10} {}^*K_2(\text{A.23}, q = 2) = (2.75 \pm 0.08)$. Since we have quantitative information as to the temperature dependence of $\log_{10} {}^*\beta_1$, cf. [76CHO/UNR], we correct the first complexation constant to 25°C: $\log_{10} {}^*\beta_1(\text{A.23}, q = 1, 298.15 \text{ K}) = 4.79$ by using $\Delta_r H_m(\text{A.22}, q = 1) = -10.7 \text{ kJ}\cdot\text{mol}^{-1}$ (taken as independent of ionic strength). We use the cumulative constants in our selection procedure, and we assign an uncertainty of ± 0.10 to $\log_{10} {}^*\beta_1$, and a larger one of ± 0.15 to $\log_{10} {}^*\beta_2$ because we use the latter value unchanged at 25°C.

[66CAS/MAG]

The authors carried out electrophoretic, chromatographic, anion and cation exchange measurements. The experiments were performed at 25°C. The electrophoretic experiments indicate a predominance of negatively charged complexes at ligand concentrations of $[\text{SCN}^-]_t > 6.5 \text{ M}$. The cation exchange data could be used to derive formation constants for the first three complexes. The data refer to an ionic strength of 3 M (NaClO_4), the concentration of SCN^- was varied between 0 and 2 M, and the pH was adjusted to 2 with HClO_4 . The following constants were reported: $K_1(\text{PuSCN}^{2+}, 3 \text{ M}, 298.15 \text{ K}) = 1.1$, $K_2(\text{Pu}(\text{SCN})_2^+, 3 \text{ M}, 298.15 \text{ K}) = 0.73$, and $K_3(\text{Pu}(\text{SCN})_3, 3 \text{ M}, 298.15 \text{ K}) \approx 0.25$.

[66DAN/ORL]

The authors used a solvent extraction technique at $(25.0 \pm 0.1)^\circ\text{C}$ with HTTA in benzene. The aqueous phase consisted of mixtures of HCl/HClO_4 , $\text{HNO}_3/\text{HClO}_4$, and HCl/HBr , to study the complexation of Pu^{4+} with Cl^- , NO_3^- , and Br^- , respectively. The complex extracted in the organic phase was shown to be $\text{Pu}(\text{TTA})_4$ exclusively.

In the chloride system, the extraction experiments with chloride concentrations varying between 10^{-4} and 4 M gave evidence for the formation of two complexes: PuCl^{3+} and PuCl_2^+ . The formation of the 1:2 complex is not visible from the graphical plot, but its inclusion improves the fit in the computer refinement. The resulting formation constants were $\beta_1 = (2.00 \pm 0.06)$ and $\beta_2 = (0.16 \pm 0.03)$. The uncertainties given appear very small, and it is not obvious how they were obtained. We use $\log_{10} \beta_1 = (0.30 \pm 0.20)$ in our evaluation, and we consider the second formation constant too uncertain to be selected.

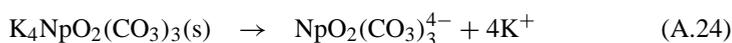
For the bromide system, the authors could identify the formation of PuBr^{3+} and PuBr_2^+ from the graphical plot of the distribution coefficient vs. the bromide concentration ($0.01 \text{ M} \leq [\text{Br}^-]_t \leq 4 \text{ M}$). They corrected for the formation of $\text{Pu}(\text{IV})$ chloride complexes and derived the following formation constants: $\beta_1 = (10.0 \pm 0.5)$ and

$\beta_2 = (4.4 \pm 0.5)$. Again, the uncertainties given appear very small and do not include any systematic errors. Since Danesi, Orlandini and Scibona's [66DAN/ORL] constant for the formation of PuCl^{3+} is consistent with our evaluation, *cf.* Figure 18.1, we use $\log_{10} \beta_1(\text{PuBr}^{3+}) = (1.00 \pm 0.20)$, convert it to molal units, $\log_{10} \beta_1 = (0.96 \pm 0.20)$, and correct it to $I = 0$ by using $\Delta\varepsilon = -(0.29 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}$ from the corresponding U(IV) system [92GRE/FUG]: $\log_{10} \beta_1 = (1.76 \pm 0.60)$. For the 1:2 complex, PuBr_2^{2+} , the authors reported $\log_{10} \beta_2(18.16, q = 2) = (0.64 \pm 0.05)$ in a 4 M HCl/HBr solution. An uncertainty of ± 0.30 would be more realistic. The correction to $I = 0$ using $\Delta\varepsilon(18.16, q = 2) = -(0.56 \pm 0.14) \text{ kg}\cdot\text{mol}^{-1}$ from the corresponding U(IV)-F reaction [92GRE/FUG] yields $\log_{10} \beta_2^{\circ}(18.16, q = 2) = (0.7 \pm 0.7)$. This corrected value is too uncertain to be included in the selected data set of the present review.

For the nitrate system, extractions were carried out using 4 M $\text{H}(\text{ClO}_4, \text{NO}_3)$ solutions with nitrate concentrations ranging from 0.001 to 4 M and 6 M $\text{H}(\text{ClO}_4, \text{NO}_3)$ solutions with nitrate concentrations ranging from 0.005 to 3.5 M. The experiments appear to have been done carefully, but the measured distribution constants are very small, *i.e.*, the error in D_0/D is large. This is especially the case for solutions in which the nitrate concentration is greater than 1 M. Also considering the large changes in the ionic medium, the values of the formation constants for complexes other than the 1:1 complex are judged to be too uncertain to be accepted in the present review. A recalculation of distribution data for $I = 4$ M, taking into account the activity coefficient changes and considering only the first complex, has been attempted. The resulting constant, $\log_{10} \beta_1 = (0.97 \pm 0.05)$, is in very good agreement with the value recalculated for similar conditions using the results of Grenthe and Norén [60GRE/NOR], and with the value of the authors which has been accepted, but with an increased uncertainty, $\log_{10} \beta_1 = (0.96 \pm 0.20)$. The results from the 6 M solutions were not considered further in the selection because of the high ionic strength of the solutions.

[66GOR/KLI]

$\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$ was prepared and chemically analysed in the same way as previously described for $\text{K}_4\text{PuO}_2(\text{CO}_3)_3(\text{s})$ [65IAK/GOR]. The authors indicated the X-ray diffraction pattern of this solid was similar to the pattern for $\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$. This solid was then assumed to be well characterized, and its solubility was measured at $(20 \pm 2)^\circ\text{C}$ in 0, 0.2, 1 M and 50% K_2CO_3 (probably 50 wt. % anhydrous solute; this corresponds to a 5.573 M aqueous solution). The solubility decreases with increasing initial K_2CO_3 concentration. As it is now well established that in concentrated carbonate aqueous solutions the major Np(VI) soluble complex is $\text{NpO}_2(\text{CO}_3)_3^{4-}$, the change in solubility can be attributed to the effect of an increase in the concentration of K^+ in solution on the following reaction



Ionic strength effects cannot be neglected in this medium, and the stoichiometry of the major soluble complex cannot be determined from this work alone (for the same reason, analogy with the well documented [92GRE/FUG] $\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$ can only

be qualitative; see below). In the present review, the equilibrium constant of the above reaction was calculated as follows.

First, using the formation constants of $\text{NpO}_2(\text{CO}_3)_3^{4-}$ and other equilibrium constants selected in this review, it was checked that all other soluble complexes can be disregarded for the conditions of this study. The speciation of the carbonate anions was calculated assuming first a closed system and secondly equilibrium with the air (see also [95VIT]). The effect of possible ingress of $\text{CO}_2(\text{g})$ was found to have a negligible effect on the above equilibrium for the conditions of this study. Since the authors measured the solubility after dissolving $\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$, the concentration of K^+ was estimated to be

$$[\text{K}^+] \approx 2[\text{K}_2\text{CO}_3]_i + 4[\text{Np(VI)}]_i$$

The experimental information given in the publication was $[\text{K}_2\text{CO}_3]_i$, the concentration of K_2CO_3 before $\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$ addition, and $[\text{Np(VI)}]_i$, the measured solubility. This review calculated (see also [98VIT/CAP])

$$\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{K}^+)} = -(0.62 \pm 0.42) \text{ kg}\cdot\text{mol}^{-1}$$

and the value of the standard equilibrium constant for formation of $\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$, $\log_{10} K_{s,3}^\circ(\text{A.24}) = -(7.03 \pm 0.88)$.

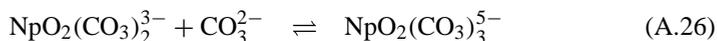
The uncertainty was deduced from the standard deviation, to which was added a contribution for a possible systematic error (0.1) in $\log_{10}[\text{K}^+]$ because the value had to be deduced from the (inadequate) original data (also see the discussions for [71MOS2, 77SIM] and [95OFF/CAP] in this appendix). This was the first experimental work that confirmed analogous chemical behaviour for U(VI) and Np(VI) in concentrated carbonate media.

[66GOR/ZEN]

Grbenko-Germanov and Zenkova prepared M-Np(V)- CO_3 solid compounds, for $M = \text{K}$ and Cs . From chemical analysis, they claimed that these compounds were $\text{M}_5\text{NpO}_2(\text{CO}_3)_3(\text{s})$, but formation of such solid phases has not been confirmed in any later publications (*e.g.*, hydrated $\text{K}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ and not $\text{K}_5\text{NpO}_2(\text{CO}_3)_3(\text{s})$ was reported [74VIS/VOL] to form in similar conditions).

The authors measured the Np(V) concentration in the “mother-liquor” (50% M_2CO_3 aqueous solution) and in the 0.2 M M_2CO_3 aqueous “wash solution”. They then equilibrated each “ $\text{M}_5\text{NpO}_2(\text{CO}_3)_3(\text{s})$ ” solid phase for one week at $(20 \pm 2)^\circ\text{C}$ with these two M_2CO_3 aqueous solutions, and in water, to measure the Np(V) solubility. The Np(V) solubility was always less than the total Np(V) concentration determined in the corresponding initial “mother-liquor” or “wash solution”. This is evidence of slow transformation of the initial M-Np(V)- CO_3 solid compounds into more stable ones, and that equilibrium was probably not attained during preparation of the initial solid phases.

In this review, an attempt has been made to interpret these solubility measurements according to the equilibria



but there is no way to check whether equilibrium was obtained prior to the measurements.

There is only one experimental result (Np(V) solubility in 0.2 M M_2CO_3) that could be used to estimate an equilibrium constant, but for this medium the Np(V) aqueous speciation is not known (*i.e.*, the $[\text{NpO}_2(\text{CO}_3)_3^{5-}]:[\text{NpO}_2(\text{CO}_3)_2^{3-}]$ ratio), because the activity coefficients are not known and are different from those in Na^+ media (in 0.2 M Na_2CO_3 aqueous solution the $[\text{NpO}_2(\text{CO}_3)_3^{5-}]:[\text{NpO}_2(\text{CO}_3)_2^{3-}]$ ratio is approximately 1.0). In the present review, this value for the ratio has been assumed, and the value for the equilibrium constant $K_{s,3}$ (A.25), was estimated but with an increased uncertainty to account for this assumption:

$$\log_{10} K_{s,3}(\text{A.25}, \text{M}^+ = \text{K}^+) = -(3.0 \pm 1.5)$$

in 0.2 M K_2CO_3 aqueous solution at $(20 \pm 2)^\circ\text{C}$. In the same way,

$$\log_{10} K_{s,3}(\text{A.25}, \text{M}^+ = \text{Cs}^+) = -(2.4 \pm 1.5)$$

in 0.2 M Cs_2CO_3 aqueous solution at $(20 \pm 2)^\circ\text{C}$, could also be estimated; but the formation of the compound $\text{CsNpO}_2\text{CO}_3(\text{s})$ is questionable (only the corresponding Am compound, $\text{CsAmO}_2\text{CO}_3(\text{s})$ has been characterised [65KEE] even though the attempted preparation of the Np compound should have been easier).

In the present review, it was assumed the solubility measured in the most concentrated K_2CO_3 aqueous solutions was controlled by the equilibrium



and hence:

$$\log_{10} K_{s,3}(\text{A.27}) = -(1.4 \pm 1.5)$$

in 5.57 M K_2CO_3 aqueous solution at $(20 \pm 2)^\circ\text{C}$. The uncertainty has been further increased because equilibrium was probably not obtained prior to measurement of the neptunium concentration.

The same type of interpretation would probably be less valid for the 50% Cs_2CO_3 media, where the Np(V) solubility is considerably higher than in the sodium or potassium aqueous solutions. Also, although there are reports in the literature about $\text{Rb}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ [79VOL/VIS, 81VOL/VIS2, 81VOL/VIS3, 81VOL/VIS] there is nothing about $\text{Cs}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$, and it is unclear whether $\text{Cs}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ was formed. Therefore, this review does not use the solubility measurements in concentrated Cs_2CO_3 aqueous solution. The thermodynamic data extracted from this publication for the potassium system are only rough estimates as the corresponding solid phases were not properly characterised.

Two Np(V) absorption spectra were also reported. The characteristic NpO_2^+ bands were notably changed on addition of concentrated carbonate solution. This was the first reported evidence of the formation of soluble Np(V) complexes. The spectra can be attributed to a mixture of $\text{NpO}_2(\text{CO}_3)_3^{5-}$ and $\text{NpO}_2(\text{CO}_3)_2^{3-}$ complexes [90RIG], but there were insufficient reported measurements for proper estimation of formation constants.

[66RYK/YAK]

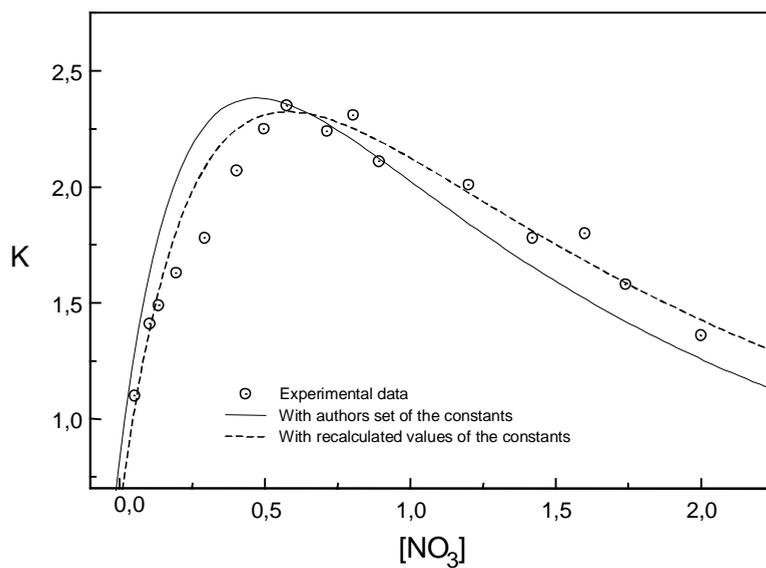
This is a spectrophotometric study of the kinetics of the reaction of $\text{Np(IV)} + \text{Np(VI)} \rightleftharpoons 2\text{Np(V)}$, carried out at $(25 \pm 0.1)^\circ\text{C}$ in 2.0 M $\text{H}(\text{ClO}_4, \text{NO}_3)$ solutions, adding nitrate through to full substitution for perchlorate. The reverse reaction, disproportionation of Np(V), was ruled out. In nitrate media, the kinetic constant initially increased linearly with nitrate concentration, then began to flatten out at higher nitrate concentrations. From this it was assumed that an activated complex nitrate-Np(IV)-Np(VI)-water had formed. To explain the flattening out, formation of nitrate complexes was assumed. Since total concentrations were measured, the rate was given by expressing the free ion concentration in terms of the total concentration and the fraction complexed. Then the assumption of which complexes form and what formation constants they should have was made by trying the simplest complexes and fitting the rate constant data. No analysis of stoichiometry of the complexes could be done since, from one set of data, constants for 3-4 complexes had to be determined. This was done by fixing arbitrarily only one complex for NpO_2^{2+} with a formation constant of 0.4 (no data are given in the paper to substantiate this assumption), and then two schemes of complexation for Np^{4+} were tested, one with only one complex, the other with two. Since the two complex hypothesis gave a better fit to the data for the dependence of the kinetic constant on nitrate concentration, this speciation was accepted and the values of the constants were determined.

By refitting the data using the authors' method, this review finds a much better fit with $\beta_1 = 1.9$ and $\beta_2 = 1$ for the formation constants of the complexes for Np(IV), using $k'_1 = 0.6$ and $k'_2 = 11.0$, instead of the set of four constants reported by the authors (2.2, 1.5, 0.82, 12.5, respectively) (see Figure A.4). The recalculated k' values with the authors' model (Eq. 12) are markedly different from those reported in Table 1 of the paper, so a calculation error is suspected. The value $\log_{10} \beta_1 = (0.34 \pm 0.20)$ is accepted, where the uncertainty has been assigned in the present review. However, other approaches to analysing the data would give a somewhat different result. Since the analysis of the kinetics of the reaction studied was based on the measurement of the concentrations of ions participating in complexation equilibria, the simplest hypothesis would be to assume only one complex for Np(IV) or even no complex at all. Even though equilibrium is not completely excluded, the reported data for K' vs. nitrate concentration have been treated as:

$$v = -d[\text{Np}^{4+}]/dt = K'(k_1 + k_2[\text{NO}_3])[\text{Np}^{4+}][\text{NpO}_2^{2+}]$$

where k_1 and k_2 are two kinetic constants to be determined together with the complexation constant(s). It can be shown that assuming a single Np(IV) complexation

Figure A.4: The kinetic data of [66RYK/YAK] plotted with the authors model and constants (full line) and using constants as recalculated in the present review (dashed curve, see text).



constant, and assuming the value of that formation constant varies with nitrate concentration because of activity effects, a better fit than that of the authors is obtained (with $\beta_1 = 2.65$), even though the authors' method assumed three complexes. Indeed, the data can even be fitted quite well assuming no complexes at all, with only a single concentration-dependent activity coefficient parameter.

[66SHI/NAZ]

The authors used a solvent extraction method with HTTA to determine the formation constants of NO_3^- and Cl^- complexes of Np(IV) at 20°C and at ionic strengths of 0.5, 1.0 and 2.0 M. The presence of Np(IV) as the only oxidation state was checked successfully with an extraction test. The ligand concentrations were varied between 0 and 2 M while maintaining a constant ionic strength of 2.0 M by using HClO_4 .

The experiments as well as their evaluation appear correct, but the authors did not give any uncertainty estimates. For chloride as a ligand, we use their values with our estimated uncertainties: $\log_{10} \beta_1(\text{NpCl}^{3+}) = (0.15 \pm 0.20)$ for $I = 0.5$ M, $-(0.04 \pm 0.20)$ for $I = 1.0$ M, and (0.04 ± 0.20) for $I = 2.0$ M. In the absence of any enthalpy data, we use these values at 25°C assuming that the temperature correction between 20°C and 25°C is not significant. For the 1:2 complex, the results $\log_{10} \beta_2(\text{NpCl}_2^{2+}) = -(0.25 \pm 0.30)$ for $I = 1.0$ M and $-(0.15 \pm 0.30)$ for $I = 2.0$ M seem acceptable, but the extrapolation to $I = 0$ of the results from different sources yields inconsistent results, *cf.* Part III, Section 9.2.2.2. The constant obtained for NpCl_3^+ at $I = 1$ M is not credible because such a complex is not expected to form under these conditions, *cf.* comments under Danesi *et al.* [71DAN/CHI].

The nitrate data were treated similarly. There is a high degree of subjectivity in calculating the constants from the experimental data. The values of some of the constants are less than the errors therein. Thus, for $I = 1.5$ M, the value selected by the authors gives a model function that is almost tangential at the lowest point of the experimental data curve. The authors reported the values $\beta_1 = 2.8$ ($I = 0.5$ M); $\beta_1 = 2.2$, $\beta_2 = 1.2$ and $\beta_3 = 0.55$ ($I = 1.0$ M); $\beta_1 = 2.3$ ($I = 1.5$ M); $\beta_1 = 2.0$ and $\beta_2 = 2.2$ ($I = 2.0$ M). Recalculation assuming two, and only two, complexes with constants calculated as the slope and intercept of the function used by the authors results in the values $\beta_1 = 4.2$ and $\beta_2 = 0.06$ ($I = 0.5$ M); $\beta_1 = 1.7$, and $\beta_2 = 1.6$ ($I = 1.0$ M); $\beta_1 = 2.6$ and $\beta_2 = 3.2$ ($I = 1.5$ M); $\beta_1 = 1.3$ and $\beta_2 = 5.0$ ($I = 2.0$ M). Because of the high ionic strength and high variation in the perchlorate and nitrate concentrations in these experiments, activity corrections as used in the present reviews [92GRE/FUG, 95SIL/BID] do not properly account for medium effects in deriving association constants from this type of data (especially higher association constants) for very weak complexes. Thus, it is assumed the activity coefficient factors, or equivalently, the concentration quotient

$$K = \frac{[\text{NpNO}_3^{3+}]}{[\text{Np}^{4+}] \cdot [\text{NO}_3^-]}$$

for a complex have the same numerical values in different media of the same ionic strength (*e.g.*, in 2 M HClO_4 or in 2 M HNO_3). A somewhat different treatment

was applied here to account for activity factor changes, and for the first complexation constant (only), extrapolated to trace nitrate concentrations, $\beta_1 = 3.0$ ($I = 0.5$ M HClO₄); $\beta_1 = 1.42$, ($I = 1.0$ M HClO₄); $\beta_1 = 1.9$ ($I = 1.5$ M HClO₄); $\beta_1 = 1.6$ ($I = 2.0$ M HClO₄) were obtained. Since this treatment yields a fit to the experimental data that is at least equally good as is found from the standard treatment, the authors' values for the formation constants of the 1:2 and 1:3 species are not accepted. The values of the constants for the first complex are well within the uncertainties of those obtained from the standard treatment above, and the values from the standard treatment, with uncertainties assigned in the present review are accepted for the first stepwise constants: $\log_{10} \beta_1(I = 0.5 \text{ M HClO}_4) = (0.62 \pm 0.20)$, $\log_{10} \beta_1(I = 1.0 \text{ M HClO}_4) = (0.23 \pm 0.20)$, $\log_{10} \beta_1(I = 1.5 \text{ M HClO}_4) = (0.41 \pm 0.20)$, $\log_{10} \beta_1(I = 2.0 \text{ M HClO}_4) = (0.11 \pm 0.20)$.

[66WAI]

In this study, Wain has measured the formal potential of the Pu(IV)/Pu(III) couple at $(25 \pm 0.1^\circ)\text{C}$ in 0.4-2 M solutions of nitric acid, as well as in 0.5 and 1 M HClO₄, and 1 M HCl. The standard calomel electrode was used as reference and the liquid junction potential was estimated by comparing the data obtained in 1 M HClO₄ with the value reported in [51RAB/LEM] obtained without liquid junction and with the hydrogen electrode as reference. The values compare relatively well, which is unexpected due to the possibility of precipitation of KClO₄ in the liquid junction. From the difference in the values of the potential measured in 1 M and 0.5 M (in fact this last value is interpolated) HNO₃ with the potential in solutions of equal concentrations of HClO₄, the author calculated the formation constant for the complex PuNO₃³⁺ as $\beta_1 = 5.3$ at 0.5 M HNO₃ and $\beta_1 = 5.6$ at 1 M HNO₃. In the calculation it was assumed that Pu(III) does not form nitrate complexes and that the redox potential at zero HNO₃ concentration should become equal to that in 0.5 M or 1 M HClO₄ solutions (almost identical values were measured in HClO₄ by the author).

Recalculations show the redox potentials in nitric acid solutions could equally well be explained by activity effects without complexation. Since only one measurement was used to determine the value of the formation constant, and because of possible problems related to Pu(III) complexation and potassium perchlorate precipitation, the results from this study are not used further in the present review.

[67DAV]

In this report on the solubility behaviour of amorphous and colloidal hydroxides, values are reported on the solubility product of Pu(OH)₄(am). It is unlikely that the plutonium in solution was predominantly in the +4 oxidation state under the conditions of at least some of the experiments. The large value for $\log_{10} K_{s,0}$ for material precipitated at a pH value of 3 is similar to that reported by Perez-Bustamante [65PER]. The problem is discussed further under the entry for that reference.

[67DEN/SHE]

The authors have studied the solubility of $\text{PuO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$ [67DEN/SHE2] in phosphoric acid solutions in the concentration range 0.02-5.88 M at 25°C. No constant ionic medium was used, and no analysis of the solid phase after the equilibration was reported. Initially a qualitative spectrophotometric study indicated a displacement of the infrared absorption band of Pu(VI) to longer wavelengths in the presence of phosphate, but the composition and the formation constants of the complexes could not be determined due to the insignificant change of the molar absorptivities. The increase in the solubility was explained as resulting from the formation of the complexes $\text{PuO}_2\text{HPO}_4(\text{aq})$ and $\text{PuO}_2\text{H}_2\text{PO}_4^+$, while the complex $\text{PuO}_2(\text{H}_2\text{PO}_4)_2(\text{aq})$ was proposed on the basis of the isolation of a solid compound with a 1:2 plutonium:ligand ratio at the highest phosphoric acid concentration. Electrophoresis experiments demonstrated that dioxoplutonium(VI) enters in the composition of cationic complexes for H_3PO_4 concentrations 0.02-0.206 M, while the decrease in cationic species at higher ligand concentrations was explained by the authors as the result of formation of the neutral $\text{PuO}_2(\text{H}_2\text{PO}_4)_2(\text{aq})$. Regardless, the formation constant for this complex could not be determined, since the authors observed both a change in the solid phase and a partial reduction of Pu(VI) to Pu(IV) for phosphoric acid concentrations higher than 5.88 M.

The calculation of the formation constants was done by analyzing the solubility data obtained in the interval $0.02 \text{ M} < [\text{H}_3\text{PO}_4] < 0.2 \text{ M}$. In the data analysis the species $\text{PuO}_2\text{HPO}_4(\text{aq})$ and $\text{PuO}_2\text{H}_2\text{PO}_4^+$ were considered. There was no experimental evidence for the formation of the $\text{PuO}_2\text{HPO}_4(\text{aq})$ complex. Apparently, its existence and stability constant $\log_{10} \beta(\text{PuO}_2\text{HPO}_4(\text{aq})) = 8.17$, together with the solubility product for the solid phase $\log_{10} K_{\text{s},0} = -12.51$ was taken from a previous work [65DEN/SHE]. These values were used by the authors [67DEN/SHE] together with the solubility data to determine the formation constant for the complex $\text{PuO}_2\text{H}_2\text{PO}_4^+$ as $\log_{10} \beta(\text{PuO}_2\text{H}_2\text{PO}_4^+) = (3.93 \pm 0.13)$. Since the values of these previously determined constants used with the solubility data to obtain $\beta(\text{PuO}_2\text{H}_2\text{PO}_4^+)$ have been rejected in the present review because of probable phase changes in the earlier study (see comments on [65DEN/SHE] in this appendix), and also because of the changes in the activity coefficients with the increase of the phosphoric acid concentration due to the variation of the ionic strength, the results reported in this work are not accepted in the present review.

[67DEN/SHE2]

The authors reported the synthesis of three solid compounds formed in the dioxoplutonium(VI)-phosphate system, namely $\text{NH}_4\text{PuO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}(\text{s})$, $\text{PuO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$ and $\text{PuO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{s})$. Powder X-ray diffraction spectra showed the first compound to be isostructural with the corresponding dioxouranium(VI) compound $\text{NH}_4\text{UO}_2\text{PO}_4 \cdot 3\text{H}_2\text{O}(\text{s})$, while only chemical analysis was used to characterize the two other compounds. The solid $\text{PuO}_2(\text{H}_2\text{PO}_4)_2 \cdot 3\text{H}_2\text{O}(\text{s})$ was obtained by mixing $\text{PuO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$ with a 5 M solution of phosphoric acid

for 14 days. All three compounds were reported to be stable with respect to changes in the oxidation state of plutonium over a period of several months.

[67ERM/STA]

Although this paper does not give any hydrolysis constants for Np(III) or Pu(III), the extraction constants K_{ex} with HTTA in benzene are determined for Am(III), Cm(III) and Fm(III). That system has been used by several authors for obtaining actinide hydrolysis constants. This paper therefore serves as a useful reference, as the experiments and results seem reliable.

[67GEL/MOS]

The data in this paper may have predated the data in [62GEL/MOS]. The experiment is identical but the results are reported in terms of a single complex, $\text{PuO}_2(\text{CO}_3)_2^{2-}$ with a stability of $\log_{10} \beta_2 = 15$. No hydroxy-complexes appear in this interpretation. No description is given of the solid phases used in these solubility experiments and therefore no reliance can be placed on these results.

[67MOS/ESS]

The authors measured the solubility of $\text{Th}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{s})$ at 0.35 M HClO_4 while varying the concentration of $\text{H}_3\text{PO}_4(\text{aq})$ between 10^{-4} and 1.5 M. The solubility data for the thorium system were explained in terms of the formation of aqueous complexes of the general composition $\text{Th}(\text{HPO}_4)_n^{4-n}$ with $n = 1$ to 3. Based on these data, the data on the analogous Pu(IV) system [60DEN/MOS2, 60DEN/MOS] and the results of the analysis of the solubility data on the U(IV) system [64MAR/VER], the authors proposed interpolated values for the stability constants of four aqueous complexes of the general composition $\text{Np}(\text{HPO}_4)_n^{4-n}$ with $n = 1$ to 4



$$\log_{10} \beta_n(\text{A.28}, n = 1, \text{unreported temperature}, I \rightarrow 0) = 12.4$$

$$\log_{10} \beta_n(\text{A.28}, n = 2, \text{unreported temperature}, I \rightarrow 0) = 23.1$$

$$\log_{10} \beta_n(\text{A.28}, n = 3, \text{unreported temperature}, I \rightarrow 0) = 32.0$$

$$\log_{10} \beta_n(\text{A.28}, n = 4, \text{unreported temperature}, I \rightarrow 0) = 41.0$$

and a value for the solubility product of the corresponding solid.

Since the chemical model used by the authors in the corresponding Pu(IV) system (see comments for [60DEN/MOS2] and [60DEN/MOS] in this appendix) has not been accepted, the Np(IV) constants estimated in this work are also rejected in the present review.

[67NAI/RAO]

This describes a cation exchange study carried out at 28°C in 1 to 1.28 M H(ClO₄, HSO₄) with the Pu(III) oxidation state maintained using 0.1 M KI under a N₂ atmosphere. Pu(III) complexing by I⁻ was ignored in interpretation. The value used for the HSO₄⁻ dissociation quotient appears to be much lower than appropriate. The Pu isotope used was not specified (probably ²³⁹Pu). Equilibrium was not demonstrated rigorously but the 24 hours equilibration time appears to be adequate for equilibrium to have been attained. Data have been provided on which to base error estimates. Results were interpreted to indicate that both SO₄²⁻ (PuSO₄⁺) and HSO₄⁻ (Pu(HSO₄)₂⁺) can complex Pu(III) in acid media, but this result is based on the erroneously low HSO₄⁻ dissociation constant used by the authors, the inability of exchange resins to quantitatively extract anionic complexes in strong acid (see the discussion of [78RAO/BAG]), and evidence from electrical migration studies [76FAR/BUC]. Data were re-evaluated using a quadratic statistical model (see [83NAS/CLE2]), and the dissociation constant of HSO₄⁻ of [51ZEB/ALT] was extrapolated to temperature using the enthalpy determined by [59ZIE] (see [76FAR/BUC]).

[68AHR/BRA]

This is a very careful study of the fluoride complexation of NpO₂²⁺ carried out by using an extraction technique with dibutyl phosphate in CCl₄ as the organic phase. The aqueous phase contained 1 M HClO₄ and various amounts of HF(aq). The authors added a small amount (0.2 mM) of permanganate to prevent Np(VI) from being reduced. The temperature of the experiment was 21°C, and the measurements were carried out at three different total concentrations of Np(VI): 0.09, 0.22 and 0.44 mM. All precautions have been taken, and the evaluation of the experimental data was performed with a graphical method. The advantage of graphical methods is that, for simple chemical systems, it is usually possible to verify or reject a chemical model by plotting the experimental data as a linear, model-dependent function. It is easy to recognise a deviation from linearity by eye, and it is usually possible to distinguish such a deviation from the scatter in the data. In such a way, the authors showed convincingly that their model, which considers only the formation of a 1:1 and a 1:2 complex, correctly interprets the experimental data up to a HF(aq) concentration of 4.51 M. The reported constants appear very reliable, and we use the reported values and uncertainties in our evaluation in Part III, Section 9.2.1.4: $\log_{10} \beta_1 = (0.93 \pm 0.11)$ and $\log_{10} \beta_2 = (1.11 \pm 0.10)$, and assume the effect of the difference in temperature is negligible within the stated uncertainties.

[68AHR/BRA2]

This describes a thorough distribution study using dibutyl phosphate as the extractant in carbon tetrachloride. A holding oxidant (permanganate) was used. A non-linear least squares approach was used to recalculate the association quotients from the data presented. On this basis $\log_{10} \beta(\text{NpO}_2\text{SO}_4, \text{aq})$ was found to be (0.75 ± 0.12) and

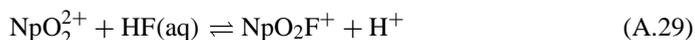
$\log_{10} \beta(\text{NpO}_2(\text{SO}_4)_2^{2-}) = (0.78 \pm 0.14)$. These data may be corrected from 294.15 K to 298.15 K using the enthalpies of reaction determined by [86ULL/SCH] and the auxiliary data for the deprotonation of HSO_4^- . Although the errors are fairly large, the results are reliable. Note that the dissociation of HSO_4^- under experimental conditions was determined by the authors.

[68HUB/HOL]

This paper describes what appears to be a carefully performed combustion experiment to determine the enthalpy of formation of neptunium dioxide, and the reported results and uncertainties are accepted in the present review.

[68KRY/KOM]

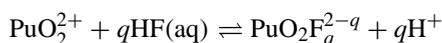
The first formation constant for the Np(VI)-HF system,



was reported at 25°C in 2.11 M and 1.04 M HClO_4 solutions. The authors used the cation exchange method of Fronæus [51FRO]. The reported values of $\log_{10} {}^*\beta_1(\text{A.29}, I = 2.11 \text{ M}) = (2.11 \pm 0.03)$ and $\log_{10} {}^*\beta_1(\text{A.29}, I = 1.04 \text{ M}) = (2.20 \pm 0.02)$ are inconsistent with the values of other studies. The IAEA review [92FUG/KHO] related the discrepancy to the fact that the authors did not take into account the formation of a 1:2 complex, $\text{NpO}_2\text{F}_2(\text{aq})$. However, by using the constants of the Np(VI) fluoride system as selected in the IAEA review, we estimate that, at $I = 1.04 \text{ M}$, only about 3% of Np(VI) were present as 1:2 complex at the highest HF(aq) concentration, and at $I = 2.11 \text{ M}$, the maximum proportion of 1:2 complex was about 1%. However, Np(VI) has oxidising properties which are enhanced in the presence of fluoride and in acidic media. Organic ion exchangers were reported to be slowly oxidised by Np(VI), see [68AHR/BRA] and references cited therein, and there is little doubt that this is what happened during the experiments of Krylov, Komarov and Pushlenkov [68KRY/KOM]. In their review of aqueous coordination complexes of neptunium, Patil, Ramakrishna and Ramaniah [78PAT/RAM] arrived at the same conclusion. The measurements reported in [68KRY/KOM] are thus most probably not representative of Reaction (A.29), and the data from this study are discarded in the present review.

[68KRY/KOM2]

The authors reported formation constants for the equilibria

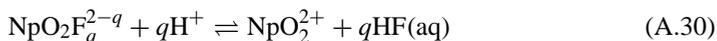


with $q = 1, 2, 3$ and 4, from cation exchange measurements in both 1 M and 2 M HClO_4 . The reported constants are inconsistent with expectations and with the results of other studies [84CHO/RAO, 85SAW/CHA]. As in the study on Np(VI) fluoride

complexation [68KRY/KOM], the most probable reason for the discrepancy is partial reduction of Pu(VI) to Pu(IV). This reduction is particularly favoured in acidic solutions, in the presence of an organic ion exchange resin, and also is favoured because of the high stability of the Pu(IV) fluoride complexes. The authors did not use any holding oxidant to prevent or control reduction, and the results of this study are not given any credit in the present review.

[68SON/MUS]

This paper presents only a short summary of redox potential measurements of the Np(VI)/Np(V) couple in the presence of fluoride. The method and theory is described in sufficient detail, but no information is given on the experimental conditions. The authors reported dissociation constants for the following reactions:



$K(\text{A.30}, q = 1) = 0.11$, $K(\text{A.30}, q = 2) = 0.54$ and $K(\text{A.30}, q = 3) = 10$, at $\text{pH} = 1$, $I = 2.1 \text{ M}$ (NaClO_4) and 25°C . The range of fluoride concentrations used was not reported by the authors. Since the constants reported for the 1:1 and the 1:2 complexes are in reasonable agreement with those of other studies, we use them in our evaluation with an estimated uncertainty of ± 0.4 in the logarithmic constants, in order to reflect the lack of experimental details.

[68ZAI/ALE]

This paper reports a study in which relatively pure $\text{PuO}_2\text{OH}(\text{am})$ was obtained, and the (room temperature ?) solubility product was determined from the initial pH of precipitation from a nitrate solution of Pu(V). A value of $K_1 = 0.5 \times 10^{-9}$ was reported, corresponding to $\log_{10}^*K_1 = 4.7$ for



This is from the same experiment reported in less detail in [64GEL/ZAI].

[68ZAI/ALE2]

A sparingly soluble (no solubility data are reported) compound of Pu(V) was synthesized from a nitric acid solution of Pu(V) by addition of $(\text{NH}_4)_2\text{HPO}_4$. Chemical analysis of the solid showed a PuO_2^+ to NH_4^+ ratio of 1:1, while the water content and the amount of HPO_4^{2-} were calculated by difference. From these results the formula $\text{NH}_4\text{PuO}_2\text{HPO}_4(\text{s})$ was proposed.

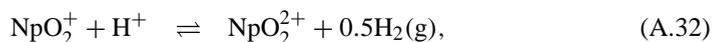
[69COH/FRI]

During an electromigration study in 1 M NaOH solution, Np(V) moved to the anode which should indicate that the major Np(V) species is anionic. An ion exchange (cation resin Dowex 50) investigation led to the same conclusion. However, it is not

clear whether special precautions had been taken to protect the NaOH solutions from $\text{CO}_2(\text{g})$ in order to avoid any (anionic) carbonate complex formation. The Np(V) absorption spectrum in 1 M tetramethylammonium reported in this work had a peak around 1010 nm which should be attributed to a mixed hydroxy-carbonate soluble complex [84VAR/BEG, 90RIG, 91VIT/OLI, 98VIT/CAP].

[69FUG/BRO]

The enthalpy of solution of $\text{NpO}_2(\text{OH})_2(\text{s})$ was measured in 1 M HCl and 1 M HClO_4 . No reliable value for $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, 1 \text{ M HCl})$ seems to have been reported. However, an estimate of the enthalpy of transfer of NpO_2^{2+} from $\text{H}_2\text{O}(\text{l})$ to 1 M HCl(aq) of $(2.4 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$ at 298.15 K can be made based on information for the analogous uranium system [83FUG/PAR, 92GRE/FUG]. From this, $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, 1 \text{ M HCl}, 298.15 \text{ K}) = -(858.3 \pm 5.3) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated in the present review. Using this value and $\Delta_f H_m^\circ(\text{H}_2\text{O}, 1 \text{ M HCl}, 298.15 \text{ K}) = -(285.85 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$ [65PAR, 2000RAN/FUG], the value $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{cr})) = -(1376.9 \pm 5.3) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated. Fuger and Oetting estimated $\Delta_f H_m^\circ(\text{Np}^{4+}, 1 \text{ M HClO}_4) = (\Delta_f H_m^\circ(\text{Np}^{4+}, \text{aq}) + 0.42) \text{ kJ}\cdot\text{mol}^{-1}$ [76FUG/OET] (*i.e.*, $-(555.60 \pm 4.2) \text{ kJ}\cdot\text{mol}^{-1}$). Using this, the enthalpies of reaction, $\Delta_f H_m^\circ$ (A.31) = $(149.082 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ$ (A.32) = $(117.449 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1}$



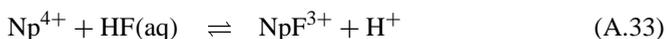
in 1 M HClO_4 based on the values selected in Section 7 and $\Delta_f H_m^\circ(\text{H}_2\text{O}(\text{l}), 1 \text{ M HClO}_4) = -(285.82 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$ based on Parker's assessment [65PAR], $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{s})) = -(1378.6 \pm 4.5) \text{ kJ}\cdot\text{mol}^{-1}$.

[69KEL/FAN]

The data reported in this study are fragmentary which leads to difficulties in assessing the validity of the results. The value of the reduction potential Pu(VI)/Pu(IV) = $-(0.60 \pm 0.05) \text{ V}$ (error estimated in the present review) *vs.* the calomel electrode ($-(0.36 \pm 0.05) \text{ V vs. SHE}$) was measured in 1 M Na_2CO_3 solution at room temperature (25 ± 2)°C. The controlled potential reduction of molar Na_2CO_3 solutions with initial ratios of U(VI)/Pu(VI) varying from 6.25:1 to 2.5:1, followed by heating the solution to 80°C, resulted in a series of homogeneous hydrated precipitates of the form (U, Pu) $\text{O}_2(\text{s})$ with the same ratio of U/Pu as in the original solutions. X-ray powder patterns were used to confirm that the solid solution series was homogeneous.

[69KRY/KOM]

The authors reported equilibrium constants at 25°C for the reaction



at ionic strengths of 1 M and 2 M (HClO₄). They used the cation exchange method of Fronæus [51FRO]. The results of Krylov, Komarov and Pushlenkov [69KRY/KOM3], who performed the same experiments in HNO₃ solutions, are also discussed here. The constants were obtained from distribution measurements at HF(aq) concentrations between 8×10^{-5} and 3×10^{-3} M and are listed in Table A.2. While Patil and Ramakrishna [75PAT/RAM] observed constant values up to a HF(aq) concentration of only 3×10^{-4} M, the results of the present two studies seem to remain fairly constant up to the maximum HF(aq) concentration of 3×10^{-3} M. In other words, Krylov and coworkers [69KRY/KOM, 69KRY/KOM3] can explain their data in terms of the formation of NpF³⁺, while Patil and Ramakrishna [75PAT/RAM] need to consider NpF₂²⁺ as an additional complex. We cannot find any evident shortcoming in the evaluation or performance of the experiments. However, a systematic error is indicated. We take account of this unidentified systematic error by increasing the uncertainties, see below.

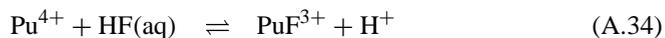
Table A.2: Equilibrium constants referring to Reaction (A.33) as reported in [69KRY/KOM] (HClO₄) and [69KRY/KOM3] (HNO₃).

Background electrolyte	$\log_{10} {}^*\beta_1(\text{A.33})$ ($I = 1$ M)	$\log_{10} {}^*\beta_1(\text{A.33})$ ($I = 2$ M)
HClO ₄ [69KRY/KOM]	(4.56 ± 0.04)	(4.70 ± 0.05)
HNO ₃ [69KRY/KOM3]	(4.23 ± 0.10)	(4.11 ± 0.03)
HNO ₃ (corrected for the formation of NpNO ₃ ³⁺ by this review)	(4.74 ± 0.15)	(4.75 ± 0.15)

It is obvious that the constants are systematically lower in HNO₃ media compared to HClO₄ media. This is due to the formation of nitrate complexes of Np⁴⁺. We use our selected constants to correct for the formation of NpNO₃³⁺ in nitrate media, $\log_{10} \beta_1(I = 1 \text{ M}) = (0.50 \pm 0.16)$ and $\log_{10} \beta_1(I = 2 \text{ M}) = (0.49 \pm 0.19)$. The corrected values, listed in the last row of Table A.2, are now very close to those measured in HClO₄ solutions. The results suggest only a small influence of the inert salt medium and the ionic strength on the equilibrium constant of Reaction (A.33). The constants measured in perchlorate media and the corrected ones from nitrate media are used in the evaluation of the standard values, but the uncertainties in the logarithmic values are increased to ± 0.30 to cover the unidentified systematic error (see above).

[69KRY/KOM2]

The authors reported equilibrium constants at 25°C for the reaction



at ionic strengths of 1 M and 2 M (HClO₄) from distribution measurements using a cation exchange resin. The results of Krylov, Komarov and Pushlenkov [69KRY/KOM4], who performed the same experiments in HNO₃ solutions, are also

discussed here. The constants were obtained from distribution measurements at HF(aq) concentrations between 6×10^{-5} and 10^{-3} M and are listed in Table A.3. Krylov and coworkers [69KRY/KOM2, 69KRY/KOM4] could explain their data in terms of the formation of PuF_3^{3+} , and it was not necessary under these conditions to include a 1:2 complex in the model.

Table A.3: Equilibrium constants referring to Reaction (A.34) as reported in [69KRY/KOM2] (HClO_4) and [69KRY/KOM4] (HNO_3).

Background electrolyte	$\log_{10} {}^*\beta_1(\text{A.34})$ ($I = 1$ M)	$\log_{10} {}^*\beta_1(\text{A.34})$ ($I = 2$ M)
HClO_4 [69KRY/KOM2]	(4.20 ± 0.08)	(4.45 ± 0.03)
HNO_3 [69KRY/KOM4]	(4.04 ± 0.08)	(3.78 ± 0.01)
HNO_3 (corrected for the formation of PuNO_3^{3+} by this review)	(4.66 ± 0.15)	(4.64 ± 0.16)

It is obvious that the constants are systematically lower in HNO_3 solutions [69KRY/KOM4] compared to HClO_4 solutions [69KRY/KOM2]. This is due to the formation of nitrate complexes of Pu^{4+} . We use our selected constants to correct for the formation of PuNO_3^{3+} in nitrate media, $\log_{10} \beta_1(I = 1 \text{ M}) = (0.50 \pm 0.16)$ and $\log_{10} \beta_1(I = 2 \text{ M}) = (0.49 \pm 0.19)$. The corrected values, listed in the last row of Table A.3, are then significantly higher than those measured in HClO_4 solutions. In particular, it is noted that the constant measured at $I = 1$ M (HClO_4) differs considerably from the one determined in nitric acid solution and corrected for nitrate complexation. We estimate that the formation of the 1:2 complex, PuF_2^{2+} , should be significant at the higher concentrations of HF(aq) used in these experiments. However, the possible influence of the 1:2 complex should also affect the values determined in the HClO_4 solutions, and the lack of including the 1:2 complex can therefore not explain the discrepancy. The constants measured in perchlorate media and the corrected ones from nitrate media are used in the evaluation of the standard values, but the uncertainties in the logarithmic values are increased to ± 0.30 in HClO_4 and to ± 0.40 in HNO_3 media to cover the systematic errors.

[69KRY/KOM3]

See comments under Krylov and Komarov [69KRY/KOM].

[69KRY/KOM4]

See comments under Krylov and Komarov [69KRY/KOM2].

[69MET/GUI]

This is a solvent extraction study of the hydrolysis of Pu(IV) for an aqueous medium of ionic strength 1.0 M (H/LiClO₄). No values for the hydrolysis constants are derived in this paper.

[69MOS]

This publication is a compilation of stability constants of actinide complexes with various ligands. Values for nitrate, sulphate, carbonate and phosphate complexes, as determined in previous work, published and unpublished, were reported together with the author's estimates. For the phosphate system, constants for Np(III) complexes with H₂PO₄⁻ were included, estimated on the basis of the results for Pu(III), Am(III) and Cm(III) published in a later paper [71MOS4]



$$\log_{10} \beta_n(\text{A.35}, n = 1, \text{unreported temperature}, I \rightarrow 0) = 2.40$$

$$\log_{10} \beta_n(\text{A.35}, n = 2, \text{unreported temperature}, I \rightarrow 0) = 3.73$$

$$\log_{10} \beta_n(\text{A.35}, n = 3, \text{unreported temperature}, I \rightarrow 0) = 5.64$$

$$\log_{10} \beta_n(\text{A.35}, n = 4, \text{unreported temperature}, I \rightarrow 0) = 6.2$$

and estimates at $I = 0$ for the Pu(III) constants later reported in [71MOS4]:



$$\log_{10} \beta_n(\text{A.36}, n = 1, \text{unreported temperature}, I \rightarrow 0) = 2.39$$

$$\log_{10} \beta_n(\text{A.36}, n = 2, \text{unreported temperature}, I \rightarrow 0) = 3.70$$

$$\log_{10} \beta_n(\text{A.36}, n = 3, \text{unreported temperature}, I \rightarrow 0) = 5.63$$

$$\log_{10} \beta_n(\text{A.36}, n = 4, \text{unreported temperature}, I \rightarrow 0) = 6.2$$

Since the experimentally determined constants for the Pu(III) in [71MOS4] have been rejected in the present review, the same holds for the corresponding Np(III) complexes. Moskvina includes also constants for complexes of Np(VI) with both H₂PO₄⁻ and HPO₄²⁻ and for Pu(VI) with HPO₄²⁻, reported to have been obtained in a solvent extraction study at an ionic strength 0.5 M.



$$\log_{10} \beta(\text{A.37}, \text{unreported temperature}, I = 0.5 \text{ M}) = 1.70$$

$$\log_{10} \beta(\text{A.37}, \text{unreported temperature}, I \rightarrow 0) = 2.33$$



$$\log_{10} \beta(\text{A.38, unreported temperature, } I = 0.5 \text{ M}) = 7.18$$

$$\log_{10} \beta(\text{A.38, unreported temperature, } I \rightarrow 0) = 8.18$$



$$\log_{10} \beta(\text{A.39, unreported temperature, } I = 0.5 \text{ M}) = 1.66$$

$$\log_{10} \beta(\text{A.39, unreported temperature, } I \rightarrow 0) = 2.33$$

The experimental study cited here by Moskvin has not been available to this review, and probably was never published. Hence these data have been rejected.

The value reported for the formation of a carbonate complex of Pu(VI) ($\text{PuO}_2\text{CO}_3\text{HCO}_3^-$) is not included in the determination of best values.

[70AL-/WAI]

Fluoride and sulphate complexation were investigated at 25°C and five different ionic strengths: 0.1, 0.2, 0.3, 0.4 and 0.5 M (HClO_4). The authors measured the redox potentials of mixtures of Np(V) and Np(VI) as a function of fluoride and sulphate concentrations.

In the fluoride system, no complexation of Np(V) was observed, because the acidity used in these experiments was too high to allow $\text{NpO}_2\text{F}(\text{aq})$ to form. The potential changes measured during the titration with fluoride solution were interpreted by the authors in terms of the formation of NpO_2F^+ and $\text{NpO}_2\text{F}_2(\text{aq})$. The auxiliary data used by them are compatible with ours for the protonation of fluoride ion, and the formation of HF_2^- is negligible in the systems investigated. The authors reported $\log_{10} {}^*\beta_1$ values between 1.11 ($I = 0.5 \text{ M}$) and 1.20 ($I = 0.1 \text{ M}$), and $\log_{10} {}^*\beta_2$ values between 1.14 ($I = 0.5 \text{ M}$) and 1.20 ($I = 0.3$ and 0.4 M), *cf.* Table 9.5. The meaning of the reported uncertainties is unknown, but they are no doubt grossly underestimated. We use the reported $\log_{10} {}^*\beta_1$ values in our evaluation, and we assign uncertainties of ± 0.20 to each of them. The 1:2 complex was only present in small amounts in the experiments of [70AL-/WAI], and the error in $\log_{10} {}^*\beta_2$ is therefore considerable. In none of the titration experiments was more than 10% of the Np(VI) present as $\text{NpO}_2\text{F}_2(\text{aq})$, even at the highest fluoride concentrations employed. We assign uncertainties of ± 0.40 to these values.

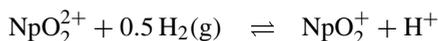
The Np(V)/Np(VI) redox couple was also measured as a function of SO_4^{2-} concentration at acid strengths from 0.1 to 0.5 M. The authors calculated a first stability constant for the Np(VI)- SO_4^{2-} complex assuming no Np(V) complexes. This assumption appears reasonable given the relative strengths of the Np(V)- and Np(VI)-sulphate complexes. The disulphato complex was only observed in a single experiment. This may be because only a small excess of SO_4^{2-} over NpO_2^{2+} was used in these experiments. In most cases, the linear least squares approach and the non-linear least squares approach yield essentially indistinguishable results. Revised values using the non-linear approach were calculated and used in determining best values. No estimate of precision was possible for the single determination of the association quotient for the

disulphato complex. This unique determination was not used in selecting a best value for disulphato complex.

[70AL-/WAI2]

Mixtures (1:1) of Np(V) and Np(VI) was titrated with chloride and nitrate at $(25 \pm 0.01)^\circ\text{C}$ and at three different ionic strengths (0.3, 0.4 and 0.5 M (HClO_4)) for chloride and four (0.4, 0.5, 0.6 and 0.8 (HClO_4)) for nitrate. This was a very careful potentiometric study, $[\text{Np}]_{\text{tot}} = 3.96 \times 10^{-4}$ M. The chloride concentration was varied between 0.01 and 0.14 M, and the nitrate concentration between 0.03 and 0.21 M. By assuming that the formation of Np(V) complexes can be neglected, the authors derived the following formation constants: $\beta_1(\text{NpO}_2\text{Cl}^+, I = 0.3 \text{ M}) = (0.48 \pm 0.03)$, $\beta_1(\text{NpO}_2\text{Cl}^+, I = 0.4 \text{ M}) = (0.44 \pm 0.04)$, and $\beta_1(\text{NpO}_2\text{Cl}^+, I = 0.5 \text{ M}) = (0.45 \pm 0.03)$, and $\beta_1(\text{NpO}_2\text{NO}_3^+, I = 0.4 \text{ M}) = (0.105 \pm 0.005)$, $\beta_1(\text{NpO}_2\text{NO}_3^+, I = 0.5 \text{ M}) = (0.110 \pm 0.005)$, $\beta_1(\text{NpO}_2\text{NO}_3^+, I = 0.6 \text{ M}) = (0.130 \pm 0.006)$ and $\beta_1(\text{NpO}_2\text{NO}_3^+, I = 0.8 \text{ M}) = (0.115 \pm 0.004)$. The uncertainties given by the authors are certainly greatly underestimated. The amounts of complexes formed in these experiments were very small. In fact, under the experimental conditions of this investigation, the proportion of total Np(VI) complexed by chloride was never higher than 6%, and the Np(VI) complexed by nitrate was never higher than 2%. Hence, the changes in the electrode potential were extremely small (up to 1.3 mV in the chloride system, and up to 0.5 mV in the nitrate system.). Since the experimental method is reliable, we use the constants reported in [70AL-/WAI2] in our selection procedure, but we assign them comparatively high uncertainties of ± 0.40 in $\log_{10} \beta_1$ for the chloride system.

For the reaction studied:



the measured reduction potential for solutions containing mixtures of nitrate and perchlorate is:

$$E(\text{mV}) = E^\circ + 59.16 \log_{10} \frac{[\text{NpO}_2^{2+}] \cdot p_{\text{H}_2}^{0.5}}{[\text{NpO}_2^+] \cdot [\text{H}^+]} + 59.16 \log_{10} \frac{\gamma_{\text{NpO}_2^{2+}, \text{mix}}}{\gamma_{\text{NpO}_2^+, \text{mix}} \cdot \gamma_{\text{H}^+, \text{mix}}} + E_j$$

where activity coefficients in the mixtures are denoted by the subscript "mix". Since the potential was also measured in perchloric acid, the difference can be expressed:

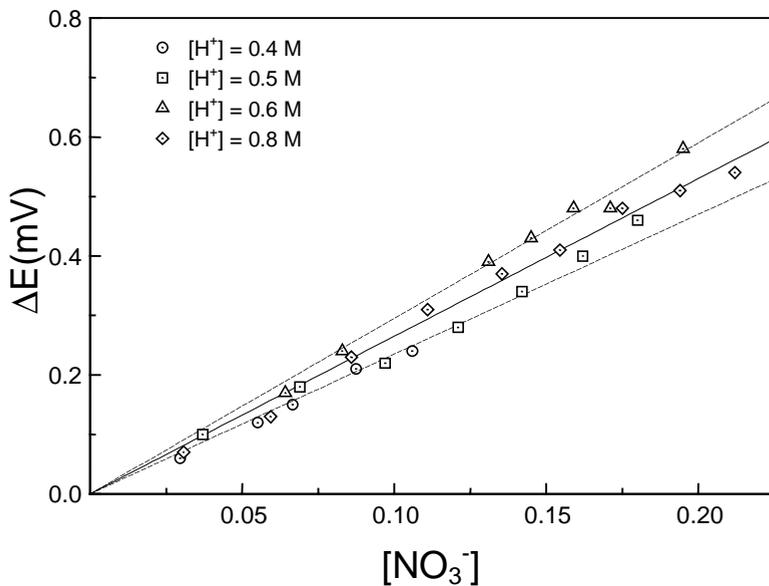
$$\Delta E(\text{mV}) = 59.16 \log_{10} \frac{\gamma_{\text{NpO}_2^{2+}, \text{mix}}}{\gamma_{\text{NpO}_2^+, \text{mix}} \cdot \gamma_{\text{H}^+, \text{mix}}} - 59.16 \log_{10} \frac{\gamma_{\text{NpO}_2^{2+}, \text{ClO}_4^-}}{\gamma_{\text{NpO}_2^+, \text{ClO}_4^-} \cdot \gamma_{\text{H}^+, \text{ClO}_4^-}} + E_j$$

Hence, if standard SIT equations and interaction coefficients are used for various γ_i , ΔE is expressed as,

$$\Delta E - E_j = 59.16 (\Delta \varepsilon(\text{NpO}_2^{2+}) - \Delta \varepsilon(\text{NpO}_2^+) - \Delta \varepsilon(\text{H}^+)) [\text{NO}_3] \dots$$

where $\Delta \varepsilon(i) = \varepsilon_{(i, \text{NO}_3^-)} - \varepsilon_{(i, \text{ClO}_4^-)}$.

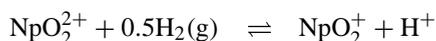
Figure A.5: Experimental data of [70AL-/WAI2]. The full and dotted lines correspond to $59.16 (0.045 \pm 0.005) [\text{NO}_3^-]$.



In this case, the distinction between formation of very weak complexes while using the standard SIT interaction coefficients and assigning all the experimentally measured potential differences to activity effects becomes blurred. For example, from the experimental data for the nitrate solutions (Figure A.5) this review estimates that values of $(\Delta\varepsilon(\text{NpO}_2^{2+}) - \Delta\varepsilon(\text{NpO}_2^+) - \Delta\varepsilon(\text{H}^+)) = 0.044 \pm 0.005 \text{ kg}\cdot\text{mol}^{-1}$ could explain the data for all ionic strengths. The increase in the slope is not regular (the slope is slightly smaller at $I = 0.8 \text{ M}$ than at 0.6 M) and taking into account the extremely small ΔE values together with the possibility of changes in E_j , these slope changes very possibly reflect small experimental errors. Any nitrate complexes must be very weak, and if the results are interpreted in terms of complexation rather than just activity effects, a high uncertainty (± 0.50) must be assigned to the authors' values. The experiments were sensitive, but the amount of complexation under the conditions of the experiments is small.

[70BRA/COB]

Brand and Cobble determined the potential of the reaction



at seven different HClO_4 concentrations at various $\text{NpO}_2^{2+}/\text{NpO}_2^+$ concentration ratios. Using an extended version of the Debye-Hückel theory, they plotted $E^{o'}$ as a function

of ionic strength and extrapolated to infinite dilution to obtain $E^\circ = (1.236 \pm 0.01)$ V. Comparison of this value with the formal potential $E^\circ = (1.13630 \pm 0.00016)$ V of Sullivan *et al.* [61SUL/HIN] gives a 0.1 V difference between the formal and the standard potential. The authors recommended this value to be used as a constant correction for deriving $\text{MO}_2^{2+}/\text{MO}_2^+$ standard potentials from measured formal potentials. As Riglet, Vitorge and Grenthe [87RIG/VIT] pointed out later, Brand and Cobble used the mean activity coefficients of $\text{NpO}_2(\text{ClO}_4)_2$, NpO_2ClO_4 , and HClO_4 and not the values of (individual) activity coefficients in the mixture. Riglet, Vitorge and Grenthe [87RIG/VIT] reinterpreted the experimental data using the specific interaction theory (SIT).

The authors also carried out a limited set of measurements of the solubility of $\text{NpO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ in water (reporting a saturation molality of (2.95 ± 0.26) at $(25 \pm 0.2)^\circ\text{C}$). From this and mean ion activity coefficients from the corresponding uranium system [51ROB/LIM], $\Delta_r G_m^\circ = -(12.3 \pm 1.1)$ $\text{kJ}\cdot\text{mol}^{-1}$ was calculated for the dissolution of the salt. This review applies a SIT correction using $\varepsilon_{(\text{NpO}_2^{2+}, \text{NO}_3^-)} = (0.24 \pm 0.06)$ $\text{kg}\cdot\text{mol}^{-1}$ and obtains $\Delta_r G_m^\circ = -(14.0 \pm 2.4)$ $\text{kJ}\cdot\text{mol}^{-1}$. Because of the high ionic strength of the system ($I = 8.895$ M), this correction does not lead to a more reliable value, and Brand and Cobble's original value is used in determining the values of $S_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K})$ and $\Delta_f G_m^\circ(\text{NpO}_2^{2+}, \text{aq}, 298.15 \text{ K})$ in Section 7.2.

The enthalpy of solution in water of the nitrate salt was also measured. The result, (21.59 ± 0.564) $\text{kJ}\cdot\text{mol}^{-1}$, was corrected for hydrolysis to (18.82 ± 1.67) $\text{kJ}\cdot\text{mol}^{-1}$ by Fuger and Oetting [76FUG/OET]. The correction was calculated using hydrolysis constants for UO_2^{2+} that are not the same as the ones selected in the present review for NpO_2^{2+} . However, the differences are probably within the uncertainty assigned by Fuger and Oetting, and their recalculation is accepted in the present review.

[70CAS/ORL]

This paper is a report of a polarographic study of the reduction of Pu(IV) to Pu(III) and the oxidation of Pu(III) to Pu(IV) in 1 M sodium carbonate at 25°C . The electrochemical study was apparently thorough, and the values reported for the half-wave potential of the reduction (-0.95 V *vs.* SCE or -0.71 V *vs.* SHE) and the oxidation (-0.553 V *vs.* SCE or -0.31 V *vs.* SHE) are in reasonable agreement with later polarographic work (see [86LIE/KIM]), but differ from the potentiometric determination of the formal potential of the Pu(IV)/Pu(III) couple made by Fedoseev, Peretruxhin and Krot [79FED/PER] (-0.495 V *vs.* SHE).

[70LAH/KNO]

This is a solvent extraction study performed at $(20 \pm 1)^\circ\text{C}$ using tri-*n*-octylamine (TOA) 0.5 M in xylol as extractant and 8 M $\text{H}(\text{ClO}_4, \text{NO}_3)$ mixtures in the aqueous phase. The oxidation state of the actinides was maintained as follows: Pu(III) with Fe(II) sulphamate, Pu(IV) with NaNO_3 ; Pu(VI) with the oxidant KBrO_3 , Np(IV) with Fe(II) sulphamate, Np(V) with urea. The nitrate concentration was varied from 0 to 8 M. The

extraction mechanism is complicated ([78PAT/RAM] state that perchlorate is extracted), and no data on distribution coefficients are reported to enable a reviewer to carry out a recalculation. The values of the constants together with semilogarithmic fraction diagrams calculated with these constants are the only data reported in this work. Because of the high and variable ionic strength, the complicated extraction mechanism and the lack of experimental details, the constants reported in this work are rejected in the present review.

[70MOS]

This paper describes a spectrophotometric study at $I = 0.3 \text{ M HNO}_3$. Temperature and experimental details are not provided. At the low acidities of this experiment we anticipate problems with the formation of hydrolysis products and air oxidation of Pu(IV). The results of these experiments are not included in the recommended value determinations.

[70PAU]

In this report, values of -1.90 and -1.91 were given for $\log_{10} \beta_{\text{Hydr}}$ based on spectrophotometric experiments using two different cuvettes. The values for this mixed constant rest on at least two assumptions, (a) that the molar absorptivity for the hydrolysed species at 960.4 nm is very small compared to the molar absorptivity for Np^{4+} , (b) that no hydrolysis beyond the first hydrolysis step occurs for pH values below 2.

Assumption (b) is inconsistent with the results of Sullivan and Hindman [59SUL/HIN] who found evidence for polymerization at acid concentrations less than 0.02 M . Furthermore, examination of the raw data in Table 6 of [70PAU] indicates the absorption does not change smoothly with pH, for pH values above 1.65. Thus, the absorbances at higher pH are probably influenced by the formation of hydrolysis species other than NpOH^{3+} , and these measurements should not be used in the data analysis. This leaves, in essence, duplicate measurements at only five concentrations, from which at least two constants (β_1 and the molar absorptivity of NpOH^{3+}) must be determined. In this review the data were fitted assuming uncertainties of 0.005 in the absorbances in the 1.0 cm cell and 0.10 in the absorbances in the 0.5 cm cells. Various schemes were tried, and it was found that a significantly better fit was obtained if both the molar absorptivity of Np^{4+} and NpOH^{3+} at 960.4 nm were allowed to vary. Similar fitting parameters were obtained whether the data from the two cuvettes were analysed separately or together, nor was any statistically significant difference found in the ratio of the cuvette path lengths from that calculated using their nominal values. The fitted value of the molar absorptivity of Np^{4+} was approximately 139 cm^{-1} , very similar to the maximum value reported in Table 3 of [70PAU] for Np^{4+} in 1.0 M aqueous HClO_4 . The value of the molar absorptivity of NpOH^{3+} was calculated to be 67 cm^{-1} (inconsistent with assumption (b), above), and thus the ratio of the molar absorptivities is 0.48. Sullivan and Hindman [59SUL/HIN] reported the ratio of the molar absorptivity of NpOH^{3+} to that of Np^{4+} to be 0.14. The fitted value of β_1 is 0.0605 (molal units).

After correction to $I=0$, using the specific-ion interaction coefficients $\varepsilon_{(\text{Np}^{4+}, \text{ClO}_4^-)} = (0.84 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{NpOH}^{3+}, \text{ClO}_4^-)} = (0.50 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ (estimated), $\log_{10}^* \beta_1 = -(0.18 \pm 0.50)$ is calculated in the present review. The rather large uncertainty is an estimate, and is a consequence of the sparse data, the rather arbitrary cut-off for the omission of the low acidity measurements in the present data evaluation, and the degree of correlation of the fitted values of $^* \beta_1$ and the molar absorptivity of NpOH^{3+} .

[70UEN/HOS]

The results of thermogravimetric and X-ray powder pattern studies along with elemental analysis were used to identify a solid compound, $(\text{Co}(\text{NH}_3)_6)_2\text{Pu}(\text{CO}_3)_5 \cdot 4\text{H}_2\text{O}(\text{s})$. No new thermodynamic data were reported.

[71DAN/CHI]

The authors used an extraction technique with HTTA in *o*-xylene at 25°C and $I = 4 \text{ M}$ (ClO_4^-) maintaining $[\text{H}^+]_t = 1 \text{ M}$ and $[\text{Na}^+]_t = 3 \text{ M}$. The oxidation states of neptunium were checked before and after the experiments in the aqueous as well as in the organic phase. The Np(IV) solutions of $> 0.5 \text{ M}$ HNO_3 required addition of 0.01 M Fe(II) sulphamate as a holding reductant, since oxidation of Np(IV) was noticed for total nitrate concentrations greater than 0.5 M. The absence of polynuclear complexes was shown for Np concentrations up to 0.045 M.

Danesi *et al.* [71DAN/CHI] interpreted the results of the Np(IV) chloride experiments in terms of two models, one including two, the other three chloride complexes. No details on the evaluation procedure and the method for calculating the standard deviations are given. In the model with two complexes, the fitting exercise resulted in $\beta_1(\text{NpCl}^{3+}) = (0.77 \pm 0.06)$ and $\beta_2(\text{NpCl}_2^{2+}) = (0.79 \pm 0.06)$, whereas in the model with three complexes the resulting values were $\beta_1(\text{NpCl}^{3+}) = (0.92 \pm 0.06)$, $\beta_2(\text{NpCl}_2^{2+}) = (0.27 \pm 0.14)$ and $\beta_3(\text{NpCl}_3^+) = (0.25 \pm 0.07)$. The authors preferred the first set of constants because the standard deviation of β_2 was increased when a third complex was added to the model. This result indeed shows that fitting exercises have to be carried out with great care. Information on the overall goodness-of-fit (*e.g.*, the sum of the squares of the deviations) was not provided, although this is a very important parameter to compare the performance of different models. It is possible that the standard deviations listed by the authors reflect the variation in the goodness-of-fit around the best value of the respective constants, but even if this is so, the mode of calculation must be known to relate the reported uncertainties to those of other studies. In light of these questions, we accept the values of the 1:2 model with significantly increased uncertainties: $\log_{10} \beta_1(\text{NpCl}^{3+}) = -(0.11 \pm 0.30)$ and $\log_{10} \beta_2(\text{NpCl}_2^{2+}) = -(0.10 \pm 0.50)$.

For the Np(IV) nitrate complexation results, recalculation was rendered difficult by several factors. The raw data were not provided, and any recalculation had to rely on use of values digitised from the published figures. No value of D_0 was reported

(from the figures, $D_0 = 0.135$ has been estimated). The procedure used by the authors to obtain values for the activity coefficients of HNO_3 from the work of Davis and De Bruin [64DAV/BRU], (needed to back-calculate the free nitrate ion concentration) is not clear. A maximum value of 3.6 M nitrate can be estimated from the figure, and as the H^+ concentration is 1 M, the maximum concentration of nitrate is calculated to be 3.7 M [64DAV/BRU]. The authors state 4 M was reached. It appears that activity coefficients of HNO_3 for concentrations greater than 1 M have been used for the (H, Na) NO_3 mixtures. The authors reported $\log_{10} \beta_1 = -(0.15 \pm 0.12)$ and $\log_{10} \beta_2 = -(0.74 \pm 0.12)$. Here, from the recalculation, considering only formation of the 1:1 complex, $\log_{10} \beta_1 = -(0.12 \pm 0.10)$ is obtained, which was then recalculated for 4 M HClO_4 before using it in the selection procedure. Only the value for the first complexation constant is accepted in the present review, but with an increased uncertainty, $\log_{10} \beta_1 = -(0.15 \pm 0.30)$.

For the Np(V) chloride system, Danesi *et al.* [71DAN/CHI] proposed a model with two complexes, which they withdrew later [74DAN/CHI] when they realised, based on new measurements, that the liquid junction potential of their electrode system in the case of Cl^- was larger than they had assumed. A re-evaluation of their data showed that no complex formation between NpO_2^+ and Cl^- could be observed under their conditions (*i.e.*, up to a chloride concentration of about 2.3 M at an ionic strength of 4 M).

The measurements of the Np(VI)/Np(V) potential in nitrate media, when plotted against the nitrate concentration, show deviations from linearity only at high nitrate concentrations (≥ 1.5 M). Attempts to explain the slight curvature in terms of a single Np(VI) complex were successful only for an association constant of less than 0.01, and $\Delta\varepsilon(\text{NpO}_2^{2+}) \leq \Delta\varepsilon(\text{NpO}_2^+)$. Despite the determination of the liquid junction potential in a later paper [74DAN/CHI], changes in the junction potential when using a calomel electrode in such different media are likely. These data are considered unreliable, and are not used in the present review.

In the Np(VI) chloride system, the fitting of the extraction data resulted in the same value for the constant of the 1:1 complex, no matter whether or not a 1:2 complex was included in the model. We use this value in our evaluation with an increased uncertainty: $\log_{10} \beta_1(\text{NpO}_2\text{Cl}^+) = -(0.16 \pm 0.20)$. After the re-evaluation of their redox potential measurements on the Np(V)/Np(VI) system, Danesi *et al.* [74DAN/CHI] derived a formation constant for the Np(VI) chloride complex with the new evidence that no chloride complex of Np(V) is formed. Since the resulting value is independent of the extraction value from above, we use it too in our evaluation and assign it the same uncertainty: $\log_{10} \beta_1(\text{NpO}_2\text{Cl}^+) = -(0.05 \pm 0.20)$.

The extraction results suggest the nitrate complexes are about half an order of magnitude weaker than the chloro complexes, and the “complexation” could be as easily accounted for by selecting appropriate activity coefficients as by invoking nitrate complexes of NpO_2^{2+} . The authors reported $\beta_1 = (0.21 \pm 0.03)$ ($\log_{10} \beta_1 = -(0.68 \pm 0.14)$) for the formation constant of the first nitrate complex. This is not consistent with the value from the potentiometric work reported in the same paper, and results at least in part because the constants are negligibly small and other activity coefficient effects are of the same order of magnitude.

[71MOS]

This reports on a distribution study of Np(IV) nitrate complexes and a spectrophotometric study of the Pu(IV) nitrate system. The distribution study was carried out at $(25 \pm 1)^\circ\text{C}$, using the extractant TBP (tri-*n*-butylphosphate) in the organic phase and 2 M and 4 M $\text{H}(\text{ClO}_4, \text{NO}_3)$ solutions in the aqueous phase. The organic phase was previously equilibrated with solutions containing all components except Np(IV), so the species $\text{HNO}_3 \cdot \text{TBP}$ was in equilibrium before the start of the distribution measurements. The dependence of the extraction reaction on the TBP concentration was checked in 1 M HNO_3 and on the acid concentration in $\text{LiNO}_3 - \text{HNO}_3$ mixtures. The treatment of data was done using the Fomin-Majorova and Fronaeus integral method. Complexes of the general formula $\text{Np}(\text{NO}_3)_n^{4-n}$ with $n = 1 - 4$ were found to form with the overall stability constants calculated with both methods as follows: $I = 2$ M (Fomin): $\beta_1 = 6.8, \beta_2 = 20.6, \beta_3 = 35.3, \beta_4 = 34.3$. (Fronaeus): $\beta_1 = 6.8, \beta_2 = 20.0, \beta_3 = 35.5, \beta_4 = 36.0$. $I = 4$ M (Fomin) $\beta_1 = 5.2, \beta_2 = 12.0, \beta_3 = 16.8, \beta_4 = 14.5$. Recalculation with an alternate treatment considering activity effects explicitly in the mixed electrolyte solutions and only the 1:1 complex leads to $\beta_1 = 5.7 \pm 0.1$, consistent with the values reported by the author. In the present review, only the average reported value for the first complexation constant $\log_{10} \beta_1 = (0.78 \pm 0.2)$ (the uncertainty was estimated in the present review) is accepted.

The spectrophotometric study of the Pu(IV) nitrate complexes was performed in nitric acid media of various concentrations less than 1 M. The ionic strength was not kept constant. From the measurements the author determined $\log_{10} \beta_1 = 0.38$, and $\log_{10} \beta_2 = 0.43$. No recalculation is possible as no experimental data were reported. These values are rejected in the present review.

[71MOS2]**a) Np(IV)**

The solubility of Np(IV) was measured in 0.15 to 2.20 M $(\text{NH}_4)_2\text{CO}_3$ aqueous solutions, together with the absorption spectrum of one of these solutions. The pH was also measured. This was the first experimental work from which a value for a formation constant of a Np(IV) soluble complex in concentrated carbonate media was proposed. The value has been extensively cited and used. Unfortunately, as Rai and Ryan [85RAI/RYA] later pointed out, there are many reasons to conclude that the interpretation of the experiments was “completely erroneous”. The present review agrees with this statement of Rai and Ryan. Nevertheless, Moskvin’s proposed species and value are still being used. Therefore, we feel it necessary to comment again on the inconsistencies in Moskvin’s experimental procedures and interpretation. Np(IV) was introduced as $\text{Np}(\text{OH})_4 \cdot x\text{H}_2\text{O}(\text{s})$, prepared as in [71MOS3]. Moskvin implicitly assumed, that this solid controlled the solubility during his measurements, but he did not report any characterisation of his solid phase after equilibration, and there is reason to believe the solid may have been transformed to a carbonate-containing solid (see also [95VIT]). The experimental conditions are similar to those reported elsewhere for preparation of solid M' -actinide(IV) carbonates ($M'^+ = \text{Na}^+, \text{K}^+ \text{ or } \text{NH}_4^+$). The solubility results

are not very different from those found for the Ce(IV) or Th(IV) systems under similar conditions [73DER/FAU3, 73DER/FAU], where the solubility is apparently controlled by $\text{Na}_6\text{M}^{\text{IV}}(\text{CO}_3)_5 \cdot 12\text{H}_2\text{O}(\text{s})$, and is due to at least one strong carbonate complex.

Moskvin assumed, that the enhanced solubility of Np(IV) in carbonate solutions was due to $\text{Np}(\text{OH})_4\text{CO}_3^{2-}$, and then proposed its formation constant, $\log_{10} \beta_{4,1} = (53.045 \pm 0.015)$. From a calculation exactly parallel to that described by Rai and Ryan [85RAI/RYA], but using values from the present review, (see the discussion on [85RAI/RYA] in this appendix), it is shown that this formation constant is certainly less than 10^{47} . In a similar paper on plutonium(IV), where more details on their calculations are provided, Moskvin and Gel'man [58MOS/GEL] earlier proposed the formation of $\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ with a similar value for the formation constant. In both cases the interpretation is incorrect (also see the discussion of [58MOS/GEL] in this appendix). The numerical values are similar only because the methodology is the same, and because Np(IV) and Pu(IV) are chemical analogues. Rai and Ryan [85RAI/RYA] give "a variety of reasons for completely rejecting such carbonate formation constant values".

There are no details about the calibration of the pH electrode in this set of experiments. The medium was strongly buffered, but the exact pH cannot be calculated because the partial pressures of $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ are not known. There is as much as a 0.6 unit difference between the pH values reported by Moskvin and the ones that we calculate (see also [95VIT]). The measured pH value also varied too much as a function of $[(\text{NH}_4)_2\text{CO}_3]$, and this is certainly due to variations in the liquid junction potentials. The inconsistencies may also be due, in part, to some uncontrolled exchange between the working solutions and the air, or to some other aspect of the experimental procedure, that is not well described.

Moskvin reported the absorption spectrum of the supernatant of the 1.5 M $(\text{NH}_4)_2\text{CO}_3$ solution, for which he measured a solubility of 0.0174 M of Np(IV). Neither Np(V), nor Np(VI) can be detected in this spectrum, and it can be attributed to Np(IV). Similar spectra for wavelengths above 500 nm have been reported by other groups [77SAI/UEN, 81WES/SUL, 84VAR/HOB, 93LI/KAT, 95VIT, 96DEL/VIT]. Below 500 nm the base line of the spectrum reported by Moskvin rises, and this can reasonably be attributed to the effect of small particles of solid in suspension in the Moskvin's Np saturated solution.

When it is controlled by the solid $\text{Np}(\text{OH})_4(\text{s})$, the solubility of Np(IV) in neutral and basic solutions is very low (less than 10^{-8} M [85RAI/RYA], also see Section 8.1.4 of this review). There is no other published experimental work that has been performed in exactly the same carbonate medium, but there is also no evidence of any contradiction between Moskvin's data and other published work [95VIT]. Only Moskvin's interpretation is "unbelievable", as it relies on "completely erroneous assumptions" and is certainly "completely incorrect" [85RAI/RYA]. All the published solubility studies are consistent with the formation of $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$ complexes, whose stability is similar to the corresponding U [92GRE/FUG] and Pu [92CAP] complexes. The species $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$ certainly exist under some conditions, and complexes with similar stoichiometries have been proposed for Ce(IV)[73DER/FAU3], Th(IV) [73DER/FAU3, 97FEL/RAI], U(IV) [92GRE/FUG, 98RAI/FEL] and Pu(IV) [92CAP, 98CLA/CON].

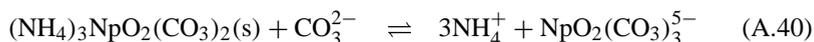
b) Np(V)

In a Np(V) solubility study also reported in this publication, Moskvin proposed the stoichiometry of Np(V) soluble carbonate complexes ($\text{NpO}_2\text{OHCO}_3^{2-}$ and $\text{NpO}_2\text{OH}(\text{CO}_3)_2^{4-}$), and their stability constants. The author did not try any other model (*i.e.*, set of soluble complexes and solid phases). There was no proof offered for his model, which is not consistent with later work. The experimental solubility measurements in concentrated $(\text{NH}_4)_2\text{CO}_3$ solutions, using either $\text{NpO}_2\text{OH}(\text{s})$ or hydrated $\text{NH}_4\text{NpO}_2\text{CO}_3(\text{s})$ solids as starting materials, are compatible with Np(V) behaviour in concentrated carbonate media found in previous [66GOR/ZEN] and later studies [77SIM, 84VIT, 86GRE/ROB, 91KIM/KLE, 94NEC/KIM]. No characterisation of the solid phase (assumed not to change during the equilibrations) was reported. The initial solid phase had little influence on most of the solubility results, indicating that at least one of the initial solid phases was transformed during the solubility equilibration [98VIT/CAP]. No indication was given as to the method of pH calibration (junction potential, ionic strength effects). It was assumed the free carbonate concentration, $[\text{CO}_3^{2-}]$, was equal to the total carbonate concentration; this is incorrect as the measured pH values were always less than the $\text{p}K_a$ value for the first protonation step for CO_3^{2-} .

In carrying out the present review, attempts were made to reinterpret the data from this study. It has been assumed that, on addition of $(\text{NH}_4)_2\text{CO}_3$ to the solution, $\text{NpO}_2\text{OH}(\text{s})$ solid was transformed into a hydrated $\text{NH}_4\text{NpO}_2\text{CO}_3(\text{s})$, which was slowly transformed into a thermodynamically more stable (hence less soluble) hydrated $(\text{NH}_4)_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ solid in the most concentrated $(\text{NH}_4)_2\text{CO}_3$ aqueous solutions (2 and 2.2 M). The data for 2 and 2.2 M $(\text{NH}_4)_2\text{CO}_3$ solutions were therefore rejected, and the $\text{NpO}_2\text{OH}(\text{s})$ solubility data were also excluded because the results were scattered, suggesting equilibrium was not always achieved. The Np(V) complexation constants and the specific interaction coefficients selected or estimated in the present review were used, but the uncertainty has been increased for the values estimated by analogy: $\varepsilon_{(\text{NH}_4^+, \text{CO}_3^{2-})} \approx \varepsilon_{(\text{K}^+, \text{CO}_3^{2-})} = (0.02 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{NH}_4^+, \text{HCO}_3^-)} \approx \varepsilon_{(\text{Na}^+, \text{HCO}_3^-)} = (0.0 \pm 0.2) \text{ kg}\cdot\text{mol}^{-1}$. Values for $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{NH}_4^+)}$ and $K_{s,3}(\text{A.25}, \text{M}^+ = \text{NH}_4^+) = K_{s,3}\beta_3 = [\text{NH}_4^+][\text{NpO}_2(\text{CO}_3)_3^{5-}]/[\text{CO}_3^{2-}]^2$ were determined by fitting two different models to the data. One model assumed the 1:2 complex was important (and required a fixed value of $\log_{10} K_3^\circ(\text{A.26}) = (-0.87)$ to achieve convergence and yield a value for $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{2-}, \text{NH}_4^+)}$, the other that only the limiting complex was important. Both models resulted in a value for $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{NH}_4^+)}$ near 0.6 a surprisingly large positive value that again leads to questions about whether Moskvin's solutions were at equilibrium.

The values $-(2.6 \pm 1.0)$, $-(2.8 \pm 0.4)$, $-(3.0 \pm 0.3)$, $-(2.9 \pm 0.2)$ and $-(2.9 \pm 0.3)$ were calculated in the present review for $\log_{10} K_{s,3}$ for solutions 0.2, 0.6, 1.0, 1.25 and 1.5 M in $(\text{NH}_4)_2\text{CO}_3$, respectively. The solid phase was not characterised by the author so this review has tabulated (Table 12.4) only the value calculated for 0.6 M $(\text{NH}_4)_2\text{CO}_3$ (this is similar to the value for the corresponding sodium system as calculated from the data selected in the present review). At higher ammonium carbonate

concentrations it is reasonable to assume equilibrium was not achieved because of slow transformation of the solid into one with a higher $\text{NH}_4:\text{Np}$ ratio. The apparent solubility product values do not change markedly with increasing ammonium carbonate concentration, especially for solutions ≥ 1.0 M, and are quite different from the value estimated for the corresponding potassium salt as estimated in the present review (see the discussion on [66GOR/ZEN] in this appendix). This is surprising as K^+ and NH_4^+ cations often have similar chemical behaviour. The $K_{s,3}$ (A.25) values in ammonium and potassium media are treated in this review only as rough estimates for poorly characterised phases. From the measurements in 2.2 M $(\text{NH}_4)_2\text{CO}_3$ aqueous solutions the constant for the following equilibrium,



was estimated in the present review to be $\log_{10} K_{s,3}(\text{A.40}) = -(2.6 \pm 0.5)$ in 2.2 M $(\text{NH}_4)_2\text{CO}_3$ aqueous solution (again only as a guideline to the value, as the solid phase was not characterised). This $K_{s,3}(\text{A.40})$ value is similar to the corresponding one in potassium media as estimated by this review (see the discussion for [66GOR/ZEN] in this appendix). Thus, the constant for the quotient $\log_{10}(K_{s,3}(\text{A.40})/K_{s,3}(\text{A.25}))$ is estimated in the present review as $-(0.3 \pm 0.6)$ in 2.2 M $(\text{NH}_4)_2\text{CO}_3$ aqueous solution.

c) Np(VI)

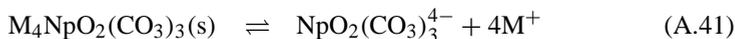
In a Np(VI) study also reported in this publication, the solubility of $(\text{NH}_4)_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$ in $(\text{NH}_4)_2\text{CO}_3$ aqueous solutions, and the solubility of $\text{NpO}_2(\text{OH})_2(\text{s})$ in $(\text{NH}_4)_2\text{CO}_3$ aqueous solutions, were measured by dissolution of the solid phases. There is very little information provided as to the experimental procedures, and the interpretation given by the author is not consistent with later work (see Sections 12.1.2.1.2 and 12.1.2.2.1) and with those for the analogous U(VI), and Pu(VI) systems. The author ignored the fact that the free carbonate concentration was not equal to the total carbonate concentration, and he did not try to show that the interpretation he gave was the only possible one, or that it could explain the published chemical information on this type of system. The stoichiometries proposed in this publication for two of the soluble Np(VI) carbonate complexes, $\text{NpO}_2(\text{OH})_2\text{CO}_3^{2-}$, and $(\text{NH}_4)_2\text{NpO}_2(\text{CO}_3)_2(\text{aq})$, were completely incorrect, and the value of the equilibrium constant involving $\text{NpO}_2(\text{CO}_3)_2^{2-}$ was erroneous. When it is correctly reinterpreted, this experimental work confirms chemical analogy between U(VI) and Np(VI) chemistry in carbonate media (see also the discussion on [66GOR/KLI] in this appendix).

The comparison between the solubility results and the amount of $(\text{NH}_4)_2\text{CO}_3$ used in these measurements, indicates that the amount of carbonate or ammonium ions due to the Np(VI) solid dissolution, can be disregarded (except when no $(\text{NH}_4)_2\text{CO}_3$ at all was added). Speciation, except for Np(VI), should have been almost the same before and after the Np(VI) solid dissolution (although this approximation is less valid when calculating a solubility product where $[\text{NH}_4^+]^4$ is involved).

The speciation was calculated in the same way explained previously [95VIT] for Np(IV) data. The reported measured pH values do not correspond to the values calcu-

lated in the present review [98VIT/CAP]. No experimental details were provided for the pH measurements (calibration, junction potentials nor activity coefficients). Different pH values are reported for solutions with the same initial $(\text{NH}_4)_2\text{CO}_3$ concentrations for the two sets of experiments. This suggests experimental errors, possibly systematic errors. As in the review and recalculations for the part of this publication dealing with Np(IV) or Np(V), calculated speciation (and not pH measurements) were used for the reinterpretation. This procedure could introduce systematic errors, and allowance has been made for this in the final estimation of the uncertainties. For aqueous solutions with $(\text{NH}_4)_2\text{CO}_3$ concentrations greater than 0.5 M, both sets of solubility measurements gave the same total solution concentration of neptunium, regardless of the starting material. Furthermore, this was the same solubility as previously published [66GOR/KLI] for K_2CO_3 aqueous solutions [98VIT/CAP].

The simplest and most consistent interpretation is to assume that the solubility was controlled by the equilibrium



(where $\text{M} = \text{NH}_4$). The calculations were carried out as described in this appendix for [66GOR/KLI]. The calculated values for the solubility product $K_{s,3}$ and the value on extrapolation to $I = 0$ (SIT regression), are essentially the same values that were found for $\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$ in K_2CO_3 media (as calculated from the data of Gorbekov-Germanov and Klimov [66GOR/KLI] in this appendix) within the uncertainty limits (the cations K^+ and NH_4^+ are often found to show similar behaviour in aqueous solutions).

For $\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$	$\log_{10} K_{s,3}^\circ (\text{A.41}) = -(7.03 \pm 0.88)$
for $(\text{NH}_4)_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$	$\log_{10} K_{s,3}^\circ (\text{A.41}) = -(7.44 \pm 0.30)$
for $\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$	$\log_{10} K_{s,3}^\circ = -(5.34 \pm 0.16)$

From the data from [66GOR/KLI, 71MOS2] as reinterpreted in this appendix, and from the data of [92GRE/FUG, 95GRE/PUJ], respectively. The following ε values are also obtained:

$\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{K}^+)}$	$= -(0.62 \pm 0.42) \text{ kg}\cdot\text{mol}^{-1}$	(from data of [66GOR/KLI])
$\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{NH}_4^+)}$	$= -(0.78 \pm 0.25) \text{ kg}\cdot\text{mol}^{-1}$	(from data of [71MOS2])
$\varepsilon_{(\text{UO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+)}$	$= -(0.01 \pm 0.11) \text{ kg}\cdot\text{mol}^{-1}$	[92GRE/FUG, 95GRE/PUJ]
$\varepsilon_{(\text{UO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+)}$	$= -(0.13 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$	(from $\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$ solubility [92GRE/FUG])

The uncertainties are deduced from statistical analysis after the ionic strength corrections. This gives an estimate of ± 0.66 in the logarithm of the solubility product for the random part of the uncertainty. As for the interpretation of [66GOR/KLI], this review estimated an logarithmic uncertainty of ± 0.4 for possible systematic errors in the speciation. Finally it was checked again whether any known soluble complex of Np(VI)

other than $\text{NpO}_2(\text{CO}_3)_3^{4-}$ could contribute to the solubility for the experimental conditions described by Moskvin [71MOS2]. It was found that $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$ could contribute a few percent to the total solution concentration of neptunium (this is a rough estimate since the value of the activity coefficient must be estimated) in the less concentrated solutions. However, the effect of the relatively minor amounts of this species on the calculated solubility product values should be less than the uncertainties.

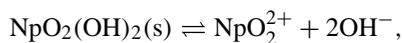
No realistic thermodynamic interpretations could be found to account for the other solubility data obtained by dissolving the $\text{NpO}_2(\text{OH})_2(\text{s})$ solid phase (when the measured solubilities were not the same as those in the experiments in which $(\text{NH}_4)_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$ was used as starting material). None of them gave results consistent with the other chemical information on actinide(VI) systems in aqueous carbonate media [98VIT/CAP].

This means that the corresponding data might be evidence of a new solid phase containing less carbonate than $(\text{NH}_4)_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$, but it could also simply be interpreted as the result of slow dissolution of the initial Np(VI) compound. No further quantitative interpretation of those data was attempted. NH_4^+ and K^+ often have very similar behaviour and this is also found here. The standard values for the $\text{K}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$ and $(\text{NH}_4)_4\text{NpO}_2(\text{CO}_3)_3(\text{s})/\text{NpO}_2(\text{CO}_3)_3^{4-}$ equilibrium constants calculated in this appendix from data of [66GOR/KLI] and [71MOS2] are the same (within the uncertainties), while they are smaller than the value for the corresponding tetrasodium dioxouranium(VI) compound (however, these comparison values rely heavily on the values assigned to the activity coefficients). The $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{NH}_4^+)}$ value calculated here from Moskvin's data [71MOS2] is similar to the value for $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{K}^+)}$ calculated in this review (in this appendix) from data of Gorbenko-Germanov and Klimov [66GOR/KLI], but is quite different from $\varepsilon_{(\text{UO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+)}$ selected in this series [92GRE/FUG, 95GRE/PUJ], or determined [92GRE/FUG] from the solubility of $\text{Na}_4\text{UO}_2(\text{CO}_3)_3(\text{s})$ in aqueous NaClO_4 media. Ionic strength effects do not seem to be exactly the same when Na^+ is exchanged for K^+ , or along the actinide series.

[71MOS3]

Moskvin [71MOS3] has reported the solubility of “ $\text{NpO}_2(\text{OH})_2(\text{s})$ ” at 20°C as a function of pH ($I < 0.1$). The solid was apparently not well characterised initially, nor does it appear that the material was re-examined after equilibration with the aqueous solutions. No proof was presented that equilibrium was achieved. It appears likely the solid was primarily the hydrated hydroxide, *i.e.*, $\text{NpO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{s})$ [64BAG/LAI, 75BEL/IL’], or hydrated oxide [96KAT/KIM], or possibly $\text{NpO}_3 \cdot 4\text{H}_2\text{O}(\text{s})$

Moskvin reported $\log_{10} K_{s,0} = -22.1$ for the reaction



but his analysis of the experimental solubility data is not self-consistent, and contains several errors. Attempts to apply activity corrections and/or modify the hydrolysis constants for NpO_2^{2+} did not significantly improve the agreement. The proposed

hydrolysis scheme includes the species $\text{NpO}_2(\text{OH})^+$, $\text{NpO}_2(\text{OH})_2(\text{aq})$, $\text{NpO}_2(\text{OH})_3^-$, $(\text{NpO}_2)_2(\text{OH})_3^+$ and $(\text{NpO}_2)_2(\text{OH})_5^-$, but no real reason was offered as to why this set of species was preferred to any other.

Recalculation of Moskvín's data for pH values of 3.5 to 6 (in which range formation of anionic hydrolysis species or carbonate complexes would be unlikely), assuming the hydrolysis constants in Section 8.1.2 and using the appropriate activity coefficient corrections, demonstrates a regular drift in $\log_{10}^*K_s$ from 5.0 to 7.4.

Nevertheless, the results do indicate the solubility product, *K_s , at 20°C is, on average, approximately 10^6 . The calculations should be least complicated for the measurements at low pH, and the short equilibration times (6 to 8 hours) will tend to cause the solubility to be overestimated. Therefore, a value of $10^{(5.5 \pm 1.5)}$ can be estimated from this work, a value which is not inconsistent with the later (and possibly more accurate) value based on the work of Kato *et al.* [96KAT/KIM] (though it has not been firmly established that both studies measured the solubility of the same solid).

Np(V) solubility measurements in a narrow pH domain ($6.5 < \text{pH} < 6.7$) were used to calculate the $\text{NpO}_2\text{OH}(\text{s})$ solubility product: $\log_{10}([\text{NpO}_2^+][\text{OH}^-]) = -(9.03 \pm 0.07)$ at low ionic strength. Hence, (assuming that the authors have calculated $K_{s,0}$ from pH measurements using $K_w = 14.0$) $\log_{10}^*K_{s,0} = (4.97 \pm 0.07)$. The experimental results do not deviate greatly from other similar studies [76SEV/KHA, 85LIE/TRE]; but, there is no indication as to how the pH electrode was calibrated. For the neptunium(V) hydrolysis constant, the proposed value of $^*\beta_1$ is based on two assumptions: (1) 100% hydrolysis of NpO_2^+ to $\text{NpO}_2\text{OH}(\text{aq})$ at pH = 8.6, and (2) the equilibrium concentration of neptunium over $\text{NpO}_2\text{OH}(\text{s})$ in water at a pH value of 8.6 is 7.9×10^{-6} M [71MOS2]. However, the solubility from [71MOS2] is three and a half orders of magnitude lower than the solubilities in Table 3 of [71MOS3] (for pH values of 6.6). This means either the model invoking only one hydrolysis step in the pH range 6.6 to 8.6 is incorrect, or the two sets of solubility measurements are inconsistent. The author has estimated the $\text{NpO}_2\text{OH}(\text{aq})$ formation constant ($\log_{10} K_1 = 3.9$, and hence $\log_{10}^*K_1 = -10.1$) but, since the pH domain is too narrow, this calculation has no meaning. Inherently, the value proposed for the hydrolysis constant is based on only one experimental point (at pH = 8.6), and the reported value for the hydrolysis constant would suggest that less than 5% of the neptunium(V) would be hydrolysed to $\text{NpO}_2\text{OH}(\text{aq})$ at a pH value of 8.6.

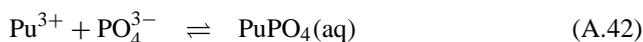
The experimental results reported for Np(IV) in this paper were apparently preliminary. The solid " $\text{Np}(\text{OH})_4 \cdot x\text{H}_2\text{O}(\text{aq})$ " was only aged for one day, and the reported solubilities are consistent with the solid being slightly less stable than the material used in the solubility experiments of Rai *et al.* [87RAI/SWA].

[71MOS4]

In this work Moskvín studied the phosphate complexation of Pu(III) through solubility measurements of $\text{PuPO}_4 \cdot x\text{H}_2\text{O}(\text{s})$, while the cation exchange method was used to study the phosphate complexes of Pu(III), Am(III) and Cm(III).

The composition of the solid was verified only by chemical analysis, and no water content was reported. The solubility was measured at $(20 \pm 1)^\circ\text{C}$, in an ionic medium

of 0.5 M NaClO₄, over the pH range 0.3 to 7.2. The author explained the solubility data by assuming formation of the complex PuPO₄(aq):



with $\log_{10} \beta(\text{A.42}, 0.5 \text{ M NaClO}_4) = 19.2$, and obtained for the reaction:



$$\log_{10} K_{s,0}(\text{A.43}, 0.5 \text{ M NaClO}_4) = -24.4$$

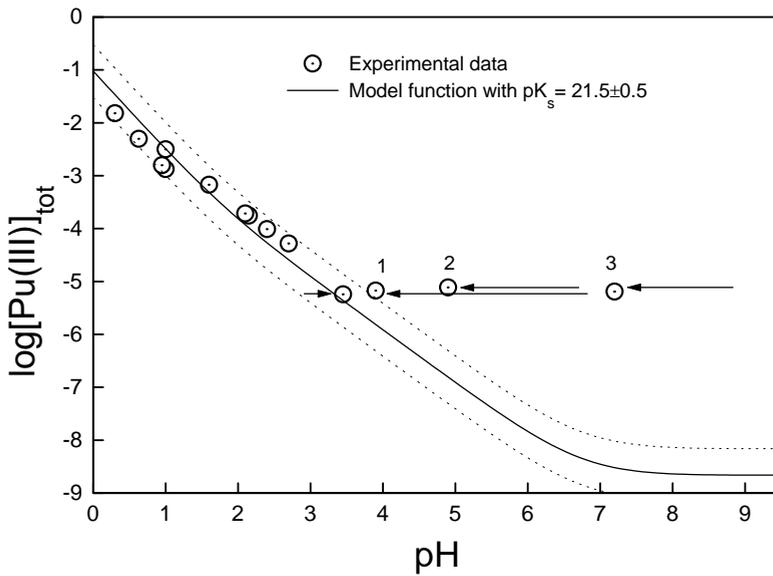
No phase verification before and after equilibration and no holding reductant or test of the oxidation state of plutonium in solution was reported. The solubility was measured only from undersaturation. The third dissociation constant of phosphoric acid as used by the author was high, even compared to values used by the same author in other works. The formation of the complex PuPO₄(aq) at very low total phosphate concentrations resulting from the dissolution of the solid at low pH is not supported by studies in similar systems.

Recent studies on phosphate complexation of trivalent lanthanides [91BYR/LEE, 89BYR/BIN] and americium [92RAI/FEL, 95SIL/BID] have shown that the stability of M(III)PO₄(aq) complexes has generally been overestimated by several orders of magnitude. The same is true in this study. If the proposed complexation constant were used, almost all the Pu(III) in the ion exchange experiments discussed in the second part of this work would be in the form of PuPO₄(aq). In that section the author considers only the formation of complexes with H₂PO₄⁻ as the ligand.

The conclusion the neutral complex was formed was based on the relatively constant solubility for pH values ≥ 4 (points 1, 2 and 3 in Figure A.6). This phenomenon was actually likely the result of experimental problems, especially if the pH shift (Table 2 in the paper and shown in the Figure A.6 by arrows) during the attainment of equilibrium is considered. Possible explanations for the acidification of the solution during the equilibration with the solid may include solution reactions involving Pu³⁺ (and at these pH values hydrolysis would be negligible), or a phase transformation of the solid to some hydroxyphosphate. As no details on the holding reductant or the filtration procedure are reported, it is also possible that Pu(III) was partially oxidized to Pu(IV), and the colloidal Pu(IV) was considered as soluble Pu(III). For these reasons the solubility data for pH > 4 were discarded and the remaining data were treated using phosphoric acid constants accepted in this review and recalculated for the given ionic medium using the interaction coefficients in Appendix B. The resulting solubility product $\log_{10} K_{s,0}(\text{A.43}, 0.5 \text{ M NaClO}_4, 20^\circ\text{C}) = -(21.5 \pm 0.5)$ was recalculated to standard conditions, using the interaction coefficient $\varepsilon_{(\text{Pu}^{3+}, \text{ClO}_4^-)} \cong \varepsilon_{(\text{Am}^{3+}, \text{ClO}_4^-)} = 0.49 \text{ kg}\cdot\text{mol}^{-1}$, and $\log_{10} K_{s,0}^\circ = -(24.57 \pm 0.80)$, was calculated. The increased uncertainty (estimated here) should account for the temperature difference and the approximate interaction coefficient.

The ion exchange study was performed using a 1.0 M NH₄Cl medium (at an unreported temperature), at a constant total phosphate concentration of 0.1 M and

Figure A.6: Solubility measurements on $\text{PuPO}_4 \cdot x\text{H}_2\text{O}(\text{s})$ from Moskvin [71MOS4]. The continuous curve represents the values calculated with the solubility product $\log_{10} K_{s,0}^\circ = -24.57$, in combination with the selected acidity constants for phosphoric acid given in Chapter 4 and the specific ion interaction equations in Appendix B. The dotted curves show the calculated uncertainty when the uncertainty in the value of $\log_{10} K_{s,0}^\circ$ is set to 0.80. The arrows show the pH shift during the attainment of equilibrium for points 1, 2 and 3 as reported in Table 1 of [71MOS4].



variable pH (between 0.3 and 4.9), as well as at constant perchloric acid concentrations (0.016, 0.25, 0.5 M) using a wide range of phosphoric acid concentrations: ($5.6 \times 10^{-5} \leq [\text{H}_3\text{PO}_4]_{\text{TOT}} \leq 9.5 \text{ M}$). The variation of the distribution coefficient with the calculated concentration of H_2PO_4^- was interpreted in terms of the formation of four complexes of the general composition $\text{Pu}(\text{H}_2\text{PO}_4)_n^{3-n}$ with $n = 1$ to 4. The cation exchange technique does not appear very useful for studying this system, as there are several ligands that could form cationic complexes with Pu(III). In stating that “when the phosphate ion concentration in solution is increased, the absorption of ions of the M^{3+} by the cation-exchange resin decreases”, the author may have neglected the sorption of potential cationic complexes such as $\text{PuH}_2\text{PO}_4^{2+}$ and $\text{Pu}(\text{H}_2\text{PO}_4)_2^+$. In fact, unrealistic negative values of the distribution constants for these species result if the speciation proposed by the author is used. Therefore the values of the complexation constants proposed by Moskvin:



$$\log_{10} \beta_n(\text{A.44}, n = 1, \text{unreported temperature}, I \rightarrow 0) = 2.40$$

$$\log_{10} \beta_n(\text{A.44}, n = 2, \text{unreported temperature}, I \rightarrow 0) = 3.73$$

$$\log_{10} \beta_n(\text{A.44}, n = 3, \text{unreported temperature}, I \rightarrow 0) = 5.64$$

$$\log_{10} \beta_n(\text{A.44}, n = 4, \text{unreported temperature}, I \rightarrow 0) = 6.2$$

are rejected in the present review.

[71RYK/BLO]

No values for complexation constants are reported in this paper.

[71SCH]

This is a preliminary report. A thorough discussion of the results is given in a later paper [75SCH].

[71SHE/GRA]

This is a qualitative spectrophotometric study of the hexanitrate complex of Pu(IV) in water-methanol mixtures of variable methanol content. No constants are reported. The authors report an increase of the complexation while increasing the methanol content of the solutions due to the lowering of the dielectric constant and the distortion of the water structure.

[72BAR/MUR]

This is a spectrophotometric study of Np(IV) complexes in 9 M $\text{H}(\text{ClO}_4, \text{NO}_3)$ mixtures with nitrate 0.02-1 M, 4 mM Np(IV). The following bands were assigned to the respective species: 960 nm to Np^{4+} , 968 nm to NpNO_3^{3+} and 981 nm to $\text{Np}(\text{NO}_3)_2^{2+}$.

The authors constructed the function $\phi = [\text{Np(IV)}]_{\text{tot}}/[\text{Np}^{4+}] = 1 + \sum \beta_i [\text{NO}_3^-]^i$ from the decrease of the peak corresponding to Np^{4+} with the increase of the nitrate concentration. Only data in the range 0.1-0.4 M NO_3^- were used to determine the constants (Figure 4 in the paper). The authors reported: $\beta_1 = 8$ and $\beta_2 = 115$ ($\log_{10} \beta_1 = 0.90$, $\log_{10} \beta_2 = 2.06$).

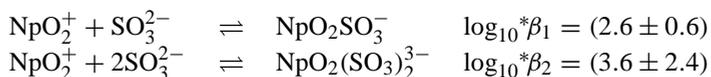
A recalculation considering activity effects for mixed electrolyte solutions explicitly (but only the 1:1 complex) in the high ionic strength solutions gave a good fit to the data for $\log_{10} \beta_1 = 1.2$, a somewhat larger value than the one proposed by the authors. Because the measurements were carried out in solutions of such high ionic strength, the calculated complexation constants are not used in determining selected values in the present review.

[72BLO/BUK]

The authors carried out spectrophotometric measurements to investigate the complex formation of Np(V) and Np(VI) with iodate, IO_3^- , at 25°C. In the case of Np(V), they observed a displacement of the UV absorption band with increasing iodate concentrations, but they judged the spectral changes too small to derive any complexation constants. In the case of Np(VI), however, the spectral changes observed when adding KIO_3 were significant. Blokhin *et al.* [72BLO/BUK] fixed the pH at 2 and the ionic strength at 0.3 M using perchlorate. They added increasing amounts of NaIO_3 up to a maximum concentration of 0.25 M. They assumed that only one complex, $\text{NpO}_2\text{IO}_3^+$, was present at iodate concentrations below 0.15 M, and they evaluated its formation constant by using experimental points up to an iodate concentration of 0.12 M. Above 0.15 M iodate, the calculated β_1 values were not constant, giving rise to the formation of higher complexes. According to our calculation using the protonation constant of iodate as published by Grenthe *et al.* [92GRE/FUG] and corrected to $I = 0.3$ M, $\log_{10} K(\text{HIO}_3) = 0.5$, 3% of the free iodate is protonated at pH = 2. Hence, the fact that the authors neglected iodate protonation in their evaluation of the experiments introduced only a small error. The resulting formation constant of $\text{NpO}_2\text{IO}_3^+$, $\log_{10} \beta_1 = 0.61$, is corrected to $I = 0$ in this review, *cf.* Part III, Section 9.2.4.2, and is selected with an increased uncertainty of ± 0.30 to reflect the lower precision of spectrophotometric measurements.

[72BLO/BUK2]

The sulphite complexes of neptunium(V) were studied by spectrophotometric methods and solid dioxoneptunium(V) sulphites of the form $\text{MNpO}_2\text{SO}_3(\text{s})$ ($\text{M} = \text{Na}^+, \text{NH}_4^+$ and K^+) were precipitated and described. The spectrophotometric study was conducted at $t = 25^\circ\text{C}$ and $I = 1$ M with NaNO_2 used to adjust ionic strength, over a range of pH. Preliminary experiments at $I = 0.1$ M indicate that HSO_3^- complexes are not formed. The results of all experiments are interpreted as the result of the formation of two complexes:



although the increased solubility of the $\text{MNpO}_2\text{SO}_3(\text{s})$ precipitates at higher but unspecified SO_3^{2-} concentrations suggest that a third complex may form. Unfortunately, the original data are not given and no correction can be made to these values to use an appropriate dissociation constant for $\text{H}_2\text{SO}_3(\text{aq})$.

The following stable solids were isolated: $\text{NaNpO}_2\text{SO}_3 \cdot \text{H}_2\text{O}(\text{s})$, $\text{NaNpO}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$, $\text{NH}_4\text{NpO}_2\text{SO}_3(\text{s})$, and $\text{KNpO}_2\text{SO}_3(\text{s})$. The physical solubility and thermal characteristics of these compounds are given in the text, however no thermodynamic data are presented.

[72CAS/MAG]

This is a potentiometric study of the hydrolysis of Pu(VI) in 1 M NaClO_4 . The authors considered the species PuO_2OH^+ , $(\text{PuO}_2)_2(\text{OH})_2^{2+}$, $(\text{PuO}_2)_2(\text{OH})_3^+$, $(\text{PuO}_2)_2(\text{OH})_4(\text{aq})$, $(\text{PuO}_2)_3(\text{OH})_5^+$, $(\text{PuO}_2)_3(\text{OH})_4^{2+}$ and $(\text{PuO}_2)_3(\text{OH})_6(\text{aq})$. Of these, $(\text{PuO}_2)_2(\text{OH})_3^+$, $(\text{PuO}_2)_2(\text{OH})_4(\text{aq})$, $(\text{PuO}_2)_3(\text{OH})_4^{2+}$ and $(\text{PuO}_2)_3(\text{OH})_6(\text{aq})$ were rejected. This appears to be a well designed study, and it is unfortunate only a small fraction of the experimental data were published. In this review, the uncertainties are estimated as ± 0.5 in $\log_{10}^*\beta$ to reflect model error and possible radiolytic effects on the plutonium oxidation state.

[72CAS/MAG2]

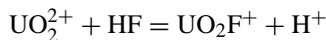
The authors reported $\log_{10}^*\beta_1 = -(5.17 \pm 0.03)$, $\log_{10}^*\beta_{2,2} = -(6.68 \pm 0.02)$ and $\log_{10}^*\beta_{5,3} = -(18.25 \pm 0.02)$ from potentiometric titrations of solutions of Np(VI) with NaOH and HClO_4 in a medium of 1 M NaClO_4 . The authors selected their hydrolysis model after careful comparison of the residuals upon fitting their data to a number of different schemes. The reported uncertainties do not reflect possible systematic errors, and in this review the estimated uncertainties in the values of $\log_{10}^*\beta$ have been estimated as ± 0.20 . The ion-interaction coefficients are assumed to be equal for the corresponding uranium and neptunium hydrolysis reactions



hence $\Delta\varepsilon_{2,2} = -(0.07 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$ and $\Delta\varepsilon_{5,3} = -(0.23 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}$. Grenthe *et al.* [92GRE/FUG] reported $\Delta\varepsilon_{1,1} = -(0.38 \pm 3.7) \text{ kg}\cdot\text{mol}^{-1}$ for formation of UO_2OH^+ , and derived $\varepsilon_{(\text{UO}_2\text{OH}^+, \text{ClO}_4^-)} = -(0.06 \pm 3.7) \text{ kg}\cdot\text{mol}^{-1}$. The uncertainty limit is chemically unrealistic, and in the absence of a more accurate value we assign a slightly more realistic uncertainty, hence $\varepsilon_{(\text{UO}_2\text{OH}^+, \text{ClO}_4^-)} = -(0.06 \pm 0.40) \text{ kg}\cdot\text{mol}^{-1}$ and $\Delta\varepsilon_{1,1} = -(0.4 \pm 0.4) \text{ kg}\cdot\text{mol}^{-1}$. From these the selected values,

$$\begin{aligned} \log_{10}^*\beta_1^\circ &= -(5.1 \pm 0.4) \\ \log_{10}^*\beta_{2,2}^\circ &= -(6.27 \pm 0.21) \\ \log_{10}^*\beta_{5,3}^\circ &= -(17.12 \pm 0.22) \end{aligned}$$

are calculated. The selected value for $\log_{10} \beta_1^\circ$ is very uncertain because of the uncertainty in $\Delta\varepsilon_{1,1}$. For the somewhat similar reaction



a very different value, $\Delta\varepsilon = -(0.03 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$, has been estimated [92GRE/FUG]. If that were the value of $\Delta\varepsilon_{1,1}$, $\log_{10} \beta_1^\circ = -4.7$ is calculated — a markedly less negative value than for the corresponding uranium [92GRE/FUG] or plutonium (Section 17.1.1) species.

[72MEF/KRO]

A number of alkali and hexamminecobalt(III) dioxoneptunium(VI) sulphate compounds were isolated in solid form and their identities confirmed by bulk analysis or by analogy to the similar U(VI) compounds. Infrared spectra of the salts in solution and thermogravimetric curves for the solids are given for some of these compounds and the analogous dioxouranium(VI) compounds. At high temperature the hexamminecobalt(III) compounds decompose to CoSO_4 and $(\text{NpO}_2)_2\text{SO}_4$. The following solids were identified: $\text{Cs}_2\text{NpO}_2(\text{SO}_4)_2(\text{s})$, $\text{Cs}_2(\text{NpO}_2)_2(\text{SO}_4)_3(\text{s})$, $\text{K}_2\text{NpO}_2(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}(\text{s})$, $(\text{Co}(\text{NH}_3)_6)_2\text{NpO}_2(\text{SO}_4)_4\cdot x\text{H}_2\text{O}(\text{s})$, where $x = 5$ or 8 and $(\text{Co}(\text{NH}_3)_6)_4\text{Cs}_6(\text{NpO}_2(\text{SO}_4)_4)_3\cdot x\text{H}_2\text{O}(\text{s})$. There are no thermodynamic data in this paper applicable to this review.

[72MEF/KRO2]

Solid Np(IV) and Np(V) sulphate compounds were isolated from solution and their identities confirmed by bulk analysis. The following compounds were identified: $\text{Co}(\text{NH}_3)_6\text{NpO}_2(\text{SO}_4)_2\cdot 3\text{H}_2\text{O}(\text{s})$, $\text{Co}(\text{NH}_3)_6\text{NpO}_2(\text{SO}_4)_2\cdot \text{K}_2\text{SO}_4\cdot x\text{H}_2\text{O}(\text{s})$, $(\text{NpO}_2)_2\text{SO}_4\cdot 5\text{H}_2\text{O}(\text{s})$, $\text{K}_4\text{Np}(\text{SO}_4)_4\cdot 3\text{H}_2\text{O}(\text{s})$, $\text{Co}(\text{NH}_3)_6\text{NaNp}(\text{SO}_4)_4\cdot 8\text{H}_2\text{O}(\text{s})$, $\text{Co}(\text{NH}_3)_6\text{NpO}_2(\text{SO}_4)_2\cdot \text{Cs}_2\text{SO}_4\cdot 8\text{H}_2\text{O}(\text{s})$, and $\text{Co}(\text{NH}_3)_6\text{NpO}_2(\text{SO}_4)_2\cdot \text{Na}_2\text{SO}_4\cdot \text{H}_2\text{O}(\text{s})$. Photomicrographs of crystal forms and thermogravimetric curves are given for some of these compounds. There are no thermodynamic data in this paper applicable to this review.

[72MET/GUI]

The hydrolysis of Pu(IV) in 1 M (Li/H)ClO₄ (also see [69MET/GUI]) was studied by solvent extraction using thenoyltrifluoroacetone (HTTA), dibenzoylmethane (HDBM) and isopropyltropolone (HITP) dissolved in benzene. The TTA extraction was found to be limited to solutions having pH values < 5 and to HTTA concentrations in benzene > 10⁻⁴ M; also, HTTA seems to reduce Pu(IV) to Pu(III). HDBM and HITP can be used in more alkaline solutions (the values of $(\log K_d + \text{p}K_a)$ for HDBM and HITP are 14.70 and 10.41, respectively, as compared to 7.98 for HTTA). Stock solutions of ²³⁸PuA₄ (A=TTA or DBM) in benzene were reported to be stable, and such solutions were used in the distribution experiments. However, the plutonium concentrations are not clearly specified. In some cases ²³⁹Pu also seems to have been used (1 mM concentration).

Liquid scintillation counting was used to measure the plutonium distributions, but no information was provided about scintillation quenching corrections.

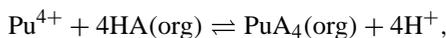
According to the authors, redox buffers are necessary as otherwise radiolysis from plutonium decay would disrupt the disproportionation equilibria between the different oxidation states. Indeed, according to data selected in the present review, Pu(IV) disproportionation cannot be neglected (*i.e.*, regardless of radiolytic processes) in solutions with pH values at which Pu⁴⁺ is expected to be hydrolyzed to PuOH³⁺. At pH values > 6, the aqueous phase was stabilized by 10⁻² M trishydroxyaminomethane (which does not complex plutonium). Pu(IV) was found to be stable in 10⁻⁴-10⁻⁵ M K₂Cr₂O₇ at pH values near 4, but not in solutions at lower or higher pH values; 10⁻⁴ M NO₂⁻ stabilizes Pu(IV) over a broader range, whereas hydroquinone causes reduction to Pu(III). In the absence of an oxidation state stabilization agent, Pu(IV) is partially reduced to Pu(III). The distribution experiments were carried out with different redox agents in different pH regions.

The variation of log D_{Pu} as f(log[HA]_{org}) had the expected slope of 4 (indicating that the dominant species were Pu⁴⁺ in the aqueous phase and PuA₄ in the organic phase) for HTTA at pH values ≤ 4-5, and for HDBM at pH values of 6.5-7.5, while for HITP this slope was only achieved in 2-3 M HClO₄. Therefore HITP was not used for studying the Pu(IV) hydrolysis. It is not clear if the Pu(IV) oxidation state was checked in the whole pH-region from < 0 to 7.5.

The relation log D_{Pu} = f(pH) was studied for HTTA (normalised to [HTTA]_{org}=10⁻²) and HDBM (normalised to [HDBM]_{org} = 5 · 10⁻⁴). The change in slope from 4 to 0.5 was attributed to the formation of aqueous hydrolysis products. Using a least squares computer program for the ≈ 100 distribution points, the following equilibrium constants were calculated:

$$\log \beta_1 = -0.45, \log \beta_2 = -0.75, \log \beta_3 = -3.3, \log \beta_4 = -6.3$$

In the paper, the “K”s used by the authors correspond to “β”s in the nomenclature of the present review. The extraction (normalisation) reaction with HTTA is



for which log K_{ex} = 7.33(1 M HClO₄); the corresponding value for HIPT is 9.4 and no K_{ex} value was given for HDBM. HIPT seems to extract Pu(OH)₂A₂ and is therefore less suitable for Pu hydrolysis studies. Also see the entries for [73MET] and [76MET/GUI].

[73DER/FAU]

The solubility, *S*, of Na₆M^{IV}(CO₃)₅·12H₂O(s) (M^{IV} = Ce or Th) in concentrated Na₂CO₃ and NaHCO₃ solutions, is practically constant in a wide range of [CO₃²⁻]: *S* = 0.0215 and 0.015 M respectively for thorium and cerium. The sodium ion concentration was kept constant (with a sodium salt ?) at 2 g·dm⁻³. The authors assumed

that CO_3^{2-} is the only ligand in the soluble complexes, but they do not discuss this assumption. The similar solubilities in Na_2CO_3 and NaHCO_3 solutions with similar carbonate ion, and sodium ion concentrations, and with similar water activities, confirms the authors' assumption. This could demonstrate that $\text{M}^{\text{IV}}(\text{CO}_3)_5^{6-}$ is the major species, but the ionic strength corrections are not as straightforward as those used by the authors. There might well have been some ion pairing between Na^+ and the anionic soluble carbonate complex. Since no data are reported for neptunium or plutonium, this work is not reviewed in more detail here. This work, and other papers from the same laboratory (e.g., [73DER/FAU2]) suggest analogous behaviour for f-block elements in the +4 oxidation state; but also see more recent papers [97FEL/RAI, 98RAI/FEL].

[73KHA/MOS]

Infrared spectra are interpreted as indicating mono and bidentate bonding of CO_3^{2-} with NpO_2^+ in $\text{NH}_4\text{NpO}_2\text{CO}_3(\text{s})$ solid; see [79VOL/TOM].

[73MET]

This dissertation is the basis for references [72MET/GUI] and [76MET/GUI].

The hydrolysis experiments were carried out with 10^{-3} - 10^{-4} M Pu in 1 M H/LiClO₄ solutions of different pH. Two problems were encountered, polymerization and changes in oxidation state (disproportionation). The solvent extraction technique employed used TTA (thenoyltrifluoroacetone), DBM (dibenzoylmethane) or IPT (isopropyltropolone) in benzene as the extractant. This procedure reduces the total free Pu concentration in the aqueous phase, thus reducing polymerization. In the complexation/distribution experiments, it was ascertained that all Pu in the beginning was in the form of $\text{Pu}(\text{TTA})_4$ (or one of the corresponding complexes) in the organic phase. At pH 6 the system was stabilized by addition of trishydroxyaminomethane. The oxidation and/or reduction to other valence states was investigated at 10^{-7} to 10^{-8} M ^{238}Pu using different redox agents, e.g., $\text{K}_2\text{Cr}_2\text{O}_7$ or NaNO_2 . The reduction of Pu(IV) to Pu(III) or oxidation to Pu(VI) was manifested by a reduction in the distribution ratio when other conditions were kept constant. As $\text{Pu}(\text{TTA})_4$ (or another of the corresponding complexes) was the only Pu-species soluble in the organic phase, one can evaluate the complexation of Pu(IV) with OH^- and citrate (CIT) from measurements of the Pu(IV) distribution between the benzene and aqueous phases (Pu-TTA complexation in the aqueous phase is known to be negligible). Plutonium (IV) hydrolysis begins even at 1 M acid concentration, and increases rapidly with increasing pH, so that at pH 3.5 $\text{Pu}(\text{OH})_2^{2+}$ dominates; at pH values close to 3.5 PuOH^{3+} is predominant. From graphical analysis, a value of $\log \beta_1 = -0.45$ was obtained, and $\log \beta_2$ was estimated as -0.75. The values $\log \beta_3 = -3.3$ and $\log \beta_4 = -6.3$ were obtained from computer refinement, where $\beta_n = [\text{Pu}(\text{OH})_n^{4-n}][\text{H}^+]^n / [\text{Pu}^{4+}]a_{[\text{H}_2\text{O}]}^n$.

In the report, the "K"s used by the author correspond to "β"s in the nomenclature of the present review.

In the citric acid studies, the solutions contained simultaneously three systems, the Pu(IV)-OH, -CIT and TTA (or DBM or ITP). The investigator claims that he has identified 10 different citric complexes (with the OH-group at the central carbon) and 6 different isocitric complexes (with the OH-group at the terminal carbon) by carrying out the extraction studies in solutions at different pH values (up to pH 7) and acid concentrations. The concentration ranges of the different species were calculated. This reviewer doubts the reliability of the formation constants presented.

[73MUS/POR]

This appears to be a preliminary report of a larger study that was never published. There are no details (*e.g.*, pH, analysis method) given as to how the reported solubility product, for $\text{PuO}_2(\text{OH})_2(\text{s})$, $\log_{10} K_{s,0} = -(24.04 \pm 0.19)$, was determined. A limiting solubility of 6.9×10^{-9} M is reported, presumably for a pH value near 8.2, but again no details were provided. The hydrolysis constants were apparently determined by analysis of the near infrared spectra, but no discussion is provided as to why any particular species was selected in any particular pH regime, or why certain species were included or omitted overall.

[73PAT/RAM]

The paper describes a study of sulphate complexation based on solvent extraction of Np(IV) and Pu(IV) from 2 M $\text{H}(\text{ClO}_4, \text{HSO}_4)$ solution using dinonylnaphthalenesulphonic acid (HDNNS). Experiments were performed at 10 and 40°C.

The results of a comparative study for Np(IV) using TTA in benzene were also presented. An incorrect linear model was used to calculate the association quotients. With the data provided, and a better quadratic model, the association constants in Table A.4 were found.

Table A.4: Values of the formation constant of NpSO_4^{2-} from the reaction of Np^{4+} with HSO_4^- based on a recalculation of the results of Patil and Ramakrishna [73PAT/RAM].

	t (°C)	HDNNS	TTA
$\log_{10} \beta$ (1)	10	(2.44 ± 0.05)	(2.42 ± 0.02)
	25	[73PAT/RAM2]	(2.48 ± 0.03)
	40	(2.51 ± 0.05)	(2.56 ± 0.08)
$\log_{10} \beta$ (2)	10	(3.95 ± 0.04)	(3.95 ± 0.01)
	25	[73PAT/RAM2]	(4.06 ± 0.02)
	40	(4.15 ± 0.03)	(4.13 ± 0.05)

In conjunction with the results from [73PAT/RAM2], the values can be used to calculate $\Delta_r H_m^\circ$ and $\Delta_r S_m^\circ$.

In the plutonium experiments, the Pu isotope was not specified, but NaNO_2 was used as holding oxidant. The Pu oxidation state was verified, and complexing by NO_2^-

was assumed negligible. A re-evaluation of the association constants and errors using a quadratic model yields $\log_{10} \beta (I)(19.4) = (2.84 \pm 0.06)$ (10 °C) and (2.72 ± 0.05) (40 °C) and $\log_{10} \beta (I)(19.5) = (4.33 \pm 0.05)$ (10 °C) and (4.39 ± 0.03) (40 °C). With similar 25°C HDNNS extraction data from [73PAT/RAM2] $\Delta_r H_m^\circ (19.4) = -(7.2 \pm 1.7)$ kJ·mol⁻¹ and $\Delta_r H_m^\circ (19.5) = (3.1 \pm 1.8)$ kJ·mol⁻¹.

[73PAT/RAM2]

This reports studies of sulphate complexation based on solvent extraction of Np(IV) and Pu(IV) from 2 M H (ClO₄, HSO₄) solution using dinonylnaphthalenesulphonic acid (HDNNS), and of Pu(IV) using TTA (thenoyltrifluoroacetone), all at 25°C.

For the neptunium system reversibility is claimed, and a holding reductant was used to prevent oxidation. Sufficient data are provided for recalculation of the association quotients and errors using a more appropriate quadratic model. The results of the recalculation yield $\log_{10} \beta_1 = (2.49 \pm 0.03)$ and $\log_{10} \beta_2 = (4.03 \pm 0.02)$.

The Pu(IV) isotope was not specified. NaNO₂ was used as a holding oxidant; the Pu oxidation state was verified and complexing by NO₂⁻ was assumed negligible. A reevaluation of the data presented in this paper using a quadratic model yields $\log_{10} \beta (I)(19.4) = (2.76 \pm 0.03)$ and (2.68 ± 0.06) and $\log_{10} \beta (I)(19.5) = (4.35 \pm 0.02)$ and (4.51 ± 0.02) .

[73RYK/BLO]

No complexation constants are reported in this paper.

[73SIM/MAT]

In this study coulometric measurements were made to determine the value of the Np(VI)/Np(V) couple in aqueous NaOH solutions (0.2 M to 10.0 M) using a platinum electrode. Care was taken to exclude CO₂(g). No systematic correction was made for the diffusion potential at the saturated KCl (calomel electrode)-sodium hydroxide interface. However, Peretrukhin and Alekseeva [74PER/ALE] provided the corrected values, presumably based on more extensive tables of the original data than those published in [73SIM/MAT]. The corrected potential for 1 M NaOH, 0.19 V vs. SHE, can be used to calculate $E^\circ = 1.83$ V when corrected as per the discussion for [77ERM/PER]. The corrected potential for 2.5 M NaOH solution is about 0.02 V more positive than found by Ermakov *et al.* [77ERM/PER] for a 2.5 M LiOH solution.

Although at concentrations of NaOH below 1 M the increase in stability of Np(VI) with increasing base concentration was reflected in a slope of the potential of the couple of -0.146 V per unit $\log_{10}[\text{NaOH}]$, the slope was nearly zero for $1 < [\text{NaOH}] < 10$ M. This work is not consistent with the experimental results published by Peretrukhin and Alekseeva [74PER/ALE], but was later supported by that of Peretrukhin and Spitsyn [82PER/SPI].

[74ARK/GUT]

The heat capacity of neptunium dioxide was determined from drop calorimetry measurements in the temperature range 350 to 1100 K. The sample was somewhat impure, containing approximately 1% iron. The results do not mesh smoothly with those obtained at lower temperatures by Westrum *et al.* [53WES/HAT]. Unfortunately, the authors [74ARK/GUT] did not report their raw data, but instead provided a table of smoothed values. They report the mean square deviation of the enthalpy values as $\pm 4.7\%$ and the scatter of the experimental (heat capacity?) points from the calculated equation as 15%. Thus, the measured values can provide only a rough guide to the heat capacity behaviour of $\text{NpO}_2(\text{cr})$ over the experimental temperature range. The extrapolated value for 300 K is approximately 20% greater than found by Westrum *et al.* [53WES/HAT] for $\text{NpO}_2(\text{cr})$, and comparison with values for $\text{UO}_2(\text{cr})$ [92GRE/FUG] and $\text{PuO}_2(\text{cr})$ [76FLO/OSB] at 298.15 K show similar differences. Nevertheless, the large disagreement between the equation from this study extrapolated to 298.15 K and the data in [53WES/HAT] is almost within the cited uncertainties! Values obtained by extrapolation of the results (228.6 to 312.7 K) from [53WES/HAT] do not differ from those in [74ARK/GUT] by more than 15% for temperatures above 400 K. In view of the large reported experimental scatter, the smoothed values reported by Arkhipov *et al.* are rejected in the present review.

[74DAN/CHI]

See comments under Danesi *et al.* [71DAN/CHI].

[74FAR/PEA]

The authors report on an ion exchange study of sulphate complexation in 2 M HClO_4 at $(25 \pm 0.1)^\circ\text{C}$. The plutonium was a mixture of ^{239}Pu , ^{240}Pu , ^{241}Pu , and ^{242}Pu . Distribution of $\text{Pu}(\text{IV})$ was determined by counting ^{241}Pu only, to avoid errors due to other radioactive isotopes that may have been present in the mixture. The time to attain equilibration was determined experimentally, and counting procedures were described in detail. Nitrite was used as a holding reductant, and complexation by NO_2^- was assumed negligible. Insufficient data were reported to allow re-evaluation of the errors. Uncertainties compiled by the authors are assumed to be 1σ , and hence, $\log_{10} \beta_1(I)(19.4) = (2.75 \pm 0.02)$ and $\log_{10} \beta_2(I)(19.5) = (4.43 \pm 0.03)$.

[74KHO/MAT]

This is a solvent extraction study of thiocyanate complexation using dinonylnaphthalenesulphonic acid in *n*-hexane. The reference temperature of the experiments was $(30 \pm 0.1)^\circ\text{C}$ and the ionic strength was kept constant at 1 M (NH_4ClO_4). The pH of the experimental solutions was about 2.8. All solutions contained 0.1 M NH_4I as a holding reductant. In order to correct for the possible formation of $\text{Pu}(\text{III})$ iodide complexes, the formation constant of a PuI^{2+} complex was determined in the same medium in a separate experiment. Up to a total iodide concentration of

0.7 M, only the first complex, PuI^{2+} , was found to be formed with a constant of $K_1(\text{PuI}^{2+}, 1 \text{ M}, 303.15 \text{ K}) = (1.09 \pm 0.07)$. This experiment was not described in more detail by the authors. For the thiocyanate complexes, the following constants were reported: $\beta_1(\text{PuSCN}^{2+}, 1 \text{ M}, 303.15 \text{ K}) = (2.18 \pm 0.17)$ and $\beta_2(\text{Pu}(\text{SCN})_2^+, 1 \text{ M}, 303.15 \text{ K}) = (4.10 \pm 0.21)$.

In order to obtain some information on the thermodynamic properties of the complexes, the authors performed additional experiments at 15, 37 and 45°C. The results are given in Figure 3 of [74KHO/MAT]. The formation constants obtained for PuSCN^{2+} are: $\log_{10} \beta_1 = 0.31$ (15°C), 0.34 (30°C), 0.33 (37°C) and 0.31 (45°C). The temperature variation of this constant is thus zero within the experimental error. The authors reported, for the formation of PuSCN^{2+} : $\Delta_r H_m(1 \text{ M}, 303.15 \text{ K}) = (0.25 \pm 0.75) \text{ kJ}\cdot\text{mol}^{-1}$.

Khopkar and Mathur [74KHO/MAT] drew attention to the “reversal” behaviour of Pu(III) and Am(III) in the thiocyanate complex stability order. They expected the 1:1 complex of Pu(III) to be less stable than that of Am(III) due to a decrease in the atomic radii. However, Choppin and Ketels [65CHO/KET] have found a higher stability for the Am(III) complex. In any case, the formation constants of the complexes PuSCN^{2+} and AmSCN^{2+} are very similar, cf. [95SIL/BID], and the differences are smaller than the estimated uncertainties.

[74MEF/KRO]

The hydrolysis of Np(III) was studied by potentiometric titration of *ca.* 0.044 millimole samples of Np(III) in 0.1 M NaClO_4 , using 0.1 M NaOH and a LPU-1 pH meter and glass(?) electrode, in a deaerated system protected from air. The experiments were carried out at 20°C (Table 1). The titrations in chloride medium at 23°C (Figure 1) were presumably not used in the final calculations of the hydrolysis constant. The Np(III) was produced by electrolysis of 0.022 M $\text{Cs}_2\text{NpCl}_6(\text{aq})$ in 0.1 M HCl using a mercury cathode in an inert atmosphere. Solutions of Pr^{3+} and Nd^{3+} were titrated in a similar manner, and the three sets of titration curves were compared to obtain the ratios of the hydrolysis constants. A ratio ${}^*\beta_1(\text{Nd})/{}^*\beta_1(\text{Pr}) = 1.35$ was obtained, in agreement with an earlier value of 1.32 [66FRO/KUM], obtained at 0.3 M NaClO_4 (25°C). The values reported in the paper by Frolova, Kumok, and Serebrennikov, [66FRO/KUM] for the first hydrolysis constants, $\log_{10} {}^*\beta_1$, are -8.43 for Nd^{3+} , and -8.55 for Pr^{3+} . The value for the first Np(III) hydrolysis constant at (25°C), ${}^*\beta_1 = (3.7 \pm 0.9) \times 10^{-8}$, was then calculated for a medium of 0.3 M NaClO_4 ($\log_{10} {}^*\beta_1 = 7.43 \pm 0.11$) using the ratios of the hydrolysis constants of Np(III) with those of Pr(III) and Nd(III).

Considering the comparison of values obtained by [66FRO/KUM] for 0.3 and 3 M NaClO_4 , from titrations using both NaOH and $\text{Ba}(\text{OH})_2$, and literature values cited by the same authors for the lanthanide ion hydrolysis constants in 3 M NaClO_4 , it seems likely that the error in the Np(III) hydrolysis constant is considerably greater than ± 0.1 . Systematic errors may also be present, and as the paper does not show any measured points, the statistical uncertainty cannot be evaluated. Using

$$\log_{10} {}^*\beta_1(I = 0) = \log_{10} {}^*\beta_1(I) + 4D + \Delta \varepsilon I - \log_{10} a_{\text{H}_2\text{O}}$$

where $D = 0.154$ for $I = 0.305$ m ($4D = 0.615$) and $\Delta\varepsilon = -0.04$ kg·mol⁻¹ is estimated by analogy from values in Table B.3, $-\log_{10}^*\beta_1^\circ = (6.8 \pm 0.3)$. The uncertainty is an estimate.

[74PER/ALE]

In this study potential measurements were made of Np(VII), Np(VI) and Np(V) in aqueous NaOH solutions (0.3 M to 14 M) using a rotating platinum electrode. The Np(V)/Np(VI) couple is apparently reversible, although gradual precipitation of a Np(V) solid occurs. The potentials are somewhat lower than those obtained from coulometric [73SIM/MAT] and potentiometric [77ERM/PER] measurements. The measured potentials decreased slightly with increasing NaOH concentration. The experimental slopes are not very precise and should be corrected for ionic strength and junction potential variations. There is no satisfactory way to estimate the junction potential changes in these experiments, and it is thus not clear whether the stoichiometries of the limiting hydroxide complexes of actinide (V) and (VI) in the present review are compatible with the measurements. The reported formal potential for Np(VI)/Np(V) is not consistent with later work of one of the authors [82PER/SPI].

[74SIM/VOL]

a) K⁺-Np(V)-CO₃²⁻ compounds

The authors do not give enough experimental information to allow an accurate interpretation to be made of this work. Nevertheless, it is quite clear that the authors have prepared pentavalent actinide carbonate compounds containing alkali metal cations. This confirms some of the results for neptunium reported in [74VIS/VOL]. The authors reported the preparation of hydrated KNpO₂CO₃(s) in 0.2 M K₂CO₃ and hydrated K₃NpO₂(CO₃)₂(s) in 0.8 M K₂CO₃ aqueous solution. The preparation conditions were such that the carbonate concentrations were respectively less and more than the [CO₃²⁻] value controlled by the equilibrium



Thus, in the present review, the equilibrium constant for this reaction is estimated as

$$\begin{aligned} \log_{10} K &= \log_{10} K_s(\text{K}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})) - \log_{10} K_s(\text{KNpO}_2\text{CO}_3(\text{s})) \\ &= -(0.6 \pm 0.9) \end{aligned}$$

b) Np(VI)/Np(V) redox couple

It was confirmed that the preparation involved a one electron exchange, and a value for the sum of the normal redox potential plus the junction potential at $(20 \pm 1)^\circ\text{C}$ was deduced. The junction potential between the working electrode and the reference electrode (a saturated calomel electrode connected with a saturated KCl bridge) was

probably less than the uncertainty in the measurements. The shift in the Np(VI)/Np(V) potential from acidic to the carbonate media was reported as

$$E_{\text{Np(VI)/Np(V) in 1 M Na}_2\text{CO}_3} - E_{\text{Np(VI)/Np(V) in 1 M HClO}_4} = -0.6 \text{ to } -0.7 \text{ V}$$

This corresponds to

$$\log_{10} \left(\beta_{3\text{Np(VI)}} / \beta_{3\text{Np(V)}} \right)_{0.2 \text{ to } 3 \text{ M K}_2\text{CO}_3} = 11.2 \pm 0.9$$

since it is now known that the two limiting complexes are $\text{NpO}_2(\text{CO}_3)_3^{4-}$ and $\text{NpO}_2(\text{CO}_3)_3^{5-}$. The change in the Np(VI)/Np(V) redox potential between 0.2 and 3 M K_2CO_3 solutions and acidic solutions was constant, which indicated the Np(V) and Np(VI) limiting complexes have the same stoichiometry. See the discussions for [75SIM] and [77SIM] in this appendix, for further quantitative interpretation and discussion of these data.

c) Reduction of Pu(VI)

The reduction potential of Pu(VI) in 0.1 and 1.0 M K_2CO_3 at 20°C was reported to be (0.30 ± 0.01) and (0.32 ± 0.01) V vs. SHE. The reduced products were identified (by X-ray diffraction studies) as a hydrated $\text{KPuO}_2(\text{CO}_3)(\text{s})$ and a $\text{K}_3\text{PuO}_2(\text{CO}_3)_2(\text{s})$ compound. The former compound precipitated during the course of the electrolytic reduction, a period of ~15 minutes, while in the latter case there was an induction period of ~24 hours. The reduction potentials are in reasonable agreement with later reported values [83WES/SUL, 86LIE/KIM, 92CAP].

[74SOL]

The systems studied consisted of metal ions ($M = \text{Pu, U, Th or Zr}$) in solutions of high concentrations of nitric acid ($\leq 6 \text{ M}$) in contact with kerosene or o-xylene containing $\leq 60 \text{ vol\% TBP or HTTA}$. The TBP and HTTA cause extraction of metal species into the organic phase. It was assumed that the extracted species in the TBP system were $\text{M(OH)}_i(\text{NO}_3)_{(4-i)}$ and in the HTTA system M(TTA)_4 , $\text{M(NO}_3)(\text{TTA})_3$ and M(OH)(TTA)_3 . In the presence of perchlorate ions it was assumed that ClO_4^- behaves similarly to NO_3^- . Extraction equations were developed for these systems, including activity factors for the high ionic strength medium. The activity factors, which were taken from various sources (reference was given to a large number of Russian papers), do not seem to have been used systematically (leading to “hypothetical activity coefficients”). In analysis of some (but not all) of the distribution measurements of metal species and of TBP and HNO_3 , corrections were made for volume changes. A set of “thermodynamic constants of M(IV) hydrolysis at $\approx 25^\circ\text{C}$ ” were given as listed in Table A.5

Here β_1° values (e.g., $\beta_1^\circ = 3.8 \cdot 10^{14}$) are defined as the thermodynamic equilibrium constants for the reactions $\text{M}^{4+} + i\text{OH}^- \rightleftharpoons \text{M(OH)}_i^{(4-i)}$. The uncertainties in the values in the Table A.5 are unstated, but are likely large - primarily due to the uncertainties with regard to the activity factors and the uncertainties in the measured distribution

Table A.5: Thermodynamic constants of M(IV) hydrolysis at $\approx 25^\circ\text{C}$ as given by [74SOL].

M(IV)	$\beta_1^\circ 10^{-14}$	$\beta_2^\circ 10^{-28}$	$\beta_3^\circ 10^{-42}$	$\beta_4^\circ 10^{-56}$	References
Zr	3.8	23.9	52.4	70	[67SOL/TSV]
Pu	0.17	0.6	3.2		[74SOL]
U	0.06				[74SOL]

ratios (however, the author's Table 6 does show good agreement between experimental and calculated distribution coefficients for the U(VI) system). No information was presented with regard to how the unstable oxidation states, U(IV) and Pu(IV), were maintained in solution. The value of the activity product of water (K_w), as used in the author's calculations, was reported as $1.27 \cdot 10^{-14}$ at all concentrations ($\text{p}K_w = 13.90$). That value was used to analyze the experimental results ($I > 0$) to obtain values of β° , and that value is used in the present review to convert the β° values to the values of $^*\beta^\circ$ presented in Table 17.3. However, the approximate average value of $\text{p}K_w$ for 20°C to 25°C at $I = 0$ is actually 14.1.

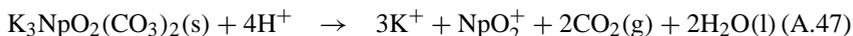
The experiments were carried out to permit semi-empirical modelling of distributions for separations processes, and the author made no claim the measurements were designed to accurately determine the hydrolysis constants. Insufficient information was provided to permit recalculation of the data. For this reason, and because the experimental conditions are ill-defined, the results of this study are not used in the present review in selection of hydrolysis or complexation constants.

[74VIS/VOL]

$\text{KNpO}_2\text{CO}_3(\text{s})$ was precipitated from concentrated 0.1-0.2 M K_2CO_3 solution. The ratio $\text{Np(V)}/\text{CO}_3^{2-}$ in the solid was determined by measuring the $\text{CO}_2(\text{g})$ released on titration with acid, and coulometric determination of the Np content. A pH-metric Np(V) titration using 0.2 M K_2CO_3 solution confirmed the stoichiometry of the $\text{KNpO}_2\text{CO}_3(\text{s})$ solid. X-Ray powder diffraction patterns indicated two $\text{K}_3\text{NpO}_2\text{CO}_3(\text{s})$ phases for which the stoichiometry was also determined by the same techniques. One precipitated from 0.8 - 1.5 M K_2CO_3 solutions and the other from 1.8-5.6 M K_2CO_3 solutions (see [54NIG/PEN]). It is quite surprising that two different solid phases with the same stoichiometry would form at equilibrium in these aqueous solutions as the variation of the water activity in these solutions was relatively small. The precipitation of the two different solid phases could be due to kinetics. Despite the comments of the authors, the X-ray diffraction patterns given in this work do not appear to support the formation of additional solid phases (either with the same stoichiometry or $\text{K}_5\text{NpO}_2(\text{CO}_3)_3(\text{s})$).

Potentiometric titration of a 0.06 M Np(V) aqueous solution with a 0.2 M K_2CO_3 aqueous solution showed that the precipitation started at $\text{pH} = 4.6$, and that the pH was buffered to $\text{pH} = 5.6$ (before the equivalence point), and the mid point for the reaction was at $\text{pH} = 5.2$. Back titration of the solid compounds, with 0.1 M HCl, showed buffering of the pH at about the same values. The mid-point of the reaction was at $\text{pH} =$

4.8, 5.2 and 6.4 respectively for hydrated $\text{K}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$, hydrated $\text{KNpO}_2\text{CO}_3(\text{s})$ and a K_2CO_3 solution. In these conditions, the free carbonate concentration, $[\text{CO}_3^{2-}]$, was certainly less than $10 \mu\text{M}$ so NpO_2^+ was not complexed, and according to the data selected by this review, the titration reactions were then



Assuming that titration caused release of $\text{CO}_2(\text{g})$ (bubbling, hence $p_{\text{CO}_2} \approx 1 \text{ atm}$), and estimating the NpO_2^+ concentration at the mid-point of the reaction to be about 0.03 M (these values were not reported in the publication [74VIS/VOL]), the first solubility product can be very crudely estimated as

$$^*\text{K}_{\text{s},0}(\text{A.46}) \approx -(10.3 \pm 2.0)$$

The results from the potentiometric titrations are not particularly consistent with later work in sodium (instead of potassium) media by the same group of authors [79VOL/VIS2], and this can be attributed to kinetic rather than thermodynamic factors (see the discussion of [79VOL/VIS2] in this appendix).

The authors also reported Np(V) solubility values in 1.2 M K_2CO_3 aqueous solutions at 20 and 80°C. If it is assumed that this solubility was controlled by the following equilibrium



then

$$\log_{10} K_{\text{s},3}(\text{A.48}) \approx -(3.4 \pm 0.5)$$

in 1.2 M K_2CO_3 aqueous solutions at 20°C, and

$$\log_{10} K_{\text{s},3}(\text{A.48}) \approx -(3.1 \pm 0.5)$$

in 1.2 M K_2CO_3 aqueous solutions at 80°C are calculated. These values are consistent with a previous estimate (see the discussion of [66GOR/ZEN]) within the uncertainties (considering the ionic strength were not the same in the two measurements). The later value [74VIS/VOL] is more accurate since the solid phase was prepared more carefully here. However, it was not possible to verify that the solid phase did not change between 20 and 80°C.

[74VOL/KAP]

Volkov *et al.* prepared hydrated $\text{KAnO}_2\text{CO}_3(\text{s})$ compounds, where An was Np, Pu or Am. They discussed the variations observed in their X-ray diffraction patterns as a function of preparation conditions and ageing. This interpretation seems reasonable (variations in the distances in the crystal lattices), but the most important information for the selection of thermodynamic data that comes from this work is that it is difficult to obtain a well characterised solid phase of this type in equilibrium with aqueous solution.

[74VOL/KAP2]

In this publication, Volkov *et al.* reported the X-ray diffraction patterns of hydrated $\text{K}_3\text{AnO}_2(\text{CO}_3)_2(\text{s})$ solid compounds, where An = Np, Pu or Am. They discussed the temperature influence on the lattice parameters. No thermodynamic data can be extracted from this work.

[75HUB/HUS]

This paper on Pu(III) hydrolysis describes some technical improvements in the radiotracer solvent extraction technique using HTTA technique in benzene from 0.2 M (Li,H)ClO₄ in the pH range 3-6. $[\text{Pu}]_{\text{tot}}$ was 10^{-5} to 10^{-8} . Hydroxylamine was added to the aqueous phase to buffer it in the proper pH-region; hydroxylamine also acts as a reducing agent. Both direct extraction and back-extraction of Pu was used; back-extraction reduces disturbances from colloids. Slow kinetics was observed, equilibrium being reached after 16 hours. The distribution values depended on the $[\text{Pu}]_{\text{tot}}$ at low pH values (*ca.* 3), but not at higher values (*ca.* 5). The distribution value also depended on the ratio $[\text{Pu(IV)}]/[\text{Pu(III)}]$.

A plot of $\log_{10}D$ versus $\log_{10}[\text{HA}]_{\text{org}}$ gives straight lines with slope 3 in the pH-range 4-6; thus aqueous complexes of Pu-TTA ought to be neglected (though at this pH-range there could be aqueous Pu(IV)-TTA complexes, as the authors admit). Normalised $\log_{10}D(\text{Pu(III)})$ versus pH plots indicates a change in slope at $\text{pH} > 3.8$ and after long agitation times. From these plots the equilibrium constants $K_{\text{ex}} = -2.5 \pm 0.3$ and $\log_{10}^*K_1 = -3.8 \pm 0.2$ ($I = 0.2$, Li^+ , H^+ , ClO_4^- , Cl^- , NH_2OH) were calculated.

There are many things that are difficult to explain about this work, *e.g.*, the slow kinetics, how the authors distinguished between Pu(III) and Pu(IV), etc. There is no information about how the “error” was obtained. The conclusions are invalidated if polymerisation occurred or Pu(IV) was present. All “Pu(III) curves” showed slow kinetics. Slow kinetics have not been observed for any of the other actinides studied. The Pu(III) equilibria, including hydrolysis, should be rapid, while Pu(IV) hydrolysis is slow in the case of polynuclear complex formation. Because oxidation is thermodynamically more likely at higher pH (> 3), the reviewer suspects that some Pu(IV) formed and was being slowly hydrolysed. This would explain both the kinetics and the change in slope, which then is not a result of Pu(III) hydrolysis. In conclusion, the reviewer has little confidence in these results. In principle, the Pu(III) system seems unsuitable for study by the TTA-solvent extraction technique.

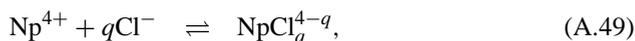
[75IOR/SHC]

NMR measurements (proton and ^{14}N resonances) in water/acetone mixtures at -105°C were reported in this paper. The authors detected the first nitrate complex for Np(VI)/water ratios < 185 (approximately 0.3 M NpO_2^{2+} if in solution in water only). The second complex was detected for Np(VI)/water ratios of 40-150. No nitrate concentrations nor formation constants were reported.

[75PAT/RAM]

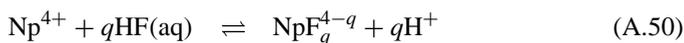
The authors used a solvent extraction technique with HTTA or dinonylnaphthalenesulphonic acid (HDNNS) in benzene. The aqueous phase contained 2 M H^+ , varying concentrations of Cl^- and $\text{HF}(\text{aq})$, respectively, and ClO_4^- as a supporting electrolyte to maintain $I = 2\text{ M}$. In the chloride complexation experiments with Np(IV), Fe(II) sulphamate was used to stabilise the oxidation state of neptunium. The temperature was kept constant during the experiments at 25°C . The experimental procedure seems satisfactory. However, no check was made to verify the proper oxidation state of Np(IV) at the end of the experiments.

For the Np(IV) chloride system,



the authors reported $\beta_1(\text{A.49}, q = 1) = (0.9 \pm 0.1)$ and $\beta_2(\text{A.49}, q = 2) = (0.7 \pm 0.1)$. Giffaut [94GIF] has re-evaluated Patil and Ramakrishna's experiments and obtained slightly different values due to improvement of the fit in the lower range of the chloride concentrations: $\beta_1(\text{A.49}, q = 1) = (1.0 \pm 0.1)$ and $\beta_2(\text{A.49}, q = 2) = (0.6 \pm 0.1)$. We use these results in our selection procedure, but we increase the uncertainties: $\log_{10} \beta_1(\text{A.49}, q = 1) = (0.00 \pm 0.20)$ and $\log_{10} \beta_2(\text{A.49}, q = 2) = -(0.22 \pm 0.40)$.

For the Np(IV) fluoride system,



the authors reported $\log_{10} {}^*\beta_1(\text{A.50}, q = 1) = (4.62 \pm 0.01)$ from HDNNS extraction. The evaluation of the HTTA extraction studies was done with a one- and a two-complex model, resulting in $\log_{10} {}^*\beta_1(\text{A.50}, q = 1) = (4.72 \pm 0.01)$ using only the points at $[\text{HF}(\text{aq})] < 3 \times 10^{-4}\text{ M}$, and $\log_{10} {}^*\beta_1(\text{A.50}, q = 1) = 4.60$ and $\log_{10} {}^*\beta_2(\text{A.50}, q = 2) = 7.49$ using all the points up to $[\text{HF}(\text{aq})] = 10^{-3}\text{ M}$. The uncertainties given by the authors are grossly underestimated. We use the independent results from this study, *i.e.*, $\log_{10} {}^*\beta_1$ from the HDNNS extraction and $\log_{10} {}^*\beta_1$ and $\log_{10} {}^*\beta_2$ from the HTTA extraction, and we assign uncertainties of ± 0.20 ($\log_{10} {}^*\beta_1$) and ± 0.40 ($\log_{10} {}^*\beta_2$).

[75RAG/RAM]

The authors used a solvent extraction technique with HTTA or dinonylnaphthalenesulphonic acid (HDNNS) in benzene to study the bromide complexation of Th^{4+} , Np^{4+} and Pu^{4+} . Vanadate was used as a holding oxidant for Pu^{4+} rather than nitrite as used earlier [73PAT/RAM2], because nitrite was found to oxidise bromide to bromine under

these conditions. For Np^{4+} , the holding oxidant used was Fe(II) sulphamate. The aqueous phase contained varying concentrations of HBr, and HClO_4 as a background electrolyte, so that $[\text{H}^+]_t = 2 \text{ M}$ and $I = 2 \text{ M}$. The temperature was kept constant at 25°C .

The constants obtained in this study are lower than from those of other studies (*cf.* the Pu(IV) bromide system in Part IV, Section 18.2.3.2), and Fuger *et al.* [92FUG/KHO] stated that they “appear abnormally low in the case of thorium and neptunium mono and dibromo complexes”. The reported formation constants for NpBr^{3+} and NpBr_2^{2+} are $\log_{10} \beta_1(\text{NpBr}^{3+}) = -(0.21 \pm 0.01)$ and $\log_{10} \beta_2(\text{NpBr}_2^{2+}) = -(0.57 \pm 0.03)$. A possible cause for the deviation is the uncertainty about the actual oxidation state of neptunium. Another possibility is the formation of complexes higher than actinide(TTA)₄, and it is presently not possible to qualify this statement because no formation constants for complexes such as actinide(TTA)_n⁴⁻ⁿ are available. If we use $\Delta\varepsilon_1 = -0.29 \text{ kg}\cdot\text{mol}^{-1}$ (equal to the corresponding uranium(IV) [92GRE/FUG] and plutonium(IV) system, see Part IV), we will obtain $\log_{10} \beta_1^\circ(\text{NpBr}^{3+}) = 1.0$, which is 0.46 and 0.6 logarithmic units lower than the value for UBr^{3+} and PuBr^{3+} , respectively. This does not correspond to the tendency in the complex formation constants of the series U-Np-Pu, and we cannot accept this value here.

[75SCH]

This is a careful potentiometric study of the hydrolysis of Pu(VI) (0.01 to 0.15 M) in 3 M NaClO_4 . The major hydrolysis species were identified as $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ and (possibly metastable) $(\text{PuO}_2)_4(\text{OH})_7^+$. Considering possible model error and radiolysis effects, the reviewer estimates the uncertainties in the logarithm (base 10) of the equilibrium constants for these two species as ± 0.5 . The authors could find no convincing evidence for PuO_2OH^+ in their solutions, and this would indicate $\log_{10} K_{11}$ is less than -5.5 .

[75SIM]

This is careful work to determine the electrochemical equilibrium



in HClO_4 , H_2SO_4 and Na_2CO_3 aqueous solutions. The formal potentials reported in this publication were probably not corrected for the junction potentials. The experimental set up used seems to give relatively small junction potentials; but it was possibly more than the value of the uncertainty reported by the author (0.01 V). In a later study [77SIM] the same author estimated that the junction potential was less than 0.01 V in similar media, but the uncertainty could still be more than this value (see the discussion for [77SIM] in this appendix).

The value of the formal potential in a non-complexing medium (1.18 ± 0.01) V/SHE is not consistent (within the uncertainty estimated by the author) with

the value selected in this review (1.14 ± 0.01) V/SHE: the difference between the two values is 0.04 V. The discrepancy is probably due to some systematic error (junction potential, calibration of the reference electrode). The ΔE values

$$E_{\text{Np(VI)/Np(V) in 1 M Na}_2\text{CO}_3} - E_{\text{Np(VI)/Np(V) in 1 M HClO}_4} = -(0.71 \pm 0.01_4) \text{ V}$$

is also different (by at least 0.05 ± 0.03 V) from the value calculated with the thermodynamic data selected in the present review. It is consistent with the previous measurement of the author [74SIM/VOL]

$$E_{\text{Np(VI)/Np(V) in 1 M Na}_2\text{CO}_3} - E_{\text{Np(VI)/Np(V) in 1 M HClO}_4} = -0.6 \text{ to } -0.7 \text{ V}$$

Since enough reliable data in HClO₄ and Na₂CO₃ media are published elsewhere (see Table 12.1) these results could be simply rejected; the value in carbonate medium can be retained, increasing its uncertainty to at least 0.02 V, which is reasonable for the possible calibration systematic deviation indicated above. In the present review an uncertainty of 0.05 V was actually used to ensure that it is really greater than the unknown junction potential. From this uncertainty and ΔE , this review calculated

$$\log_{10} (\beta_{3\text{Np(VI)}}/\beta_{3\text{Np(V)}})_{0.1 \text{ to } 2 \text{ M Na}_2\text{CO}_3 \text{ or K}_2\text{CO}_3} = (12.0 \pm 1.2)$$

to be compared with

$$\log_{10} (\beta_{3\text{Np(VI)}}/\beta_{3\text{Np(V)}})_{0.2 \text{ to } 3 \text{ M K}_2\text{CO}_3} = (11.2 \pm 0.9) \quad [74\text{SIM/VOL}]$$

The data proposed in this work, are consistent with those published by the same author earlier in similar carbonate media [74SIM/VOL] and later in similar or identical carbonate media [77SIM]; but it is (0.044 ± 0.017) V greater than a more recent published value [95OFF/CAP]. Later information by the same author on this subject [77SIM] allows an estimation of the uncertainty in the calibration of his reference electrode (see the discussion of [77SIM] in this appendix). The value was apparently overestimated by 0.021 V; however the reference electrodes in the two sets of experiments [75SIM, 77SIM] were not the same. Therefore, the above value was not corrected by 0.021 V in the present review. Nevertheless, this illustrates that the 0.05 V uncertainty estimated above, is reasonable.

[75UEN/SAI]

Np(V) solubility was measured in 0.05 to 1.6 M Na₂CO₃ solutions. The ionic strength was allowed to vary. In the most concentrated Na₂CO₃ solutions, the solid was probably slowly transformed to Na₃NpO₂(CO₃)₂(s) [66GOR/ZEN, 81VOL/VIS4, 86GRE/ROB, 93LEM/BOY, 95NEC/RUN, 98VIT/CAP].

Np(V) absorption spectra in 0.5 to 2 M Na₂CO₃ solutions reported in this work, are similar to those obtained by others [66GOR/ZEN, 90RIG].

The authors did not interpret their results, but these appear to be consistent with the Np(V) solubility predicted by using the data selected by this review, assuming equilibrium with the air, and considering NaNpO₂CO₃(s), NpO₂CO₃⁻, NpO₂(CO₃)₂³⁻

and $\text{NpO}_2(\text{CO}_3)_3^{5-}$. However, too many parameters are involved for the number of reported experimental data, and the results of this publication are not used in the present review for selection of thermodynamic values, since too many parameters were not controlled in the experiments. Rough values from $-(3.04 \pm 1.25)$ (0.07 M Na_2CO_3) to $-(1.72 \pm 0.39)$ (0.4 M Na_2CO_3) for $\log_{10} K_{s,3}$ (A.25, $M^+ = \text{Na}^+$) and $-(11.22 \pm 0.35)$ for $\log_{10} K_s^\circ(\text{NaNpO}_2\text{CO}_3(\text{s}))$ are calculated assuming values for the other constants as selected in this review (also see [98CAP/VIT]).

In the 1.2 and 1.6 M Na_2CO_3 solutions, the measured solubilities were lower than the solubilities as calculated above. This is evidence of the precipitation of a new solid phase, which was almost certainly $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$, [77SIM, 79VOL/VIS, 81VOL/VIS2, 81VOL/VIS3, 81VOL/VIS]. These solubilities should then be interpreted in terms of the following equilibrium

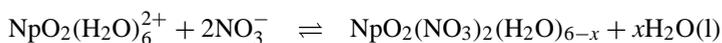


for which this review estimates $\log_{10} K_{s,3}(\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})) < -0.43$ in 1.6 M Na_2CO_3 solution.

[75VAS/AND]

This reports on a spectrophotometric study in the near infrared region (1213 nm band of intraorbital transitions). No complex was observed up to 2 M nitrate, and the band disappeared at 14 M nitrate. At 1110 nm a new band was observed at concentrations of nitrate greater than 2 M, reaching a maximum at 12 M. For concentrations of nitrate higher than 12 M a third species was formed.

The stoichiometry of the complex was deduced by comparison with known salt spectra in acetone. It is possible that even at the low (self) concentrations of the salt, such weak complexes have a non negligible dissociation in acetone solutions, since their dissolution shows a certain interaction with the solvent. By analyzing the water activity of the nitric acid solutions, it was concluded that the nitrate in the complex was bidentate, with four moles of water being displaced. The authors' value of the complexation constant does not correspond to the standard definition, but to the reaction:



$x = 4$ as determined experimentally. In order to compare it with other values obtained for solutions with nitric acid concentrations less than 2 M, the reported value should be divided by $\sim(50.1)^4 = 6.3 \times 10^6$, which corresponds to the lowest water concentration where it was assumed valid. Thus, a value of ~ 0.009 instead of 55000 has to be used for comparison with other constants, expressed only in terms of the concentrations of nitrate, metal and complex.

The constant was determined by taking the differences of large numbers, $4 \log_{10}[\text{H}_2\text{O}]$ varies between 4.6 and 6.8, $2 \log_{10}[\text{NO}_3^-]$ varies between 0.6 and 2.6. Then working with a solution 1.4×10^{-3} M in total neptunium, ratios of $[\text{NpO}_2(\text{NO}_3)_2(\text{aq})]/[\text{NpO}_2^{2+}]$ between 0.001 and 40 have been measured. This means

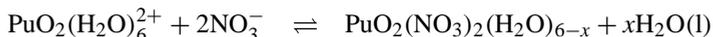
very low concentrations have been determined, then used in an expression which transforms to:

$$4 \log_{10}[\text{H}_2\text{O}] - 2 \log_{10}[\text{NO}_3^-] = \log_{10} K - \log_{10}([\text{NpO}_2(\text{NO}_3)_2(\text{aq})]/[\text{NpO}_2^{2+}])$$

As the ionic medium was not kept constant, the activity factors probably varied greatly. The value of the constant has little significance, and is not accepted in the present review.

[75VAS/AND2]

This is a spectrophotometric study performed in 0.1-20 M HNO_3 . The absorption of 1.4 mM Pu(VI) solutions at 800-850 nm at an unspecified temperature were measured. For 0.1-2 M HClO_4 , HCl , and HNO_3 solutions the Pu(VI) spectra did not change, and it could be concluded no complexes were formed. Between 1-11 M nitrate an isosbestic point was observed, the 831 nm band decreased and disappeared at 14 M, while a new band appeared at 815 and increased. At concentrations of nitrate greater than 11 M the isosbestic point disappeared and another new peak appeared, on the basis of which formation of another new species was deduced. From the similarity of the spectra to those of solutions of the salts $\text{PuO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ and $\text{NH}_4\text{PuO}_2(\text{NO}_3)_3(\text{s})$ in acetone, speciation was proposed. By analysing the water activity it was concluded that the nitrate in the complex is bidentate with four moles of water being displaced. By plotting $[\text{PuO}_2(\text{NO}_3)_2]/[\text{PuO}_2^{2+}]$ versus $[\text{NO}_3^-]^2/[\text{H}_2\text{O}]^4$ an equilibrium constant of $(4.5 \pm 0.5) \times 10^4$ or $\log_{10} \beta_2 = (4.65 \pm 0.05)$ was calculated. This result is noted in the IAEA review [92FUG/KHO] as being 2-4 \log_{10} units higher than other results. In fact the constant does not correspond to the standard definition used in this review, it corresponds to the reaction:



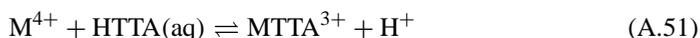
$x = 4$ as determined experimentally. To compare it with other values obtained in less than 2 M HNO_3 , it should be divided by $\sim(50.1)^4 = 6.3 \times 10^6$, which corresponds to the lowest water concentration where it would be assumed to be valid. So a value of ~ 0.007 instead of 55000 has to be used for comparison with other constants, expressed only in terms of the concentration of nitrate, metal and complex.

The constant was determined by taking differences between large numbers, see comments on [75VAS/AND]. As the ionic medium was not kept constant, the activity factors undoubtedly varied greatly. The value of the constant has little significance, and is not accepted in the present review.

[76BAG/RAM]

This supplements the solvent extraction study of [76BAG/RAM2] at 25°C and in 2 M HClO_4 and reports extension of the work to Np(IV). The techniques used were identical to those of [73PAT/RAM] and [73PAT/RAM2]. Thenoyltrifluoroacetone (TTA) was used as the extractant in two different solvents (benzene and *n*-heptane). The focus

of this paper was on the determination of the formation constants of the aqueous TTA complexes of Np(IV) and Pu(IV), respectively. In addition to the constants *K_1 (A.51, M = Np) = (48 ± 2) and *K_1 (A.51, M = Pu) = (83 ± 5) ,



the complexation constants of the 1:1 and 1:2 complexes of fluoride and sulphate have been reported for Np(IV) and Pu(IV).

From the neptunium HSO_4^- experiments, sufficient data are provided to allow recalculation using a non-linear least squares model, but the errors in $\log_{10} \beta_1$ and $\log_{10} \beta_2$ are large because of the small number of data points. Because of the large errors in these determinations, the results, although consistent with previous results, are ignored in the calculation of best values.

The constants for the reaction of Np^{4+} with $\text{HF}(\text{aq})$, corrected for aqueous TTA complexing, are used in the selection procedure in Part III, Section 9.2.1.2 with estimated uncertainties: $\log_{10} {}^*\beta_1(\text{NpF}^{3+}, I = 2 \text{ M}) = (4.70 \pm 0.15)$ and $\log_{10} {}^*\beta_1(\text{NpF}_2^{2+}, I = 2 \text{ M}) = (7.38 \pm 0.30)$.

In the plutonium experiments, ${}^{238}\text{Pu}$ or ${}^{239}\text{Pu}$ was used. Based on the data given in this paper $\log_{10} \beta_1(I)$ (19.4) = (2.73 ± 0.18) and (2.80 ± 0.13) and $\log_{10} \beta_2(I)$ (19.5) = (4.66 ± 0.07) and (4.47 ± 0.08) . We have not made any correction for aqueous TTA complexing of Pu(IV) on these data or any other data set used for evaluating the complexation constants for the sulphato complexes. The maximum effect is likely to be approximately 6 % in $\beta_1(I)$ (19.4) or $\beta_2(I)$ (19.5) (*i.e.*, it is within the range of the variation of the measurements themselves). The constants for the reaction of Pu^{4+} with fluoride, corrected for aqueous TTA complexing, are used in the selection procedure in Part IV, Section 18.2.1.2 with estimated uncertainties: $\log_{10} {}^*\beta_1(\text{PuF}^{3+}, I = 2 \text{ M}) = (4.64 \pm 0.15)$ and $\log_{10} {}^*\beta_1(\text{PuF}_2^{2+}, I = 2 \text{ M}) = (7.62 \pm 0.30)$.

[76BAG/RAM2]

The purpose of this study was to review earlier solvent extraction studies of Pu(IV) complexation by different authors, as well as to remeasure these systems, in particular with regard to controlling the Pu(IV) oxidation state before and after the experiments. In the absence of a holding oxidant (which in principle may interact with other components in the system and thus introduce systematic errors), Pu(IV) may be reduced to Pu(III) which is much less readily extractable than Pu(IV). The presence of this extra unextracted plutonium may be mistakenly interpreted as evidence for the formation of hydrophilic complexes. Also, in earlier studies, the complex formation of Pu(IV) and TTA^- in the aqueous phase was neglected. Such complexation was taken into account in this study [76BAG/RAM2], although it should be mentioned that the correction factor is very small.

The method used was solvent extraction, with HTTA, dinonylnaphthalenesulphonic acid (HDNNS), and tributylphosphate (TBP) as extractants, and an aqueous phase containing varying proton concentrations, as well as sulphate, nitrate, chloride and fluoride, respectively, as aqueous ligands. The temperature was reported as $(25 \pm 0.1)^\circ\text{C}$

(assumed here to be $(25.0 \pm 0.5)^\circ\text{C}$, with temperature stability of $\pm 0.1^\circ\text{C}$ for the solutions during equilibration), and the ionic strength was kept constant at 2 M H(X, ClO_4), where X represents the aqueous ligand. The authors tested NaBrO_3 , NH_4VO_3 , HNO_2 and $\text{K}_2\text{Cr}_2\text{O}_7$ as holding oxidants for Pu(IV) and found good performance of all except $\text{K}_2\text{Cr}_2\text{O}_7$ which acted as oxidant for Pu(IV). In fact they found a similar trend when using HNO_2 as a holding oxidant, but they interpreted this effect in terms of complexation of Pu^{4+} by nitrite, and estimated a constant of ${}^*\beta_1(\text{PuNO}_2^{3+}) = 100$ for the reaction of Pu^{4+} with HNO_2 in 2 M HClO_4 . Both ${}^{239}\text{Pu}$ and ${}^{238}\text{Pu}$ were used.

These measurements have been carried out carefully, and we consider the results obtained by using vanadate as a holding oxidant very reliable. In the case of chloride as a ligand we use $\log_{10} \beta_1(\text{PuCl}^{3+}, I = 2 \text{ M}) = (0.15 \pm 0.20)$ in our extrapolation to obtain a selected value at $I = 0$. For the fluoride system we use $\log_{10} {}^*\beta_1(\text{PuF}^{3+}, I = 2 \text{ M}) = (4.64 \pm 0.20)$ and $\log_{10} {}^*\beta_2(\text{PuF}_2^{2+}, I = 2 \text{ M}) = (7.61 \pm 0.40)$. The fluoride data were later measured by the same authors at 10°C [77BAG/RAM].

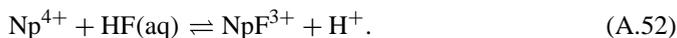
For the weak nitrate complexes (2 M in $\text{HClO}_4/\text{NO}_3$, $\text{HNO}_3 \leq 1 \text{ M}$) the reported values of the formation constants are $\beta_1 = (4.44 \pm 0.06)$ and $\beta_2 = (13.1 \pm 0.1)$. The results as recalculated in the present review yield $\log_{10} \beta_1 = (0.65 \pm 0.02)$ and $\log_{10} \beta_2 = (1.11 \pm 0.01)$. A different treatment of the medium effects at constant ionic strength to estimate the changes of the activity coefficients while substituting large amounts of the perchlorate ion by nitrate resulted in a slightly higher value for β_1 ($\log_{10} \beta_1 = (0.78 \pm 0.07)$), and gave no indication of formation of a dinitrate complex (This calculation procedure [98SPA/PUI] is different from the one generally used in the reviews in this series [92GRE/FUG, 95SIL/BID], in which the SIT is used only to estimate activity coefficient changes for constants measured at various ionic strengths. The hypothesis generally made in the uranium and americium volumes, was that in all weak complexation studies, to a first approximation, the activity coefficients do not change as perchlorate is substituted for nitrate, provided the total ionic strength is maintained constant. If, qualitatively, it was felt that the medium changes are too large, the data were discarded. In the present review the accepted procedure continues to be the same as in the previous volumes [92GRE/FUG, 95SIL/BID].). Thus, the value ($\log_{10} \beta_1 = (0.65 \pm 0.20)$ from the standard recalculation) is accepted for the formation constant for the first complex, but with an increased uncertainty because of the large changes in the ionic medium, and only the value for the first complex is accepted.

A re-evaluation of the sulphate complexation data in this paper gives $\log_{10} {}^*\beta_1(\text{PuSO}_4^{2+}) = (3.00 \pm 0.17)$ and (2.95 ± 0.14) and $\log_{10} {}^*\beta_2(\text{Pu}(\text{SO}_4)_2) = (4.59 \pm 0.11)$ and (4.45 ± 0.11) . The TBP data set was not provided and errors were not calculated by the authors. As a result the TBP results are not included in the determination of recommended values. One data set given in this paper is identical to one reported in [76BAG/RAM]. The results were also used to postulate a mixed $\text{NO}_3^- - \text{SO}_4^{2-}$ complex, although no other reports of this complex have been found.

[76CHO/UNR]

Choppin and Unrein studied the thermodynamic parameters of the formation of the mono-fluoride complexes of Am(III), Cm(III), Bk(III), Cf(III), Th(IV), U(IV) and

Np(IV) at 25°C. Np(IV) was studied by solvent extraction with dinonylnaphthalenesulphonic acid (HDNNS) at $I = 1$ M (HClO₄):



The experiments were carried out at 10, 25 and 40°C to obtain some information on $\Delta_r H_m$. The authors evaluated their measurements in terms of the formation of a 1:1 complex and reported the following values for the formation of NpF³⁺ at $I = 1$ M (HClO₄): $\log_{10} {}^*\beta_1(\text{A.52}, 283.15 \text{ K}) = (4.71 \pm 0.03)$, $\log_{10} {}^*\beta_1(\text{A.52}, 298.15 \text{ K}) = (4.60 \pm 0.02)$ and $\log_{10} {}^*\beta_1(\text{A.52}, 313.15 \text{ K}) = (4.52 \pm 0.02)$. No check of the linearity of the distribution coefficient was presented, and the reader has thus no assurance that the oxidation state Np(IV) was stable during the experiment. The similarity of these values to the corresponding Th(IV) constant and to other Np(IV) constants from the literature gives some confidence that the +4 oxidation state was maintained. The constant at 25°C is considered in the evaluation of $\log_{10} {}^*\beta_1^\circ$ in the present review, using an uncertainty of ± 0.20 in $\log_{10} {}^*\beta_1$.

From the three constants at 10, 25 and 40°C we obtain an average enthalpy of $\Delta_r H_m(\text{A.52}) = -(10.7 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$, where the error spans the range of values obtained. Assuming that this value does not depend strongly on the ionic strength, we can combine it with $\Delta_r H_m^\circ$ of the protonation reaction of F⁻, $\Delta_r H_m^\circ = (12.2 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$ [92GRE/FUG], and we obtain $\Delta_r H_m^\circ(\text{A.53}) = (1.5 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$.



This value is slightly lower than the one of Choppin and Unrein [76CHO/UNR], because they used a different value for the enthalpy of protonation of F⁻. This value is accepted in the present review.

[76FAR/BUC]

This is a report of a very careful ion exchange study at 25°C in 1 and 2 M H(ClO₄, HSO₄). Hydroquinone was used as the holding reductant under an N₂ atmosphere (in preference to ascorbic acid which was tried but had a number of undesirable properties). The results were interpreted as indicating that the protonated SO₄²⁻ ligand does not participate in the complexing of Pu(III). The plutonium isotope was not specified but distribution coefficients were evaluated using β -active ²⁴¹Pu. The dissociation constant of HSO₄⁻ was taken from experiments of [68AHR/BRA2] (20°C, $I = 1$ M) and [51ZEB/ALT] (25°C, $I = 2$ M), and extrapolated to temperature using the enthalpy of ionization determined by [59ZIE] (see [74FAR/PEA] for discussion of this choice of data). The raw experimental data were not provided and therefore the values have been accepted without re-evaluation.

[76FRO/CHI]

This paper describes a study of oxidation of neptunium(IV) by persulphate ions in carbonate solutions. The equilibrium $p\text{CO}_2$ in this medium was practically constant,

but it was not buffered. It then could have increased during (or before) the experiment (through equilibration with the air) inducing a decrease of pH. At equilibrium, the pH would increase with increasing concentration of K_2CO_3 . The authors did not measure the pH. No information about the stoichiometry of the species, and no thermodynamic data, can be deduced from this work or from the companion paper [76FRO/CHI2].

[76FRO/CHI2]

See Appendix A discussion of [76FRO/CHI].

[76HUB/HUS]

Thermodynamic functions were determined for formation of actinide citrate- and actinide hydroxy-complexes. The paper does not contain any new information on hydrolysis, except that $\log_{10} K_{ex}$ and $-\log_{10} \beta_1^*$ increase by 0.10-0.15 log units when the temperature increases from 20°C to 25°C. A table summarises $\log_{10} K_{ex}$ and $\log_{10} \beta_1^*$ values obtained in earlier work. The experimental work was primarily concerned with the higher actinides, and no new experimental work on plutonium hydrolysis was reported.

[76MET/GUI]

This paper on hydrolysis and complexation of Pu(IV) (submitted in 1973) was based on [73MET] and contains some of the same information as [72MET/GUI]. This review should be read in connection with those for the two other references.

Here the Pu concentration, when using ^{238}Pu , is given as 10^{-7} to 10^{-8} M, a concentration at which only mononuclear species of Pu should be found. In other (earlier) investigations ^{239}Pu was used at 10^{-3} to 10^{-4} M. The experimental technique was well described, and various important parameters, *e.g.*, mixing time (a dependence on mixing time would indicate unstable redox conditions) were investigated. However, the effect on counting rate due to variations in scintillation quenching caused by varying concentrations of HTTA or HDBM in the organic phase, does not seem to have been investigated. Such a variation could affect the hydrolysis constant values calculated from the variation of the distribution ratio of Pu, D, vs. pH. In Figure 4 of this paper a graphical analysis yielded the same hydrolysis constant values presented elsewhere [72MET/GUI, 73MET].

The paper again summarised the study of Pu complexation by citric acid. From the depression of the extraction of Pu(IV) with increasing concentration of citric acid in solution at different pH values, equilibrium constants were calculated for the formation of a number of Pu-citrate complexes. No attempt was made to test the model by minimising the number of species. There is little proof that the species assumed to exist in certain pH-citric acid concentration regions actually do exist.

[76PAT/RAM]

This is a solvent extraction study of fluoride and sulphate complexation at 25°C using dinonylnaphthalenesulphonic acid in benzene as the extractant. The aqueous phase contained 2 M HClO₄ and 0.01 M K₂Cr₂O₇ as a holding oxidant for Np(VI) and Pu(VI). The procedure is satisfactory, but the authors did not mention if they had checked the concentration of the holding oxidant or the oxidation state of the actinides at the end of the experiments to ensure that the actinides had not been reduced. The measurements with U(VI) were described in the uranium review of this series [92GRE/FUG].

For the fluoride experiments, the authors varied the HF(aq) concentration between 0.05 and 0.5 M. They evaluated the data in terms of the formation of a 1:1 complex only. However, according to our estimates, the concentration of 1:2 complex was probably not negligible in some solutions. We use the resulting value in our evaluation, but with a low weight by using an uncertainty of ± 0.5 in $\log_{10} {}^*\beta_1(\text{NpO}_2\text{F}^+)$. In the case of Pu(VI), the constants obtained with the same evaluation procedure are large at low HF(aq) concentrations and a factor of about five smaller at higher HF(aq) concentrations. The authors suspected partial reduction to Pu(IV) in spite of the holding oxidant used. The resulting constant for the Pu(VI) fluoride complex has to be discarded.

The formation of sulphate complexes of Np(VI) and Pu(VI) was also studied in 2 M H(ClO₄, HSO₄). Cr₂O₇²⁻ was used as holding oxidant. The plutonium isotope (not specified) was most likely ²³⁹Pu. The solution composition varied markedly, and activity coefficients may have varied correspondingly. No correction was made for that effect. There is no indication of the time required to reach equilibrium or whether equilibrium was obtained. For Pu(VI), the results are consistent with the formation of a 1:1 complex but, because of large experimental errors, there is no evidence for the formation of the weak 1:2 complex. A re-evaluation of the data, using a quadratic statistical model, yields an estimate of $\log_{10} \beta_1(\text{PuO}_2\text{SO}_4) = (1.08 \pm 0.10)$, and $\beta_2(\text{PuO}_2(\text{SO}_4)_2^{2-})$ is indistinguishable from zero. For the Np(VI) system, reanalysis leads to $\log_{10} \beta_1(\text{NpO}_2\text{SO}_4) = (1.00 \pm 0.05)$ and $\log_{10} \beta_2(\text{NpO}_2(\text{SO}_4)_2^{2-}) = (0.87 \pm 0.19)$.

[76SEV/KHA]

In this work values are reported for the first hydrolysis constant of NpO₂⁺, as determined by potentiometric titration and by spectrophotometry. Despite the evidence from the electrophoresis experiments reported in the same paper, the formation of more highly hydrolysed aqueous neptunium(V) species was not considered.

The analysis of the potentiometric data, obtained at low ionic strength (0.02 M), relies on the rather weak assumption that, past the pH at which hydrated neptunium hydroxide begins to precipitate (pH = 7.46 for titration of 1.068×10^{-2} M NpO₂NO₃ at 23°C), further addition of base will not change the equilibrium concentration of NpO₂OH(aq) in solution. There is no reason this should be true, nor is the (assumed) rather high stability of NpO₂OH(aq) compatible with other solubility studies [71MOS3, 85LIE/TRE] or with the authors' own reported "limiting" solubility of

7.2×10^{-5} M in 1 M NaOH. The temperature of the solubility study is not reported, nor is the method of calibrating the pH electrode discussed.

During the titration, a second break in the pH curve was observed around pH = 11 for approximately $\text{Np(V)}/\text{OH} = 2$. The authors tentatively attributed this pH variation to $\text{NaNpO}_3(\text{s}) (= \text{NaNpO}_2(\text{OH})_2(\text{s}) - \text{H}_2\text{O})$ precipitation; but this is not consistent with their electromigration work, nor with the shape of their potentiometric titration curve in this pH domain.

The spectrophotometric results ($I \approx 0.001$, 20°C) were analysed assuming the peak at 981 nm could be ascribed to NpO_2^+ , and the peak at 991 nm to $\text{NpO}_2\text{OH}(\text{aq})$. A good isosbestic point was found at about 985 nm, which lends credence to the reported value of $\log_{10}^*\beta_1 = -8.89$.

Unfortunately, $\text{NpO}_2\text{CO}_3^-$ also has a peak near 990 nm [90NIT/STA, 90RIG], and no special precautions to exclude $\text{CO}_2(\text{g})$ from the solutions were noted. Cohen and Fried [69COH/FRI] reported that in 1 M tetramethylammonium hydroxide solutions the 980 nm peak is shifted to approximately 1020 nm, but no mention was made of a peak near 990 nm in less basic solutions. It would appear that the reported value is an upper limit for the first hydrolysis constant, and is accepted as such (for 25°C , without correction for the difference in temperature) in this review.

[76SHI/STE]

This paper presents evidence of the formation of a carbonate complex of Np(VII) in ~ 0.5 M K_2CO_3 solutions at pH 6 to 10; but the stoichiometry of the complex was not determined.

[76VOD/KOL]

This is a report of a proton magnetic relaxation study of the complexes of NpO_2^+ with a variety of ligands in aqueous media of unspecified temperature and composition. The authors concluded that NpO_2^+ did not form strong complexes with Cl^- , NO_3^- and SO_4^{2-} in their solutions, and reported limiting values for the formation constants for the 1:1 complexes as $\beta_1(\text{NpO}_2\text{L}) < 0.2$ (probably reflecting a detection limit) for all the above ligands. This value is consistent for that found this review for the β_1 for formation of the $\text{NpO}_2\text{SO}_4^{2-}$ complex. The same holds for the nitrate complexation of Pu(VI), for which a value $\beta_1(\text{PuO}_2\text{NO}_3^+) < 0.5$ was reported. The results reported in this paper appear reliable, but in the absence of solution specifications, cannot be used in this compilation. For the Pu(VI) chloride system, the authors reported a formation constant of $\beta_1(\text{PuO}_2\text{Cl}^+) = 1.0$, again without giving the composition of the aqueous solution nor the temperature.

[76VOL/VIS]

In this publication, Volkov *et al.* discussed their previous results [74VOL/KAP, 74VOL/KAP2]. No thermodynamic data could be extracted from this publication.

[77BAG/RAM]

The paper on complexation of Pu(IV) describes results of solvent extraction experiments using TTA and HDNNS at 10°C in 2 M HClO₄. The plutonium used was ²³⁹Pu and ²³⁸Pu, with V(V) as a holding oxidant.

For the sulphato complexes the values $\log_{10} \beta_1(I)$ (19.4) = (2.71 ± 0.03) and (2.88 ± 0.07) and $\log_{10} \beta_2(I)$ (19.5) = (4.58 ± 0.01) and (4.38 ± 0.05) were determined, and in conjunction with previous measurements at 25°C using the same solutions and extractants [76BAG/RAM, 76BAG/RAM2], $\Delta_r H_m^\circ$ (19.4) = (2.4 ± 3.5) kJ·mol⁻¹ and (7.2 ± 3.0) kJ·mol⁻¹ and $\Delta_r H_m^\circ$ (19.5) = (8.6 ± 1.4) kJ·mol⁻¹ and (7.5 ± 2.3) kJ·mol⁻¹.

The authors also reported formation constants for the 1:1 and 1:2 Pu(IV) fluoride complexes at 10°C. A comparison with the values at 25°C [76BAG/RAM2] yields a picture consistent with the study of Nash and Cleveland who performed measurements at 1, 7.5, 15 and 25°C. The values of [84NAS/CLE] are preferred to those of [77BAG/RAM] for the evaluation of the reaction enthalpies, because they span a larger temperature range.

For the nitrate complexes, the reported constants are $\beta_1 = (3.72 \pm 0.08)$ and $\beta_2 = (14.2 \pm 0.1)$ as determined from a total of six experimental *D* values measured at nitrate concentrations from 0.2 to 1.0 M. As was the case for the values at 25°C [76BAG/RAM2], only the value for the first stepwise constant is accepted after recalculation, but with an increased uncertainty because of the large changes in the medium between the various solutions, $\log_{10} \beta_1 = (0.56 \pm 0.30)$.

[77CUI/MUS]

In this conference paper values are reported for the formation constants of complexes of azide, cyanide and thiocyanate ions with Np(V) and of azide ion with Pu(III). More details of this study were provided in later papers from the same group [77MUS/MAR, 78MUS/MAR2, 78MUS/MAR, 83MUS/CUI].

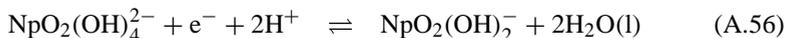
[77DUP/GUI]

This is an extraction study of the hydrolysis of Np⁴⁺. The authors reported values for the first two monomeric hydrolysis constants of Np⁴⁺ for an aqueous medium of 1 M LiClO₄, based on measurements with solutions having acid concentrations as low as 10⁻³ M. The effects of possible impurities in the LiClO₄ were not discussed. Despite warnings in the paper about the risk of oxidation to non-extractable Np(V), there is no discussion as to whether the extent of oxidation was actually checked – for *D*-values of 100, a conversion of 1% of the neptunium to Np(V) would reduce the observed *D*-value by a factor of two. It is not clear what justification exists for the restriction of the model to two hydrolysis species, nor for the selection of Np(OH)₂²⁺ as the second species (see [92GRE/FUG] for a discussion of the selection of hydrolysis species of U(IV)). Unfortunately, the raw data are not available for recalculation, the figures are not adequate to allow recovery of the data (there are inconsistencies between Figures 1 and 2), nor did the authors propose uncertainties for their selected

constants or discuss possible correlation. In the present review, the reported value for the LiClO₄ medium has been used with the specific ion interaction theory coefficients $\varepsilon_{(\text{Np}^{4+}, \text{ClO}_4^-)} = (0.84 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{NpOH}^{3+}, \text{ClO}_4^-)} = (0.50 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ (estimated) to calculate $\log_{10}^* \beta_1^\circ = (0.56 \pm 0.5)$. Similarly, using $\varepsilon_{(\text{Np}(\text{OH})_2^{2+}, \text{ClO}_4^-)} = (0.4 \pm 0.2) \text{ kg}\cdot\text{mol}^{-1}$ (estimated), $\log_{10}^* \beta_2^\circ = -0.1$ can be calculated; however, this value is rejected because of the lack of details concerning hydrolysis beyond the first deprotonation step.

[77ERM/PER]

In this study, measurements were made of the Np(VI)/Np(V) and Pu(VI)/Pu(V) couples in aqueous LiOH solutions (2.5 M to 4.0 M). The potentials were measured relative to a mercuric oxide electrode. Using $\Phi = 0.881$ [59ROB/STO], ($a_{\text{H}_2\text{O}} = 0.924$) and the specific ion interaction theory coefficients, including the estimated values $\varepsilon_{(\text{NpO}_2(\text{OH})_3^-, \text{Li}^+)} = (0.05 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$, $\varepsilon_{(\text{NpO}_2(\text{OH})_4^{2-}, \text{Li}^+)} = -(0.05 \pm 0.10) \text{ kg}\cdot\text{mol}^{-1}$, values of E° can be calculated for the reactions involving the most probable hydrolysis species. Assuming the Np(V) species to be $\text{NpO}_2(\text{OH})_2^-$, the potentials $E^\circ = 0.153 \text{ V}$, 0.987 V and 1.821 V for Reactions (A.54), (A.55), (A.56), respectively, are calculated using the data for the 2.5 M LiOH solutions.



From these and the selected formation constant for $\text{NpO}_2(\text{OH})_2^-$, $\log_{10}^* \beta_2^\circ$ (8.2) = $-(23.6 \pm 0.5)$, and assuming only one non-polymeric Np(VI) hydrolysis species in the hydroxide solutions, the calculated possible hydrolysis constants for NpO_2^{2+} are $\beta_2^\circ = 10^{-6.6}$, $\beta_3^\circ = 10^{-(20.7 \pm 1.7)}$ or $\beta_4^\circ = 10^{-(34.8 \pm 1.7)}$. The value for β_2° is not consistent with the hydrolysis constants measured in acidic solutions, and it is concluded in this review that $\text{NpO}_2(\text{OH})_2(\text{aq})$ is not the predominant Np(VI) hydrolysis species in highly alkaline solutions. The latter two constants are similar to the values selected for the corresponding uranium species [92GRE/FUG].

The measured potentials do not vary significantly with changing hydroxide concentration, but the hydroxide concentrations and ionic strengths are correlated. Therefore, it is not possible to distinguish between the hydrogen ion dependence of the potentials and activity effects.

[77SAI/UEN]

Np(IV), (V) and (VI) were precipitated in 0.05 to 0.8 M Na₂CO₃ aqueous solutions using the hexamminecobalt(III) cation. The composition of the solid phase (or phases ?) were deduced from chemical analysis. Absorption spectra were shown for aqueous solutions containing neptunium in each valence state.

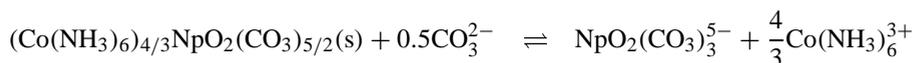
a) Np(IV)

The Np(IV) carbonate solution and solid were prepared by addition of an acidic Np⁴⁺ solution to carbonate solutions. The authors state that they had to centrifuge the solution to remove some undissolved hydroxide. This is consistent with the known behaviour of actinide(IV) species, and it would be expected for plutonium that freshly precipitated polymeric hydroxide would react with the concentrated carbonate solutions. Confirmation is supplied by the absorption spectrum of the resulting 7.04 mM Np(IV) solution in 1 M (NH₄)₂CO₃, which is the spectrum of the known [71MOS2, 95VIT, 96DEL/VIT] Np(IV) carbonate limiting complex.

Addition of the large hexamminecobalt(III) cation lowers the solubility as expected. The composition of the solid was proposed from chemical analysis (and by analogy with the Th and Pu systems [70UEN/HOS]): [Co(NH₃)₆]₂[Np(CO₃)₅]·4H₂O. The solubility increases with the concentration of Co(NH₃)₆Cl₃, and also with the concentration of (NH₄)₂CO₃ except for the last solution in 0.9 M (NH₄)₂CO₃. This behaviour could be attributed to the formation of a soluble complex with unknown stoichiometry, perhaps containing the hexamminecobalt(III) cation, or could be attributed to strong ionic strength effects, possibly ion pairing of the highly negative Np(IV) carbonate limiting complex with the ammonium cation or/and with again the hexamminecobalt(III) cation. No unique qualitative interpretation can be proposed, and no thermodynamic data can be derived from this work.

b) Np(V)

Saito and Ueno introduced Np(V) into concentrated Na₂CO₃ and Co(NH₃)₆Cl₃ aqueous solutions. From chemical analysis, they assumed that the solid compound (Co(NH₃)₆)₈(NpO₂)₆(CO₃)₁₅(s) was formed. According to this interpretation, the solubility should be controlled by the following equilibrium



The solubility was parallel to, and differed by less than a factor of two from, values calculated for hydrated Na₃NpO₂(CO₃)₂(s) using data selected in the present review (including activity coefficient corrections on the shape of the solubility curve). This does not seem reasonable, since the stoichiometries of the two dissolution reactions (and ratio of carbonate to neptunium in the solids) are completely different. This result might be (at least partially) explained by activity coefficient effects (the value of $\varepsilon_{(\text{Co}(\text{NH}_3)_6)^{3+}, \text{CO}_3^{2-}}$ is not known and its contribution cannot be estimated), so no conclusion can be reached as to the validity of Saito and Ueno's interpretation. However, the present review does not accept that formation of (Co(NH₃)₆)₈(NpO₂)₆(CO₃)₁₅(s) is proven, or that the compound is stable in contact with any aqueous solution.

c) Np(VI)

For Np(VI), it was concluded that the solid contained the same proportion of Np and carbonate as in the soluble complex NpO₂(CO₃)₃⁴⁻ which is known to be the major soluble complex for the conditions used by the authors. The solubility was expected

to be almost constant when the ionic strength of the solution was changed; but experimentally, this was not found to be so. The measured solubility increased by two orders of magnitude in aqueous solutions when the concentration of aqueous Na_2CO_3 was increased from 0.05 to 0.8 M. This may have resulted from formation of some unknown intermediate or limiting soluble species possibly stabilised by the hexamminecobalt(III) cation (or because of some special ionic strength effects in the presence of the large cation). Kinetic effects could also be responsible for this behaviour. The results of this study are not used in the present review.

[77SIM]

This publication reports very useful experimental work on Np(V) and Np(VI) chemistry in concentrated carbonate media. It is the first publication in which the stoichiometry of a soluble Np(V) carbonate complex is reasonably well established (it is the limiting complex). It is also the first publication that produced reliable measurements of the Np(VI)/Np(V) redox couple in carbonate media from which the stoichiometry of the Np(VI) carbonate limiting complex was correctly deduced.

a) Np(V)

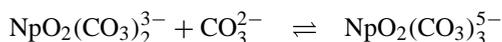
The solubility of a well-characterised sample of $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ was studied in 0.25 to 1 M Na_2CO_3 solution at constant ionic strength ($I = 3$ M, NaNO_3) where this solid is stable [81VOL/VIS2, 86GRE/ROB]. Simakin's interpretation assumed that the solubility was controlled by the equilibrium



Using the (scanned) experimental solubility data from Figure 2 of the publication, then (also see [98CAP/VIT])

$$\log_{10} K_{s,3}(\text{A.57}) = -1.46 \pm 0.09 \quad \text{at } I = 3 \text{ M NaNO}_3.$$

A further attempt was made in the present review to improve the treatment of the data by also considering K_3 , the constant of the equilibrium A.26



For this, K_3 and $K_{s,3}$ were fitted simultaneously and $\log_{10} K_{s,3}(\text{A.57}) = -(1.47 \pm 0.08)$ and $\log_{10} K_3(\text{A.26}) = 1.79$ (at $I = 3$ M NaNO_3) were obtained. This determination of K_3 is not very reliable since the contribution of $\text{NpO}_2(\text{CO}_3)_2^{3-}$ to the solubility was always less than 7%, which is less than the experimental accuracy. If the K_3 value is set to the value calculated from the data selected in the present review ($\log_{10} K_3 = 2.51$ at $I = 3$ M NaNO_3), the value obtained for $\log_{10} K_{s,3}(\text{A.57})$ (at $I = 3$ M NaNO_3) is practically the same ($-(1.46 \pm 0.09)$).

b) Np(VI)/Np(V) redox couple

The redox potentials of the Np(VI)/Np(V) and Am(VI)/Am(V) couples were measured in 0.1 to 2 M Na_2CO_3 or K_2CO_3 aqueous solutions. The author estimated that the junction potential was less than 0.01 V. It appears that the quantity referred to by the author

as the “junction potential” was the overall calibration correction for the reference electrode. This interpretation has been used in the present review, and it has been found to yield reliable results (see below) that appear to be consistent with the only other published measurements of the Np(VI)/Np(V) redox potential [90RIG, 95OFF/CAP] in which the junction potentials were explicitly taken into account. Therefore, the author’s estimate of uncertainty as 0.01 V is accepted. This is approximately the same value as calculated in the present review after SIT extrapolation to zero ionic strength (see also [98VIT/CAP]). The author reported that the uncertainty in each separate experiment (mainly attributed to reproducibility of the reference electrode calibration) was 0.001 V.

It was earlier confirmed [75SIM] that for the conditions of these experiments the variations of the potential with the concentration of CO_3^{2-} are small, and probably are due only to junction potential and ionic strength effects. The author concluded that the limiting carbonate complexes of Np(V) and Np(VI) have the same stoichiometry. This was later confirmed by others [95OFF/CAP] as discussed elsewhere in this review. The stoichiometry of the limiting complex of Np(V) was determined by measuring the solubility of $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$, S , at constant (and high) ionic strength. The nature of the equilibrium solid was confirmed by X-ray diffraction, and Yu.F. Volkov, who published extensively on these solids, was given acknowledgement for identification of the material. The value of $\log_{10} S$ increased with a slope of 1 as a function of $\log_{10}[\text{CO}_3^{2-}]$, from which the author concluded that solubility was controlled by the reaction



that the limiting complex of Np(V) is $\text{NpO}_2(\text{CO}_3)_3^{5-}$, and hence that the limiting complex of Np(VI) is $\text{NpO}_2(\text{CO}_3)_3^{4-}$. This was the first firm evidence (and proper interpretation) of the stoichiometry of the limiting carbonate complexes of Np(V) and Np(VI).

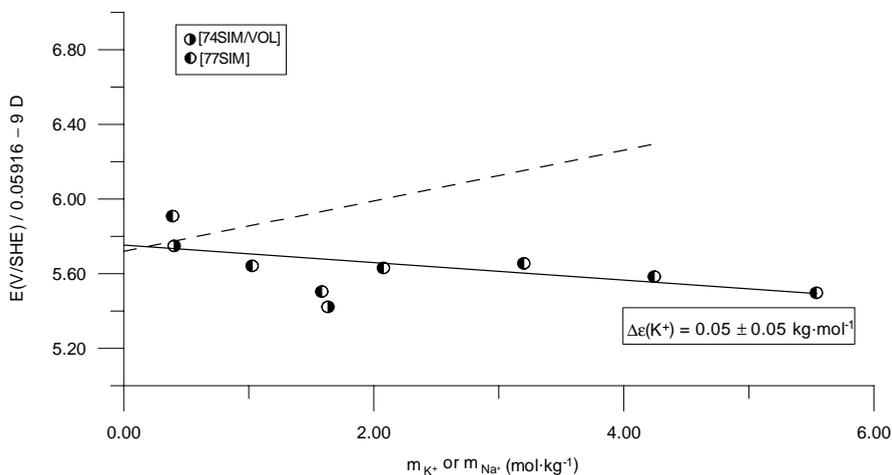
The author assumed that only monomeric soluble complexes could be formed, and did not demonstrate this explicitly. It is now recognized (for uranium [92GRE/FUG], and in the present review for Np and Pu) that a polynuclear carbonate actinide(VI) complex, $(\text{AnO}_2)_3(\text{CO}_3)_6^{6-}$, can be stable under certain chemical conditions (for Np(VI), see [86GRE/RIG] and [90RIG]). Fortunately $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$ is not a predominant species under the experimental condition used here (in [77SIM]). It was also demonstrated later [90RIG] that no Np(V) polymeric carbonate complex is stable (at least for these conditions).

The shifts of potentials between those in the carbonate media and in non-complexing media (*e.g.*, 1 M HClO_4) for all actinide(VI)/(V) couples is reported to be about 0.7 V. This is approximately the same as can be calculated for uranium [92GRE/FUG] and americium [95SIL/BID], and this confirms a previous estimate by the same author [75SIM].

The author measured the difference in potential between the saturated calomel electrode (potential usually assumed to be 0.244 V vs. SHE) used as a reference electrode for this set of experiments, and a AgCl/Ag reference electrode ($(0.222_3 \pm 0.001_6)$ V

vs. SHE). The calomel electrode would be expected to have a low junction potential, and the potential difference was found to be 0.044 V. This is only 0.021 V more than is calculated from the standard values used in the present review. The magnitude of the discrepancy is not unusual.

Figure A.7: Comparison of extrapolations to $I = 0$ of the formal potential for the $\text{NpO}_2(\text{CO}_3)_3^{4-} + e^- \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-}$ redox equilibrium, using the SIT with data from measurements in aqueous K_2CO_3 (not corrected for the dissociation of the Np(V) limiting complex). The dotted line shows the regression line based on selected measurements in Na^+ media (*cf.* Figure 12.1).



There were a number of possible sources of systematic error that were incorporated in this difference. Among these are differences in a_{Cl^-} in 1 M (or 1 m) KCl or NaCl solutions, and differences in the junction potential when a S.C.E. was being calibrated as opposed to when it was being used in a test solution. In the present review, it is assumed that all these possible systematic errors were taken into account by measuring the apparent “junction potential”. The uncertainties in the “junction potential” deduced from a SIT regression results are 3 and 12 mV in Na_2CO_3 and K_2CO_3 media, respectively. This is then consistent with the value (10 mV) estimated by the author and with later work selected by this review [90RIG, 95OFF/CAP].

Figure 1 in the paper was used to deduce values of the original experimental data. The “junction potentials” were calculated (Table 1 of [77SIM]) first using linear interpolation (or extrapolation for the last point), then shifting the value to obtain 0.000 V in 1 M K^+ or Na^+ solution (*i.e.*, 0.5 M K_2CO_3 or Na_2CO_3 respectively) where it should be near 0. Finally these corrections give a practical potential of the reference calomel

electrode of $0.266_3 + 0.021 - 0.043 = 0.244_3$ V/SHE in the 0.5 M K_2CO_3 solution: this value is exactly the theoretical one. The text has been assumed to be correct and standard values have been calculated by linear regression (*cf.* Appendix B), see Table A.6.

Table A.6: Standard potentials ($I = 0$) from measurements of the Np(VI)/Np(V) redox couple in aqueous carbonate media.

$-\Delta\varepsilon$ $\text{kg}\cdot\text{mol}^{-1}$	E° V/SHE	Medium	Reference of experimental data
$-(0.047\pm 0.051)$	$(0.3404\pm 0.0093)^{(a)}$	K_2CO_3	[77SIM]
$-(0.026\pm 0.042)$	$(0.3352\pm 0.0077)^{(b)}$	K_2CO_3	[77SIM]
(0.120 ± 0.043)	(0.3398 ± 0.0054)	Na_2CO_3	[77SIM]
(0.081 ± 0.025)	$(0.3469\pm 0.0031)^{(a)}$	Na_2CO_3	[77SIM]
(0.142 ± 0.049)	(0.3377 ± 0.0075)	Na_2CO_3	[95OFF/CAP]
(0.121 ± 0.043)	$(0.3416\pm 0.0067)^{(a)}$	Na_2CO_3	[95OFF/CAP]
(0.053 ± 0.048)	(0.3540 ± 0.0081)	Na_2CO_3	[95OFF/CAP] except 0.22 M Na_2CO_3
(0.050 ± 0.048)	$(0.3547\pm 0.0080)^{(a)}$	Na_2CO_3	[95OFF/CAP] except 0.22 M Na_2CO_3
(0.110 ± 0.033)	$(0.3433\pm 0.0049)^{(a)}$	Na_2CO_3	[77SIM, 90RIG] [95OFF/CAP]
(0.136 ± 0.037)	$(0.3384\pm 0.0056)^{(c)}$	Na_2CO_3	[77SIM, 90RIG] [95OFF/CAP]

(a) Without correction for $\text{NpO}_2(\text{CO}_3)_3^{5-}$ dissociation.

(b) Correction for $\text{NpO}_2(\text{CO}_3)_3^{5-}$ dissociation calculated assuming $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{K}^+)} = \varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{5-}, \text{Na}^+)}$.

(c) Values selected in this review.

The $\Delta\varepsilon$ values appear to be different for Na^+ and K^+ aqueous media (Figure A.7). Although this difference is (barely) within the calculated uncertainties, it is also possibly the result of different ion-pairing interactions between the highly charged complex(es) and the alkali metal cations. The numerical $\Delta\varepsilon$ values found here are quite reasonable, and are in good agreement with later work [95OFF/CAP] for Na_2CO_3 media. Also, the extrapolated value of the standard potential from measurements in sodium and potassium carbonate solutions appear to be in fair agreement.

[77VOL/VIS]

$\text{NaNpO}_2\text{CO}_3\cdot n\text{H}_2\text{O}(s)$ ($n=3.5$) was obtained in 5 mM to 100 mM Na_2CO_3 solutions, when heated from 30 to 130°C. Five different crystalline phases ($n = 3.5, 3, 2, 1, 0$) were identified. Their X-ray powder diffraction patterns are listed and the diffraction patterns are very complex. This may result in part from a few poorly crystallised

compounds rather than a large number of different ones. The structures of the proposed solid compounds were not really identified. In 0.3 to 1.8 M Na₂CO₃ solutions, Na₃NpO₂CO₃(s) solid was obtained (see [79VOL/TOM]).

[78BED/FID]

The authors used a stationary organic phase containing diethylhexylphosphate (HDEHP) as an adsorbent for their extraction chromatography experiments. This paper has been reviewed for the uranium book of this series [92GRE/FUG], where the resulting constants for UO₂Cl⁺ and UO₂Cl₂(aq) were accepted with increased uncertainties. The IAEA review [92FUG/KHO] stated that the results of [78BED/FID] are in general slightly lower than those of other studies. A reason for lower values could be a partial reduction to An⁴⁺ (An=actinide) and complete immobilization. The authors [78BED/FID] assumed that no reduction occurred during their experiments because no new peaks appeared in the elution curve, but they did not do any sensitivity analysis to verify this assumption. In fact, a partial reduction of AnO₂²⁺ to An⁴⁺ might not be visible in the elution curve because An⁴⁺ is much more firmly attached to the stationary phase. The authors, however, assumed that only AnO₂²⁺ adsorbed on the stationary phase.

In the case of neptunium, we accept their value for the 1:1 complex and we estimate the uncertainty to be ±0.2: $\log_{10} \beta_1(\text{NpO}_2\text{Cl}^+, I = 2 \text{ M}) = -(0.04 \pm 0.20)$. A comparison with other values, in particular after extrapolation to $I = 0$, cf. Part III, Section 9.2.2.4, shows that the value of [78BED/FID] is markedly higher than those of other investigations. Hence, there is no indication of partial reduction of Np(VI) to Np(IV).

[78MOS/POZ]

See comments under [79MOS/POZ].

[78MUS]

Because of the inherent uncertainty in calculating activity coefficients for species in the very high ionic strength ($I \approx 9$) medium used for the solubility measurements, these solubilities are not used in the determination of $K_{s,0}$ for NpO₂OH(am) in the present review. The author noted that the plot of log(solubility) against pH gave a straight line with slope -1 . From this he deduced that there were no polynuclear soluble complexes. This conclusion may be correct, but the extent of oligomerisation can never be deduced from solubility measurements over a single solid (in this particular case, any polynuclear complex with charge $+1$, (NpO₂)_p(OH)_{p-1}⁺ would lead to the same result).

[78MUS/MAR]

It is not clear whether the spectrophotometric measurements were done at constant ionic strength. The table of formation constants indicates the values were obtained for

solutions with “ $\mu=5$ ” (probably primarily 2 M solutions of NaCN(aq), using NaClO₄ and HClO₄ as added electrolytes), although elsewhere the medium is described simply as “2M NaCN”. The evidence presented for the stoichiometry of the limiting complex is sparse, and although there may be several complexes, insufficient information is presented to substantiate the formation of five different complexes. Figures A.1 and A.2 (but not their captions) appear to have been transposed in this paper. Solubility equations for two complex solids NaNpO₂(CN)₂·xH₂O and NpO₂CN·yH₂O were also reported for $I=5$, but even if the solids have been correctly identified, insufficient information exists to propose values for lower ionic strength media. The authors’ analysis does not take into account possible formation of NpO₂OH(am) even in solutions with pH values >9, and no values based on this work are selected in the present review.

[78RAO/BAG]

The paper describes a very careful ion exchange study of sulphate complexation of Pu(III) using dinonylnaphthalenesulphonic acid in 1 and 2 M HClO₄ at 25°C. The predominant plutonium isotope was ²³⁹Pu. After the extraction, it was confirmed that the plutonium was still Pu(III). Only 30 minutes were allowed for equilibration. No check was done to ensure equilibrium was attained. Data were interpreted as indicating that no HSO₄⁻ complexes had formed. HSO₄⁻ constants were taken from the same sources as in [76FAR/BUC]. Data of [67NAI/RAO] were re-evaluated to include I⁻ complexing. The association quotient for Pu(III)I²⁺ was taken from [74KHO/MAT] (measurements made in 1 M NH₄(ClO₄⁻, I⁻) at 30°C). In the present review, the data have been re-evaluated using a quadratic statistical model to yield log₁₀ β₁ = (0.80 ± 0.05) and (0.77 ± 0.03) and log₁₀ β₂ = (0.69 ± 0.12) and (0.88 ± 0.09) at $I = [\text{H}^+] = 1$ and 2 M respectively.

[78RAO/BAG2]

This is a solvent extraction study with thenoyltrifluoroacetone (TTA, in the case of neptunium) and dinonylnaphthalenesulphonic acid (HDNNS, for both neptunium and plutonium). The experiments with Np(IV) were carried out at 10, 25 and 40°C, those with Pu(III) at 25°C only. The ionic strength was maintained at 2 M with HClO₄ and NaClO₄, and the H⁺ concentration was 1 M. Formation constants were reported for three SCN⁻ complexes of Np(IV) and for two SCN⁻ complexes of Pu(III). The experiments with HDNNS gave results that are compatible with those of the TTA experiments. The reported results are summarised in Table A.7.

The authors also extracted Np(IV) as a function of TTA and H⁺ concentration, and they showed that a neutral Np(TTA)₄ complex was the only species extracted into the organic phase, and that all the Np(IV) thiocyanate complexes remained in the aqueous phase. According to the authors, a holding reductant (such as iodide as used by Khopkar and Mathur [74KHO/MAT]) is not needed due to the reducing properties of the thiocyanate ion.

A spectrophotometric study of the absorption bands of Np(IV) in the absence and presence of thiocyanate showed that the absorption peaks shifted to higher wavelengths

Table A.7: Formation constants of thiocyanate complexes reported in [78RAO/BAG2] at different temperatures. $[H^+] = 1 \text{ M}$, $I = 2 \text{ M}$ (Na, H)(SCN, ClO₄).

Equilibrium	Method	t (°C)	$\log_{10} \beta$ ($I = 2 \text{ M}$)	$\Delta_r H_m$ (kJ·mol ⁻¹)
$\text{Np}^{4+} + \text{SCN}^- \rightleftharpoons \text{NpSCN}^{3+}$	TTA	10	(1.53 ± 0.01)	-7.1
	TTA	25	(1.49 ± 0.07)	
	HDNNS	25	(1.48 ± 0.06)	
$\text{Np}^{4+} + 2 \text{SCN}^- \rightleftharpoons \text{Np}(\text{SCN})_2^{2+}$	TTA	40	(1.40 ± 0.01)	-9.3
	TTA	10	(2.25 ± 0.03)	
	TTA	25	(2.06 ± 0.08)	
	HDNNS	25	(2.26 ± 0.05)	
$\text{Np}^{4+} + 3 \text{SCN}^- \rightleftharpoons \text{Np}(\text{SCN})_3^+$	TTA	40	(2.13 ± 0.03)	-13.1
	TTA	10	(2.61 ± 0.03)	
	TTA	25	(2.53 ± 0.02)	
	HDNNS	25	(2.50 ± 0.03)	
	TTA	40	(2.34 ± 0.04)	
$\text{Pu}^{3+} + \text{SCN}^- \rightleftharpoons \text{PuSCN}^{2+}$	HDNNS	25	(0.33 ± 0.03)	
$\text{Pu}^{3+} + 2 \text{SCN}^- \rightleftharpoons \text{Pu}(\text{SCN})_2^+$	HDNNS	25	$-(0.30 \pm 0.26)$	

with increasing thiocyanate concentration. This may be an indication for the formation of inner-sphere complexes. On the other hand, as stated in [92FUG/KHO], the enthalpy changes are considerably smaller than for the corresponding U(IV) complexes [92GRE/FUG], and a firm conclusion about the type of complexes formed is not possible on this basis.

The thiocyanate complexes of Pu(III) are weak, and the second overall formation constant is even negative (*i.e.*, the stepwise value is $\log_{10} K_2 = -0.63$). Hence, the effect that was interpreted by the authors with the formation of a 1:2 complex is probably simply due to activity factor changes.

In our evaluation to derive the recommended constants, we accept the constants for the formation of NpSCN^{3+} , $\text{Np}(\text{SCN})_2^{2+}$, $\text{Np}(\text{SCN})_3^+$ and PuSCN^{2+} from this study. It should be noted that the uncertainties given by the authors, *cf.* Table A.7, resulted from the fitting procedure and reflect only precision, not accuracy. Hence, it is estimated that the real uncertainties are considerably larger. From the formation constants of the Np(IV) thiocyanate complexes at 10, 25 and 40°C, the authors derived enthalpy values, *cf.* Table A.7. However, the uncertainties are considerable, firstly due to the small temperature dependency of the constants and the comparatively high uncertainties resulting from the fitting procedure (see Table A.7), secondly due to the equivocal temperature variation of β_2 . Nevertheless, we use these enthalpy data as a guideline.

[78RAO/PAT]

The authors used near infrared spectroscopy to study several inorganic complexes of Np(V). The measurements were performed at an ionic strength of 2 M (NaClO₄) and at ~23°C. From the changes in the molar absorptivities of the 980 nm adsorption band

of Np(V) in the presence of ligands, association quotients were determined for complexes of the type $\text{NpO}_2\text{L}(\text{aq})$, where L^- is F^- , IO_3^- or NO_2^- . The authors report $\beta_1(\text{NpO}_2\text{F}(\text{aq}), 2 \text{ M}, 296.15 \text{ K}) = 22.3$, $\beta_1(\text{NpO}_2\text{IO}_3(\text{aq}), 2 \text{ M}, 296.15 \text{ K}) = 3.8$, $\beta_1(\text{NpO}_2\text{NO}_2(\text{aq}), 2 \text{ M}, 296.15 \text{ K}) = 1.39$. Unfortunately, the spectra used to derive these constants are not presented in the paper (the nitrite spectra are shown in the summary paper [79KUS/GAN]). The authors stated that the evaluation of the absorption measurements confirmed the presence of only one complex (1:1) within the ranges of ligand concentrations used. The constants for the Np(V) fluoride and iodate complexes are in good agreement with those of other studies, and they are accepted with increased uncertainties due to the absence of experimental results: $\log_{10}\beta_1(\text{NpO}_2\text{F}, \text{aq}, I = 2 \text{ M}) = (1.35 \pm 0.30)$, and $\log_{10}\beta_1(\text{NpO}_2\text{IO}_3, \text{aq}, I = 2 \text{ M}) = (0.58 \pm 0.30)$. The nitrite constant is not accepted, because the effects can be equally well explained by medium effects, see comments about the corresponding extraction study [79RAO/GUD].

[78SAI/UEN]

The paper describes the solubility of Np(IV), Np(V), and Np(VI) in solutions of sulphuric acid and ammonium sulphate in the presence of hexamminecobalt(III). The bulk chemistry of the resulting solids is given, but it is not clear whether one or more compounds are included in the precipitates. There are no thermodynamic data useful for this review.

[78WOO/MIT]

This paper identifies the complex with a ratio of $\text{PuO}_2^{2+}:\text{CO}_3^{2-}$ of 1:3 in mixtures of NaClO_4 and Na_2CO_3 held at $I=0.15$ and $\text{pH}= 11.4$. The 1:3 complex is clearly dominant in this pH and ionic strength range. The initial Pu(VI) form(s) is unknown in this experiment but might be calculated from compilations of Pu(VI)-OH⁻ species. The association quotient (K_3) is calculated from the unknown form(s) to be $1.73 \pm 0.22 \times 10^3$ ($\log_{10} K_3 = 3.24$).

[79BEL/SMI]

In this paper, enthalpies of reaction are reported for $\text{NpO}_2(\text{OH})_2(\text{s})$ and $\text{Np}_2\text{O}_5(\text{cr})$ with 0.04 M FeCl_2 in 6 M HCl containing 0.004 M $\text{Na}_2\text{SiF}_6(\text{cr})$. The enthalpies of formation were then calculated from the enthalpies of solution of $\text{Cs}_2\text{NpCl}_6(\text{cr})$ [71FUG/BRO], $\text{CsCl}(\text{cr})$, $\text{FeCl}_2(\text{cr})$ and $\text{FeCl}_3(\text{cr})$ in the same solvent. Because $\Delta_f H_m^\circ(\text{Cs}_2\text{NpCl}_6(\text{cr}))$ is used, the result is also contingent on the values selected for $\Delta_f H_m^\circ(\text{MCl}_4(\text{cr}))$ and $\Delta_{\text{sln}} H^\circ(\text{MCl}_4(\text{cr}))$ in 1 M HCl [69FUG/BRO, 71FUG/BRO].

Aside from the enthalpies of formation of the iron species, the key piece of auxiliary data needed to calculate $\Delta_f H_m^\circ$ for $\text{Np}_2\text{O}_5(\text{cr})$ and $\text{NpO}_2(\text{OH})_2(\text{s})$ is $\Delta_f H_m^\circ(\text{NpCl}_4, 6 \text{ M HCl}, 0.04 \text{ M FeCl}_2, 0.004 \text{ M Na}_2\text{SiF}_6)$, and that can be calculated from:

(a) the difference

$$\Delta_{\text{sln}} H^\circ(\text{Cs}_2\text{NpCl}_6(\text{cr}), 1 \text{ M HCl}) - \Delta_{\text{sln}} H^\circ(\text{Cs}_2\text{NpCl}_6(\text{cr}), 6 \text{ M HCl}, 0.04 \text{ M}$$

FeCl₂, 0.004 M Na₂SiF₆)

(b) the difference

$\Delta_{\text{sln}}H^\circ(\text{CsCl}(\text{cr}), 1 \text{ M HCl}) - \Delta_{\text{sln}}H^\circ(\text{CsCl}(\text{cr}), 6 \text{ M HCl}, 0.04 \text{ M FeCl}_2, 0.004 \text{ M Na}_2\text{SiF}_6)$

(c) $\Delta_f H_m^\circ(\text{NpCl}_4(\text{s}))$

(d) $\Delta_{\text{sln}}H^\circ(\text{NpCl}_4(\text{cr}), 1 \text{ M HCl})$

The value of $\Delta_{\text{sln}}H^\circ(\text{Cs}_2\text{NpCl}_6(\text{cr}), 6 \text{ M HCl}, 0.04 \text{ M FeCl}_2, 0.004 \text{ M Na}_2\text{SiF}_6)$ for the first difference expression has not been measured, but $\Delta_{\text{sln}}H^\circ(\text{Cs}_2\text{NpCl}_6(\text{cr}), 6 \text{ M HCl})$ has been reported [71FUG/BRO]. Thus, if the effect of the Na₂SiF₆, FeCl₂ and FeCl₃ in solution in the 6 M HCl on the enthalpy of solution of Cs₂NpCl₆(cr) is negligible, $\Delta_f H_m^\circ(\text{Np}_2\text{O}_5(\text{s}))$ and $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{s}))$ can be calculated from the data. This assumption was implicit in the calculations of Belyaev *et al.*

The reported enthalpy of solution for CsCl(cr) in the solvent mixture (10.94 kJ·mol⁻¹) [79BEL/SMI] is somewhat less than the value (11.90 ± 0.13) kJ·mol⁻¹ reported by Fuger and Brown [71FUG/BRO] for dissolution of CsCl(cr) in 6 M HCl. The latter is a more precise result than that of Belyaev *et al.* whose stated uncertainty of “± 0.10” kJ·mol⁻¹ is apparently a misprint for ± 1.0 kJ·mol⁻¹. The differences in the final concentrations of CsCl (0.01 M in Fuger and Brown [71FUG/BRO], 0.015 to 0.020 M in Belyaev *et al.* [79BEL/SMI]) are too small to explain the difference in the enthalpies of solution, as are the small amounts of FeCl₂ and Na₂SiF₆ in the solutions of the latter group.

Fuger and Brown [73FUG/BRO] proposed $\Delta_f H_m^\circ(\text{Np}^{4+}, 1 \text{ M HCl}) - \Delta_f H_m^\circ(\text{Np}^{4+}, 6 \text{ M HCl}) = -(19.0 \pm 1.4) \text{ kJ}\cdot\text{mol}^{-1}$ based on the available enthalpy of solution data for the actinide(IV) halides and caesium chloro-complexes, and not exclusively on the more limited data for the caesium neptunium(IV) chloro-salt. Using $\Delta_f H_m^\circ(\text{Np}^{4+}, 1 \text{ M HCl}) = -(551.9 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ (Section 7), the value $\Delta_f H_m^\circ(\text{Np}^{4+}, 6 \text{ M HCl}) = -(532.9 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated [2000RAN/FUG]. A heat of $-(2.2 \pm 0.8) \text{ kJ}\cdot(\text{mol Np})^{-1}$ was determined for the effect of complexation by 0.005 M Na₂SiF₆ in 1 M HCl [69FUG/BRO], and Eyring and Westrum [50EYR/WES] reported an effect of $-1.3 \text{ kJ}\cdot(\text{mol Th})^{-1}$ in 6 M HCl. Therefore, a contribution of $-(1.7 \pm 0.6) \text{ kJ}\cdot(\text{mol Np})^{-1}$ would also be expected from the effect of the 0.004 M Na₂SiF₆ in 6 M HCl (assuming the complexation constant is sufficiently greater than unity and thus that essentially all the Np(IV) was complexed) [76FUG/OET]. (However, it is noted that Fuger and Brown [73FUG/BRO] did not apply such a correction to the data [71FIT/PAV] for UCl₄ when deriving their equation used to calculate $\Delta_f H_m^\circ(\text{Np}^{4+}, 6 \text{ M HCl})$). Hence, $\Delta_f H_m^\circ(\text{Np}^{4+}, 6 \text{ M HCl}, 0.04 \text{ M FeCl}_2, 0.004 \text{ M Na}_2\text{SiF}_6) = -(534.6 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$.

The experimental enthalpies of solution of FeCl₂(cr) and FeCl₃(cr) in the (6 M HCl, 0.04 M FeCl₂, 0.004 M Na₂SiF₆) solvent have substantial uncertainties. Nevertheless, the values are reasonable, and no better literature values could be found. Parker and Khodakovskii [95PAR/KHO] have recently recommended CODATA consistent values for several iron species and compounds. They recommend $\Delta_f H_m^\circ(\text{FeCl}_2(\text{cr})) = -(341.16 \pm 0.6) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{FeCl}_3(\text{cr})) =$

$-(395.66 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$, and these values are used in the present calculations. Then, using $\Delta_f H_m^\circ(\text{H}_2\text{O}, 6 \text{ M HCl}, 0.04 \text{ M FeCl}_2, 0.004 \text{ M Na}_2\text{SiF}_6) = -(286.65 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{HCl}, 6 \text{ M HCl}, 0.04 \text{ M FeCl}_2, 0.004 \text{ M Na}_2\text{SiF}_6) = -(153.40 \pm 0.11) \text{ kJ}\cdot\text{mol}^{-1}$ (both values from [2000RAN/FUG] based on Parker [65PAR] for 6 M HCl solutions), $\Delta_f H_m^\circ(\text{NpCl}_4, 6 \text{ M HCl}, 0.04 \text{ M FeCl}_2, 0.004 \text{ M Na}_2\text{SiF}_6) = -(1148.2 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$. Hence, $\Delta_f H_m^\circ(\text{NpO}_2(\text{OH})_2(\text{s})) = -1363 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{Np}_2\text{O}_5(\text{s})) = -2142 \text{ kJ}\cdot\text{mol}^{-1}$.

The reported analyses suggest the composition of the “ Np_2O_5 ” used in the calorimetry experiments was actually closer to $\text{NpO}_{2.59}$. If this is assumed to be so, $\Delta_f H_m^\circ(\text{NpO}_{2.59}(\text{s})) = -1086 \text{ kJ}\cdot\text{mol}^{-1}$.

[79CHI/TAL]

The authors measured the influence of fluoride concentration on the equilibrium of the Pu(IV)/Pu(III) redox couple. The experiments were performed at “room temperature”, reported as $\sim 25^\circ\text{C}$, and at $I = 1 \text{ M}$ (HClO_4). Chitnis *et al.* [79CHI/TAL] assumed that only Pu^{4+} was complexed by fluoride, and that fluoride complexing of Pu^{3+} was negligible. This assumption appears reasonable. The procedure is satisfactory, and the authors used a two-complex model to interpret the data. The formation constant of the 1:1 complex, PuF^{3+} , in acidic solution is reported as $\log_{10} {}^*\beta_1(\text{PuF}^{3+}, I = 2 \text{ M}) = (4.66 \pm 0.07)$, to which we assign an uncertainty of ± 0.20 . The formation constant of the 1:2 complex, PuF_2^{2+} , has a greater uncertainty, because it formed to less than 30% during the experiments. We accept the reported value with an increased uncertainty: $\log_{10} {}^*\beta_2(\text{PuF}_2^{2+}, I = 2 \text{ M}) = (7.32 \pm 0.40)$.

[79FED/PER]

a) Np(V)/Np(IV) redox potential

The formal potential of the Np(V)/Np(IV) and Np(IV)/Np(III) redox couples were measured respectively by potentiometry, probably at a mercury electrode, and in 1 M K_2CO_3 solution by polarography. There is not much experimental detail. The Np(IV) carbonate solution was prepared by adding solid oxalate. As expected the attainment of the Np(V)/Np(IV) equilibrium was slow. The authors waited seven hours, but this may not have been long enough for this type of equilibrium and for this methodology. The authors indicate it was difficult to obtain a stable measurement using the electrode: “... only an extremely approximate value close to 0.1 V” was finally proposed. This value was confirmed by Varlashkin *et al.* [84VAR/HOB] (with no better precision for the same reason), and again recently by Vitorge and his co-workers [95VIT, 96DEL/VIT, 98VIT/CAP]. Thus any thermodynamic data calculated from this will have a very large uncertainty.

The concentrations of the major species would not be strongly affected by changes of carbon dioxide partial pressure above the solutions, but if the difference between an open and closed system (with inert cover gas) is considered [95VIT, 96DEL/VIT], p_{CO_2} can increase by almost 10^3 , and this would increase the redox potential of the solution by more than 0.3 V, and induces an error of almost 6 orders of magnitude in

the determination of the formation constant of $\text{Np}(\text{CO}_3)_5^{6-}$. In this review, calculations have been done assuming that the potential was controlled by the two limiting complexes, $\text{NpO}_2(\text{CO}_3)_3^{5-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$ (see the discussion on [81WES/SUL] in this appendix). The equilibrium can then be written

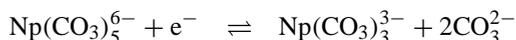


Even if we assume an overall uncertainty of only 0.2 V (and the authors seem to have estimated an uncertainty of 0.1 V for the instability of the measurement and 0.1 V for possible junction potential problems without even considering the $p\text{CO}_2$ problem), with $\varepsilon_{(\text{Np}(\text{CO}_3)_5^{6-}, \text{Na}^+)}$ as estimated in Chapter 12.1.2.1.4, and other values selected in this review, $\log_{10} \beta_5^{\circ}(\text{Np}(\text{CO}_3)_5^{6-}) = (38.1 \pm 3.7)$ is calculated. This assumes the experimental solutions were in equilibrium with air, an assumption which is consistent with later measurements [95VIT, 96DEL/VIT, 98VIT/CAP] (see Chapter 12.1.2.1.4).

For comparison, the value for the corresponding uranium reaction is (34.1 ± 1.0) [92GRE/FUG, 95GRE/PUJ], and the value selected by Capdevila [92CAP] for the plutonium reaction was (32.2 ± 2.0) . The values are in marginal agreement, but the uncertainty in the value from this paper [79FED/PER] is particularly large.

b) Np(IV)/Np(III) redox potential

Fedoseev, Peretrukhin and Krot also measured the formal potential of the Np(IV)/Np(III) couple at a dropping mercury electrode in 1 M K_2CO_3 solution. They proposed -1.32 V at 25°C . This value was later confirmed [84VAR/HOB]. The uncertainty must be quite substantial, since “all the waves [of Np and Pu(IV)/(III)] in carbonate media are irreversible”. There is no information on the liquid junction potential, and we assume an uncertainty of 0.1 V (*i.e.*, that it was the same as in the measurement of the formal potential of the Np(V)/Np(IV) couple). By analogy with Am(III) [95SIL/BID], we assume that the Np(IV)/Np(III) redox equilibrium can here be written



Exposure of the 1 M K_2CO_3 solution to atmospheric $\text{CO}_2(\text{g})$ has little influence on the free carbonate concentration and on this equilibrium. The required specific interaction coefficient $\varepsilon_{(\text{Np}(\text{CO}_3)_3^{3-}, \text{K}^+)}$ = $-(0.15 \pm 0.07)$ $\text{kg}\cdot\text{mol}^{-1}$, is estimated by analogy with the Am(III) - Na^+ system, *i.e.*, $\varepsilon_{(\text{Np}(\text{CO}_3)_5^{6-}, \text{K}^+)}$ = $-(0.73 \pm 0.68)$ $\text{kg}\cdot\text{mol}^{-1}$, by analogy with Na^+ solutions [95VIT, 96DEL/VIT] (*cf.* Section 12.1.2.1.4.a). Values for the uncertainties have been increased because the values are estimated. Using these and the standard potential of the $\text{Np}^{4+}/\text{Np}^{3+}$ redox couple selected in this review (Chapter 7.4), we calculate $\log_{10}(\beta_5^{\circ}(\text{Np}(\text{CO}_3)_5^{6-})/\beta_3^{\circ}(\text{Np}(\text{CO}_3)_3^{3-})) = (20.13 \pm 2.27)$. Hence, $\log_{10} \beta_3^{\circ}(\text{Np}(\text{CO}_3)_3^{3-}) = (15.49 \pm 2.51)$ using $\log_{10} \beta_5^{\circ}(\text{Np}(\text{CO}_3)_5^{6-}) = (35.62 \pm 1.07)$ as estimated in this review (Chapter 12.1.2.1.4.a).

c) Np(V)/Np(III) redox potential

The value of $\beta_{3,\text{Np(III)}}^\circ/\beta_{3,\text{Np(V)}}^\circ$ (11.2 ± 1.8) can be calculated from the two measurements of Fedoseev, Peretrakhin and Krot, and this should lead to a more satisfactory value for $\beta_{3,\text{Np(III)}}^\circ$ because the major uncertainties (the values of the liquid junction and estimated stability of the limiting complex of Np(IV)) cancel. Using the value $\log_{10} \beta_3^\circ = 5.50$ for Np(V) from the present review, $\log_{10} \beta_3^\circ = 16.7$ for the Np(III) carbonate complex is calculated. This compares well with the value (15.2 ± 0.6) for the formation constant of the corresponding americium complex [95SIL/BID], and with $\log_{10} \beta_3^\circ$ (15.49 ± 2.51) based on the Np(IV/III) couple in carbonate solutions (*cf.* Section 12.1.2.1.5).

d) Pu formal potentials

Potentiometric measurements of the irreversible formal potential of the Pu(IV)/Pu(III) couple in 1 M K_2CO_3 were reported. The formal potential is $-(0.495 \pm 0.030)$ V vs. SHE and has a variation with temperature of -0.63 mV/°C. On the basis of these results the Gibbs energy of oxidation was found to be 47.7 kJ·mol⁻¹ and the entropy of reaction to be -60.8 J·K⁻¹·mol⁻¹. These values appear reliable but due to the absence of independent information concerning the stoichiometry of the Pu(III) limiting complex, the irreversibility of the formal potential and the lack of information concerning the ionic strength dependence of the stability of the limiting and precursor Pu(IV) complexes, this value cannot be used to determine the nature and stability of the Pu(III) carbonate complex(es). A reduction potential was reported for the Pu(V)/Pu(IV) couple ($+0.6$ V), but no details were given concerning the experiments giving rise to this value, and it differs significantly from other reported values.

[79KUS/GAN]

This is a summary of earlier work of this research group and a short presentation of new results from solvent extraction studies. The constants reported for the formation of NpI^{3+} were obtained from extraction studies using HTTA and HDNNS (dinonylnaphthalenesulphonic acid): $\beta_1 = 0.8$ (HTTA) and 1.3 (HDNNS). The aqueous solution contained 1 M H^+ and had an ionic strength of 2 M (probably using perchlorate as background anion as was done in earlier studies), and the experiments were carried out at 25°C. Formation constants of iodide complexes of Th(IV) were also reported, as well as of oxalate complexes of Th(IV), Np(IV) and Pu(IV), of nitrite complexes of Am(III), Cm(III), of nitrate complexes of Np(IV), and of thiocyanide complexes of Tm(III). Although the experimental details are not given in this paper, it can be assumed that the extraction studies were carried out at the same level of care as the earlier studies of this group, *e.g.*, [75PAT/RAM, 76BAG/RAM2]. We therefore accept the following values with our estimated uncertainties: $\log_{10} \beta_1(\text{NpI}^{3+}, I = 2 \text{ M}) = -(0.10 \pm 0.30)$ (from the HTTA experiment) and (0.11 ± 0.30) (from the HDNNS experiment).

The values reported for the association constants of Np^{4+} with nitrate ($\beta_1 = 3.4$, $\beta_2 = 4.8$, at $I = 6$ M) are new. However, because the measurements were carried out at such a high ionic strength, and few experimental details were provided, these reported values are not accepted in the present review.

In addition, the first complexation constants of Np(V) complexes with nitrate, chloride, sulphate, thiocyanide, iodate, fluoride, nitrite and acetate were presented. The extraction data are reported in the source study [79RAO/GUD], and they are discussed under that entry below. Table 7 of [79KUS/GAN] contains, for iodate, fluoride and nitrite as ligand, three additional values for β_1 , put in parentheses and reported to be the results of spectrophotometric measurements. These measurements are reported in [78RAO/PAT] and are discussed under that entry above. Note that the figures in [79KUS/GAN] seem to be incorrectly placed: the figure placed at figure caption 14(a) appears to be Figure 14(b), the one placed at figure caption 14(b) looks like Figure 15, and the one placed at figure caption 15 in fact seems to be Figure 14(a).

[79MOS/POZ]

The comments in this entry also refer to the [78MOS/POZ] entry. Apparently the experiments and the tabulated results (including typographical errors) are identical. For some experiments, more detail is given in the earlier reference.

The authors give stability constants for the Np(V) and Pu(V) complexes with a number of inorganic and organic ligands based on a method involving co-precipitation of the free actinide cations with amorphous $\text{Fe}(\text{OH})_3$ at $20 \pm 2^\circ\text{C}$ in $\text{pH} = 8.5$ solutions of NH_4Cl . Experimental data describing the stability of the species in Table A.8 is either tabulated or plotted in [78MOS/POZ] or [79MOS/POZ].

Table A.8: Stability constants of Np(V) and Pu(V) complexes with various ligands as given in [78MOS/POZ] and [79MOS/POZ].

Composition of the complex	Ionic medium (M $\text{NH}_4(\text{Cl,L})$)	Ligand concentration (M)	$\log\beta(\pm 2\sigma)$	
			NpO_2^+	PuO_2^+
MO_2SO_3^-	1.0	0.1 – 0.28	(1.50 ± 0.05)	
$\text{MO}_2(\text{SO}_3)_2^{3-}$	1.0		(3.01 ± 0.4)	
MO_2SO_4^-	~ 1.5	0.15 – 0.6	(1.04 ± 0.4)	
$\text{MO}_2\text{HCO}_3(\text{aq})^{(c)}$	0.25	0.05 – 0.13	(2.15 ± 0.05)	
$\text{MO}_2(\text{HCO}_3)_2^{(c)}$	0.25	0.01 – 0.13	$(3.66 \pm 0.10)^{(a)}$	(1.90 ± 0.10)
$\text{MO}_2(\text{HPO}_4)^-$	$1.0^{(b)}$	0.05 – 0.34	(2.90 ± 0.11)	(2.39 ± 0.04)
$\text{MO}_2(\text{PO}_4)^{2-}$	$1.0^{(b)}$	0.05 – 0.30	(5.78 ± 0.25)	

^(a) Result given in [78MOS/POZ] only.

^(b) Given, presumably incorrectly, as 0.1 M in the papers.

^(c) The stoichiometry of this species was not confirmed, and this review considers that the numerical value of the corresponding stability constant is in contradiction with later experimental work.

The wide range of ligand concentration means that there are ionic medium effects influencing the precision of all of these determinations, particularly in the case of the bicarbonate and SO_4^{2-} experiments. This is a problem common to many experiments

dealing with the stability of weak complexes. There is also uncertainty as to the identity of the complexes, in the case of PO_4^{3-} and CO_3^{2-} complexes, as it is impossible to determine the number of protons associated with a complex based on experiments performed at constant pH. In the case of $\text{NpO}_2^+ - \text{PO}_4^{3-}$ there is an additional problem with the assignment of stability constants: the data in the paper are more compatible with a series of higher order complexes of the form of either $\text{NpO}_2(\text{HPO}_4)_n^{1-2n}$ or $\text{NpO}_2(\text{PO}_4)_n^{n-3}$, with $n = 1 - 2$ or greater (the protonation of the ligand cannot be determined from these experiments), than the single $\text{NpO}_2\text{PO}_4^{2-}$ species proposed. The variation in the ionic medium is sufficiently high and the experimental details sufficiently sparse in all of the experiments that this data cannot be used to select stability constants. Nonetheless, the results concerning the SO_3^{2-} complexes, where the experimental problems are fewer, and the remaining qualitative and semi-quantitative results are useful for the purposes of this review.

[79RAO/GUD]

The authors used a solvent extraction technique, with dinonylnaphthalenesulphonic acid (HDNNS) in benzene as the extractant, to study the complex formation between NpO_2^+ and Cl^- , NO_3^- , F^- , NO_2^- , SO_4^{2-} , SCN^- and IO_3^- at 25°C. In the aqueous phase the ionic strength is maintained at 2 M (NaClO_4). This is a careful study, and the extraction of uncharged complexes into the organic phase was verified by spectroscopy.

Three extraction experiments were carried out for iodate as a ligand, at iodate concentrations of 0.05, 0.10 and 0.15 M. The constant obtained is $\beta_1(\text{NpO}_2\text{IO}_3, \text{aq}) = (2.1 \pm 0.1)$. According to this constant, the proportions of $\text{NpO}_2\text{IO}_3(\text{aq})$ formed in the three experiments are 9, 17 and 24%, respectively. The amounts of complex formed are thus not very large, and the uncertainty in the resulting constant is high at such low complexation degrees. We hence accept the reported formation constant of the 1:1 complex, but we assign it a larger uncertainty: $\log_{10} \beta_1(\text{NpO}_2\text{IO}_3, \text{aq}, I = 2 \text{ M}) = (0.32 \pm 0.30)$.

In the case of fluoride, the authors discussed some other studies, *e.g.* [70AL-/WAI], in which it was concluded that the neutral complex $\text{NpO}_2\text{F}(\text{aq})$ did not form. They related these observations to the high acid concentrations in the experiments, and they showed that at pH = 5 the complex formation of Np(V) with fluoride is significant. They found a constant of $\beta_1(\text{NpO}_2\text{F}, \text{aq}) = (9.8 \pm 0.8)$. We accept the formation constant reported here, but assign it a larger uncertainty, because there was a slight trend in the resulting values in Table 3 [79RAO/GUD]. In our evaluation, we select $\log_{10} \beta_1(\text{NpO}_2\text{F}, \text{aq}, I = 2 \text{ M}) = (0.99 \pm 0.10)$, *cf.* Section 9.2.1.3.

Only one sulphato complex was found. Recalculation using the tabulated data and, assuming that pH ≥ 3 (and therefore $[\text{SO}_4]_{\text{TOT}} = [\text{SO}_4^{2-}]$), yields $\log_{10} \beta_1 = (0.45 \pm 0.10)$. For the nitrate complexation study, the experiments were carried out at pH 5 to maintain neptunium as Np(V). The aqueous phase consisted of 2 M Na (ClO_4 , NO_3) mixtures with a maximum nitrate ion concentration of 1 M. Only 4 measurements of K_d were performed. A spectrophotometric test for the Np(V) peak in the organic phase was run after extraction with TBP from 6 M NaNO_3 — a much higher concentration of ligand than the one used in the measurements. The authors reported $\beta_1 = (0.28 \pm$

0.03), *i.e.*, $\log_{10} \beta_1 = -(0.55 \pm 0.05)$. A re-evaluation of these data considering activity effects from the large changes in the ionic medium in this work, leads to the conclusion that the system can be treated neglecting complexation, with $\Delta\varepsilon(\text{NpO}_2^+) = 0.1 \text{ kg}\cdot\text{mol}^{-1}$ in perchlorate and nitrate media.

The nitrite complexation was studied in a similar way, and the authors reported $\beta_1 = 0.9 \pm 0.1$, *i.e.*, $\log_{10} \beta_1 = -(0.05 \pm 0.05)$ from extraction data. The spectrophotometric test for the Np(V) peak in the organic phase, after extraction with THA(Cl) from 0.5 M NaNO_2 solutions, resulted surprisingly negative, even though extraction was observed ($K_d \approx 0.3$). The peak of Np(V) reappeared in the extract after stripping neptunium into 2 M NaClO_4 , and the authors consider this behaviour unexplained. A re-calculation of the data considering activity coefficient changes resulting from the large changes in the ionic medium, leads to the conclusion that the system can be treated neglecting complexes, with $\Delta\varepsilon(\text{NpO}_2^+) = 0.28 \text{ kg}\cdot\text{mol}^{-1}$ in perchlorate and nitrite media.

Concerning the complex formation of Np(V) with thiocyanate, special attention was given to the maintenance of the oxidation state of neptunium, because thiocyanate ion is able to reduce Np(V) to Np(IV) under the conditions chosen in the experiment ($2 \text{ SCN}^- \rightleftharpoons 2 \text{ e}^- + (\text{SCN})_2(\text{aq})$, $E^\circ = 0.77 \text{ V}$ [78RAO/BAG2]). The authors found that irregularities during the experiments, such as changes in valence states, can be ruled out. They determined, for the formation of $\text{NpO}_2\text{SCN}(\text{aq})$, a constant of $\beta_1(I = 2 \text{ M}) = (2.1 \pm 0.1)$, *i.e.*, $\log_{10} \beta_1(I = 2 \text{ M}) = (0.32 \pm 0.02)$. As an attempt to extrapolate this value to $I = 0$, we use $\Delta\varepsilon(12.46, q = 1) = -0.30 \text{ kg}\cdot\text{mol}^{-1}$ from $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = 0.25 \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{SCN}^-, \text{Na}^+)} = 0.05 \text{ kg}\cdot\text{mol}^{-1}$, *cf.* Appendix B. The resulting value is $\log_{10} \beta_1^\circ(\text{NpO}_2\text{SCN}, \text{aq}, 298.15 \text{ K}) = 0.08$.

[79VOL/TOM]

Structures are proposed for $\text{NaNpO}_2\text{CO}_3(\text{s})$ and $\text{LiNpO}_2\text{CO}_3(\text{s})$ (heated to 250°C) based on an X-Ray powder diffraction study. In these two compounds, the Np atoms are in NpO_2CO_3 layers that are isostructural to UO_2CO_3 layers in Rutherfordine (UO_2CO_3). There are mono and bidentate CO_3^{2-} , which is in agreement with conclusions of some earlier infrared work [73KHA/MOS], but not with a later discussion by the same authors [81VOL/VIS4]. Several changes in the structure are possible, and in some of these changes (but not all of them) Na and Np atoms can be exchanged. As in [77VOL/VIS], crystallographic changes were attributed to temperature changes; but the ageing of the solid in equilibrium with the solution at room temperature, was not studied, so care is required if solubility measurements over $\text{NaNpO}_2\text{CO}_3(\text{s})$ are used in the determination of formation constants of the carbonate complexes. The conclusion of this structural study seems reasonable, but it deals with only one of several possible explanations of the powder X-ray diffraction patterns.

[79VOL/VIS]

This report summarises the work of Volkov *et al.* work on the structure of actinide(V) carbonate solid compounds. Most of the information was also published elsewhere

[74VIS/VOL, 74VOL/KAP, 74VOL/KAP2, 76VOL/VIS, 77VOL/VIS, 79VOL/TOM, 79VOL/VIS2, 81VOL/VIS, 81VOL/VIS3, 81VOL/VIS4, 81VOL/VIS2].

[79VOL/VIS2]

A solid, stated by the authors to be $\text{Na}_{0.6}\text{NpO}_2(\text{CO}_3)_{0.8}(\text{s})$ (written elsewhere [84VOL/KAP] as $\text{Na}_{0.75}(\text{NpO}_2)_{1.25}\text{CO}_3(\text{s})$), was precipitated from 2 mM bicarbonate solution. Heating this solid, led to another phase and finally to $\text{NaNpO}_2\text{CO}_3(\text{s})$. X-Ray powder diffraction patterns of these solids were obtained and reported; they were interpreted according to the structure proposed in [79VOL/TOM], which allows continuous variation of the Np/Na ratio in the solid. Later solubility studies [81VOL/VIS4, 83MAY, 84VIT, 98VIT/CAP] did not confirm this interpretation (see the discussion of [84VIT] in this appendix).

Results of potentiometric titrations of Np(V) with Na_2CO_3 and NaHCO_3 solutions are presented. They indicate $\text{NaNpO}_2\text{CO}_3(\text{s})$ precipitates and, only in Na_2CO_3 solutions, formation of a solid or soluble compound with a Np(V)/CO_3^{2-} ratio equal to 2. The shapes of the potentiometric titration curves shown in this publication indicate that equilibrium was probably not attained during the experiments, and at least some of the compounds may well have only been metastable phases, and unsuitable for the determination of solubility products. The shape and the position of the potentiometric titration curves obtained in a medium containing K^+ (instead of Na^+) were not consistent with a previous study by the same group of authors [74VIS/VOL]. This was not discussed. For these reasons this work (including the proposed stoichiometry of the solid phases) is not credited in the present review.

[80ALL/KIP]

These are estimated values, only.

[80PAR/THO]

The PHREEQE code permits the calculation of the distribution of aqueous species in solutions given the total concentrations of ions and association quotients selected by the user. The code contains an internal data base for the major elements, and ion pairs. The model uses iterative calculations to determine a best solution and is based on the ion association model of chemical behaviour. Three activity formulations are used in this code:

- 1) For the major elements for which size parameters (a_i, b_i) are known the activity of an ion is calculated from:

$$\log_{10} \gamma_i = \frac{-Az_i^2\sqrt{I}}{1 + Ba_i\sqrt{I}} + b_i I$$

where γ_i is the activity of the i th species, A and B are the Debye-Hückel parameters, z_i is the ionic charge, and I is the ionic strength.

- 2) For ions for which size parameters are not known the Davies approximation is used:

$$\log \gamma_i = -Az_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

- 3) The activity of water is calculated from

$$a_{\text{H}_2\text{O}} = 1 - 0.017 \sum_{i=1}^I m_i$$

where $\sum_{i=1}^I m_i$ is the sum of the molalities of all dissolved anions, cations, and neutral species.

The internal thermodynamic data base used in the calculations is current to September, 1986, and contains CODATA revisions to 1989 [90NOR/PLU].

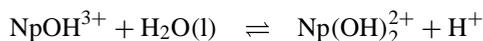
The activity approximations used in the PHREEQE model are known to work well at ionic strengths up to ~ 0.1 molal and have been shown to reproduce solubility experiments in natural systems up to the range of ~ 1 molal. Our use of this numerical code was confined to experiments where the bulk of the measurements were within this range.

[80RAI/SER]

The solubility results for hydrated $\text{PuO}_2(\text{am})$, for pH values from 3.9 to 7.8, are compatible with those of a later study by one of the same authors [84RAI]. In both papers it is suggested the solubility product of hydrated $\text{PuO}_2(\text{am})$ may not be properly determined using these high pH data, as reliable measurements of the redox potential could not be made (*cf.* the discussion of [84RAI] and also the comments in that paper).

[80SCH/GOR]

This is a pulse radiolysis study designed to obtain information concerning the reduction of Np(V) to Np(IV). The value for the first hydrolysis constant of NpO_2^+ was obtained as a fitting parameter. The pH range for the experiments was 3.0 to 7.0, and the (conductivity) data are very scattered for experiments with pH values between 6 and 7. The authors report $\log_{10}^* \beta_1 = -(8.75_{-0.5}^{+1.0})$. This value appears to represent a valid upper limit for the hydrolysis constant, but, based on the experimental data, the selected lower limit is apparently arbitrary. In the same paper, the authors report a value of $\log_{10} K = -(4.5 \pm 0.5)$ for the reaction



The experiments were carried out in solutions having pH values between 3 and 7, and $\text{Np}(\text{OH})_2^{2+}$ was considered to be an important product in the reduction of NpO_2^+ to Np(IV) solution species. Surprisingly, at the higher end of the pH range, $\text{Np}(\text{OH})_3^+$

and $\text{Np}(\text{OH})_4(\text{aq})$ or $\text{Np}(\text{IV})$ polymeric hydrolysis products do not seem to have been treated as possible major equilibrium species. Although the value is reasonable, and is based on a fit to the experimental transient conductivity data as a function of pH, it is concluded in the present review that there were too many unknown (and unconfirmed) parameters in the data analysis for this value to be accepted. No blank conductivity measurements (in $\text{Np}(\text{V})$ solutions at different pH and without radiolysis) are reported. Also, there is insufficient evidence that $\text{Np}(\text{OH})_2^{2+}$ is a major species of $\text{Np}(\text{IV})$ in the pH range of the experiment.

[80SOL/ZAK]

Aqueous mixtures of $< 2.7 \text{ M HNO}_3$ and $< 4.4 \text{ M}$ acetic acid in various proportions were extracted into *n*-dodecane containing 30 vol% TBP. From the molar ratios in the organic phase, the concentrations being determined by potentiometric titration, it was concluded that nitric acid is extracted as the species $\text{HNO}_3 \cdot \text{TBP}$, and acetic acid as $(\text{CH}_3\text{COOH})_2 \cdot \text{TBP}$. Equilibrium constants were calculated, assuming that acetic acid only appeared as a dimer, and that no HNO_3 ion pairs were formed. Calculated distribution ratios for HNO_3 and acetic acid agreed well with predicted values for this model.

In the presence of $\text{Pu}(\text{IV})$, it was concluded that the extracted species were $\text{Pu}(\text{OH})_i(\text{NO}_3)_{(4-i)} \cdot \text{TBP}$ or $\text{Pu}(\text{OH})_2(\text{CH}_3\text{COOH})_2$. The Pu concentration was $420 \text{ mg} \cdot \text{dm}^{-3}$, *i.e.*, about $1.8 \cdot 10^{-3} \text{ M}$, but no information is given about how the valence state was ascertained, nor about the extraction technique used, nor the procedures for evaluation of the experimental results. With $i=0$, the coordination number N of Pu is 10, while for $i=3$, $N=7$; the reviewer therefore doubts the formula for the extracted Pu-species. Using activity factors taken from references, the “thermodynamic constant” for the reaction $\text{Pu}^{4+} + 4\text{OH}^- \rightleftharpoons \text{Pu}(\text{OH})_4(\text{aq})$ was calculated to be $3.5 \cdot 10^{56}$. Using this value and the equilibrium constants from Solovkin [74SOL], the distribution ratio of $\text{Pu}(\text{IV})$ was calculated and found to agree well with experimental tests. The distribution measurements also yielded formation constants for the mixed hydroxy and nitrate or acetate complexes, assuming the activity coefficients are 1.00 for uncharged species at all acid concentrations (see Table A.9).

Table A.9: Formation constants for neutral plutonium(IV) complexes as given by [80SOL/ZAK].

Complex	β
$\text{Pu}(\text{NO}_3)_4$	380
$\text{Pu}(\text{OH})(\text{NO}_3)_3$	$4.8 \cdot 10^4$
$\text{Pu}(\text{OH})_2(\text{NO}_3)_2$	$1.2 \cdot 10^3$
$\text{Pu}(\text{OH})_3(\text{NO}_3)$	9.8
$\text{Pu}(\text{OH})_2(\text{CH}_3\text{COOH})_2$	93

No comparison was given with other possible models, and insufficient information

was provided to permit recalculation of the results. For this reason, and because the experimental conditions are ill-defined, the results of this study are not used in the present review in selection of hydrolysis or complexation constants.

[81BIL]

Absorption spectra (960 to 1020 nm) of Np(V) in 3.2 to 160 mM carbonate solutions have been measured at various pH values. They were not interpreted quantitatively in terms of aqueous species. There is no indication as to the pH electrode calibration, and it seems that the ionic strength was not constant. Therefore, only a rough quantitative reinterpretation is possible (also see [98VIT/CAP]). A 0.808 mM NpO_2^+ solution did not show any spectral change up to pH = 5.30 in 20 mM CO_3 solution. In 16 mM carbonate solution ($\log_{10}[\text{CO}_3^-] = -4.8$), at pH = 7.10, the characteristic peak for $\text{NpO}_2\text{CO}_3^-$ [90RIG] had appeared and the intensity of the NpO_2^+ peak was reduced by a factor of 4.3. Hence $\log_{10} K_1 = (5.5 \pm 0.5)$. At pH 9.75 in 8 mM carbonate solution ($\log_{10}[\text{CO}_3^-] = -1.8$) the characteristic band for $\text{NpO}_2(\text{CO}_3)_2^{3-}$ [90RIG] appeared, and the peak for $\text{NpO}_2\text{CO}_3^-$ nearly disappeared, thus $\log_{10} K_2 > 2$. Another experiment at pH > 11.1, where $[\text{CO}_3^-]$ is less in doubt, leads to $\log_{10} K_2 = (2.5 \pm 0.5)$. The characteristic band for $\text{NpO}_2(\text{CO}_3)_3^{5-}$ in 0.16 M is less than in 0.018 M carbonate solution. If this is due to $\text{NpO}_2(\text{CO}_3)_3^{5-}$ formation [90RIG] then $\log_{10} K_3 = (1.4 \pm 1)$. These values are not in particularly good agreement with those proposed in this review, probably because the estimates of the free carbonate concentrations are not sufficiently accurate (because of the poor experimental methodology and measurements). The results from this study were not used in the data selection in the present review.

[81LUN/HUL]

The work was done using a procedure described in [81LUN]. Hydration numbers for actinide(III) ions are 13-17 (inner plus outer sphere). For the lanthanide(III) ions in water the inner sphere hydration number is 9 for La-Nd, 8.5 for Sm-Gd, and 8 for Dy-Yb. The outer sphere numbers are, correspondingly, *ca.* 4, *ca.* 5 and *ca.* 6. All experiments were carried out at pH < 1 in 1 M Na(H)ClO₄. Some ion-pair metal perchlorate formation constants are given (estimated at zero ionic strength) but these values are not used in the present review.

[81PAT/RAM]

This is an extended abstract with few experimental details. No data are provided. The authors used a solvent extraction technique with HTTA and sodium dinonylnaphthalenesulphonate (NaDNNS) in benzene. Interesting results are provided for Np(V)- SO_4^{2-} complexing at I = 8.5 M, but there is no easy way of correcting the value for comparison to values obtained at lower ionic strengths.

In the case of Np(IV) iodide complexation, the aqueous phase contained 1 M H^+ at an ionic strength of 2 M (maintained by using perchlorate as an inert anion), and HTTA was used as extractant. The concentrations of iodide were 0.0, 0.4, 0.6, 0.8

and 1.0 M. The authors corrected the resulting value of $\beta_1(\text{NpI}^{3+}) = 0.8$ for aqueous TTA complexes and obtained $\beta_1(\text{NpI}^{3+}) = 1.1$. There is no obvious reason to discard the reported formation constant, and since it is not completely clear if this study is independent of the one presented in [79KUS/GAN], we increase the uncertainty. In our evaluation we use $\log_{10} \beta_1(\text{NpI}^{3+}, I = 2 \text{ M}) = (0.04 \pm 0.30)$. The authors also reported solvent extraction results on nitrate complexation of Np(V) at 25°C, again using NaDNNS in benzene. The aqueous phase had a very high ionic strength ($I = 8.5 \text{ M}$) using an unspecified electrolyte (probably sodium perchlorate) at $\text{pH} = 3-4$. For the nitrate complex of Np(V) the value of the constant reported is exactly the same as the one reported in [79RAO/GUD] with the same experimental conditions but $I = 2 \text{ M}$. The measured changes in the distribution coefficient are better explained as resulting from activity coefficient changes rather than from the formation of a complex.

[81RAI/SWA]

The experimental work shows that the plutonium(IV) polymer seems to have solubility properties intermediate between those of $\text{Pu}(\text{OH})_4$ and PuO_2 . The Pu(IV) polymer does not seem to form stable suspensions at pH values above 5.

[81VOL/VIS]

This work is an extension of the previous paper [81VOL/VIS4] about the exchange of simple cations with $\text{MO}_2^+(\text{V})$ cations. As is the case for this previous publication, [81VOL/VIS4], the discussion proposed in this paper was not supported by sufficient experimental verification.

[81VOL/VIS2]

Hydrated $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$, $\text{Na}_4\text{NpO}_2(\text{CO}_3)_{2.5}(\text{s})$, and $\text{Rb}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ were precipitated in (respectively) 0.3 to 1.7, 2.4 M Na_2CO_3 and 1 to 3.8 M Rb_2CO_3 solutions. The X-Ray powder diffraction patterns of these solids were obtained and reported. This review concludes the X-ray diffraction pattern shown for $\text{Na}_4\text{NpO}_2(\text{CO}_3)_{2.5}(\text{s})$ could be interpreted equally well as resulting from a poorly crystallised hydrate (also see [98VIT/CAP]).

[81VOL/VIS3]

Crystal structures for hydrated $\text{M}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ ($\text{M} = \text{Na}, \text{K}, \text{Rb}$) are proposed based on powder X-ray crystallographic data. They are not exactly isostructural, but all have layers containing Np atoms, with the CO_3^{2-} ions being bidentate. This Np(V)-containing layer also incorporates one third of the alkali metal cations. The rest of the alkali metal ions go into interlayer positions, and are susceptible to ion exchange (as is also the case for the Na^+ ions in $\text{NaNpO}_2\text{CO}_3(\text{s})$) [79VOL/VIS2, 98VIT/CAP] (cf. the discussion of [84VIT] in this appendix).

The difference in structure could explain the relatively slow transformation of $\text{NaNpO}_2\text{CO}_3(\text{s})$ to $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ [66GOR/ZEN].

[81VOL/VIS4]

This is a general discussion of the work about actinide(V) carbonate solid compounds in the nine previous publications of this series [74SIM/VOL, 74VIS/VOL, 74VOL/KAP, 74VOL/KAP2, 77VOL/VIS, 79VOL/TOM, 79VOL/VIS2, 81VOL/VIS2, 81VOL/VIS3]. $\text{NaNpO}_2\text{CO}_3(\text{s})$ is no longer proposed as isostructural to rutherfordine [79VOL/VIS2]; but there is no additional experimental evidence for the new interpretation. The general explanation of the structure changes seems reasonable; but some of the results were not confirmed. Some of the proposed non-stoichiometric solid compounds may have been kinetic artefacts. Only one possible non-stoichiometric compound was proposed [79VOL/VIS2], but this study was not completely convincing ([84VIT, 98VIT/CAP] and discussion of [79VOL/VIS2, 84VIT] in this appendix). Later Np(V) solubility studies in sodium carbonate/bicarbonate media showed no evidence of non-stoichiometric compounds.

[81WES/SUL]

Np(V) was electrolysed in 1 M carbonate and in 1 M bicarbonate solutions by controlled potential electrolysis at -1.8 V to produce Np(IV). Water was also partially reduced. Only the use of a platinum electrode was reported, but almost certainly a mercury electrode was used. The same methodology was used later [84VAR/HOB] with some difficulties. One Np(IV) absorption spectrum in 1 M Na_2CO_3 or NaHCO_3 solution is reported. The spectrum does not vary from pH 8.3 to 11.2 and is the same as has been reported elsewhere [77SAI/UEN, 84VAR/HOB, 93LI/KAT, 95VIT, 96DEL/VIT] for Np(IV) in concentrated carbonate media. This is evidence, that a limiting complex is formed under these conditions. The measurements by Fedosseev *et al.* [79FED/PER] were carried out under similar conditions. No thermodynamic data and no stoichiometry can be deduced from this work.

The redox potential of the Np(VI)/Np(V) couple was measured in 1 M Na_2CO_3 and 1 M NaHCO_3 solutions. The authors stated that their measurement, 0.221 V/S.C.E., was in very good agreement with previous work [74SIM/VOL, 77SIM]. Only the value reported for a 1 M Na_2CO_3 medium, is consistent with the value proposed in the present review (also see [98VIT/CAP]). The Na^+ concentration and ionic strength were different in the different buffer media, and therefore a difference would be expected between potentials measured in the different media. The authors did not report nor discuss such differences, and also may not have taken the junction potentials into account. For these reasons, the value from this paper was not used in the present review.

[82ALC/ROB]

This paper does not contain any thermodynamic data for review. It reports excellent structural information concerning the solid phase $2\text{NpO}_2\text{SO}_4 \cdot \text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}(\text{s})$.

[82MOR/FUG]

This paper reports a determination of the enthalpy of formation of $\text{Ba}_2\text{MgNpO}_6$. The enthalpy of formation of MgCl_2 in 1 M HCl is calculated from the CODATA [89COX/WAG] values for Mg^{2+} and Cl^- and the difference ($5.86 \text{ kJ}\cdot\text{mol}^{-1}$) in the enthalpies of solution of $\text{MgCl}_2(\text{cr})$ in 1 M HCl and in water reported by Shin and Criss [79SHI/CRI]. The reported enthalpy of reaction of $\text{Ba}_2\text{MgNpO}_6$ with 1 M HCl is used with this and other auxiliary data selected in the present review (see Chapter 13 and the entry for [83MOR/WIL] in Appendix A) to obtain $\Delta_f H_m^\circ(\text{Ba}_2\text{MgNpO}_6, \text{cr}, 298.15 \text{ K}) = -(3096.9 \pm 8.2) \text{ kJ}\cdot\text{mol}^{-1}$.

[82NAI/CHA]

Hydrolysis constants were determined by potentiometric titration (“Bjerrum-Calvin pH titration technique”) for trivalent Pu, Am, Sm and Eu in 1 M NaClO_4 . Data analysis using the method of weighted least squares was a Bjerrum type analysis (\bar{n} functions). The calculated curves deviate systematically from the experimental points for Pu(III), but less so for Am(III), and are quite good for Sm(III) and Eu(III). Results are reported in Table A.10.

Table A.10: Hydrolysis constants for trivalent Pu, Am, Sm and Eu as given by [82NAI/CHA].

Metal ion	${}^*\beta_1$	${}^*\beta_2$	$-\log_{10}{}^*\beta_1$	$-\log_{10}{}^*\beta_2$
Pu(III)	$2.75 \pm 0.16 \times 10^{-6}$		5.56 ± 0.03	
	$2.85 \pm 0.17 \times 10^{-6}$		5.54 ± 0.03	
Am(III)	$9.32 \pm 0.94 \times 10^{-8}$		7.03	
Sm(III)	$1.46 \pm 0.06 \times 10^{-9}$	$1.85 \pm 0.16 \times 10^{-16}$	8.84	15.73
Eu(III)	$7.59 \pm 0.30 \times 10^{-9}$	$3.55 \pm 0.33 \times 10^{-16}$	8.12	15.45

The points in Fig. 1 and 2 of [82NAI/CHA] indicate that the errors should be considerably larger for Pu than given in the table. In the case of Pu and Am the total metal concentrations were $\leq 0.04 \text{ mM}$, and polymer formation was unlikely. The approach and technique seem very good, and the results, as shown in the figures appear significant. The discrepancy between the Pu and the Am data seems too large. For Pu, the discrepancy between the calculated curve and experimental data is substantial. This indicates the plutonium solution may not have been pure Pu(III), but perhaps contained some Pu(IV). This would explain the differences. Therefore the values are rejected in the present review.

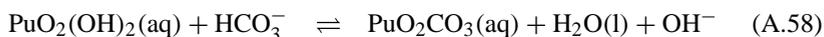
[82PER/SPI]

The Np(VI)/Np(V) redox potential was found to be approximately constant in aqueous 1 to 15 M NaOH solutions. This agrees with the results of Simakin *et al.* [73SIM/MAT], but not with previous work of one of the authors [74PER/ALE].

[82SUL/WOO]

Spectrophotometric and calorimetric data were used to calculate the stability constants for complexes with $\text{PuO}_2^{2+}:\text{CO}_3^{2-}$ ratios of 1:1 and 1:2. On the basis of the observation that initial and final pH values of the solutions were the same and the initial form of Pu(VI) was $\text{PuO}_2(\text{OH})_2(\text{aq})$ at pH = 8.3, the 1:1 complex was assumed to be of the form $\text{PuO}_2\text{OHCO}_3^-$. This is not a necessary conclusion. Sufficient HCO_3^- was added to convert all of the $\text{PuO}_2(\text{OH})_2(\text{aq})$ to $\text{PuO}_2(\text{CO}_3)_2^{2-}$ with no impact on the final pH.

By analogy to the stoichiometry for the corresponding carbonate complexes of UO_2^{2+} and NpO_2^{2+} , the reported equilibrium constant ($\beta_1(I = 0.1) = 463 \pm 60$, ($\log_{10} \beta_1 = 2.67 \pm 0.60$)) was determined spectrophotometrically and is assumed to refer to the following reaction



As there is no change in the net charge for this reaction, the extrapolation procedure yields a standard state formation constant identical to that reported for 0.1 M.

At 0.1 M ionic strength and pH = 8.3 the equilibrium constant for the reaction



is reported as $\log_{10} \beta_2 = 4.36 \pm 1.00$.

The enthalpy of the reaction is taken: (1) from the temperature dependence of the stability constant measured spectrophotometrically, $-(6.3 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$ (data re-evaluated by the reviewers) and (2) from the calorimetric results, $-(1.46 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$.

The mean of these values with the uncertainties expanded to include the range from both values, $-(3.9 \pm 4.8) \text{ kJ}\cdot\text{mol}^{-1}$, is used by this review.

[82WES/MUL]

The paper describes the preparation, X-ray powder pattern and visible and near-IR spectra of $\text{Np}(\text{OH})_2\text{SO}_4$. Although the compound is well characterised structurally, there are no thermodynamic data useful for this review.

[83HAL/OLI]

This describes a thorough extraction study of sulphate complexation of Np(V) using HDNNS in *n*-heptane. Experiments were performed at $I = 0.5, 1.0$ and 2.0 M and $t = 5, 25$ and 45°C . Insufficient data have been provided for the results to be recalculated, and the reported values are used here. It is unclear whether the reported uncertainties reflect 1σ or 2σ . We assume 1σ . Only monosulphate complexes were observed. All $[\text{SO}_4]_{\text{T}}$ was assumed to be $[\text{SO}_4^{2-}]$. This is a reasonable assumption over the pH range of the experiment (4 to 7). The data at 25°C can be used in the assessment of the best values, and enthalpies of reaction can be calculated using the remaining results.

[83HEL]

The paper describes an X-ray diffraction study of compounds of the form $M_2NpO_2SO_4 \cdot xH_2O(s)$ and $M_2NpO_4(s)$ where $M = Cs$ or Rb and $x = 10, 4,$ and 0.5 . The most highly hydrated forms were precipitated from room temperature solutions and the dehydrated forms prepared on heating. Other compounds described are: $K_2NpO_2(SO_4)_2 \cdot H_2O(s)$, $Na_2NpO_2(SO_4)_2 \cdot H_2SO_4 \cdot 7H_2O(s)$, $Na_2NpO_2(SO_4)_2(s)$, $(NpO_2)_2SO_4(s)$, $(H_3O)_2Na_2NpO_2(SO_4)_3 \cdot 2H_2O(s)$, $Na_2NpO_2(SO_4)_2 \cdot H_2SO_4(s)$, $NH_4HNpO_2(SO_4)_2 \cdot 3H_2SO_4(s)$, $(NH_4)_2NpO_2(SO_4)_2 \cdot 3H_2SO_4 \cdot 4H_2O(s)$, $NpO_2SO_4 \cdot H_2SO_4 \cdot 6H_2O(s)$, and $NpO_2SO_4 \cdot H_2SO_4 \cdot 2.5H_2O(s)$. Bulk analyses and water content were provided for some of these solids and X-ray diffraction peak heights for most. Comparison was made to analogous U compounds. There are no thermodynamic data useful for this review.

[83KIM/LIE]

The results on complexation of Pu(IV) in carbonate-bicarbonate solutions were obtained from a series of solubility studies of $^{238}PuO_2(s)$ at a constant ionic strength of 1.0 at room temperature (probably $20^\circ C$). The solubilities are given as a function of pH that varied from 2 to 10 (the higher pH values were fixed by the ratio of CO_3^{2-}/HCO_3^-) and were measured after equilibration periods of 4 to 12 months. Spectrophotometric evidence supports the contention that Pu(IV) was the predominant oxidation state in the initial solutions, but the oxidation state later in the experiment was not confirmed. The stability of the initial solid phase ($^{238}PuO_2(s)$ prepared from the amorphous hydroxide calcined at $700^\circ C$ for 6 hours) was not verified during the experiment and the authors postulated that an alternative phase, $Pu(OH)_2CO_3(s)$, might have been the solubility limiting phase in these experiments. No verification of the identity of the phase was made. The authors were aware that radiation effects on the solutions could give rise to ambiguities in the interpretation of the solubility data and they considered the calculated values to be "preliminary". Polymers, which may have formed in the course of some of the experiments, especially at low total CO_3^{2-} concentrations, were not considered by the investigators. The data describing Pu(IV) hydrolysis was taken from Baes and Mesmer [76BAE/MES]. The data were interpreted as resulting from a sequence of carbonate complexes up to the pentacarbonato complex, and included one mixed hydroxycarbonate, $PuOHCO_3^+$. The stability of plutonium carbonate was taken as given in the work of Moskvin and Gelman [58MOS/GEL] and, as a result, all of the remaining calculated values were biased by this ill-chosen value (see comments in this appendix for [58MOS/GEL]). Unfortunately, no attempt was made to perform a sensitivity analysis which would have permitted some of these candidate complexes to be eliminated. In the absence of the original data, we cannot perform these calculations ourselves. We therefore give zero weight to the calculated values of stability constants for these Pu(IV) carbonate complexes. However, the observed rapid increase in plutonium solubility in high carbonate solutions is strong evidence that the limiting species is at least a tri-carbonato species.

[83MAR/HOF]

The paper reports the preparation and X-ray powder patterns of members of the $\text{NH}_4(\text{U, Pu})\text{O}_2(\text{CO}_3)_3(\text{s})$ solid solution series. Heats of formation of solid compounds were calculated, but no stability constants measured or estimated.

[83MAY]

After Simakin's paper in 1977 [77SIM] that established the stoichiometry of the Np(V) carbonate limiting complex, this is the first reliable work from which the stability of the soluble carbonate complexes could be calculated. This review used this experimental work and followed most of the interpretation of the author to select thermodynamic data.

The solubility of $\text{NaNpO}_2\text{CO}_3(\text{s})$ was measured at $8.08 < -\log_{10}[\text{H}^+] < 10.99$, and for different partial pressures of $\text{CO}_2(\text{g})$ in 1.0 M NaClO_4 . The pH electrode was properly calibrated in concentration units ($-\log_{10}[\text{H}^+]$ and not pH). The solid phase, $\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}(\text{s})$, was aged for 8 days, was analysed to establish its Np(V): CO_3^{2-} ratio and was characterised from its X-ray diffraction pattern. An attempt was made to independently vary the hydroxide and free carbonate concentrations. The formation constants as reported by the author and those recalculated in the present review are shown in Table A.11.

Table A.11: Results from refitting Maya's solubility data for Np(V) in carbonate solutions.

	[83MAY] values	Recalculated values
$\log_{10} K_{s,1}$	$-(10.14 \pm 0.04)$	$-(10.12 \pm 0.35)$
$\log_{10} \beta_1$	(4.49 ± 0.06)	(4.57 ± 0.35)
$\log_{10} \beta_2$	(7.11 ± 0.07)	(7.03 ± 0.24)
$\log_{10} \beta_3$	(8.53 ± 0.09)	(8.52 ± 0.41)
$\log_{10} {}^*\beta_1$	$-(9.12 \pm 0.15)$	$-11^{(a)}$
$\log_{10} {}^*\beta_2$		$-23^{(a)}$
1.96σ	0.104	0.097

^(a) fixed value.

The author also measured $\log_{10} {}^*K_1 = (9.55 \pm 0.02)$ and $\log_{10} {}^*K_2 = (6.03 \pm 0.04)$ for protonation of carbonate in the perchlorate medium. There are small differences between these values and those used in the present review, (9.59 ± 0.05) and (6.13 ± 0.05) , and in how effects of ionic strength on calibration were handled, however this was found to have no effect on values of the final calculated formation constants and solubility product.

In the paper " $-\log_{10} Q_{\text{H}} = (9.12 \pm 0.15)$ " was reported, whereas initial reanalysis in this review yielded a value of $\log_{10} {}^*\beta_1 = -9.47$. Furthermore, no significant change to the other fitted equilibrium constants, or to the value of χ^2 , resulted even if a fixed

value of $\log_{10}^*\beta_1 = -11.5$ was used. Therefore, in this review, it is concluded that the first hydrolysis constant of NpO_2^+ is not well defined by the data in [83MAY], and it was not included in the final set of fitted constants.

There are some other minor problems or potential problems with this paper. The solid $\text{NaNpO}_2\text{CO}_3 \cdot 3.5\text{H}_2\text{O}(\text{s})$ may not have been as well-characterised as supposed, because several complicated X-ray diffraction patterns of general formula $\text{NaNpO}_2\text{CO}_3 \cdot x\text{H}_2\text{O}(\text{s})$ or $\text{Na}_{0.6}\text{NpO}_2(\text{CO}_3)_{0.8} \cdot x\text{H}_2\text{O}(\text{s})$ have been published, and there are indications [81VOL/VIS4] that well crystallised material is difficult to obtain (X-ray analysis was performed before, and not after, solubility equilibration, and thus solid phase transformations during the equilibration of the initial solid with the aqueous solution could not be detected. A similar study with many more experimental points [84VIT, 86GRE/ROB, 98VIT/CAP] indicates that this type of phenomenon is possible, and also that $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ is the thermodynamic stable phase when $[\text{CO}_3^{2-}] > 0.01 \text{ M}$.

There are too few experimental points to know from statistical error analysis whether the solubility product law could be verified, and too few experimental points were presented to perform a proper statistical error analysis. The sensitivity analysis was based on the fact that solubilities were essentially dependent only on $[\text{CO}_3^{2-}]$ even when the carbon dioxide gas partial pressure was varied within the same batches. This procedure would have been more convincing if details had been given concerning the calculation of $[\text{CO}_3^{2-}]$ and $[\text{HCO}_3^-]$ from the measured $-\log_{10}[\text{H}^+]$ values. Also, because the low $-\log_{10}[\text{H}^+]$ values and high $[\text{CO}_3^{2-}]$ values were strongly correlated, a proper sensitivity analysis for formation of $\text{NpO}_2(\text{CO}_3)_2^{3-}$ and $\text{NpO}_2(\text{CO}_3)_3^{5-}$ was not possible. Finally, the method is incapable of determining whether the solution species are polymeric.

But, as stated above, these problems are relatively minor. There is evidence from later work (e.g., [90RIG]) that Maya's interpretation was correct. There is very little other work in this field based on correct experimental procedures, especially with properly measured pH values.

[83MOR/WIL]

The enthalpy of reaction of $\text{Sr}_3\text{NpO}_6(\text{cr})$ with 1 M HCl and the reaction cycles from this paper are used to recalculate $\Delta_f H_m^\circ(\text{Sr}_3\text{NpO}_6, \text{cr}, 298.15 \text{ K}) = -(3125.8 \pm 5.9) \text{ kJ} \cdot \text{mol}^{-1}$ using CODATA compatible data based on Busenberg, Plummer and Parker [84BUS/PLU, 89COX/WAG], and this value is accepted in the present review. The value $\Delta_f H_m^\circ(\text{NpO}_2^+, 1 \text{ M HCl}, 298.15 \text{ K}) = -(858.3 \pm 5.3) \text{ kJ} \cdot \text{mol}^{-1}$ used in these calculations is based on an estimated enthalpy of transfer from water of $(2.4 \pm 2.4) \text{ kJ} \cdot \text{mol}^{-1}$. The enthalpy of formation of $\text{Ba}_3\text{NpO}_6(\text{cr})$ is recalculated to be $-(3085.6 \pm 9.6) \text{ kJ} \cdot \text{mol}^{-1}$ using $\Delta_f H_m^\circ(\text{BaCl}_2, \text{cr}, 298.15 \text{ K}) = -(855.15 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$ (see Section 13.2.1) and the enthalpy of solution of $\text{BaCl}_2(\text{cr})$ in 1.0 M aqueous HCl as determined (1.0109 M) by Cordfunke, Konings and Ouweltjes [90COR/KON].

[83NAS/CLE]

This describes the results of a TTA extraction study of Pu(IV) complexation with sulphate in 1 M and 2 M H^+ , but 2 M (ClO_4 , HSO_4) ionic strength, at 10, 25, and 35°C. No data were provided to independently estimate errors. The data reduction procedure uses a more appropriate non-linear (quadratic) regression model to estimate thermodynamic parameters and errors. In our re-evaluation of the results of other authors we have used this quadratic model. The authors interpret their data to indicate that one of the ligands is not deprotonated. We have recalculated their results on the basis of deprotonation of all ligands. $\Delta_r H_m^\circ$ (19.4) = (18.6 ± 0.6) $\text{kJ}\cdot\text{mol}^{-1}$ and $\Delta_r H_m^\circ$ (19.5) is indistinguishable from 0. The results in [83NAS/CLE2] concerning Pu(IV) recapitulate the results reported here.

[83NAS/CLE2]

The sulphate complexation experiments with Pu(III) involved ion exchange at 2.7, 10, 16.5, and 25°C in 1 and 2 M H^+ , but at 2 M ionic strength (ClO_4 , HSO_4). The predominant isotope was ^{239}Pu and the plutonium oxidation state was verified at the end of each experiment. Example data on which to base error estimates were provided for the Pu(III) experiments, and 1σ errors were reported for all thermodynamic parameters. Additional data was provided by Dr. Nash. A different (and probably more appropriate) statistical approach is used by [83NAS/CLE2] to calculate association quotients than is used by other authors performing similar experiments. The [83NAS/CLE2] procedure correctly weights the individual distribution measurements over the whole range of SO_4^{2-} concentrations. The results of this analysis suggested to the author that PuSO_4^+ and $\text{PuSO}_4\text{HSO}_4(\text{aq})$ are the principal complexes in strong acids. A reanalysis of the results of this experiment indicates that the data are also consistent with the formation of $\text{Pu}(\text{SO}_4)_2^-$ in lieu of $\text{PuSO}_4\text{HSO}_4(\text{aq})$. Our reanalysis gives $\log_{10} \beta_2(I = 2.2 \text{ m})$ and using $\varepsilon = (0.32 \pm 0.20)$ $\text{kg}\cdot\text{mol}^{-1}$, $\log_{10} \beta_2^\circ$, see Table A.12.

Table A.12: Values of the formation constant of $\text{Pu}(\text{SO}_4)_2^-$ from the reaction of Pu^{3+} with HSO_4^- based on a recalculation of the results of Nash and Cleveland [83NAS/CLE2].

t (°C)	H^+ (M)	I (m)	$\log_{10} \beta_2(I)$	$\log_{10} \beta_2^\circ$
2.7	1	2.2	(0.59 ± 0.09)	(1.70 ± 0.24)
10.0	1	2.2	(0.51 ± 0.18)	(1.64 ± 0.29)
16.5	1	2.2	(0.42 ± 0.22)	(1.56 ± 0.31)
25.0	1	2.2	(0.11 ± 0.20)	(1.28 ± 0.30)
25.0	2	2.2	(0.25 ± 0.26)	(1.42 ± 0.39)

On the basis of the first four results at $I = 2.2$ m (under identical pH conditions), $\Delta_r H_m^\circ(2) = (-33 \pm 16)$ $\text{kJ}\cdot\text{mol}^{-1}$.

For a discussion of the results on the Pu(IV) sulphate system presented in the same paper, see the Appendix A discussion of [83NAS/CLE].

[83SCH/GOR]

a) Neptunium

The authors have studied hydrolysis of Np(VI) by the pulse radiolysis transient conductivity technique for solutions with pH values between 2.2 and 6.5. Only the first hydrolysis step is considered in their analysis. Both the oxidation of Np(V) to Np(VI) and the reduction of Np(VI) to Np(V) were considered. The resultant values for \log_{10}^*K were similar, 5.5 and 5.4, respectively. The high pH results from the reduction experiments may be suspect because the results of Cassol *et al.* [72CAS/MAG2] suggest polymer formation becomes important in the 5×10^{-4} M Np(VI) solutions between pH values of 4 and 5. Indeed, in Figure 6 of reference [83SCH/GOR], the curve fit to the data is poor above pH 4.5.

b) Plutonium

The authors have studied hydrolysis of Pu(VI) by the pulse radiolysis transient conductivity technique. A limited set of experiments for the reduction of Pu(VI) yielded a value for $\log_{10}^*K_{11}$ of 6.3. As in the case for the experiments on neptunium, this assumes no polymer formation below a pH value of 5 for the 5×10^{-4} M solution of $\text{PuO}_2(\text{ClO}_4)_2$. This assumption is open to debate (see Part IV, Section 17.1.1).

[83WES/SUL]

Spectra were presented for Pu(VI) and Pu(IV) in 1 M NaHCO_3 and Pu(V) in 1 M Na_2CO_3 . For Pu(VI) the spectra in NaHCO_3 and Na_2CO_3 were reported to be identical. The values for the reduction potentials of the Pu(VI)/Pu(V) couple (0.11 V vs. SCE or 0.352 V vs. SHE) and for the Pu(IV)/Pu(III) and Pu(V)/Pu(III) couples (-1.0 V vs. SCE or -0.76 V vs. SHE) are in reasonable agreement with other published results (see the tabulation in [86LIE/KIM]). There is insufficient information about the experimental details in this short publication to make an accurate assessment of the uncertainties. For the purposes of the present review the uncertainties are assumed to be ~ 0.1 V (2σ).

[84BLA/MAD]

Blanc and Madic determined the thermal temperature coefficients $(dE/dT)_{\text{therm}}$ of the $\text{NpO}_2^{2+}/\text{NpO}_2^+$, $\text{PuO}_2^{2+}/\text{PuO}_2^+$, $\text{Np}^{4+}/\text{Np}^{3+}$ and $\text{Pu}^{4+}/\text{Pu}^{3+}$ redox couples. Potential differences were determined in a cell with two platinum electrodes that had temperature gradients imposed on them. The values determined for the thermal and isothermal temperature coefficient of the standard potentials, and for $\Delta_r S^\circ$ are given in Table A.13. The variations of the values of $\partial E/\partial T$ as a function of ionic strength for the (IV/III) couples are rather strange (especially for Np, where there may have been problems maintaining the oxidation state ratio). The thermoelectric powers for the (VI/V)

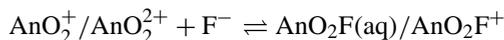
Table A.13: Values of temperature coefficients for standard potentials from Blanc and Madic [84BLA/MAD].

	$(\partial E^\circ/\partial T)_{\text{therm}} / \text{V}\cdot\text{K}^{-1}$	$(\partial E^\circ/\partial T)_{\text{isotherm}} / \text{V}\cdot\text{K}^{-1}$	$\Delta_r S^\circ / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
Pu ⁴⁺ /Pu ³⁺	$\sim (0.0021 \pm 0.0004)$	$\sim (0.0019 \pm 0.0004)$	(183±39)
Np ⁴⁺ /Np ³⁺	$\sim (0.0021 \pm 0.0004)$	$\sim (0.0019 \pm 0.0004)$	(183±39)
PuO ₂ ²⁺ /PuO ₂ ⁺	0.00085	0.00065	
NpO ₂ ²⁺ /NpO ₂ ⁺	0.00043	0.00023	

couples at I=1 are approximately +0.2 and +0.6 mV.K⁻¹ for Np and Pu respectively. Blanc and Madic then claimed values of +0.43 and +0.85 mV.K⁻¹ for I=0. Using the authors' equation 5 [59DEB/LIC] leads to values of $\partial E^\circ/\partial T$ of +0.23 and +0.65 mV.K⁻¹ as in the table above. In the present review, because of the cycles used, a more useful value would be $\partial E^\circ/\partial T(1 \text{ M HClO}_4)$. Based on the graphs in the paper, the values of $(\partial E^\circ/\partial T)$ might be expected to be approximately 0.0 and +0.4 mV.K⁻¹, respectively, for the Np and Pu couples. These values differ by no more than 0.5 mV.K⁻¹ from those determined from measurements of the potentials at different temperatures (*cf.* Figure 16.1), but the theoretical basis for the thermoelectric power values is not as strong. Therefore, the values of Blanc and Madic [84BLA/MAD] are not used in in this review in determining the selected values of the entropies for the aqua ions.

[84CHO/RAO]

The authors used a solvent extraction technique to determine the formation constants of UO₂F⁺ and NpO₂F(aq) and a potentiometric method with a fluoride ion selective electrode to determine the formation constants of UO₂F⁺, NpO₂F⁺ and PuO₂F⁺. All results refer to the following type of reaction (An=actinide):



The experiments were carried out at 23°C, at pH = 2.96 and at a constant ionic strength of 1 M (NaClO₄). Apparently, the two independent results of Choppin and Rao for UO₂F⁺ were missed in the uranium review of the present series [92GRE/FUG]. The formation constants, $\log_{10} \beta_1(\text{UO}_2\text{F}^+, I = 1 \text{ M})$, were reported by Choppin and Rao [84CHO/RAO] as (4.52 ± 0.10) from solvent extraction and (4.70 ± 0.07) from potentiometry. The first value is fully consistent with the selection of the uranium review [92GRE/FUG], while the second one is slightly higher. The authors did not mention what value they used for the protonation constant of fluoride, and this could be the source of a small error, but is insufficient to explain the difference. However, the results of this study seem to be reliable, and we include the following values in our selection procedure in Parts III and IV, Sections 9.2.1.3, 9.1.2.4 and 18.2.1.4: $\log_{10} \beta_1(\text{NpO}_2\text{F}^+, I = 1 \text{ M}) = (4.27 \pm 0.15)$, $\log_{10} \beta_1(\text{PuO}_2\text{F}^+, I = 1 \text{ M}) = (4.22 \pm 0.20)$, and $\log_{10} \beta_1(\text{NpO}_2\text{F, aq}, I = 1 \text{ M}) = (1.26 \pm 0.30)$. We have increased the re-

ported uncertainties by a factor of 2.5 to 3 to take account of the unknown protonation constant used for fluoride ion and the fact that small proportions of 1:2 complexes of actinide(VI) may have been present at higher fluoride concentrations.

[84KAS/JOS]

In this study the potential difference (with respect to the calomel electrode) required to reduce Np(VI) to Np(V) was recorded as a function of HF(aq) or HSO_4^- concentration. The study was carried out at 23°C (“room temperature”) in 0.5 M HClO_4 ($I = 0.5$ M) (and also in 0.5 M $\text{HClO}_4 + 0.5$ M NaClO_4 ($I = 1$ M) for the fluoride complexation measurements). The authors assumed that no Np(V) complexes were formed in the course of the experiments. It should be mentioned that precipitation of KClO_4 (s) might occur at the liquid junction between the saturated calomel electrode and the HClO_4 solution, and that such a precipitation will influence the measured potentials. However, this systematic error cancels to some extent since no absolute values were used but only potential changes resulting from different ligand concentrations.

The HF(aq) concentrations used were 2.5×10^{-2} M, 5×10^{-2} M, 0.1 M and 0.15 M, and $[\text{Np}]_t = 5 \times 10^{-2}$ M. In addition, Np concentrations of 3×10^{-4} M and 1.2×10^{-3} M were used at the two lowest HF(aq) concentrations. The procedure is satisfactory. The proportion of the proposed 1:2 complex, NpO_2F_2 (aq), reached 18% at most, and the values reported for ${}^*\beta_2$ are thus less certain than those for ${}^*\beta_1$. We use these values in our evaluation in Part III, Section 9.2.1.4, and we assign uncertainties of ± 0.2 in $\log_{10} {}^*\beta_1$, and ± 0.4 in $\log_{10} {}^*\beta_2$.

Our recalculated association quotient for formation of NpO_2SO_4 (aq) is based on a linear least squares model. Given the range of reported experimental errors a non-linear approach does no better. There is no evidence for the disulphato complex. Recalculated errors have been increased slightly to account for possible errors in the estimation of the protonation constant for SO_4^{2-} .

[84KIM/BER]

This paper contains a set of solubility data for a solid initially identified as $\text{PuO}_2(\text{OH})_2$ (s), although the nature of the solid was not determined after the equilibration period of “several months”. The experiments were done using ${}^{238}\text{PuO}_2(\text{OH})_2$ (s) in 0.1 M NaClO_4 . The isotope ${}^{238}\text{Pu}$ has a half life shorter than that of ${}^{239}\text{Pu}$ by a factor of approximately 270, and both isotopes decay primarily through the production of 5 MeV α -particles. Thus, autoradiolysis would be expected to be much greater for ${}^{238}\text{Pu}$ than for ${}^{239}\text{Pu}$. It would be expected the oxidation state of the solution species, especially for solutions having relatively high ${}^{238}\text{Pu}$ concentrations, would no longer have been primarily Pu(VI) after the long equilibration period. The authors’ Figure 4 refutes this. Apparently trace quantities of chloride (and hence hypochlorite [93PAS/KIM]) were present as an impurity in the solutions, and this helped maintain the plutonium as Pu(VI), at all values of pH, despite the short half-life ${}^{238}\text{Pu}$ isotope having been used [94KIM]. Rai and Ryan [82RAI/RYA] also reported Pu(VI) as

the major solution species (along with Pu(IV) polymer) resulting from a mixing $^{238}\text{PuO}_2(\text{cr})$ with water for 1266 days.

However, there is a problem with the data analysis. It is not possible to mathematically distinguish contributions of different species having the same total charge. Thus the ratios of the concentrations of PuO_2^{2+} to $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ and PuO_2OH^+ to $(\text{PuO}_2)_x(\text{OH})_{2x-1}^+$ will remain constant at all values of pH. Kim *et al.* [84KIM/BER] proposed six species, and listed six equilibrium constants (including the solubility product). However, only four independent parameters (related to species having charges of two, one, zero and minus one) could be produced from their data analysis.

In Lierse and Kim [86LIE/KIM], the same results are shown with $\log_{10}[\text{Pu}]_{\text{TOT}}$ plotted against the pH value. The sum of the pH value plus the value of $-\log_{10}[\text{OH}^-]$ in [84KIM/BER] is 14.0, perhaps suggesting the hydroxide concentrations are actually activities. The later reference indicates values of $\log_{10} K_{s,0}$ and $\log_{10} \beta_1$ were fixed in the data analysis, using average values from the literature. If the reported constants are used to calculate the solubilities, a line with much less curvature is calculated than is shown in the diagram of either reference.

(NOTE: This set of comments was discussed with Professor Kim who concurred [94KIM]; also see [86LIE/KIM].)

Reanalysis of the data (Figure 3 of [84KIM/BER]) by a non-linear least squares treatment (equally weighted values of $\log_{10}[\text{Pu}]_{\text{TOT}}$) leads to the following equations:

$$\begin{aligned}\log_{10}[*K_{s,0} + 2*\beta_{22}*K_{s,0}^2] &= (6.915 \pm 0.182) \\ \log_{10}[*\beta_{11}*K_{s,0} + x*\beta_{(2x-1)x}*K_{s,0}^x] &= (1.337 \pm 0.050) \\ \log_{10}[*\beta_{21}*K_{s,0}] &= -(8.078 \pm 0.11) \\ \log_{10}[*\beta_{31}*K_{s,0}] &= -(20.04 \pm 0.16)\end{aligned}$$

In writing the equations derived from the reanalysis, PuO_2^{2+} , PuO_2OH^+ , $\text{PuO}_2(\text{OH})_2(\text{aq})$, $\text{PuO}_2(\text{OH})_3^-$ and $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ have been considered, as has one additional singly charged polymeric species (*e.g.*, $(\text{PuO}_2)_3(\text{OH})_5^+$ or $(\text{PuO}_2)_4(\text{OH})_7^+$). Although the data do not uniquely define the solubility product and hydrolysis constants for the system, these equations can be used to investigate the bounds on the values. For example, if $*K_{s,0} < 10^5$, $*\beta_{22} > 10^{-3.4}$ (*i.e.*, large enough $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ would be a major species even in low pH solutions – this has not been noted in spectrophotometric and potentiometric studies). Conversely, if $*\beta_{22} < 10^{-5.5}$, still a rather large value, $*K_{s,0} > 10^{6.0}$ ($K_{s,0} \approx 22$), a value lower than all the reported experimental values with the exception of the value $*K_{s,0} > 10^{6.3}$ derived from the work of Pashalidis *et al.* [95PAS/KIM].

[84LIE/KIM]

This is a report of a differential pulse polarographic study of Pu(IV)/Pu(III), Pu(III)/Pu(IV), Pu(VI)/Pu(V) and Pu(V)/Pu(III) couples in 1 M sodium carbonate solutions at 20°C. Plutonium solutions were prepared electrolytically and oxidation state speciation was confirmed by spectrophotometry. The values reported (identical

with those in [86LIE/KIM]) are in reasonable agreement with others. As none of these reported redox reactions are reversible (the exception is the Pu(VI)/Pu(V) [86LIE/KIM] but reversibility was not observed in this study), it is impossible to estimate stability constants of carbonate complexes using these data.

[84MAD/BEG]

This is a Raman spectroscopic study of the hydrolysis of dioxoplutonium(VI). Bands were tentatively assigned to the hydrolysis species $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ and $(\text{PuO}_2)_4(\text{OH})_7^+$. The higher hydrolysis species had a spectrum that did not appear similar to that of the uranium 5:3 species. Using the (room temperature ?) spectra for 0.1 M Pu(VI) in a 1.0 M ionic strength medium (0.26 M ClO_4^- , adjusted with NaCl), formation constants were calculated for the 2:2 and 7:4 species, although a value was also calculated assuming the 5:3 species was formed rather than the (spectroscopically) more reasonable 7:4 species. No evidence for a 1:1 hydrolysis species was found in these rather concentrated solutions. The nature of the hydrolysis species at high pH (13.3) was not established.

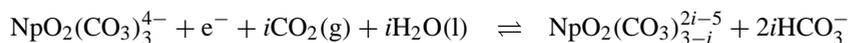
[84MAY]

The aim of this work was to deduce the speciation of Np(VI) in bicarbonate and carbonate aqueous solutions using potential measurements and potentiometric titrations. The author pointed out, that results obtained from the two different techniques were not in good agreement.

Maya did not use exactly the same values for the carbonate protonation constants as selected in the present review. However this does not result in major inconsistencies when comparisons are made between his results and the results of calculations carried out by Vitorge and Capdevila [98VIT/CAP].

a) Measurements of the potential of the Np(VI)/Np(V) couple

The author encountered a number of experimental difficulties (precipitation, irreversible electrode behaviour and lack of reproducible behaviour at the solid electrode) while measuring the potential of the Np(VI)/Np(V) redox couple. A saturated calomel reference electrode was used; but there was no mention of how the author estimated the junction potential. Therefore, in the present review, the uncertainties in the reported $E^{o'}$ values were increased by 30 mV. The potential measured in the most concentrated $[\text{CO}_3^{2-}]$ solution was constant, and its numerical value is consistent with the values observed of several other authors only if the uncertainty is increased. This potential increased with $\log_{10} p\text{CO}_2$ by (0.114 ± 0.019) , (0.110 ± 0.012) and (0.095 ± 0.016) mV/ $\log_{10} p\text{CO}_2$ units at 55, 27 and 14 mM of total alkalinity, respectively. This corresponds to (1.93 ± 0.16) , (1.85 ± 0.21) and (1.60 ± 0.28) CO_2 molecules exchanged with each electron. Slope analysis for potential *versus* alkalinity suggests these data can be interpreted in terms of the following equilibrium in bicarbonate media (where $[\text{HCO}_3^-] \approx$ alkalinity is constant in a wide domain for each set of experiments):



where i is between 1 and 2 (but closer to 2). This is consistent with Np(VI) and Np(V) chemistry: the complexes of Np(VI) are more stable than those of Np(V). The Np(V) limiting complex, $\text{NpO}_2(\text{CO}_3)_3^{5-}$, should dissociate at higher alkalinities before the Np(VI) complex.

Maya's calculations did not take into account the possible formation of $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$ [86GRE/RIG, 90RIG, 98VIT/CAP]. However, the redox measurements were carried out at very low total Np concentrations (approximately $2\mu\text{M}$), and neglecting this polynuclear species should, at worst, result in only a small systematic error.

In Maya's original calculations the formation constants for the tri- di- and mono-carbonato complexes of Np(V) were fixed, (from Maya's previous work for similar conditions [83MAY]), and his values are consistent with those selected in the present review. The model can reasonably predict the experimental data. The main explanation for the shape of the curve showing the variation of the redox potential, is the dissociation of the Np(V) limiting complex, $\text{NpO}_2(\text{CO}_3)_3^{5-}$, into $\text{NpO}_2(\text{CO}_3)_2^{3-}$, $\text{NpO}_2\text{CO}_3^-$ and NpO_2^+ . The values for the equilibrium constants for the dissociation equilibria for $\text{NpO}_2(\text{CO}_3)_3^{4-}$, have a relatively minor effect on the curve fitting. Therefore, one cannot rely on the results of such curve fitting.

There also are other possible systematic errors:

- The total Np(VI) concentrations are not known with any degree of accuracy.
- The possible formation of other (monomeric) Np(VI) hydrolysis species cannot be ruled out.
- The best fit to the data shows a systematic error at high carbonate concentration. This is a classical fitting artefact due to the small number of experimental data in these experimental conditions. The fitting does not distinguish between random scatter of the points and systematic deviations.

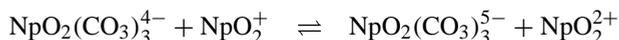
If the results for the high carbonate solutions are most heavily weighted, the (constant) formal potential $E_{\text{NpO}_2(\text{CO}_3)_3^{4-}/\text{NpO}_2(\text{CO}_3)_3^{5-}}^{\circ}$ of the reaction



is recalculated to be (0.4263 ± 0.044) V/SHE (the unweighted statistical "best fit" value is (0.445 ± 0.036) V/SHE). Within the (large) uncertainty, this value agrees with other values from the literature, (0.4615 ± 0.0035) V/SHE [77SIM] and (0.460 ± 0.017) V/SHE [95OFF/CAP]. The value of the formation constant of the Np(VI) limiting complex, β_3^{VI} , is obtained from the shift between the Np(VI)/Np(V) potential measured here ($E_{\text{NpO}_2(\text{CO}_3)_3^{4-}/\text{NpO}_2(\text{CO}_3)_3^{5-}}^{\circ}$) and its value in 1 M HClO₄ ($E_{\text{NpO}_2^{2+}/\text{NpO}_2^+}^{\circ} = (1.140 \pm 0.007)$ V/SHE) [89RIG/ROB]

$$\log_{10} \left(\beta_3^{\text{VI}} / \beta_3^{\text{V}} \text{ in } 1 \text{ M NaClO}_4 \right) = (12.06 \pm 0.75)$$

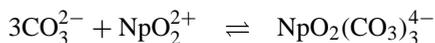
for



and finally using, as above, $\log_{10} \beta_3^V = (8.54 \pm 0.3)$ [83MAY]

$$\log_{10} \left(\beta_3^{VI} \text{ in } 1 \text{ M NaClO}_4 \right) = (20.59 \pm 0.76)$$

for



Fixing the $E^{\circ'}$ $_{\text{NpO}_2(\text{CO}_3)_3^{4-}/\text{NpO}_2(\text{CO}_3)_3^{5-}}$ value at (0.4263 ± 0.044) V/SHE instead of using the value from the best least-squares fit, has a relatively small effect on the value of $\log_{10}(\beta_3^{VI}/\beta_3^V \text{ in } 1 \text{ M NaClO}_4)$, but there is more influence on the values of the second and third ($\text{NpO}_2^{2+}/\text{CO}_3^{2-}$) dissociation constants. The value of $\log_{10}(\beta_2/\beta_3) = -(4.85 \pm 1.05)$ is changed to $-(5.72 \pm 1.96)$ and the value of $\log_{10}(K_2 \cdot K_3) = -(11.47 \pm 2.14)$ is changed to $-(11.14 \pm 1.97)$.

Hence,

$$\log_{10} \beta_1(1 \text{ M NaClO}_4) \leq (9.46 \pm 2.11)$$

$$\log_{10} \beta_2(1 \text{ M NaClO}_4) \leq (14.87 \pm 2.10)$$

The β_i values estimated here for Np(VI) are of the same order of magnitude as those of uranium, $\log_{10} \beta_1(1 \text{ M NaClO}_4) = (8.44 \pm 0.07)$, $\log_{10} \beta_2(1 \text{ M NaClO}_4) = (15.67 \pm 0.13)$ recalculated using values in [92GRE/FUG]. The value of β_3 is slightly smaller for Np(VI) than for U(VI), but the measurements of β_1 and β_2 are not accurate enough to demonstrate any differences between the U and Np systems. As already mentioned, the values of β_i/β_3 calculated here (and hence the β_i values deduced from them) are only rough estimates.

b) Potentiometric titrations of Np(VI) in carbonate media

Aqueous HClO₄ was added to a Np(VI) carbonate solution in which carbon dioxide gas, pre-equilibrated with an aqueous solution of the same ionic strength, was bubbling through the working solution to maintain a constant value of p_{CO_2} . The ionic strength was constant (1 M NaClO₄), and $\log_{10}[\text{H}^+]$ was measured with a glass electrode that had been calibrated using concentration standards. The author tried different models (sets of complexes) to interpret his potentiometric data, and using the known formation constants of some of the simple hydroxide complexes [72CAS/MAG2] as fixed parameters, gave the corresponding curve-fitting results. It was concluded that in addition to the known simple hydrolysis products, the limiting complex of Np(VI) reacted to form $\text{NpO}_2(\text{CO}_3)_2^{2-}$ and $(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$. Formation constants were calculated for these species. As mentioned by Maya, the curve-fitting results themselves, are not sufficient to determine a unique model or set of species. Independent qualitative chemical information was used to choose an interpretation, and the selected model was probably not correct for the following reasons:

First, the statistical analysis was not really correct because:

- The values of some fitted parameters were correlated, indicating some of the experimental parameters had not been varied sufficiently (approximately the same

total Np(VI) concentration was used for all the measurements, and too narrow a domain of CO₂(g) partial pressure was used).

- Calculations using different models did not result in clear differences in the overall least-square sum, \sum . Therefore, it is not clear (considering only the statistical results) whether other species exist or not.

Second, as observed by the author, the overall formation constants deduced from these potentiometric titrations do not agree with those deduced from the equilibrium potential measurement data. The values for only one of the pairs of stepwise constants, β_i/β_3 , are consistent.

Third, there are several problems in the selection of species or chemical problems that could cause small systematic errors.

- According to Maya, the final product of the titrations was NpO₂²⁺. The assumption was then made that NpO₂(CO₃)₂²⁻(aq) is a major intermediate product, but, surprisingly, not NpO₂CO₃(aq) which is the intermediate species between NpO₂(CO₃)₂²⁻ and NpO₂²⁺. Reanalyses of the equilibrium potential measurement data, and consideration of behaviour in the analogous uranium system indicate that NpO₂CO₃(aq) is probably stable over a broader range of conditions than NpO₂(CO₃)₂²⁻.
- Maya concluded (NpO₂)₃(CO₃)₆⁶⁻ was not important because slightly poorer fits to his data were obtained using models that included this species. However, based on later work, the stability of the species (NpO₂)₃(CO₃)₆⁶⁻ is now well established [86GRE/RIG, 90RIG]. The absorption spectrum of (NpO₂)₃(CO₃)₆⁶⁻ has been clearly detected [86GRE/RIG, 90RIG] in solutions similar to those used for Maya's measurements [84MAY].
- It has also been observed [86GRE/RIG, 90RIG] that, in contrast to the behaviour of the analogous solid in the U(VI) and Pu(VI) systems, precipitation of NpO₂CO₃(s) is quite slow. Recent solubility measurements [98VIT/CAP], suggest that some of Maya's solutions were probably supersaturated with respect to Np(VI). This might have introduced systematic deviations in the titration data; and there are no indications that the solutions were checked for possible precipitation or colloid formation [90RIG].

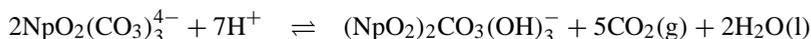
Any attempted reanalysis of the data is open to question because not all the data were provided in the original publication and because there are some inconsistencies and obvious typographical errors in the author's Table 1 (a list of the values used in the present review are presented in [98VIT/CAP]). Although the author used different carbon dioxide gas partial pressures, and varied the ratio of hydroxide to carbonate ligand, further experiments with higher carbon dioxide gas partial pressures and different total Np(VI) concentrations would be required to generate data to unequivocally determine the stoichiometries of the important species, and to obtain accurate values for their formation constants. This is particularly the case for any polymeric mixed-ligand species.

The chemical conditions for some of the measurements of the potential of the Np(VI)/Np(V) couple were similar to those of the potentiometric titrations. Nevertheless, the results cannot be plotted on a single curve as a function of $[\text{CO}_3^{2-}]$. As the total concentration of Np(VI) was approximately three orders of magnitude greater in the titration experiments, the two sets of experiments, taken together, provide evidence of formation of at least one polymeric Np(VI) complex containing hydroxide anions. Curve-fitting indicates that none of the known hydroxide Np(VI) complexes can be identified as the intermediate complex(es). Thus, this work provides the first (and essentially the only) experimental evidence of the formation of (at least) one polymeric Np(VI)-OH complex that also contains carbonate as a ligand.

The author fitted the overall formation constants, $\beta_{a,b,x}$ for the equilibria $a\text{NpO}_2^{2+} + b\text{CO}_2(\text{g}) + (b+x)\text{H}_2\text{O} \rightleftharpoons (\text{NpO}_2)_a(\text{CO}_3)_b(\text{OH})_x^{2a-2b-x} + (2b+x)\text{H}^+$ which (as explained above) refer to the free species, NpO_2^{2+} . This is always a minor species [98VIT/CAP], and the complexation reactions involving this species are probably not directly measurable. For this reason the equilibrium constants ($\beta'_{a,b,x} = \beta_{a,b,x}/\beta_{1,3,0}^a$) for the dissociation of the limiting complex $a\text{NpO}_2(\text{CO}_3)_3^{4-} + (b-3a)\text{CO}_2(\text{g}) + (b+x-3a)\text{H}_2\text{O} \rightleftharpoons (\text{NpO}_2)_a(\text{CO}_3)_b(\text{OH})_x^{2a-2b-x} + (2b+x-6a)\text{H}^+$ should be used.

Graphical analysis [98VIT/CAP] indicates that many possible complexes could form on hydrolysis of $\text{NpO}_2(\text{CO}_3)_3^{4-}$ at lower partial pressures of $\text{CO}_2(\text{g})$. Among others, these include the species $(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$, $(\text{NpO}_2)_3(\text{OH})_7^-$ or $(\text{NpO}_2)_3(\text{OH})_8^{2-}$ (analogous to species proposed for uranium [92GRE/FUG, 95PAL/NGU]). Curve-fitting results (many different approaches have been used [98VIT/CAP] in preparing this section of the present review) lead to similar conclusions if we accept not only the best fit but also those that are within reasonable confidence limits ($\pm 1.96 \sigma_{\text{min}}$) of the “best fit” set. The fit proposed by Maya is only one among the many possible that give quite reasonable results. The values calculated for the formation constants for several of the more likely species are highly correlated. This review accepts the numbers he proposed; but only as possible maximum values, and then only for the equilibria corresponding to $\beta'_{a,b,x}$ and not $\beta_{a,b,x}$ (NpO_2^{2+} was always a minor species). To limit the discussion, this review considered only the species analogous to those proposed in the TDB uranium review [92GRE/FUG] or those suggested recently by Palmer and Nguyen-Trung [95PAL/NGU]).

There is evidence [86GRE/RIG, 90RIG] that for conditions similar to those used by Maya, $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$, could not be neglected [98VIT/CAP] in the buffering region during the titrations at the highest carbon dioxide gas partial pressure. A formation constant for this species is proposed, and incorporated in the other recalculations. For $(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$, the value proposed by the author is marginally consistent with later work [86GRE/RIG, 90RIG]. By analogy with uranium, Maya’s value for the formation constant is accepted in the present review with an uncertainty of ± 1.0 in $\log_{10} K$ for



The simple dicarbonato complex, $\text{NpO}_2(\text{CO}_3)_2^{2-}$, was undoubtedly only a minor species in Maya’s solutions, and the formation constant he proposed is clearly an over-

estimate. In the present review, Maya's value for the formation constant is also accepted as a limiting value.

Maximum values for the formation constants of $(\text{NpO}_2)_3(\text{OH})_7^-$ and $(\text{NpO}_2)_3\text{CO}_3(\text{OH})_3^+$ (*i.e.*, $(\text{NpO}_2)_3\text{O}(\text{OH})_2\text{HCO}_3^+$) are also proposed. Calculations show these could well have formed as minor species during Maya's titrations [84MAY]. The calculated values are similar to those selected for the uranium analogues [92GRE/FUG], but there is no firm evidence that these species actually exist. The species $(\text{UO}_2)_3(\text{OH})_8^{2-}$ was not selected in the uranium review [92GRE/FUG], but was proposed to explain the results of a recent study [95PAL/NGU]. The formation of the analogous neptunium species, $(\text{NpO}_2)_3(\text{OH})_8^{2-}$, as a minor species is also not inconsistent with the data from Maya's titrations, and the maximum value compatible with Maya's data has been calculated in the present review. The recently proposed [95PAL/NGU] species $(\text{UO}_2)_3(\text{OH})_{10}^{4-}$ also was not selected in the uranium review [92GRE/FUG]; however, if a maximum value of the formation constant for $(\text{NpO}_2)_3(\text{OH})_{10}^{4-}$ is estimated based on the value proposed for the uranium species [95PAL/NGU], calculations indicate that this species would not have been detectable during Maya's titrations [84MAY]. A more detailed re-interpretation is given in [98VIT/CAP].

Table A.14: Table of values and limiting values of formation constants based on re-assessment of Maya's potentiometric titration data in 1 M NaClO_4 aqueous solution [84MAY].

	Present review	Selected [84MAY]	Calculated but rejected [84MAY]	Uranium analogue [92GRE/FUG]
$\log_{10} \beta'_{3,6,0}$	(42.82 ± 1.06)		(42.06 ± 0.80)	(40.41 ± 0.41)
$\log_{10} \beta'_{2,1,3}$	(41.75 ± 1.46)	(41.76 ± 0.94)		(39.88 ± 0.60)
$\log_{10} \beta'_{1,2,0}$	$< (12.47 \pm 0.47)$	(12.47 ± 0.35)		(10.92 ± 0.12)
$\log_{10} \beta'_{3,0,7}$	< 63.33		(62.35 ± 1.47)	(57.5 ± 2.1)
$\log_{10} \beta'_{3,1,3}$	< 75.42		(75.42 ± 0.71)	(70.59 ± 0.60)
$\log_{10} \beta'_{3,0,8}$	< 55.45			$(51.29 \pm 0.15)^*$

* Species not accepted in [92GRE/FUG]; comparison value from [95PAL/NGU]

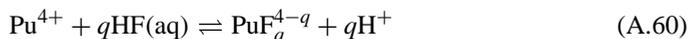
$\log_{10} \beta'_{3,6,0}$	$3\text{NpO}_2(\text{CO}_3)_3^{4-} + 6\text{H}^+ \rightleftharpoons (\text{NpO}_2)_3(\text{CO}_3)_6^{6-} + 3\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}$
$\log_{10} \beta'_{2,1,3}$	$2\text{NpO}_2(\text{CO}_3)_3^{4-} + 7\text{H}^+ \rightleftharpoons (\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^- + 5\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}$
$\log_{10} \beta'_{1,2,0}$	$\text{NpO}_2(\text{CO}_3)_3^{4-} + 2\text{H}^+ \rightleftharpoons \text{NpO}_2(\text{CO}_3)_2^{2-} + \text{CO}_2(\text{g}) + \text{H}_2\text{O}$
$\log_{10} \beta'_{3,0,7}$	$3\text{NpO}_2(\text{CO}_3)_3^{4-} + 11\text{H}^+ \rightleftharpoons (\text{NpO}_2)_3(\text{OH})_7^- + 9\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}$
$\log_{10} \beta'_{3,1,3}$	$3\text{NpO}_2(\text{CO}_3)_3^{4-} + 13\text{H}^+ \rightleftharpoons (\text{NpO}_2)_3\text{CO}_3(\text{OH})_3^+ + 8\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}$
$\log_{10} \beta'_{3,0,8}$	$3\text{NpO}_2(\text{CO}_3)_3^{4-} + 10\text{H}^+ \rightleftharpoons (\text{NpO}_2)_3(\text{OH})_8^{2-} + 9\text{CO}_2(\text{g}) + \text{H}_2\text{O}$

[84MUL/GOR]

In the course of this kinetic work, Mulac *et al.* measured the redox potential of the actinide(VI)/actinide(V) couple by cyclic voltammetry in Na₂CO₃ aqueous solution for An = U, Np and Pu. The actual Na₂CO₃ concentration was not clearly reported, but it was probably 0.05 M. There is no indication of the junction potential. For these reasons, this review did not use the data reported in this work. The actinide(VI)/actinide(V) couple was written as AnO₂(CO₃)₃⁴⁻/AnO₂(CO₃)₃⁵⁻ in this publication, which is correct in concentrated Na₂CO₃ aqueous solution; however, in 0.05 M Na₂CO₃ aqueous solution the dissociation of the actinide(V) limiting complex should probably not be neglected. A more detailed re-interpretation is given in [98VIT/CAP].

[84NAS/CLE]

Nash and Cleveland's primary aim was to explain, with the help of the thermodynamics of fluoride complexation of Pu(IV), a plutonium solubility as high as 10⁻⁷ M in a groundwater of pH = 9.3 that contained 2.7 mM fluoride. Their interest lay also in checking if temperature variations could have a significant impact on fluoride complexation. They used a solvent extraction technique with the extractant HTTA in benzene at 25°C. In one experimental set, the ionic strength of the aqueous solution was kept constant at *I* = 2 M, maintained by HClO₄, and the 1:1 and 1:2 formation constants were determined at 1, 7.5, 15 and 25°C. In another experimental set the background electrolyte was a mixture of 1 M NaClO₄ and 1 M HClO₄, and the plutonium concentration was varied by a factor of about three. The experimental procedure is satisfactory. The authors reported enthalpies of the equilibria



for *q* = 1 and 2, from the determinations between 1 and 25°C: Δ_rH_m(A.60, *q* = 1, *I* = 2 M) = -(3.08 ± 0.32) kJ·mol⁻¹ and Δ_rH_m(A.60, *q* = 2, *I* = 2 M) = -(14.4 ± 1.8) kJ·mol⁻¹. The Van't Hoff plots ([84NAS/CLE], Figure 2) show a slight scattering of the data, especially for the 1:2 complex. Since the authors assigned different uncertainties to each constant, we prefer to use these uncertainties in a weighted linear regression according to the outline in Appendix C.3. We obtain Δ_rH_m^o(A.60, *q* = 1, *I* = 2 M) = -(3.13 ± 2.15) kJ·mol⁻¹ and Δ_rH_m^o(A.60, *q* = 2, *I* = 2 M) = -(13.4 ± 4.9) kJ·mol⁻¹. These constants are accepted. We assume that their ionic strength dependence is small, and that they are also valid at *I* = 0.

The authors corrected the resulting constants to *I* = 0 by estimating the activity coefficients. We prefer to use the specific ion interaction equation for this correction, and we use the constant determined at 25°C in 2 M H⁺, as well as the average from the three determinations in 1 M H⁺, in our evaluation of log₁₀ *β₁^o(A.60, *q* = 1) and log₁₀ *β₂^o(A.60, *q* = 2). We assign an uncertainty of ±0.20 to all values.

[84PER/SAP]

This paper reports solubility boundaries with respect to the Pu(IV) concentration in aqueous solution and pH. The boundary position, if interpreted with respect to Pu⁴⁺ as

the sole plutonium(IV) solution species (as suggested by the slopes drawn in Figure 1), indicates $\log_{10} K_{s,0}^{\circ} = -(53.0 \pm 0.2)$. The study appears to have been done carefully, but it is not clear how the expected disproportionation of Pu(IV) was accounted for, nor was allowance made for the highly probable occurrence of Pu(IV) as PuOH^{3+} in the solutions. In estimating the solubility product of $\text{Pu}(\text{OH})_4(\text{am})$ in the present review, the data from this paper were not used.

[84RAI]

Amorphous plutonium(IV) hydrous oxide was contacted with acidic nitrate solutions for 83 days at $(22 \pm 2)^{\circ}\text{C}$. Care was taken to identify the oxidation states of the solution species. The electrochemical potentials of the solutions were also determined. Solubilities were measured for pH values from 0.5 to 4.9. Below a pH value of 4, the total plutonium in solution changed with time in parallel with the potentials, as the predominant solution species were found to be species of Pu(V) and Pu(VI) for pH values greater than 1. The reasonable values derived for the Pu(V) and Pu(VI) redox couples make a strong case for this study.

It is not clear why the oxidation potential of the solution is so high (undoubtedly disproportionation of Pu(IV) is involved, but α -radiolysis might be expected to lead eventually to a lower average oxidation state). However, formation of Pu(V) and Pu(VI) from Pu(IV) in HClO_4 solutions also has been demonstrated by Capdevila [92CAP].

The author claims the solubility results are compatible with those of [80RAI/SER2], but suggests the solubility product of hydrated $\text{PuO}_2(\text{am})$ could not be properly determined from the earlier study, as the redox potential was not well poised.

The equilibrium constants in this study were corrected to $I = 0$ by the author using the Davies' equation and a series of hydrolysis and complexation constants from the literature.

Recalculation using the selected value for the first hydrolysis constant and $\text{p}K_w = -14.1$ at 22°C [59ROB/STO] for just the data from solutions 202 and 203 results in $\log_{10} K_{s,0} = -(57.4 \pm 0.1)$.

[84REE/DAN]

Rees and Daniel have done a cation exchange study of the Np(V) phosphate system to be able to account for phosphate complexation in a study of complexes of organic ligands in the presence of phosphate buffers. The experiments were carried out in a 0.1 M NaClO_4 medium, at a constant pH value of 7.5, at 10, 25 and $(35 \pm 0.5)^{\circ}\text{C}$. The total phosphate concentration was varied between 10^{-3} and 10^{-2} M. The small effect of hydrolysis was measured in separate experiments and accounted for in the calculation of the constants of the phosphate system. Even though at constant pH no conclusions can be reached about which of the phosphate ions acts as ligand, data analysis together with the results in [64MOS/PER] suggest that $\text{NpO}_2\text{HPO}_4^-$ is the predominant species in the given experimental conditions.

For the reaction:



the authors reported $\log_{10} \beta_1(\text{A.61}, 0.1 \text{ M NaClO}_4) = (3.11 \pm 0.19)$ at 10°C , (2.36 ± 0.42) at 25°C and (2.06 ± 0.39) at 35°C . From the temperature variation of the complexation constant the authors also reported the thermodynamic quantities $\Delta_r H_m(\text{A.61}, 0.1 \text{ M NaClO}_4, 298.15 \text{ K}) = -69.9 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S_m(\text{A.61}, 0.1 \text{ M NaClO}_4, 298.15 \text{ K}) = -188 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

There was no information provided about the recalculation of the constants of phosphoric acid at the given ionic strength and temperature, and no total phosphate concentrations were reported. A recalculation performed in which the total phosphate was first calculated from the reported HPO_4^- concentrations, the pH and the thermodynamic constants of phosphoric acid resulted in essentially no variation in the values of the constants for 10 and 25°C , while at 35°C no such calculations could be performed. This is because from the values in the last column of Table 3 of [84REE/DAN], a D_0 value that varies between 7.7 and 9.2 has been used at 35°C , while a constant value of 11.52 was used at the two other temperatures.

A weighted linear regression of $\ln \beta_1$ vs. $1/T$ (K^{-1}) for the measurements at 10 and 25°C , using the auxiliary values for HPO_4^{2-} from Table 5.1 of the present review, results in $\Delta_r H_m(\text{A.61}, 0.1 \text{ M NaClO}_4, 298.15 \text{ K}) = -(52 \pm 50) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S_m(\text{A.61}, 0.1 \text{ M NaClO}_4, 298.15 \text{ K}) = -(127 \pm 167) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

The recalculated value of this complexation constant at 25°C , $\log_{10} \beta(\text{A.61}, 0.1 \text{ M NaClO}_4) = (2.42 \pm 0.42)$ is used in the selection of a final value for the constant. Extrapolation of the value to $I = 0$ with the SIT equations and interaction coefficients in Appendix B (in fact the interaction coefficient term at this low ionic strength is very small, since also $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = 0.25 \text{ kg}\cdot\text{mol}^{-1}$, (Table B.3) and $\varepsilon_{(\text{Na}^+, \text{HPO}_4^{2-})} = -0.30 \text{ kg}\cdot\text{mol}^{-1}$ (Table B.5) and the interaction coefficient of the single charged complex is small) results in:

$$\log_{10} \beta^\circ(\text{A.61}, I = 0, 298.15 \text{ K}) = (2.86 \pm 0.45)$$

[84VAR/BEG]

The authors reported quasi-reversible formal potentials for the Pu(VI)/Pu(V) and the Np(VI)/Np(V) couples in 2 M Na_2CO_3 : 0.11 V and 0.23 V vs SCE, respectively.

The authors did not make an assessment of uncertainties associated with their measurements (assumed to be $\pm 0.01 \text{ V}$ in this review). Also, the possibility of systematic errors associated with non-negligible junction potentials was not discussed or evaluated. The reported values are given no weight in the determination of the stability constants of neptunium and plutonium carbonate complexes. The experimental work on the neptunium system described in this report was also discussed in a paper [84VAR/HOB].

[84VAR/HOB]

This work was issued in preliminary form as part of [84VAR/BEG]. A value of the Np(VI)/Np(V) redox potential in 2 M Na₂CO₃ aqueous solution is reported. No indication was given about the calibration of the reference (saturated calomel) electrode and the junction potential correction. This could explain the observed differences between their potentials and those from the careful previous work of Simakín [77SIM]. Addition of NaOH to a solution of the Np(VI) carbonate limiting complex, NpO₂(CO₃)₃⁴⁻, was found to lead to reduction of Np(VI) (possibly by water or hydroxide ion) to Np(V).

The Np(V) absorption spectrum in (probably 2 M) Na₂CO₃ solution showed complexation as was found previously in the work of Billon [81BIL]. The addition of 0.02 to 1.3 M NaOH solutions demonstrated the formation of new complex(es), and NpO₂(OH)₂⁻ should not be stable enough to explain the spectral variations. The formation of mixed hydroxo-carbonate complex(es) [90RIG, 98VIT/CAP] is probable.

The preparation of Np(IV) in carbonate solution, the absorption spectra and the electrochemical measurements repeated and confirmed previous work [81WES/SUL]. We carried out the same calculations discussed in this appendix for [79FED/PER].

Cyclic voltammetry of Np(V) in 2 M Na₂CO₃ solution confirmed the previous [79FED/PER, 81WES/SUL] electrochemical observations. The reduction to Np(IV) is not reversible and is observed only at -1.7 V (at pH = 12.9), where [79FED/PER] Np(IV) is quantitatively reduced to Np(III). The reduction peak is shifted toward more negative values (-1.8 V) at [OH⁻] = 0.25 M, and its shape changes with a “pre-peak” at -1.63 V at pH = 10.9. This stabilisation of Np(V) can certainly be explained by the formation of a mixed OH-CO₃ complex of Np(V), for which some spectral evidence is shown in this publication, and which later was confirmed [90RIG, 98VIT/CAP].

The precipitation of Np(III) is mentioned by the authors; but as is the case for Am(III), Np(III) is quite soluble in this medium. However, Np(OH)₃(s) could precipitate directly on the electrode, where the electrolysis of water can locally produce a high enough quantity of OH⁻ anion. This type of process is well known for electrodeposition on solid electrodes. This also would explain why the precipitate is re-dissolved in the bulk solution when the electrolysis is stopped. However, this will not occur (as the authors suggest it will) in other cases, where Np(OH)₄(s) can also precipitate (see below). The changes in the shape of the electrochemical peaks could be due to some side chemical reaction such as



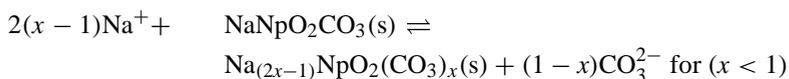
precipitation of Np(IV), and/or formation of an intermediary complex. The authors had difficulties in electrolysing the neptunium in their solution to Np(IV) and in keeping it stable in that oxidation state. As explained in the discussion on [79FED/PER] in this appendix (see also [95VIT]), the instability of the potential can be due to ingress of carbon dioxide gas into the solution. In addition, the water was also electrolysed during the preparation. This generated some OH⁻ that also reacted with carbon dioxide gas. A small increase of [OH⁻] would be enough to dissociate the carbonate limiting complex of Np(IV) (into Np(OH)₄(aq) or another unidentified Np(IV) complex containing the hydroxide anion). This would result in the precipitation

of solid Np(IV) hydroxide. In our opinion, this was clearly a problem during this work. Only because they did not identify this problem did the authors conclude they could not confirm the previous work of Wester and Sullivan [81WES/SUL]. No thermodynamic data can be deduced from these Np(V)/Np(IV) or Np(IV)/Np(III) studies. No new information on Np(IV) nor Np(III) is revealed in this work.

[84VIT]

This conference paper reports many experimental results (shown on figures), their interpretation (on figures and in tables), and literature comparisons and reinterpretations. The experimental data were preliminary results. Np(V) was precipitated in NaHCO₃ aqueous solution. The solid compound was equilibrated in this aqueous solution at constant ionic strength (3 M NaClO₄) under CO₂(g) bubbling. The pH was decreased and increased, so that Np(V) solubility measurements (over more than 3 orders of magnitude) were obtained from both dissolution and precipitation. The experimental results were reasonably reproducible, but they were more scattered (± 0.4 in $\log_{10}[\text{Np}]_{\text{TOT}}$) near the minimum solubility (a few μM Np(V)), than in more acidic media (± 0.2 in $\log_{10}[\text{Np}]_{\text{TOT}}$), or than was found later in more basic solutions [86GRE/ROB, 90RIG, 98VIT/CAP].

The X-ray diffraction pattern of the solid was identical to one previously published [79VOL/VIS2] for a solid prepared by heating at 350°C and assumed [79VOL/VIS2] initially to be Na_{0.6}NpO₂(CO₃)_{0.8}(s). Two models, one assuming (as a “best” fit to the data) the solid to be hydrated Na_{0.72}NpO₂(CO₃)_{0.86}(s), the other assuming it to be hydrated NaNpO₂CO₃(s), were equally consistent with the experimental solubility data. This suggested that at least some of the compounds prepared by Volkov’s group were simply poorly crystallised 1:1:1 solids, that equilibrium conditions had not been attained in their experiments, and that there was little evidence for formation of a series of stable Np(V) solids of varying stoichiometry with equilibria described by



The quantitative results are discussed elsewhere in this appendix (discussions for [86GRE/ROB, 90RIG]).

[84VOL/KAP]

This publication is an interesting review paper on the stability of some carbonate and other actinide solid compounds, but it does not contain any thermodynamic data.

[85BID/TAN]

Liquid-liquid extraction was used to measure the Np(V) carbonate complex formation constants. The technique used is very interesting, because Np(V) has been used at a concentration lower than the solubility or spectrophotometric detection limit. However,

the chemical system is very complicated, and it is not certain that all the necessary corrections can be done properly (from independent experimental measurements). Even then, mixed complex formation is often not easy to detect. All that can reasonably be done to avoid the drawbacks of the technique has been done. The pH was controlled with a buffer (TRIS) that should not have interfered, the extractants (TOMA and TTA) were involved in some side reactions but these have been taken into account (as much as possible). For these reasons we believe that when no carbonate was added, there was no evidence of $\text{NpO}_2\text{OH}(\text{aq})$ formation (compared with possible side reactions) up to $\text{pH} = 9.2$ and $\log_{10}^*K_1 \ll -9$.

Although a value for the first hydrolysis constant of NpO_2^+ was reported in this paper, no uncertainty was stated. Using the reported constant, it is calculated that in the pH range of the experiments a maximum of 20% of the neptunium was present as $\text{NpO}_2\text{OH}(\text{aq})$ and, for most of the experiments, less than 10% of the neptunium was present as $\text{NpO}_2\text{OH}(\text{aq})$. On this basis it would appear that the reported hydrolysis constant has a large inherent uncertainty. The distribution curve for the extraction of Np(V) into the TOMA/TTA mixture (as shown in Figure 2 of [85BID/TAN]) displays very little curvature for pH values above 8.4, and does not suggest significant hydrolysis below a pH value of 9.0. It is concluded in this review that the value of the hydrolysis constant of NpO_2^+ is not well defined by the data in [85BID/TAN].

For $0.1 < [\text{CO}_3^{2-}] < 1$ mM, with $0.4 < [\text{CO}_3]_{\text{t}} < 10$ mM (in HCO_3 medium where $8.2 < \text{pH} < 9.0$) the predominant species is $\text{NpO}_2(\text{CO}_3)_2^{3-}$, and the proposed value of its formation constant, $\log_{10} \beta_2 = (7.06 \pm 0.05)$, fits the experimental results very well. However, the reported formation constant for $\text{NpO}_2\text{CO}_3^-$, $\log_{10} \beta_1 = 4.13 \pm 0.03$, does not seem to fit the results shown in the figures of the publication. A value of $\log_{10} \beta_1 = 3.80 \pm 0.36$ seems to provide a better fit. Either value leads to an under-estimation of the stability of $\text{NpO}_2\text{CO}_3^-$ compared to all the other measurements described in this review. This could be the result of a predominant side reaction in the system. An extra experiment in 0.1 M NaClO_4 , 0.1 M NaHCO_3 solution also does not fit well with the other results. Therefore, the value reported for the $\text{NpO}_2\text{CO}_3^-$ formation constant must be rejected. Experiments independently varying the pH and $[\text{CO}_3]_{\text{t}}$ and pH gave no indication that $\text{NpO}_2(\text{CO}_3)_3^{5-}$ was formed in the solutions used. A statistical treatment of the data suggested a systematic error, probably the result of an unidentified chemical problem with the liquid-liquid extraction experiment. For this reason, data from this publication have been disregarded.

[85CÔM]

This report includes preliminary reports of work discussed elsewhere [84VIT, 85KIM, 86GRE/ROB, 90RIG].

[85EIS/KIM]

The paper describes a laser-induced photo-acoustic spectrophotometric study of Pu(IV) in carbonate media. The Pu(IV) stock solution in 1 M Na_2CO_3 was prepared by the addition of Pu(III) (generated electrolytically in 1 M HClO_4) to the Na_2CO_3 solution.

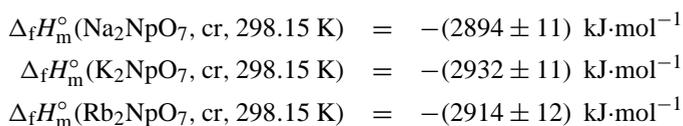
The solutions were allowed to stand for 24 hours and then filtered. The variations in the spectra with pH (varied by titration with HClO₄) were tabulated for 4 wavelengths (425, 444, 470 and 485 nm) over the pH range of 10.6 to 8.80. At pH ≤ 8.8 precipitation occurred. A statistical test (F-Test) was used to determine that the optimum number of parameters that should be used to fit all the data points (4 wavelengths, 8 different pH values) was three. The three species hypothesized were Pu(CO₃)₃²⁻, Pu(CO₃)₄⁻ and Pu(CO₃)₅⁶⁻. Note that the stoichiometry of these species was not uniquely determined by the spectrophotometric experiment. This interpretation is not consistent with that of Capdevila [92CAP]. The difference may be due to the assignment by the authors of statistical significance to fairly small variations found in the absorbance spectra. A qualitative review of the spectra suggests that only two complexes may be necessary to account for the observations.

[85EWA/GOR]

In this solubility study a limiting neptunium concentration of 10^{-8.1} M “Np(OH)₄” was measured under reducing conditions over a rather limited pH range (10 to 13). Sodium dithionite was used to maintain reducing conditions. The use of ²³⁵Np in carrier ²³⁷Np by this group allowed more accurate analysis of the low concentrations of neptunium than was possible in the work of Rai and Ryan [85RAI/RYA].

[85FUG]

The enthalpies of reaction of the dineptunates with 1 M HCl from this paper are used with auxiliary data consistent with the present review (see the discussion in the Appendix A entries of [92GRE/FUG] for the references labelled as [74OHA/HOE2] and [74OHA/HOE4] in that volume, including the heats of solution of the alkali metal chlorides in 1 M HCl from these references) to calculate the enthalpies of formation:



The value for the rubidium salt was considered by the author to be preliminary because the samples contained 2 to 6% Np(V). However, as the result was based on thirteen measurements (three preparations), the value is accepted in the present review with the author's large estimated uncertainty. The value $\Delta_f H_m^\circ(\text{NpO}_2^{2+}, 1 \text{ M HCl}, 298.15 \text{ K}) = -(858.3 \pm 5.3) \text{ kJ}\cdot\text{mol}^{-1}$ used in these calculations is based on an estimated enthalpy of transfer from water of $(2.4 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$.

[85GEN/FUG]

The enthalpies of reaction are used with auxiliary data selected in the present review (see [92GRE/FUG] and the entries for [82MOR/FUG, 83MOR/WIL] in this

appendix) to obtain $\Delta_f H_m^\circ(\text{Ba}_2\text{CaNpO}_6, \text{cr}, 298.15 \text{ K}) = -(3159.3 \pm 7.9) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\circ(\text{Ba}_2\text{SrNpO}_6, \text{cr}, 298.15 \text{ K}) = -(3122.5 \pm 7.8) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\circ(\text{Sr}_3\text{PuO}_6, \text{cr}, 298.15 \text{ K}) = -(3042.1 \pm 7.9) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\circ(\text{Ba}_3\text{PuO}_6, \text{cr}, 298.15 \text{ K}) = -(2997 \pm 10) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\circ(\text{Ba}_2\text{MgPuO}_6, \text{cr}, 298.15 \text{ K}) = -(2995.8 \pm 8.8) \text{ kJ}\cdot\text{mol}^{-1}$, $\Delta_f H_m^\circ(\text{Ba}_2\text{CaPuO}_6, \text{cr}, 298.15 \text{ K}) = -(3067.5 \pm 8.9) \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{Ba}_2\text{SrPuO}_6, \text{cr}, 298.15 \text{ K}) = -(3023.3 \pm 9.0) \text{ kJ}\cdot\text{mol}^{-1}$. The value $\Delta_f H_m^\circ(\text{PuO}_2^{2+}, 1 \text{ M HCl}, 298.15 \text{ K}) = -(819.6 \pm 7.0) \text{ kJ}\cdot\text{mol}^{-1}$ used in these calculations is based on an estimated enthalpy of transfer from water of $(2.4 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$.

[85INO/TOC]

Inoue and Tochiyama studied Np(V) carbonate complexes in 1 M NaClO₄ aqueous solutions, using a liquid-liquid extraction technique similar to that used by Bidoglio, Tanet and Chatt [85BID/TAN], and interpreted their results in terms of the complexes $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2(\text{CO}_3)_2^{3-}$. They determined formation constants that are not in accord (within the uncertainties as estimated by the authors) with a previous solubility study [83MAY] in the same medium. No information was provided as to the procedure used to calibrate the glass electrode. The 101 data points of Inoue and Tochiyama were less scattered than the 71 points from [85BID/TAN]. In the present review, Figure 2 of the paper [85INO/TOC] was scanned, and models were curve-fit to redetermine the formation constants, $\text{NpO}_2(\text{CO}_3)_i^{(1-2i)}$. In contrast to the results of the reanalysis of the data of Bidoglio, Tanet and Chatt (see the discussion in this appendix), theoretical $\log_{10} D$ vs. $\log_{10}[\text{CO}_3^{2-}]$ curves fit the experimental data of Inoue and Tochiyama with no systematic deviations. The results were consistent (within uncertainties) with those initially proposed by the authors, but with those from Maya's solubility study only if larger uncertainties (0.3 to 0.5 in the $\log_{10} \beta$ values) were assumed. However, the liquid-liquid extraction results [85INO/TOC] were judged less likely to be reliable because of the possible errors in pH calibration, and these results were not used in the present review to select thermodynamic data.

[85INO/TOC2]

This paper describes a solvent extraction study at 25°C using HTTA and phenanthroline as extractants in methylbutanol or dichloromethane. The ionic strength of the aqueous phase was maintained at $I = 1 \text{ M}$ with NaClO₄. The ²³⁹Np isotope was used.

The authors reported formation constants for the following complexes: $\text{NpO}_2\text{F}(\text{aq})$, NpO_2F_2^- , $\text{NpO}_2\text{SO}_4^-$, $\text{NpO}_2\text{H}_2\text{PO}_4(\text{aq})$, $\text{NpO}_2(\text{H}_2\text{PO}_4)_2^-$, $\text{NpO}_2\text{HPO}_4^-$, and $\text{NpO}_2(\text{HPO}_4)_2^{3-}$. Although these constants are in fair agreement with those of other studies, the authors leave some open questions concerning the experimental conditions: no check was done for the oxidation state of neptunium (Np(V) may have been reduced to Np(IV) in the organic layer), no indication was given as to whether equilibrium was reached or could be confirmed. The reagents used are uncommon in solvent extraction experiments, and the effect of the buffer on the distribution ratio is

unknown. The measurements are not tabulated in detail. However, error propagation rules appear to have been used properly.

For the fluoride system, the pH was between 6.6 and 7.6, and the authors used fluoride concentrations up to $[F^-]_t \approx 0.25$ M. At such high concentrations, they could observe the formation of a 1:2 complex, $NpO_2F_2^-$. We tentatively accept their values, and assign quite large uncertainties to the reported constants to allow for the missing information concerning the experimental conditions: $\log_{10} \beta_1(NpO_2F, aq, I = 1 M) = (1.39 \pm 0.30)$ and $\log_{10} \beta_2(NpO_2F_2^-, I = 1 M) = (2.07 \pm 0.50)$.

For the sulphato and phosphato complexes, the reported errors are assumed to be 1σ . These results are reported here “as is” (without attempting recalculation), but they were not used in the determination of “best values” for the formation constants.

In the case of the Np(V)-phosphate system, from the variation of model functions in the pH interval 4.60-7.94, the following species and the corresponding stability constants were proposed: $NpO_2H_2PO_4(aq)$, $NpO_2(H_2PO_4)_2^-$, $NpO_2HPO_4^-$, and $NpO_2(HPO_4)_2^{3-}$. As the authors recognized, it is difficult to have considerable amounts of the Np(V) complex with $H_2PO_4^-$ in solutions having pH values greater than 4.5. Furthermore, in the case of such weak complexes, it is difficult to estimate the effects of medium changes during the titration - see the discussion of [64MOS/PER] in this appendix. As for the HPO_4^{2-} complexes, there is little agreement among different studies as to the Np(V) speciation at higher pH. Thus, even though negligible amounts of $NpO_2(HPO_4)_2^{3-}$ are calculated to be present in the conditions of the study of Morgenstern and Kim [96MOR/KIM], calculations also indicate that their proposed species, $NpPO_4^{2-}$, would form in large amounts in this study [85INO/TOC2], especially for the three titrations at $pH > 7$.

[85KIM]

This report (as for [85CÔM]) includes a summary of work published elsewhere [85BID/TAN, 90RIG].

[85KRU/RAI]

These authors measured the solubility of Np(IV) hydrous oxide in the presence of metallic Fe and $Na_2S_2O_4$, respectively, to avoid oxidation of Np(IV). The aim of this study was to check if fluoride concentrations up to 100 ppm ($\sim 5 \times 10^{-3}$ M) had any influence on the Np(IV) solubility, or probably rather if such fluoride concentrations could increase the neptunium concentration beyond the detection limit. The measured concentrations of neptunium, with or without addition of fluoride, were all at the detection limit of the liquid scintillation counter (7.7×10^{-9} M). The authors suggested that “fluoride complexes of tetravalent actinides, and Np(IV) in particular, do not measurably increase the solubility of tetravalent actinide solids in near-neutral to alkaline solutions”. This conclusion cannot be based on the solubility experiments but may nevertheless be correct as a condition-specific statement, because a concentration as high as 100 ppm fluoride may not be sufficient to compete effectively with hydroxide

for Np(IV) complexation at neutral to alkaline pH. However, one must not be misled to conclude that Np(IV) fluoride complexes are non-existent.

[85LIE/TRE]

Lierse, Treiber and Kim measured the solubility of $\text{NpO}_2\text{OH}(\text{s})$ as a function of pH ($6.8 < \text{pH} < 13$) in 1 M NaClO_4 . There is no indication as to how the glass electrode was calibrated, although corrections are provided in a later publication from the same group [92NEC/KIM], but also see the discussion of [91KIM/KLE] in this appendix. The measurements in neutral to alkaline solutions indicate that, for solutions having pH values greater than ~ 11.5 , Np(V) exists predominantly in an anionic form. There is no indication that the solid in equilibrium with the solution was characterised after equilibration with the solution, nor that the same solid was at equilibrium with the solutions having different values of pH (again additional information was provided by Neck, Kim and Kanellakopoulos [92NEC/KIM]). Nevertheless, the good linearity of the logarithm (base 10) of the equilibrium neptunium concentration as a function of pH between pH values of 6.8 and 10.8 (with a slope essentially equal to -1.0) suggests these measurements are of good quality.

Values of $\log_{10} \beta_1 = (2.33 \pm 0.62)$, $\log_{10} \beta_2 = -(4.89 \pm 0.05)$ and $\log_{10} K_{s,1} = -(8.81 \pm 0.05)$ were reported (for a medium of 1.05 m NaClO_4). Revised values ($\log_{10} \beta_1 = (2.11 \pm 0.62)$, $\log_{10} \beta_2 = -(4.45 \pm 0.18)$ and $\log_{10} K_{s,1} = -(8.59 \pm 0.07)$) were later published [92NEC/KIM] and are used here. The ion product for water in the medium is calculated as $10^{-13.80}$ using the specific ion interaction theory. The values $\log_{10} \beta_1^{\circ} = -(11.81 \pm 0.62)$, $\log_{10} \beta_2^{\circ} = -(23.54 \pm 0.18)$ and $\log_{10} K_{s,1}^{\circ} = (5.33 \pm 0.07)$ can then be calculated using $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.25 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$, $\varepsilon_{(\text{NpO}_2(\text{OH})_2^-, \text{Na}^+)} = -(0.01 \pm 0.07) \text{ kg} \cdot \text{mol}^{-1}$ (estimated).

The increase in Np(V) solubility at pH > 11 is not consistent with the work of Ewart *et al.* [86EWA/HOW] (Figure 8.3). This solubility increase was attributed to $\text{NpO}_2(\text{OH})_2^-$ formation, but this is only one possible interpretation. The authors used filters with different pore sizes (220 down to 1 nm). Only use of the filter with the smallest pore size resulted in slightly lower solubilities at $11.5 < \text{pH} < 12.5$, but not at $12.5 < \text{pH} < 13$. As pointed out by the authors, the interpretation of this small difference is not clear.

There is no way to verify whether the $[\text{CO}_3^{2-}]$ was low enough ($\log_{10}[\text{CO}_3^{2-}] < -5$) to avoid formation of $\text{NpO}_2\text{CO}_3^{2-}$ or other Np(V)-OH- CO_3 anionic complexes. If there were sufficient carbonate to cause precipitation of $\text{NaNpO}_2\text{CO}_3(\text{s})$, and the formation constants for carbonate complexes in the same medium as determined by Maya are used, $\log_{10}[\text{NpO}_2\text{CO}_3^-] = -5.6$, $\log_{10}[\text{NpO}_2(\text{CO}_3)_2^{3-}] = -18.3 + \text{pH}$, $\log_{10}[\text{NpO}_2(\text{CO}_3)_3^{5-}] = -32.2 + 2\text{pH}$ and $\text{NpO}_2\text{CO}_3^-$ is the predominant aqueous neptunium(V) species at $6.0 < \text{pH} < 12.8$ and $\text{NpO}_2(\text{CO}_3)_2^{3-}$ predominates at $12.8 < \text{pH} < 13.9$. $\text{NpO}_2(\text{OH})_2(\text{CO}_3)_2^{5-}$ [91VIT/OLI, 98VIT/CAP] may also form. Therefore, the formation of an anionic Np(V) hydrolysis species is not proven, and the discrepancy with the work of Ewart *et al.* remains. Nevertheless, at present, this, with the work in [92NEC/KIM] is probably the most believable hydrolysis study of Np(V).

[85RAI/RYA]

In this paper measurements of the solubility of “neptunium (IV) hydrous oxide” were reported for the pH range 6 to 14. A strong reducing agent was used: $\text{Na}_2\text{S}_2\text{O}_4$, Fe or Zn, “that in general maintained redox potentials close to the boundary at which water is reduced to produce H_2 ”. In other cases, $10^{-4.4}$ to $10^{-7.5}$ M solubility was found and attributed to Np(V) or Np(VI). The measured Np(IV) solubilities were found to be a little less than 10^{-8} M: $10^{-7.7}$ to $10^{-8.45}$ M using liquid scintillation α -counting. The detection limit for the analytical method for neptunium is claimed to be $10^{-8.3}$ M, and the results indicated the solubility is near to or less than this value. However, the total solubilities of uranium(IV) and plutonium(IV) species seem to be less than $10^{-8.3}$ M (of the order of 10^{-9} – 10^{-10} M) for conditions in which the IV oxidation state predominates in solution. The lack of experimental details about the pH measurements (which pH buffers were used for calibration; was the junction potential taken into account; was it really pH or $-\log_{10}[\text{H}^+]$?); are of little importance here.

Table A.15: Calculation of the maximum value of the formation constant of some complexes of Np(IV), $\text{Np}(\text{CO}_3)_i(\text{OH})_j^{4-2i-j}$, from the [85RAI/RYA] solubility measurements and comparison with the values proposed in the literature ($\log_{10} \beta_{i,j} = \log_{10}[\text{Np(IV)}] - \log_{10} K_s - i \log_{10}[\text{CO}_3^{2-}] + (4 - j) \log_{10}[\text{OH}^-]$).

	$\log_{10} \beta_{i,j}$ upper limit values		$\log_{10} \beta_{i,j}$ values		
	[85RAI/RYA]	this review	U ^(a)	Np	References for Np
* β_5	-24.7	-25.5			
β_1	22.5	30.4			
β_2	27.9	33.1			
β_3	33.2	35.8		(37±1.2)	[89MOR/PRA]
β_4	38.5	38.4	35	(41.1±1.4)	[89MOR/PRA]
β_5	41.6	40.7	34		[79FED/PER]
					E(V/IV)
				(36.4±3.1)	[79FED/PER]
					E(IV/III)
β_{22}		41.9		(45.69±0.44)	[90PRA/MOR]
β_{24}		47.8		(53.07±0.44)	[90PRA/MOR]
β_{14}		46.5		(53.05±0.02)	[71MOS2]

^(a) Uranium values from [92GRE/FUG, 95GRE/PU] (there is a minor inconsistency in the values in the table and text of [95GRE/PU]).

The authors calculated the maximum values of the formation constants of some Np(IV) complexes that were not detected in their solubility measurement. They show convincingly that some published formation constants for the Pu(IV) carbonate complexes PuCO_3^{2+} through $\text{Pu}(\text{CO}_3)_5^{6-}$ [58MOS/GEL, 83KIM/LIE], and of the Np(IV) carbonate complex $\text{Np}(\text{OH})_4\text{CO}_3^{2-}$ [71MOS2] are much too high to be “believable”.

This review concurs with these conclusions.

To confirm this, the authors showed that Np(IV) solubility is not increased by the formation of any new soluble complex when the hydroxyl ion concentration of the solution is increased so the free carbonate concentration approaches 0.01 M.

To estimate the maximum value of the formation constant, $\beta_{i,j}$, of the complex $\text{Np}(\text{OH})_i(\text{CO}_3)_j^{4-i-2j}$, one can assume, that the solubility, S , is approximately equal to the measured solubility ($[\text{Np}(\text{OH})_4(\text{am})]$) of the neptunium solid, and $[\text{Np}(\text{OH})_i(\text{CO}_3)_j^{4-i-2j}] / [\text{Np}(\text{OH})_4(\text{aq})]$ is less than the relative uncertainty in S . Using the [85RAI/RYA] value of $K_{s,0} = -53.5$ as in [85RAI/RYA], the calculations show, that among the Np(IV) complexes proposed in the literature, only the observations of the formation of $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$ are believable. Other complexes may, of course, exist under limited conditions that have not been thoroughly investigated experimentally.

[85SAN/MUR]

The data for adsorption of plutonium on goethite provided the basis for a computational thermodynamic model that described the interaction of plutonium with an oxide surface and with dissolved ligands. The data for the adsorption of plutonium on goethite, as a function of total alkalinity from 10 to 1000 meq/l at $\text{pH} = 8.6 \pm 0.1$ and 20°C , was treated using a two parameter model that included an intrinsic adsorption constant in addition to a value of $\log_{10} \beta$ for one of the possible complexes (27.2, -7.1 and +1.4 for the species PuCO_3^{2+} , $\text{Pu}(\text{OH})_4\text{CO}_3^{2-}$ and $\text{Pu}(\text{OH})_3\text{CO}_3^-$, respectively). Given the presumably negative charge on freshly precipitated goethite at $\text{pH} = 8.6$, PuCO_3^{2+} would appear to be the most likely species in solution and to adsorb on the goethite surface. The estimate of $\log_{10} \beta$ for this species might be taken as a reasonable upper bound. The results, however, are too dependent on the adsorption model used in the study. The ionic strength was not held constant in these experiments, and there was no direct verification of the plutonium oxidation state. No useful thermodynamic information can be inferred from this data set.

[85SAW/CHA]

Sawant *et al.* investigated the formation of fluoride complexes of U(VI), Np(VI) and Pu(VI) by titrating moderately acidic solutions of these metals with fluoride solution at $I = 0.1$ M and 1 M (NaClO_4) and at a temperature of $(21 \pm 1)^\circ\text{C}$ ("room temperature"). The free fluoride concentration was measured with a fluoride-selective electrode, and appropriate corrections for the liquid junction potential were made by computing $[\text{H}^+]$ at each titration point for the Np(VI) and Pu(VI) systems. The measurements for the U(VI) system were discussed in [92GRE/FUG].

In the case of Np(VI), the results seem to be reliable, and we use the reported constants for the 1:1 and 1:2 complexes in our evaluations. Since the authors did not report any uncertainties, we estimate them to be equal to those in the study of Choppin and Rao [84CHO/RAO] who used the same method (± 0.15 in the logarithmic constants).

The Pu(VI) results on the formation of the 1:1 and 1:2 complexes are also used in our selection procedure, and we assign the same uncertainties as above (± 0.15 in the logarithmic constants).

[85SAW/RIZ]

The authors used a potentiometric method with a fluoride ion selective electrode to determine the formation constant of $\text{NpO}_2\text{F}(\text{aq})$ at room temperature (21°C) and at ionic strengths of 0.1 M and 1 M (NaClO_4).



The constant was determined by titrating the Np(V) solution in HClO_4 with a NaF solution and by measuring the free fluoride concentration at each titration step. This is, in principle, a reliable and precise method. The pH was between 2.4 and 3.0, as can be calculated with the information about $[\text{H}]_t$ in Table 2 of [85SAW/RIZ].

The authors carried out a blank titration in the absence of neptunium(V). For each titration point they calculated the quantity of fluoride bound to Np(V) from the difference in free fluoride measured in the blank and in the real titration. In this way, Sawant *et al.* [85SAW/RIZ] eliminated uncertainties in the calibration of the electrode, in the liquid junction potential, and in minor side reactions such as the formation of $\text{HF}(\text{aq})$ and HF_2^- . On the other hand, the two measured quantities of free fluoride differed by only 3 to 12% throughout the titrations, and the resulting values of fluoride bound to Np(V) are thus affected with a relative error roughly 10 to 40 times larger than that of the measured quantities. The authors also made an independent check (“Method B”) to quantify these side effects by replacing the blank titration by commonly used parameters for the liquid junction potential (calculated based on the $[\text{H}^+]$ difference on each side of the junction) and the stabilities of $\text{HF}(\text{aq})$ and HF_2^- (which the authors determined separately). They obtained $\log_{10} \beta_1(\text{A.62}, I = 0.1 \text{ M}) = 1.76$ with Method B, compared to the more reliable value of $\log_{10} \beta_1(\text{A.62}, I = 0.1 \text{ M}) = 1.51$ by using a blank titration. The evaluation of the measurements at $I = 1 \text{ M}$ shows a slight trend with increasing fluoride concentration.

This is a careful investigation, in which the authors tried to eliminate as many uncertainties and errors as possible. Yet one important parameter was not given sufficient attention: the complexation degree, \bar{n} , which represents the average number of fluorides bonded to NpO_2^+ . In the present one-complex system, \bar{n} represents the fraction of NpO_2^+ that has reacted to form $\text{NpO}_2\text{F}(\text{aq})$:

$$\bar{n} = \frac{[\text{NpO}_2\text{F}(\text{aq})]}{[\text{Np}]_t} = \frac{[\text{F}]_t - [\text{F}^-] - [\text{HF}(\text{aq})] - 2[\text{HF}_2^-]}{[\text{Np}]_t}$$

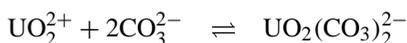
A speciation calculation to simulate the experiments of this study reveals that the fraction of Np(V), or fluoride, that reacted to form $\text{NpO}_2\text{F}(\text{aq})$, was as follows: Method A (with blank titration), $\bar{n} = 0.0012$ to 0.068 for $I = 0.1 \text{ M}$, and $\bar{n} = 0.0006$ to 0.0062 for $I = 1 \text{ M}$; Method B, $\bar{n} = 0.0014$ to 0.019 (here the authors listed the \bar{n} values they obtained, ranging from $\bar{n} = 0.0045$ to 0.1025, which is an overestimate

according to our calculations). It is certainly correct to interpret the potential difference, measured with Method A in the presence and absence of Np(V), in terms of the formation of $\text{NpO}_2\text{F}(\text{aq})$. However, the reliability of the resulting constants cannot be high. These values can only be given a small weight in the selection procedure of the present review. We use $\log_{10} \beta_1(\text{A.62}, I = 0.1 \text{ M}) = (1.51 \pm 0.50)$ and $\log_{10} \beta_1(\text{A.62}, I = 1 \text{ M}) = (1.15 \pm 0.80)$.

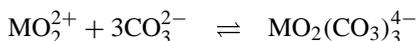
[85SCH/FRI]

This work reports the results of calorimetric titrations of uranium(VI) and neptunium(VI) in aqueous Na_2SO_4 solutions with Na_2CO_3 and (for uranium(VI)) NaHCO_3 aqueous solutions at 25°C . The uranium experiments were done at $I = 1.6 \text{ M}$ using samples containing $50 \mu\text{moles}$ of U(VI), and similar conditions were used for the neptunium experiments. The uranium part of this work has already been discussed in the NEA uranium review [92GRE/FUG], and the same reinterpretation is used in the present review.

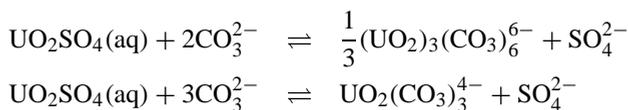
The authors [85SCH/FRI] reported enthalpy changes for



and for $M = \text{U}$ and Np



Grenthe *et al.* [92GRE/FUG] concluded that the technical quality of the enthalpy data seem to be satisfactory, but they found that the two main reactions taking place under the conditions of experiment are

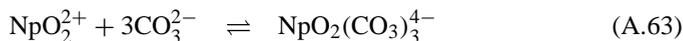


The authors gave a value of the enthalpy of the reaction

$$\Delta_r H_m(I = 0.3 \text{ to } 1.6 \text{ M Na}_2\text{SO}_4) = -(50 \pm 2) \text{ kJ}\cdot\text{mol}^{-1}$$

A re-evaluation of the three experimental determinations at high excess CO_3^{2-} concentrations yields a more realistic estimate of $\Delta_r H_m = -(50.1 \pm 12.2) \text{ kJ}\cdot\text{mol}^{-1}$.

Assuming that $\text{NpO}_2\text{SO}_4(\text{aq})$ is the only species initially present in the calorimeter, $\Delta_r H_m(\text{10.1}) = -(16.7 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$ can be used to estimate $\Delta_r H_m$ for the reaction



$$\Delta_r H_m(\text{A.63}) = -(33.4 \pm 12.2) \text{ kJ}\cdot\text{mol}^{-1}$$

consistent with the subsequent determinations made by Ullman and Schreiner [88ULL/SCH] using the same calorimeter.

[85THO/NAS]

This work reports kinetic data, mostly for uranium(VI) complexation. Neptunium(VI) species analogous to the transient U(VI) species are proposed. No values from this paper are used in the present review.

[86BRU/GRE]

The effective value of $\log_{10} K_{s,0}$, $\text{Pu}(\text{OH})_3(\text{cr})$, coprecipitated with $\text{UO}_2(\text{s})$, is reported to be 2.4 at $I = 0.5 \text{ M NaClO}_4$, 298 K *i.e.*, many orders of magnitude lower than in the pure solid. The oxidation state of the precipitated plutonium does not appear to have been confirmed. The precipitating major phase was not well defined, nor was long-term equilibrium established.

[86EWA/HOW]

The solubilities reported for $\text{NpO}_2\text{OH}(\text{s})$ fall off strongly with increasing pH above values of 11, although at low values of pH the results are in accord with those reported elsewhere, [71MOS3, 76SEV/KHA, 78MUS, 85LIE/TRE]. One possible explanation might be the coprecipitation of the neptunium with Ca-containing basic solids (the Ca^{2+} concentration in the solutions was relatively high at 0.01 M). Another possibility might be disproportionation of Np(V) in the solid phase. No analysis of the final solid was reported. The authors suggested that soluble hydroxo-Np(V) complexes did not form for kinetic reasons, but this behaviour usually occurs only for polynuclear soluble complexes, and is unlikely in these dilute solutions of dioxoneptunium(V). The temperature was also not reported (but has been assumed to be 25°C in the present review).

The solubility of the ill-defined Pu(IV) solid (probably $\text{Pu}(\text{OH})_4(\text{am})$) ranges from $10^{-9.5}$ to $10^{-10.5}$ M for pH values between 9 and 13. The oxidation state of the solution species apparently was not checked, and the stable oxidation state may be Pu(V) [94NEU/HOF]. The solution concentrations near a pH value of 8 are similar to those reported by Rai and Ryan [82RAI/RYA] for “ $^{239}\text{PuO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ ”. There are few results for pH values below 9, and the numerical results were not used in the present review although they appear compatible with those from other studies. More information about the study was provided in a later paper [92EWA/SMI].

[86GRE/RIG]

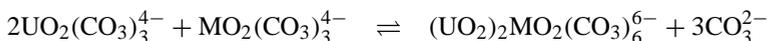
Dissociation of the limiting carbonato complexes of Np(VI) and Pu(VI), $\text{MO}_2(\text{CO}_3)_3^{4-}$, in 3 M NaClO_4 was studied in aqueous solution at $t = (22 \pm 1)^\circ\text{C}$, using a spectrophotometric technique and a potentiometric technique using a glass electrode with zero junction potential (correctly calibrated in concentration units $-\log_{10}[\text{H}^+]$). The aim of this work was mainly to show that U(VI), Np(VI) and Pu(VI) form trinuclear complexes in concentrated bicarbonate media, and this was effectively demonstrated. The original experimental data have since been published [90RIG, 98VIT/CAP].

From isobestic points and quantitative graphical interpretation the authors concluded that two species are sufficient for interpretation of the data. For constant total metal concentration, the measured molar absorptivity was plotted on a single curve as a function of the free carbonate ion concentration, regardless of the carbon dioxide gas partial pressure ($0.1 < p_{\text{CO}_2} < 1$ atm.). For NpO_2^{2+} the authors [86GRE/RIG] then concluded that the major dissociated complex contained only CO_3^{2-} ligand. The stability of the dissociated complex increased with the total metal concentration. This is direct experimental evidence that a polynuclear complex was formed (and that the interpretation proposed earlier by Maya [84MAY] was incorrect).

The results were confirmed by sensitivity analysis performed by the authors [86GRE/RIG]. The stoichiometry of the dissociated complex can readily be determined using straight forward slope analysis. This graphical interpretation was used for neptunium by Riglet [90RIG]. Sensitivity analysis performed in this [86GRE/RIG] publication showed that the dissociation equilibrium is



for $M = \text{Np}$ or Pu . The experimental data ($\log_{10}[\text{CO}_3^{2-}]$, \log_{10} (molar absorptivity)) were graphically compared with theoretical curves calculated for constant total metal concentration, assuming that there was only one major soluble dissociated complex with different possible stoichiometries. This method allowed the determination of the formation constant of the above equilibrium. In the same way for $M = \text{Np}$ or Pu



mixed equilibria were studied under the same conditions using the same experimental procedure. The corresponding equilibrium constants were determined by using the same graphical method. The results were accepted previously in the uranium volume in this series of reviews [92GRE/FUG], and were re-evaluated and extrapolated to standard state conditions by Grenthe *et al.* [95GRE/PUI]. This review accepts the stability constants and uncertainties for the mixed complexes as assigned by Grenthe *et al.* [95GRE/PUI]. However, a revised calculation is done to extrapolate the value of the stability constant for the mixed uranium-neptunium complex to $I = 0$ (*cf.* Section 12.1.2.3).

[86GRE/ROB]

a) Neptunium

This is a preliminary publication of the data in [90RIG]. There is no experimental detail in this work, which is discussed in this appendix with [90RIG]. Qualitatively, this experimental work clearly shows that for Np(V) in carbonate or bicarbonate media, $0.1 < p_{\text{CO}_2} < 1$ atm, the only ligand in the major solution species is carbonate. The limiting complex $\text{NpO}_2(\text{CO}_3)_3^{5-}$ is stable only at high ionic strength. The solid, $\text{NaNpO}_2\text{CO}_3(\text{s})$, is not well crystallised when precipitated from solutions having low carbonate concentrations ($\log_{10}[\text{CO}_3^{2-}] < -3.5$), but it is stable and well crystallised

when precipitated from oversaturated solutions ($0.1 \text{ mM} < [\text{CO}_3^{2-}] < 1 \text{ mM}$) where $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ solid precipitates slowly.

This publication also contains further experimental details related to some of the data for Np(VI) complexation as published by Grenthe, Riglet and Vitorge [86GRE/RIG]. In addition, lattice parameters of the compounds $\text{PuO}_2\text{CO}_3(\text{cr})$ and $\text{NpO}_2\text{CO}_3(\text{cr})$ are reported. These solids have the same structure as rutherfordine, $\text{UO}_2\text{CO}_3(\text{cr})$. The lattice parameters reported for $\text{NpO}_2\text{CO}_3(\text{cr})$ are reasonably consistent with those published by Thevenin, Jove and Madic [86THE/JOV] (both X-ray diffraction studies were done using the same apparatus in the same laboratory, but the samples were prepared independently).

b) Plutonium

The paper summarises a variety of carbonate complexation experiments, only two of which concern Pu(VI); (1) the stability of $(\text{PuO}_2)_3(\text{CO}_3)_6^{6-}$ and (2) the existence and stability of $(\text{PuO}_2)_2\text{UO}_2(\text{CO}_3)_6^{6-}$. The experimental procedures and results are more completely described in [86GRE/RIG].

[86LIE/KIM]

This report contains much of the experimental and calculation detail that was omitted from the papers published by this group. In particular, it clarifies two points with respect to the Pu(VI) hydrolysis study by Kim *et al.* [84KIM/BER].

First, it indicates that in the data analysis $\log_{10} K_{s,0}$ was fixed with a value of -23.0 , and that a fixed value of $\log_{10} \beta_1 = -8.3$ was also selected. These values were based on best estimates from the literature, and were not determined experimentally in any other way. The other four constants, $\beta_{2,2}$, $\beta_{2,1}$, $\beta_{5,3}$ and $\beta_{3,1}$ were then derived from the solubility data.

Second, it suggests the radiolysis from the ^{238}Pu may have resulted in reactions with the plastic container. The net result of these reactions that may have led to the plutonium remaining in the +6 oxidation state over the long equilibration period.

The value of $\log_{10} \beta_{3,1} = 10 \pm 2.1$ for the formation of the $\text{PuO}_2(\text{CO}_3)_3^{5-}$ was calculated using the Gibbs energy changes calculated from the standard potential of the Pu(V)/Pu(VI) couple, the Gibbs energy of formation of $\text{PuO}_2(\text{CO}_3)_3^{4-}$, and the reversible formal potential of the Pu(VI)/Pu(V) couple in 1 M sodium carbonate solution. The temperature was probably $\sim 20^\circ\text{C}$. A recalculation of this value, and extrapolation to zero ionic strength using the same SIT parameters as in [92CAP] results in a value of $\log_{10} \beta_3^\circ = 4.2 \pm 0.9$.

The results of a series of long-term (up to 650 days) studies on the solubility of $\text{PuO}_2(\text{s})$ were rationalized in terms of the sequential formation of the mono- through the pentacarbonato complexes of Pu(IV). The oxidation state was not verified in the course of this study, and the identity and stability of Pu(IV) hydrolysis products were taken as given from another study in this report. The tabulated values are those for 0.3 and 1 M $\text{NaHCO}_3/\text{Na}_2\text{CO}_3$ solutions at 25°C . The interpretation of these solubility studies was complicated by the effects of radiolysis on the solution and solid that

may have generated oxidizing/reducing radicals. The experimental protocol addressed the self-evident problems in this type of experiment in a satisfactory fashion. The tabulated experimental data for carbonate, hydroxide and plutonium concentrations in solution are provided and could be used for developing alternative models. We can not recommend the calculated values for the stability constants from this contribution. A qualitative consideration of the solubility data at high CO_3^{2-} concentrations, however, clearly supports the existence of tricarbonato or higher complexes.

The molar absorptivity at 486 nm for Pu(IV) in 1 M Na_2CO_3 (pH = 10.60) and 1 M NaHCO_3 (pH = 8.17) was found to be identical. This result is at odds with the observations of Capdevila [92CAP, 96CAP/VIT], which indicated that two different species with different molar absorptivities should exist in these contrasting solutions. We cannot resolve this discrepancy.

[86MAH/SAW]

See comments under Sawant *et al.* [93SAW/MAH].

[86PRY/REE]

The solubility of some actinides was measured in “simulated pore water [...] prepared by equilibrating demineralised water with crushed concrete for several months. [...] The pH was varied by addition of sodium hydroxide or hydrochloric acid.” According to the chemical analysis of the water at pH 12, $[\text{CO}_3^{2-}]$ was 30 μM . This value might be too high for a water equilibrated with cement [91VIT/TRA]. The results are in general agreement with those from a previous study [85RAI/RYA], but the measured solubility was found to be constant to a higher pH, and in this study $[\text{CO}_3^{2-}]$ was lower. Therefore, we have not used this work to estimate maximum values for formation constants of Np(IV) carbonate complexes (see the discussion for [85RAI/RYA] in this appendix).

If the measured Np(IV) solubility values are really above the detection limit, Np(IV) and Pu(IV) behave slightly differently – the Pu(IV) solubility is smaller and it increases at pH 13.

[86ULL/SCH]

This is a study of the reaction of $\text{NpO}_2(\text{ClO}_4)_2$ with Na_2SO_4 by titration calorimetry. The ion-interaction model (PHREEQE [80PAR/THO], as discussed in Appendix A of this review) was used as part of the data reduction to compensate for variation in I during the course of the experiment. The ion-interaction model gives an apparent $\Delta\varepsilon$ of $-(0.28 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ and $-(0.02 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ for the two reported complexes. The former value is in good agreement with the reported value for the monosulphatodioxouranium(VI) complex ($\Delta\varepsilon = -(0.34 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$, [92GRE/FUG]). Comparison of the reported association quotients and enthalpies of reaction for UO_2^{2+} and those selected in the uranium review [92GRE/FUG] suggest the method and the model extrapolation used are reliable.

[86WEI/HEL]

The results and discussion essentially duplicate those in [83HEL].

[87BEN/HOF]

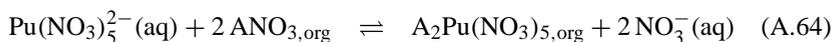
This is a UV-spectroscopic study, with no real data useful for estimating the first hydrolysis constant of PuO_2^+ .

[87DEL]

Solubility data were presented for the identification of $\text{PuO}_2(\text{OH})_4(\text{CO}_3)_2^{7-}$ along with a reported value for the equilibrium constant $\log_{10} K = (1.13 \pm 0.20)$. Data were collected at room temperature (18- 24°C) with an equilibration period of 153 days. The solutions were 3-5 molal NaOH and 0.25 to 1 molal Na_2CO_3 . Plutonium was added to these mixtures as Pu(IV) nitrate, and the concentration of plutonium in the supernatant was determined by scintillation counting. Observations made on other systems with comparable high sodium hydroxide concentrations had identified Pu(V) in the alkaline supernatants. There is an apparent ambiguity in this identification as Pu(VI) was also identified in acidified samples. The author has chosen to write the equilibrium as the addition of two carbonate ions to $\text{PuO}_2(\text{OH})_4^{3-}$, the predominant hydrolysis species reported to be found in the study. The solid phase apparently changed with time. The value for the association constant and species identification are not considered to be reliable.

[87FUK/SIE]

This is a solvent extraction study of Pu(III) nitrate complexation performed at $(25 \pm 0.1)^\circ\text{C}$ with aqueous solutions 2 M in NH_4NO_3 , and using Adogen 464 (trialkyl /C8-C10/ methylammonium nitrate) 20% in xylene as extractant. During the equilibration HNO_3 was added to the aqueous phase to obtain a pH value of 3.3. The reaction studied was [83SOK/SIE]:



where ANO_3 is the Adogen nitrate monomer. Then the distribution coefficient is:

$$D = \frac{K_5^\circ \cdot \beta_5^\circ \cdot [\text{NO}_3^-]_{\text{aq}}^3 \cdot [\text{ANO}_3]_{\text{org}}^2 \cdot f_{\text{Pu}^{3+}, \text{aq}} \cdot f_{\text{NO}_3^-, \text{aq}}^3 \cdot f_{\text{ANO}_3, \text{org}}^2 \cdot f_{\text{cpX}, \text{org}}^{-1}}{1 + \sum_{i=1}^N \beta_i \cdot [\text{NO}_3^-]_{\text{aq}}^i \cdot f_{\text{Pu}^{3+}, \text{aq}} \cdot f_{\text{NO}_3^-, \text{aq}}^i \cdot f_{\text{cpXi}, \text{aq}}^{-1}}$$

The distribution coefficients for plutonium were compared to those for several lanthanides measured using the same method. The authors assumed that activity coefficients in the aqueous and organic phases and also complexation in the different aqueous phases were identical, so only the ratio of the products of the constants $K_5^\circ \beta_5^\circ$ from the above expression remains in the ratio of the distribution coefficients. From this, differences in the standard Gibbs energy of extraction for a couple of metals were

deduced. Furthermore, K_5° was assumed constant for all metals, thus the ratio of distribution coefficients was assumed equal to the ratio of the β_5° constants. Hence, only the relative (apparent) atomic number of Pu^{3+} has been calculated from the stability of $\text{Pu}(\text{NO}_3)_5^{2-}$. This is defined as:

$$Z_{\text{Pu(III)}/G/} = z_{\text{Ln}} + \frac{\Delta G_{\text{Ln}'}^\circ - \Delta G_{\text{Pu}}^\circ}{\Delta G_{\text{Ln}'}^\circ - \Delta G_{\text{Ln}''}^\circ}$$

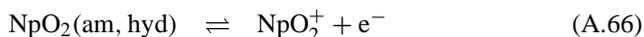
The only result in this work is that the value for this quantity for Pu(III) is 58.9, and ΔG° for the pentantrate complex is approximately $2.5 \text{ kJ}\cdot\text{mol}^{-1}$ higher than that for La, and almost equal to the analogous quantity for Pr. No value for the formation constant of the plutonium complex is reported, and the results from this study cannot be used further in this review.

[87NIT]

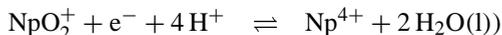
Results obtained in an experimental study of the solubility of Np, Pu, and Am in solutions of 120 ppm total carbonate were compared to calculated values. The values of the parameters used in the calculations are not given. As mixtures of oxidation states were present in the Pu experiments, useful thermodynamic solubilities cannot be determined.

[87RAI/SWA]

In this paper a value of $\log_{10} {}^*K_{s,0}(\text{A.65}) = 1.5$ for $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ was reported, based on the concentration of Np(IV) over $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in the presence of Cu(I)/Cu(II) as a redox buffer. Also, a value of $\log_{10} {}^*K_{s,0}(\text{A.65}) = 2.7$ was reported, based on the equilibrium concentration of NpO_2^+ over $\text{NpO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in the same solutions (Reaction (A.66)).



Apparently the difference in these two numbers could be reconciled if the potential for the reaction:



differs by 0.07 V from the estimate used in the IAEA compilation [76FUG/OET] for the potential of the reduction reaction. Indeed, in the present review, the value of the selected potential (0.604 V) is somewhat lower (by 0.04 V). From this potential and the average value of $\log_{10} K(\text{A.66}) = -(8.10 \pm 0.12)$, the logarithm of the equilibrium constant for the reaction when corrected to $I = 0$ is $\log_{10} {}^*K_{s,0}(\text{A.65}) = 2.0_5$.

However, the extent of hydrolysis is likely to be considerably greater than estimated by Rai, Swanson and Ryan [87RAI/SWA]. Use of the value $\log_{10} {}^*K_1 = -(0.29 \pm 1.00)$ selected in the present review for the first hydrolysis constant for Np^{4+} results in $\log_{10} {}^*K_{s,0}(\text{A.65}) = 1.0_1$ from the Np(IV) concentrations. In the present review the average value of $\log_{10} {}^*K_{s,0}(\text{A.65}) = (1.5_3 \pm 1.0)$ is used, where the uncertainty is an estimate.

[87RIG/VIT]

The authors determined the polarographic half-wave potentials of the $\text{UO}_2^{2+}/\text{UO}_2^+$ couple in NaClO_4 as a function of ionic strength ($I = 3, 2, 1, 0.5 \text{ M}$). Using a cell arrangement that eliminated liquid junction potentials, they derived $E^\circ = (0.089 \pm 0.002) \text{ V}$ using an SIT extrapolation. The authors also determined the formal potential in 1 M HClO_4 as $E^{o'} = (0.065 \pm 0.0002) \text{ V}$ and calculated $E^\circ - E^{o'} = (0.024 \pm 0.004) \text{ V}$. They recommended a correction of 0.024 V to the formal potentials in 1 M HClO_4 of all actinide couples $\text{MO}_2^{2+}/\text{MO}_2^+$ to derive their standard potentials E° . This is in contradiction to the results of Brand and Cobble [70BRA/COB] who studied the $\text{NpO}_2^{2+}/\text{NpO}_2^+$ system and derived $E^\circ = (1.236 \pm 0.010) \text{ V}$. By comparing this value to the $E^{o'} = (1.13638 \pm 0.00016) \text{ V}$ of Sullivan *et al.* [61SUL/HIN], Brand and Cobble recommended the potential difference of 0.1 V to be applied to all $\text{MO}_2^{2+}/\text{MO}_2^+$ formal potentials to derive the standard potentials. Riglet, Vitorge and Grenthe noted that Brand and Cobble used the mean activities of pure solutions of $\text{NpO}_2(\text{ClO}_4)_2$, NpO_2ClO_4 , and HClO_4 instead of the activities for the mixture in their Debye-Hückel extrapolation. Therefore, the authors reinterpreted Brand and Cobble's data using the SIT expression

$$\frac{E}{A} + 2D(I) - \log_{10} \frac{[\text{NpO}_2^{2+}]}{[\text{NpO}_2^+][\text{H}^+]} = \Delta\varepsilon \cdot m_{\text{ClO}_4^-}$$

with

$$\Delta\varepsilon = \left(\varepsilon_{(\text{NpO}_2^{2+}, \text{ClO}_4^-)} - \varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} - \varepsilon_{(\text{H}^+, \text{ClO}_4^-)} \right)$$

$$D = \frac{0.5091\sqrt{I_m}}{1 + 1.5\sqrt{I_m}}$$

and

$$A = 0.05916 \text{ V}$$

This review has also recalculated Cobble's data using a Debye-Hückel constant of 0.5091 instead of the 0.5107 used by Riglet, Vitorge and Grenthe. This however, does not change the standard potential significantly. The parameter values and the results are given in Table A.16.

To calculate $\sigma_{E/A}$ an uncertainty of 0.001 V was assumed. An unweighted linear regression resulted in $E^\circ = (1.158 \pm 0.008) \text{ V}$ and in $\Delta\varepsilon = (0.9412 \pm 0.9642) \text{ kg}\cdot\text{mol}^{-1}$. As one of the authors pointed out in her thesis [90RIG], the large error in $\Delta\varepsilon$ is likely due to the insensitivity of the ion interaction coefficients in solutions of rather low ionic strengths ($0.03 \leq I \leq 0.1 \text{ m}$). Therefore, Riglet, Vitorge and Grenthe used a more meaningful $\Delta\varepsilon = 0.04 \text{ kg}\cdot\text{mol}^{-1}$, derived from their $\text{UO}_2^{2+}/\text{UO}_2^+$ studies conducted over a range of ionic strengths from 0.5 to 3.5 m , to fit the experimental results of Brand and Cobble. The fit resulted in $E^\circ = (1.161 \pm 0.008) \text{ V}$. Although this review accepts this approach, the neptunium measurements over a wide range of ionic strengths later published from the same laboratory [89RIG/ROB] are preferred.

Table A.16: Results of recalculations of the data of Brand and Cobble [70BRA/COB].

$m_{\text{ClO}_4^-}$	$\frac{E}{A^{(a)}}$	$\sigma_{E/A^{(a)}}$
0.09100	19.66543	0.017
0.07156	19.63967	0.017
0.05709	19.56283	0.017
0.05688	19.65371	0.017
0.04192	19.56990	0.017
0.03411	19.64494	0.017

$$\frac{E^\circ}{A^{(a)}} = (19.5674 \pm 0.0595); \Delta\varepsilon = (0.9412 \pm 0.9642) \text{ kg}\cdot\text{mol}^{-1}$$

(a) $A = 0.05916 \text{ V}$

[87ROB/VIT]

This paper reports on the results of a solubility study of $\text{PuO}_2\text{CO}_3(\text{s})$ in carbonate solutions at $I = 3 \text{ M}$ and $t = (20 \pm 1)^\circ\text{C}$. Values for $\log_{10} \beta_1$, $\log_{10} \beta_2$ and $\log_{10} \beta_3$ are reported as (8.6 ± 0.3) , (13.6 ± 0.7) and (18.2 ± 0.4) , respectively, at $I = 3 \text{ M}$ and 9.2, 14.3, and 17.4, respectively, at $I = 0$ (extrapolated using the specific ion interaction method as described in Appendix B.). All of these values appear reasonable. Experiments were reversed and the composition of the solid phase monitored during each experiment. The dicarbonato trimer is described as a metastable (“oversaturated”) form of the dicarbonatodioxoplutonium(VI) monomer. Data was taken from the figure in this reference to estimate the pH range of these experiments. One of the co-authors has pointed out to the reviewer that the measured minimum solubility might actually have been the detection limit. If so, the value for β_1 in this paper may have been overestimated.

[87RÖS/MIL]

Rösch *et al.* measured the mobilities of neptunium(V) species under the influence of a constant electric field gradient. Their measurements in neutral to alkaline solutions confirmed that for solutions having pH values greater than ~ 11.5 , Np(V) exists predominantly in an anionic form. Values of $\log_{10} {}^*\beta_1 = -(10.45 \pm 0.25)$ and $\log_{10} {}^*\beta_2 = -(21.95 \pm 0.35)$ were reported (for a medium of 0.101 M NaClO_4). Correction of these values to $I = 0$ using the specific-ion interaction theory ($\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.25 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$, $\varepsilon_{(\text{NpO}_2(\text{OH})_2^-, \text{Na}^+)} = -(0.01 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}$ (estimated)) results in $\log_{10} {}^*\beta_1^\circ = -(10.46 \pm 0.25)$ and $\log_{10} {}^*\beta_2^\circ = -(22.17 \pm 0.35)$. However, the reported constants are probably mixed constants. They are identical to those reported in [90RÖS/HUN] (and probably from the same experiments). If the pH values, assumed

to be properly measured hydrogen ion activities, were incorporated by the authors to obtain mixed constants, $\log_{10}^* \beta_1^\circ = -(10.4 \pm 0.4)$ and $\log_{10}^* \beta_2^\circ = -(22.0 \pm 0.5)$, where the increased uncertainties have been estimated in the present review, in part to reflect the difficulties in estimating the activity coefficients of the neptunium species.

In the absence of other evidence confirming its existence, the proposed species $\text{NpO}_2^+ \cdot \text{H}_3\text{O}^+$ is not credited in the present review. Although complexes of cations with NpO_2^+ exist, this particular species, for which the authors propose a formation constant of 10^4 , is unlikely to have escaped detection in studies of the potential of the $\text{NpO}_2^+/\text{NpO}_2^{2+}$ couple.

[88CAN]

The values for the formation constants of the mono- and bis-carbonato complexes of Pu(III), $\log_{10} \beta_1 = 7.5$ and $\log_{10} \beta_2 = 12.4$, were calculated from an empirical power series function of the ionic radii of the trivalent lanthanides. There are no other experimental or any other empirical data concerning these complexes in the literature. Therefore these results may be useful to some investigators. However, we cannot recommend these results.

[88KLE/KIM]

The work involved a study of Pu(IV) at 3.3×10^{-7} M in 1 M Na_2CO_3 , pH = 11.2. The main adsorption band is at 484 nm, similar to that found in more concentrated solutions [85EIS/KIM, 86LIE/KIM, 92CAP]. There was no attempt made to identify the species responsible for this absorption band.

[88NAG/TAN]

The results of this study are in qualitative agreement with other recent work on Np(V). However, using $\text{p}K_w = -13.93$ and -13.8 for the 0.005 M and 0.1 M ionic strength media, respectively, the values -8.2 and -7.8 are calculated for $\log_{10}^* \beta_1$. These values are considerably less negative than found in all of the other studies. Results from the studies of Schmidt *et al.* [80SCH/GOR] and Kraus and Nelson [48KRA/NEL] would have been significantly different had the first hydrolysis constant been this large. The values from [88NAG/TAN] are rejected in the present review.

[88NAK/ARI]

The solubility of $\text{NpO}_2\text{OH}(\text{am})$ was measured as a function of pH. Solutions were equilibrated for periods from 1 day to 2 months and then filtered through a 10000 MW cutoff filter. There is no discussion about how the glass electrode was calibrated. The rather scattered solubility results were similar for solutions that had equilibrated ($T = ?$) for 1 week and 2 months, indicating equilibrium had been established. The high solubilities for pH values above 9 suggest the presence of carbonate in the solutions despite the precautions taken by the authors. The CO_2 concentration in the

solutions was estimated to be less than 0.01 mM but there is not much information in the experimental procedure discussing how this was achieved or how the calculations to do this estimation were carried out (the redox potential measurements indicate that solutions were equilibrated with the air, and this is not consistent with low CO₂ concentrations in the solutions). Experimental solubility values, when plotted against pH (7 to 12.4), are scattered and there is practically no significant pH dependency at 8 < pH < 11.5. Most of the results are not in agreement with previous solubility measurements [76SEV/KHA, 78MUS, 85LIE/TRE]. The erratic results are likely the result of carbonate complexation, and gradual ripening or dissolution of colloidal material.

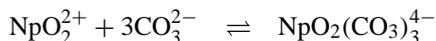
[88ULL/SCH]

The sections of this publication dealing with the uranium system were discussed in a previous volume of the NEA review [92GRE/FUG]. The paper reports results of calorimetric experiments for the heat of reaction of Np(VI) (0.0289 to 0.0447 M) and Pu(VI) (0.010 to 0.016 M), perchlorate salts in aqueous Na₂SO₄ solutions (0.15 M, for the Np(VI) solutions, 0.07 M, for the Pu(VI) solutions) with aliquots of Na₂CO₃ (0.1 to 1 M). The actinides were initially present in solution as AnO₂²⁺, AnO₂SO₄(aq) and AnO₂(SO₄)₂²⁻. By the end of each titration, the limiting carbonate complex, AnO₂(CO₃)₃⁴⁻, had formed. The distributions of the SO₄²⁻ complexes were calculated from equilibrium constants (and enthalpies) previously determined using the same apparatus, [86ULL/SCH]. The calculation procedure for the evaluation of all equilibrium constants and the enthalpy of the non-limiting complex is different from that of this review. The enthalpy of the limiting complexes is essentially model independent. It was not possible to re-evaluate this data set with the appropriate assignment of activity coefficients. The errors assigned to the equilibrium constants and the enthalpies of the intermediate carbonate complexes must be expanded to reflect the non-standard procedure.

The authors [88ULL/SCH] concluded that only the limiting carbonate complex, NpO₂(CO₃)₃⁴⁻, was formed when there was an excess of carbonate. The mean of the experimental heat of reaction values for the neptunium system, for experiments in which the final CO₃²⁻:Np ratio is > 3, is $\Delta H = -(64.5 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$. This molar enthalpy of reaction value is more negative than the value previously reported by Schreiner *et al.* [85SCH/FRI], probably because the initial sulphate concentrations were not the same. Correction of the value for sulphate complexation as done in the original paper [88ULL/SCH] by addition of 22.5 kJ·mol⁻¹ (with an uncertainty assumed equal to that found for the enthalpy of solution reported in this paper ($\pm 2.3 \text{ kJ}\cdot\text{mol}^{-1}$)) results in the value

$$\Delta_r H_m = -(42.0 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1}$$

for



This values applies in an ill-defined aqueous medium that was different for different stages of the experiment, ranging in ionic strength from 0.3 to 1.1 M.

The authors reported $\Delta_r H_m = -(41.9 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$ for the reaction. Assuming the difference results from the original authors using unrounded primary results that were unavailable to the present reviewers, we accept

$$\begin{aligned} \Delta_r H_m(0.098 \text{ to } 0.135 \text{ M Na}_2\text{SO}_4 + 0.123 \text{ to } 0.363 \text{ M Na}_2\text{CO}_3) \\ = -(41.9 \pm 3.2) \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

The values for the measured molar enthalpies of reaction remain constant (within $\pm 2.3 \text{ kJ}\cdot\text{mol}^{-1}$), after the formation of the limiting complex. Since the contributions of Na_2SO_4 dilution and of added Na_2CO_3 to the measured heat were subtracted using a blank, and since the number of moles of Np(VI) is constant in each series of titrations, then in each series of titrations when an excess of Na_2CO_3 was used the only contributions to this (undetected) variation of $\Delta_r H_m$ are due to changes in the activity coefficients [93GIF/VIT, 94GIF/VIT, 98VIT/CAP]. The experiments confirm this result for the limiting complexes.

For the heats measured before the end of titration (before the formation of the limiting complex), a linear variation with the amount of carbonate added was not found. This is evidence that intermediary species were formed. Under these conditions one expects some formation of the trinuclear carbonate complex. However, the authors [88ULL/SCH] did not interpret their data using a model incorporating $(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$. Using the limited data available, it is not possible to choose between the different possible models. However, the value for ΔH_2 reported for the neptunium system is quite different from the values reported for the corresponding uranium and plutonium systems as measured in the same work [88ULL/SCH]. This could be due to experimental kinetic problems as noted by Riglet [90RIG] for similar conditions. These problems apparently occur only for Np(VI) , but not for U(VI) or Pu(VI) . Therefore, this review does not use the ΔH_2 value reported by Ullman and Schreiner for the Np(VI) system. For the Pu(VI) system, the results were reported as the extrapolated infinite dilution values: $\log_{10} \beta_3^\circ = (18.5 \pm 1.2)$ (where the uncertainty is assigned in the present review), $\Delta_r G_{m,3}^\circ = -(105.6 \pm 6.8) \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_r H_{m,3}^\circ = -(38.65 \pm 1.00) \text{ kJ}\cdot\text{mol}^{-1}$. For the $\text{PuO}_2(\text{CO}_3)_2^{2-}$ complex: $\log_{10} \beta_2^\circ = 15.1 \pm 2.2$, $\Delta_r G_{m,2}^\circ = -(86.2 \pm 12.6) \text{ kJ}\cdot\text{mol}^{-1}$, and $\Delta_r H_{m,2}^\circ = -(27 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$. The uncertainties in $\log_{10} \beta_2^\circ$ and $\Delta_r H_{m,2}^\circ$ were expanded above those reported to account for the non-standard calculation procedure used in the original paper.

[89BUD/FED]

The structures of neptunium(V) sulphate hydrate $(\text{NpO}_2)_2\text{SO}_4 \cdot x\text{H}_2\text{O(s)}$, where $x = 6, 4.5,$ and $2,$ were characterised by IR and X-ray diffraction. Instructions are given for the preparation of these salts. No thermodynamic data are presented for evaluation.

[89FEL/RAI]

This paper reports the results of a study of the solubility of $\text{Pu(OH)}_3(\text{s})$ (^{239}Pu) in water and two high ionic strength brines. The measurements were done at $(23 \pm 2)^\circ\text{C}$,

near neutral pH, using iron powder as a holding reductant. For the work in deionized water, solubilities were at or below the detection limit of the method used to determine plutonium (liquid scintillation α -counting) for molalities of $H^+ \leq 10^{-8.5}$. It is unfortunate the details as to the length of time each sample was left before sampling were not provided, nevertheless, the work appears to have been done carefully. The results from the experiments in deionized water are accepted in the present review, and are used to obtain a value for $\Delta_f G_m^\circ(\text{Pu}(\text{OH})_3, s, 298.15 \text{ K})$, but because of the scatter and the steep slope of the plot of solubility vs. p_{cH^+} the uncertainty limit for the reported solubility product is increased ($\log_{10}^* K_{s,0} = (15.8 \pm 1.5)$). The solubility results in the brine solutions, although also from experiments that seem to have been carried out carefully, are not used in the present review both because the solutions are of such high ionic strength that the SIT formulation is probably not applicable, and because the possibility of radiolytic oxidation of plutonium in the high chloride media was not assessed.

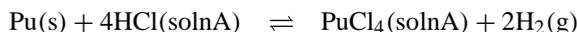
[89KIM/KAN]

This study appears to have been carefully carried out. The solubilities of $\text{Pu}(\text{OH})_4(\text{am})$ and $\text{PuO}_2(\text{cr})$ (predominantly ^{239}Pu) were measured in acidic perchlorate solutions. The amorphous solid was equilibrated for 45 d, the crystalline material for 3 a at $(20 \pm 1)^\circ\text{C}$. The authors concluded that only the measurements obtained in 1 M acid could be used to determine solubility products, although a limiting value for the solubility product of $\text{Pu}(\text{OH})_4(\text{am})$ at $\text{pH} = 1.09$ was also calculated. The reported solubility products were calculated using 25°C values for pK_w and for the activity coefficients for NaClO_4 . Furthermore, it was assumed the activity coefficients for NaClO_4 and HClO_4 are the same. Actually, they differ by more than 0.1 at 25°C [59ROB/STO]. The former problem is more severe, and the overall result is that the reported values of $K_{s,0}$ are approximately an order of magnitude greater than if the calculations were done correctly ($\log_{10} K_{s,0}(\text{Pu}(\text{OH})_4(\text{am})) = -58.8$, $\log_{10} K_{s,0}(\text{PuO}_2(\text{cr})) = -61.2$).

[89MOR/ELL]

The heats of solution of four samples of $\text{BaPuO}_3(\text{cr})$ into 1 M HCl and one sample into 4 M HCl were measured. The oxygen stoichiometry was checked during the course of the work, and the measurements were done under conditions that should have resulted in disproportionation of less than a few tenths of a percent of the $\text{Pu}(\text{IV})$. The value obtained from the dissolution into 4 M HCl was consistent with the other measurements. However, based on an assessment of the values for the enthalpies of formation of U^{4+} (6 M HCl) and U^{4+} (1 M HCl), and also the corresponding quantities for Th^{4+} , it would be expected that the value of the enthalpy of formation of Pu^{4+} in 4 M HCl would be substantially less negative than the value in 1 M HCl probably by between 5 and 15 $\text{kJ}\cdot\text{mol}^{-1}$. There would also be (probably partially compensating) differences in the other heats involving "soln A" in the authors' Table 2. Therefore, only the four heats of solution into 1 M HCl have been accepted in the present review, and using the procedures outlined in Appendix C, $\Delta_{\text{sol}}H = -(273.9 \pm 7.0) \text{ kJ}\cdot\text{mol}^{-1}$. The difference

($\Delta_f H_m^\circ(\text{PuCl}_4, 1 \text{ M HCl}) - \Delta_f H_m^\circ(\text{PuCl}_4, \text{aq})$) has been estimated [2000RAN/FUG] as $(4.6 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$. Using this and $\Delta_f H_m^\circ(\text{Pu}^{4+}, \text{aq}) = -(539.9 \pm 3.1) \text{ kJ}\cdot\text{mol}^{-1}$ (Section 16.4 of the present review), the enthalpy for the reaction



is estimated here as $-(535.3 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}$.

Therefore,

$$\Delta_f H_m^\circ(\text{BaPuO}_3, \text{cr}, 298.15 \text{ K}) = -(1654.2 \pm 8.3) \text{ kJ}\cdot\text{mol}^{-1}$$

[89MOR/PRA]

This publication is chapter 2 of Prapoto's thesis. It seems to be a first try to perform the same type of experiment reported previously by Rai and Ryan [85RAI/RYA], but the results are less accurate. The critical discussion of [85RAI/RYA] was cited, but not used. The experimental procedure used to prepare the solutions and to perform the solubility measurements led to the non-reversible formation of Np(IV) hydroxide. This precipitated and gave particles (or colloids). Despite what is said in this publication, the formation of colloids was not controlled, and its effect on the solubility is not quantitatively understood. The authors say, that they maintained constant ionic strength, and that they added NaOH to adjust the pH probably during equilibration with carbon dioxide from the air. However, this certainly would increase the ionic strength. There are also some uncertainties introduced since we do not know how the pH electrode was calibrated (pH or $-\log_{10}[\text{H}^+]$?).

The reported solubility values are higher than those well-established by Rai and Ryan [85RAI/RYA] under similar chemical conditions. The highest solubilities are obtained in contact with the air, but no Np(V) was found in the solution. The non-reversible reactions mentioned above are enough to explain this discrepancy. No thermodynamic data can be deduced from this work. The solubility increase with increasing $[\text{CO}_3^{2-}]$ is significant but for the same reasons, and because of possible systematic errors in the pH measurements, no stoichiometry can be deduced for the soluble species. There is no real evidence of formation of some unknown complex.

Finally, the authors used curve-fitting to interpret their results without any sensitivity analysis. Many hypothetical carbonate or hydroxide complexes could be used to fit those results, as they encompass such a narrow domain of chemical conditions. This is especially true when the solid was not properly prepared and reducing conditions were probably not maintained. The authors have then used their "fitted" formation constants in many subsequent papers [89PRA/MOR, 89TAN/NAG, 90PRA/MOR, 91ITA/TAN, 93PRA/YAM] that should be reinterpreted. In addition, in many of these other experiments, the chemical conditions were also not correctly controlled, and the reproducibility was not checked. Even the literature cited by the authors (especially [85RAI/RYA]) have carefully pointed out that such methodologies, interpretations and results should be avoided.

[89PRA/MOR]

Solubility studies were carried out using low initial concentrations of Np(IV) (10^{-5} to 10^{-6} M), but the equilibration time allowed (one week) was rather short. Although they do not give a great deal of experimental detail, the authors appear to have been able to successfully measure ^{237}Np to quite low concentrations (3×10^{-10} M). The measured neptunium concentrations in aqueous solutions contacted with $\text{Np}(\text{OH})_4(\text{s})$ (with $\text{Na}_2\text{S}_2\text{O}_4$ as a holding reductant) were similar to, but only slightly lower than, those reported by other groups [85EWA/GOR, 85RAI/RYA], and the results are accepted in the present review.

[89RIG/ROB]**a) $\text{NpO}_2^{2+}/\text{NpO}_2^+$ system**

Riglet, Robouch and Vitorge studied the $\text{NpO}_2^{2+}/\text{NpO}_2^+$ redox couple at a rotating platinum electrode by linear scan voltammetry and by cyclic voltammetry on a static platinum electrode. Both experiments were carried out at 20°C . The neptunium redox reaction in both experiments showed quasi-reversible behavior. From the two independent methods the potential in 1 M HClO_4 was determined to be $E^{o'} = (1.140 \pm 0.007)$ V and $E^{o'} = (1.140 \pm 0.005)$ V. From these data, this review calculates $E^{o'} = (1.140 \pm 0.004)$ V. Because the potential measurements were made at 293.15 K, and not at the standard temperature of 298.15 K, the authors applied a value of $-(0.0015 \pm 0.0010)$ V to correct to standard temperature. This temperature correction was derived from the isothermal temperature coefficient which was determined by Cohen and Hindman [52COH/HIN]. Blanc and Madic [84BLA/MAD] determined the thermal temperature coefficient for the $\text{NpO}_2^{2+}/\text{NpO}_2^+$ potential to be $(\partial E/\partial T)_{\text{therm}} = 0.00043 \text{ V}\cdot\text{K}^{-1}$ which converts to an isothermal coefficient of $(dE/dT)_{\text{isotherm}} = 0.00023 \text{ V}\cdot\text{K}^{-1}$. Using this temperature coefficient, a temperature correction of 0.0011 V would apply to the potential of Riglet, Robouch and Vitorge. The difference between both correction methods is within the standard deviation of the correction used by Riglet, Robouch and Vitorge.

Riglet, Robouch and Vitorge derived the standard potential $E^\circ = (1.162 \pm 0.011)$ V using the SIT with data from potential measurements at additional ionic strengths ($I = 2, 3$ M). The difference between the standard potential and the formal potential is $E^\circ - E^{o'} = (0.022 \pm 0.014)$ V. This difference agrees with the value of (0.024 ± 0.004) V for the $\text{UO}_2^{2+}/\text{UO}_2^+$ system [87RIG/VIT], and from the SIT treatment $\Delta\varepsilon = (0.21 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ was derived. Using $\varepsilon_{(\text{NpO}_2^{2+}, \text{ClO}_4^-)} = \varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)} = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$, $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.25 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ is obtained.

The $\text{NpO}_2^{2+}/\text{NpO}_2^+$ standard potential of Riglet, Robouch and Vitorge was found to be quasi-reversible. An undetermined kinetic step was involved in the electron transfer reaction. Although explanations were given that the half-wave potential of the reaction was not affected by this kinetically controlled transfer, the potentials are not really acceptable from a standpoint of rigorous thermodynamics. But in light of the good agreement of E° with the corrected value of Brand and Cobble [70BRA/COB, 87RIG/VIT],

and the lack of other data, this review accepts this value.

A general problem arises from the standpoint of strict thermodynamics when formal potentials are determined against a reference electrode other than the standard hydrogen electrode. For example, Riglet, Robouch and Vitorge used the cell



To compare the potential of this cell to a cell arrangement using a SHE reference electrode the potential of the following cell must be known:



Riglet, Robouch and Vitorge used the activity coefficient of HClO₄ for the left half-cell and the Cl⁻ activity coefficient calculated with the SIT for the right half-cell to correct to the standard potential. However, H⁺, Cl⁻, Na⁺, and ClO₄⁻ may have been transferred across the junction. The system is strictly not at equilibrium, because the NaClO₄ and NaCl concentrations in the left half-cell are very close to zero.

b) Pu⁴⁺/Pu³⁺ system

Riglet, Robouch and Vitorge determined the formal potential of the Pu⁴⁺/Pu³⁺ couple in 1 M HClO₄ at 293.15 K by cyclic voltammetry using a platinum electrode as $E^{\circ'}(293) = (0.959 \pm 0.005) \text{ V}$. Connick and McVey [51CON/MCV] and Rabideau and Lemons [51RAB/LEM] determined for the Pu⁴⁺/Pu³⁺ couple the formal potentials of $E^{\circ'} = (0.982 \pm 0.002) \text{ V}$ and $E^{\circ'} = (0.9821 \pm 0.0005) \text{ V}$, respectively. The data of these investigators were derived from junction potential-free emf measurements which are precise and accurate. To compare their non-standard (293.15 K) formal potential to these earlier derived potentials at standard temperature, Riglet, Robouch and Vitorge used a temperature correction of $(11 \pm 2) \text{ mV}$ which they indicated was derived by Connick and McVey [51CON/MCV]. This is incorrect. Connick and McVey's value is $(dE/dT)_{\text{isotherm}} = (0.00125 \pm 0.00004) \text{ V}\cdot\text{K}^{-1}$. Capdevila, Vitorge and Giffaut [92CAP/VIT] reported $(dE/dT)_{\text{isotherm}} = (0.00168 \pm 0.00007) \text{ V}\cdot\text{K}^{-1}$, that was determined over a wide temperature range. This review selects $(dE/dT)_{\text{isotherm}} = (0.00149 \pm 0.00008) \text{ V}\cdot\text{K}^{-1}$ (see text). Therefore, a correction of $(0.0075 \pm 0.0004) \text{ V}$ should be applied for the temperature change of the formal potential from 293.15 to 298.15 K. Correcting Riglet, Robouch and Vitorge's potential by this amount results in the formal Pu⁴⁺/Pu³⁺ potential at standard temperature, $E^{\circ'} = (0.966 \pm 0.0005) \text{ V}$. This potential is smaller by 16 mV than the potentials determined earlier, $E^{\circ'} = (0.982 \pm 0.002) \text{ V}$ by Connick and McVey [51CON/MCV], and $E^{\circ'} = (0.9821 \pm 0.0005) \text{ V}$ by Rabideau and Lemons [51RAB/LEM]. The reason for this discrepancy may be found in the problem of Riglet, Robouch and Vitorge's reference electrode, which is discussed above for the NpO₂²⁺/NpO₂⁺ system, or in the possible presence of polymeric Pu(IV) in solution which would shift the potential to more negative values. However, the most likely reason, as suggested later by Capdevila and Vitorge [95CAP/VIT], is interference between the two reversible redox couples during the measurements.

The paper of Riglet, Robouch and Vitorge misquotes a hydrogen activity correction to the formal potential as work of Connick and McVey, while this correction was actually performed by Rabideau and Lemons [51RAB/LEM, p. 2897, lines 7 to 9]. This correction, however, has no bearing on the formal potential.

Because of the large discrepancy of Riglet, Robouch and Vitorge's formal potential and the fact that there are no plausible reasons to doubt the consistent data of Connick and McVey, Rabideau and Lemons, and of Capdevila [92CAP], this review selects $E^{\circ'} = (0.982 \pm 0.002)$ V. Therefore, data of Riglet, Robouch and Vitorge at ionic strengths of 0.5, 2, and 3 M, and the resulting E° from applying the SIT to these data, were not used in the present review.

c) $\text{Np}^{4+}/\text{Np}^{3+}$ system

Riglet, Robouch and Vitorge measured the $\text{Np}^{4+}/\text{Np}^{3+}$ couple in perchloric acid at different ionic strengths ($I = 0.5, 1, 2, 3$ M) and at 293.15 and 298.15 K, using cyclic voltammetry on a hanging mercury drop electrode. Their formal potential at 298.15 K, $E^{\circ'} = (0.154 \pm 0.005)$ V agrees well with the value of Cohen and Hindman [52COH/HIN], $E^{\circ'} = (0.1551 \pm 0.0010)$ V. This leads to confidence in their data at different ionic strengths. The review accepts their standard potential $E^{\circ} = (0.218 \pm 0.010)$ V derived from the data using the SIT treatment. Exclusion of data from the measurements in 0.5 M HClO_4 solutions to minimize any deviation caused by Np^{4+} hydrolysis would result in only a minor difference in the value of E° (to 0.2164 V vs. SHE). The uncertainty interval, however, was calculated incorrectly; the corrected value, as recalculated in the present review, is $(dE/dT)_{\text{isotherm}} = (0.0016 \pm 0.0028)$ $\text{V}\cdot\text{K}^{-1}$. Because this value is derived from only two data points, it should be considered an estimate. Within the rather large uncertainty, it agrees, however, with $(dE/dT)_{\text{isotherm}} = (0.00136 \pm 0.00005)$ $\text{V}\cdot\text{K}^{-1}$ and $(dE/dT)_{\text{isotherm}} = (0.0019 \pm 0.0004)$ $\text{V}\cdot\text{K}^{-1}$ determined by Cohen and Hindman [52COH/HIN] and by Blanc and Madic [84BLA/MAD], respectively.

The difference between the standard and the formal potential

$$E^{\circ} - E^{\circ'} = (0.064 \pm 0.011) \text{ V}$$

(the value that is used in the present review) is substantially different from the 0.0024 V used by Fuger and Oetting [76FUG/OET], which they derived from literature data on $\text{Pu}^{4+}/\text{Pu}^{3+}$.

[89RÖS/DIT]

This paper describes results of an electromigration study of carrier-free ^{239}Np with added complexing ligands. The results of these colligative measurements were interpreted in terms of mobilities and association quotients for the complex ions. The results for sulphate indicate that no anionic species are formed. In order to explain this result the authors proposed that Np(V) in solution forms the complex cation NpO^{3+} . This hypothesis is at odds with a large amount of direct and indirect evidence that Np(V) exists as NpO_2^+ in solution. As we are unable to explain these results in terms of the

generally accepted model of Np(V) behavior in solution, we have given no weight to these results in our review.

[89SAW/CHA]

This seems to be a partial, preliminary publication of Sawant, Chaudhuri and Patil [90SAW/CHA2]. See the comments on that paper.

[89TAN]

The near IR spectra, 820-880 nm, were shown for 0.00125 M Pu(VI) solutions in LiOH solutions (2.5×10^{-3} to 1 M), and large changes in the spectra were reported. The smoothed spectra are not suitable for reanalysis, and although the authors proposed that $\text{PuO}_2(\text{OH})_3^-$ and $\text{PuO}_2(\text{OH})_4^{2-}$ are formed, no values for the hydrolysis constants were suggested. Nothing reported in the experimental procedure precludes carbonate complexation in the less basic solutions, so although there is evidence for at least one anionic hydrolysis species, no quantitative results are derived from this study.

[89TAN/NAG]

This is work discussing sorption and migration of Np(IV). No thermodynamic data can be deduced from this work. It uses erroneous chemical speciation from [88NAG/TAN].

[90BEN]

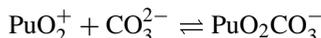
In this thesis, laser induced photoacoustic spectroscopy was used to determine the concentration of free PuO_2^+ in 0.1 M NaClO_4 solutions. From pH = 3 to 8, there was no observed spectral change; from pH = 8 to 10.75, there was a clear and systematic decrease in the magnitude of the absorptivity associated with PuO_2^+ , but there is no spectral evidence for a new soluble species. The author attributed the decrease in absorptivity to the decrease of PuO_2^+ concentration and the formation of the first hydrolysis product according to the reaction:



On the basis of this interpretation, an equilibrium constant was proposed for this reaction: $\log^* \beta_{11}(0.1\text{MNaClO}_4) = -(9.73 \pm 0.10)$. The stability diagrams provided in this work (taken from but not attributed to the Np(V) study of [90RIG]), suggest a conflicting alternative explanation: that Pu(V) may have disproportionated to Pu(IV) and Pu(VI). However, this disproportionation reaction, if possible (see [94PER/DAV]), should be slow in basic solution and there is no evidence that the measurements were delayed sufficiently to allow the redox equilibrium to be established. The lack of spectral evidence for the soluble hydrolysis species suggests still another interpretation; precipitation of $\text{PuO}_2\text{OH}(\text{am})$ may have occurred under the conditions of these experiments. Considering this latter interpretation, the stability constant given by the author, $\log^* \beta_{11}^\circ = -(9.73 \pm 0.10)$, represents only a reasonable upper bound for the stability

of the first hydrolysis species. This value is consistent with the upper limit suggested by Kraus and others [46KRA/DAM, 48KRA/NEL, 49KRA/DAM, 56KRA] who did observe and consider the effects of disproportionation in their more acidic solutions. We select the reported results as an upper limit: $\log^* \beta_{11}^\circ = -(9.73 \pm 0.10)$. Further experiments will be needed to validate this result.

Using the same technique in 0.5 M NaClO₄ with varying p_{CO_2} (0.1 – 0.5 atm) and pH = 6.25 – 7.85, Bennett determined spectra attributed to the formation of the first Pu(V)-carbonate complex according to the reaction:



Both a decrease in the PuO₂⁺ peak and an increase in another peak were observed. The evidence of carbonate complexing is clear, although the stoichiometry of the complex is poorly constrained. However, higher order complexes, PuO₂(CO₃)_n¹⁻²ⁿ, do not appear to be important in these experiments. The stability diagrams provided by the author (also from [90RIG]) suggest that disproportionation and formation of Pu(VI)-carbonate may be important, but for the same reasons outlined above, this disproportionation is unlikely. The proposed stability constant for PuO₂CO₃⁻ is (4.60 ± 0.03). Its extrapolated value at infinite dilution, $\log \beta^\circ(298 \text{ K}) = (5.12 \pm 0.14)$ (*cf.* Section 21.1.2.1.2 and Appendix B), is similar to the value found for the analogous Np(V) reaction ($\log \beta^\circ(298 \text{ K}) = (4.96 \pm 0.06)$), suggesting that the author's interpretation may be valid. The proposed value is selected. However, additional experimental work is needed to confirm the author's interpretations. The additional stability constants for Pu(V)-carbonate species reported in this work were apparently derived by analogy to the Np(V) work of [90RIG] (no citation to this source was given) and are not considered in the present review.

[90NIT/STA]

Nitsche, Standifer and Silva measured the formation constant of the first Np(V) carbonate complex by absorption spectrophotometry, in 0.1 M NaClO₄ aqueous solution. Their results are in accord with previous work of Riglet [90RIG]. The SIT was used to extrapolate their data to zero ionic strength, with other published data, but they did not use values obtained in 3 M NaClO₄ [86GRE/ROB, 90RIG]. The formation constant is consistent with the values selected in the present review, but there are some minor problems with this work.

The authors did not give the exact composition of their solution which hinders recalculation in the present review. This is unfortunate, because use of the hydrolysis constants selected in the present review suggests the authors overestimated the correction for Np(V) hydrolysis. It was reported that 28% of neptunium not complexed at a pH value of 8.5 was hydrolyzed to form NpO₂OH(aq). Since they observed an isosbestic point, they had to assume that the Np(V)-OH species had the same molar absorptivity coefficient as the NpO₂⁺ species. This was not verified, and it is quite unusual to observe actinide hydrolysis without spectral change. This is not a problem if the hydrolysis is assumed to be much weaker, and using the value for the first hydrolysis constant selected in the present review, the correction for hydrolysis should be

Table A.17: Values of the formation constant for $\text{NpO}_2\text{CO}_3^-$ in 0.1 M NaClO_4 from various analyses of the spectrophotometric measurements of Nitsche, Standifer and Silva [90NIT/STA]. A_0 and A_1 are NpO_2^+ and $\text{NpO}_2\text{CO}_3^-$ molar absorptivity respectively. \pm_A and $\pm_{\log_{10} A}$ are 1.96 standard deviations for A and $\log_{10} A$ respectively where A is the measured molar absorbance. When $\log_{10} \beta_1$ is not fitted, it is the weighted mean value calculated from each experimental measurement.

Fitted parameters	\pm_A	$\pm_{\log_{10} A}$	A_0	A_1	$\log_{10} \beta_1$
$A_1, \log_{10} \beta_1$	21.88	0.051	395	49.8	(4.73±0.17)
A_1	22.78	0.052	395	47.2	(4.74±0.17)
$A_1, \log_{10} \beta_1$	23.90	0.042	395	36.7	(4.66±0.17)
A_1	23.06	0.050	395	41.7	(4.71±0.17)
$A_1, A_0, \log_{10} \beta_1$	9.81	0.028	353	25.8	(4.51±0.06)
A_1, A_0	9.81	0.028	352	25.8	(4.51±0.06)
$A_1, A_0, \log_{10} \beta_1$	9.83	0.028	351	24.7	(4.51±0.06)
A_1, A_0	9.83	0.028	352	24.7	(4.51±0.06)
A_1			?		(4.34±0.11) ^(a)
A_1			?		(4.46±0.23) ^(b)
					(4.56±0.46) ^(c)

(a) [90NIT/STA] corrected for Np(V)-OH .

(b) [90NIT/STA] no corrections (this review).

(c) [90NIT/STA] proposed by this review.

less than the experimental uncertainty. The recalculated value (in 0.1 M NaClO₄) is $\log_{10} \beta_1 = 4.22$ instead of $\log_{10} \beta_1 = (4.34 \pm 0.11)$ as calculated in the original paper [90NIT/STA].

The glass electrode was calibrated with a standard buffer and a 4 M NaCl solution was used as a bridging electrolyte, thus there was probably some error due to junction potentials. With a linear regression analysis to check the stoichiometry and to calculate the formation constant of the equilibrium under study, the authors found a slope of 0.94. Thus, the formation constant calculated was $\frac{[\text{Np(V)}]}{[\text{NpO}_2^+][\text{CO}_3^{2-}]^{0.94}} (\text{mol}\cdot\text{dm}^{-3})^{-0.94}$, and not $\beta_1 = \frac{[\text{Np(V)}]}{[\text{NpO}_2^+][\text{CO}_3^{2-}]} (\text{mol}\cdot\text{dm}^{-3})^{-1}$ as required for consistency with the mass action law. It is possible each of these small systematic errors were negligible or that they cancelled, however there is not enough information in this publication to evaluate them accurately.

The scanned spectrophotometric results from Figure 1 of the paper were used with the $\log_{10}[\text{CO}_3^{2-}]$ values given in its Table 1 to refit the data (see Table A.17). The results are not consistent with the NpO_2^+ molar absorptivity coefficient, A_0 , reported by Nitsche, Standifer and Silva, so that was also fitted in the present review. The value $\log_{10} \beta_1 = (4.34 \pm 0.11)$ proposed in the original paper [90NIT/STA] is consistent with $\log_{10} \beta_1 = (4.51 \pm 0.06)$, the best fit value, but not with $\log_{10} \beta_1 = (4.74 \pm 0.17)$ where the A_0 was not fitted. This confirms that there is some systematic error. Calculations show that formation of the $\text{NpO}_2(\text{CO}_3)_2^{3-}$ complex had a negligible effect. The uncertainty was selected so as to overlap all the fitting results (see Table A.17). The uncertainty was then increased to ± 0.46 to also account for the uncertainty in the junction potential and in the calculation of the activity coefficient for H^+ . The final value $\log_{10} \beta_1 = (4.56 \pm 0.46)$ is fortuitously in excellent agreement with the value selected for the same medium in the present review.

[90OKA/REE]

This paper was apparently written after [91OKA/REE]. It reports the use of laser photoacoustic spectroscopy to provide evidence supporting the identification of the species responsible for absorption at 640 nm as $(\text{PuO}_2)_3(\text{OH})_5^+$. The authors also suggest the hydrolysis species formed in weakly basic solutions may be the monomeric $\text{PuO}_2(\text{OH})_2(\text{aq})$. At least some of the data analysis relies on the first hydrolysis species being PuO_2OH^+ , $\log_{10}^*\beta_1 = -5.2$ [91OKA/REE]. It is not clear how the results would be reinterpreted if the first major hydrolysis species were the dimer, as suggested by the same authors in a later paper [93OKA/REE].

[90PAZ/KUD]

This paper reports the total aqueous solution concentrations of plutonium species over $\text{Pu}(\text{OH})_4(\text{am})$ as a function of pH for pH values from 1.5 to 10.3. No check seems to have been done to identify the oxidation state of the solution species. As this information is lacking, data from this paper could not be used to obtain hydrolysis constants in the present review. It is hard to understand how the authors could fail to even dis-

cuss the problem of the oxidation state when they specifically cite Rai's paper [84RAI] in the introduction. The raw solubility results are reasonably compatible with those of Rai [84RAI] except for the most acidic solutions ($\text{pH} < 2$). For values of pH near 1.5, the solubility is one to three orders of magnitude greater than found by others [49KAS, 65PER, 84RAI]. However, even at the lowest pH value, Pu^{4+} would not be expected to be a major form of plutonium in equilibrium in solution over the solid.

[90PRA/MOR]

This is chapter 3 of Prapoto's thesis. It is an unsuccessful attempt to exactly duplicate the experiments of Rai and Ryan [85RAI/RYA]. The experimental results are not particularly consistent with those of chapter 2 of the thesis [89MOR/PRA], and the measured solubilities are higher than those well established by Rai and Ryan [85RAI/RYA] under these conditions [98VIT/CAP], see also the discussion of [85RAI/RYA] in this appendix. The authors made the same types of errors in their experimental procedures and curve fitting as in Moriyama *et al.* [89MOR/PRA] (see the discussion in this appendix). No thermodynamic data should be deduced from these measurements that are scattered, probably not representative of equilibrium conditions, and where the solid phase may have varied. Therefore the stoichiometry and the formation constants proposed by the authors are not considered further in this review.

[90RIG]

The information in this thesis formed part of the basis for several publications [86GRE/RIG, 87RIG/VIT, 89RIG/ROB]. The Np(V) solubility data are those reported in [84VIT, 86GRE/ROB, 98VIT/CAP]. The experimental methods and the interpretation used in this work were correct. The aqueous speciation was controlled at constant ionic strength (NaClO_4 media) either by $\text{CO}_2(\text{g})/\text{HCO}_3^-$ (bubbling carbon dioxide gas in an open cell) or $\text{HCO}_3^-/\text{CO}_3^{2-}$ (closed batches) buffers. For potentiometric measurements the junction potentials could be neglected because the same ionic medium (typically 3 M NaClO_4) was used for the working solutions and the reference electrode solution, and glass electrodes were calibrated in concentration units, in the same ionic medium as the working solutions. Auxiliary thermodynamic data used for $-\log_{10}[\text{H}^+]$ calibration were consistent with those used in the present review.

a) Np(V) spectrophotometric study in carbonate media

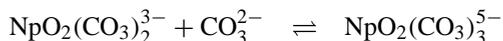
The formation of Np(V) carbonate soluble complexes in carbonic acid/bicarbonate/carbonate aqueous solutions was studied by spectrophotometry (thesis pages 140 to 151). The formation constant for $\text{NpO}_2\text{CO}_3^-$ was determined in 0.5 M NaClO_4 bicarbonate solution at $p_{\text{CO}_2} = 1$ atm, using the absorptivity at 991 nm, and 2 different Np(V) concentrations (0.460 and 0.195 mM) to confirm this complex is not polynuclear. There is only limited overlap of the main characteristic peaks of the two Np(V) species, and this method avoids systematic errors inherent in determinations from solubility measurements (see below). However, in the present review, the value was re-

Table A.18: Experimental conditions of the [90RIG] publication spectrophotometric measurements.

series n ^o	[NaClO ₄] _{ini} (M)	[Na ₂ CO ₃] _{ini} (M)	[Np(V)] _{total} (mM)	log ₁₀ [CO ₃ ²⁻] range
1	0.5	0	0.046	< -4.3
2	0.5	0	0.0195	-2.06 to -0.4
3	0.5	0	0.0218	-1.4 to -0.6
4	1	0	0.0109	-1 to -1.8
5	2	0	0.0109	-2
6	3	0	0.0054	-1.6 and -1.7
7	0	0.13 to 2	1.08	-0.89 to 0.30
8	0	0.01 to 0.1	0.2	-2 to -1

calculated from the absorbance measured at 981 nm (thesis page 225), a NpO₂⁺ peak, as this precludes interferences from the 993 nm NpO₂(CO₃)₂³⁻ band. The recalculated β₁ value is in accord with that determined by Riglet (within the uncertainties), and is reasonably accurate (Table A.19). It was used by this review in the selection of thermodynamic data extrapolated to zero ionic strength. It is consistent with the value selected in this review, and with later studies (at lower ionic strength) as reinterpreted in the present review [90NIT/STA, 94NEC/KIM]. The molar absorptivity of the NpO₂CO₃⁻ peak at 991 nm (not a NpO₂OH(aq) peak [76SEV/KHA]) was found to be 300 mol⁻¹·cm⁻¹. Although NpO₂(CO₃)₂³⁻ was barely detectable for these conditions, interference was sufficient that the spectral data at 991 nm from this NpO₂CO₃⁻ peak were not used in the present review.

The Np(V) spectral variations at 998 nm (NpO₂(CO₃)₂³⁻ absorbs at this wavelength) for 0.02 M < [CO₃⁻] < 0.4 M at different ionic strengths (0.5 to 3 M) were used to determine values for the stepwise formation constant, K₃,



and the corresponding value of Δε₃ = -(0.14 ± 0.10) kg·mol⁻¹. In the same set of experiments, spectral variations at 990 nm were used to determine values for the stepwise formation constant, K₂,



and Δε₂ = -(0.04 ± 0.10) kg·mol⁻¹.

The evaluation of Δε₂ and K₂ is very difficult because NpO₂(CO₃)₂³⁻ is the predominant species only in a very narrow chemical domain, and in some cases (at high ionic strength) perhaps not at all. Interference from either the NpO₂CO₃⁻ species at low carbonate concentrations, or the NpO₂(CO₃)₃⁵⁻ complex at high carbonate concentrations, cannot be avoided. The NpO₂CO₃⁻ peak is at a wavelength between those

Table A.19: Np(V) carbonate complexation constants deduced from the spectrophotometric measurements reported in [90RIG]. $K_i = [\text{NpO}_2(\text{CO}_3)_i^{(1-2i)}] / ([\text{NpO}_2(\text{CO}_3)_{(i-1)}^{(3-2i)}][\text{CO}_3^{2-}])$. The equilibrium constants deduced from only a part of the experimental data [90RIG] are italicised to stress that they were not used in selection of values in the present review.

	Ionic media	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$
series 7 and 8	0			$-(0.98 \pm 0.15)$
series 4 to 6	0		(1.51 ± 0.15)	$-(0.86 \pm 0.15)$
values finally proposed in [90RIG]	0	(4.7 ± 0.2)	(1.51 ± 0.15)	$-(0.86 \pm 0.15)$
this review	0.12 Na ₂ CO ₃		(1.4 ± 0.3)	
this review	0.17 Na ₂ CO ₃			(1.0 ± 0.28)
series 1	0.5 NaClO ₄	(4.30 ± 0.10)		
series 2	0.5 NaClO ₄	<i>4.41</i>	<i>3.35</i>	
series 1 and 2	0.5 NaClO ₄	<i>4.75</i>	<i>3.71</i>	
this review, data from series 7 and 8	0.18 Na ₂ CO ₃			(0.90 ± 0.2)
values finally proposed in [90RIG]	0.5 NaClO ₄	(4.3 ± 0.1)	(2.23 ± 0.07)	(1.37 ± 0.07)
this review	0.5 NaClO ₄	(4.41 ± 0.1)	(2.1 ± 0.6)	(1.13 ± 0.2)
series 7 and 8	1 Na ₂ CO ₃			(1.60 ± 0.07)
series 4 to 6	1 NaClO ₄		(2.38 ± 0.07)	(1.86 ± 0.07)
values finally proposed in [90RIG]	1 NaClO ₄	(4.3 ± 0.2)	(2.38 ± 0.07)	(1.86 ± 0.07)
this review	1 NaClO ₄			(1.48 ± 0.2)
series 7 and 8	2 Na ₂ CO ₃			(2.05 ± 0.07)
series 4 to 6	2 NaClO ₄		(2.54 ± 0.07)	(2.47 ± 0.07)
values finally proposed in [90RIG]	2 NaClO ₄	(4.6 ± 0.3)	(2.54 ± 0.07)	(2.47 ± 0.07)
this review	2			(1.96 ± 0.2)
values finally proposed in [90RIG]	3 NaClO ₄			(2.9 ± 0.2)

of NpO_2^+ and $\text{NpO}_2(\text{CO}_3)_2^{3-}$, and has an intermediate molar absorptivity, so qualitative interpretation (prior to curve fitting or to help in interpretation of the results) is not possible. Riglet noted that these problems did not cause difficulties in the study of the influence of ionic strength on the shift of the curves of absorbance vs. $\log_{10}[\text{CO}_3^{2-}]$ (to determine values of $\Delta\varepsilon_2$ and $\Delta\varepsilon_3$), and her reported values are indeed in fair agreement with the values determined in the present review from other published data (a graphical recalculation led to $\Delta\varepsilon_3 = -(0.08 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$). However, these data are not used in the selection of thermodynamic parameters in the present review. An attempt by Riglet to fit all her spectrophotometric and solubility results within the uncertainties of the measurements was unsuccessful, and she concluded this inconsistency was due to trying to simultaneously determine the unknown molar absorptivity coefficients of $\text{NpO}_2(\text{CO}_3)_2^{3-}$ from the fit of the data.

b) Np(V) solubility in sodium carbonate media

This thesis also reported and discussed a study of Np(V) solubility in carbonic acid/bicarbonate/carbonate aqueous solutions. The experimental data were those reported in several earlier publications [84VIT, 86GRE/ROB], and reports of European joint research contracts [85CÔM, 85KIM]. Sensitivity analysis was done (page 153 [90RIG]). The thermodynamic values deduced by the author and in those from recalculation in the present review are consistent within the stated uncertainties (Table A.20). Riglet noted that the main uncertainty was due to poor crystallisation of the solid phase when NpO_2^+ was the major soluble neptunium species. This seems to have been substantiated in later studies (*e.g.*, [93LEM/BOY]). As mentioned elsewhere in this appendix (see the discussion of [84VIT]), this relatively poor accuracy probably cannot be attributed to ion exchange equilibria in the solid phase as proposed by Volkov *et al.* [79VOL/VIS2]



The solids, typically hydrated $\text{Na}_{0.6}\text{NpO}_2(\text{CO}_3)_{0.8}(\text{s})$, did not usually result from lengthy equilibration with aqueous solutions. Vitorge carried out measurements [84VIT], for the chemical conditions under which NpO_2^+ was the major soluble complex by assuming the equilibrium



controlled the solubility and deduced values of the corresponding solubility product, $K_{s,x}$, and x values (Table A.21) from linear regression (the plot of $\log_{10}[\text{Np(V)}]$ vs. $\log_{10}[\text{CO}_3^{2-}]$ was a straight line with slope of approximately -1). He found the “best” stoichiometry to be $\text{Na}_{0.72}\text{NpO}_2(\text{CO}_3)_{0.86}(\text{s})$, but after several weeks a hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ was formed. Reanalysis of the data for each successive dissolution and precipitation of Np(V) indicates the linear regression results were more accurate for dissolution than for precipitation; over time the x value became closer to 1 and the $K_{s,1}$ decreased (Table A.21). This is evidence that hydrated $\text{Na}_{(2x-1)}\text{NpO}_2(\text{CO}_3)_x(\text{s})$ with $x < 1$ was formed initially, but that this solid phase was metastable, and was slowly transformed to a thermodynamic stable phase, hydrated

Table A.20: Curve fitting results of solubility measurements of Np(V) in 3 M NaClO₄ carbonate/bicarbonate/carbonic acid aqueous solutions [84VIT, 85CÔM, 85KIM, 86GRE/ROB, 90RIG]^(a). $K_{s,j} = [\text{Na}^+]^{(2j-1)}[\text{NpO}_2^+][\text{CO}_3^{2-}]^j$ is the Na_(2j-1)NpO₂(CO₃)_j(s) solubility product. $\beta_i = [\text{NpO}_2(\text{CO}_3)_i^{(1-2i)}]/([\text{NpO}_2^+][\text{CO}_3^{2-}]^i)$.

$\log_{10} K_{s,1}$	$\log_{10} K_{s,2}$	$\log_{10} \beta_1$	$\log_{10} \beta_2$	$\log_{10} \beta_3$	1.96 Σ	Reference
-10.92		4.60	8.12	10.44		[84VIT]
		4.12	8.60	10.76		[84VIT] ^(b)
-10.50	-16.40	4.60	8.12	10.44		[85CÔM]
-10.56	-12.44	5.09	8.15	10.46	0.269	[86GRE/ROB] ^(c)
±0.34		±0.57	±0.43	±0.38		
-10.63		5.33	8.13	10.56	0.114	best fit
±0.38		±0.51	±0.84	±0.41		
-10.65		5.25	8.15	10.64	0.250	this review
±0.33		±0.29	±0.46	±0.37		

(a) All values were calculated from the same set of experimental measurements, except those from Vitorge [84VIT] that used preliminary results. Minimum solubility values were used to determine $K_{s,1}$ and not the best fit obtained by minimising Σ^2 (of $K_{s,1}$ and $K_{s,1} \beta_i$), the least square sum. Uncertainties (calculated in the present review) are 1.96 standard deviations based on a weighted mean of the corresponding equilibrium constant.

(b) Assuming the formation of Na_{0.72}NpO₂(CO₃)_{0.86}(s) solid phase.

(c) Uncertainties calculated in the present review; the values were also reported elsewhere [85KIM, 90RIG].

NaNpO₂CO₃(s). This is consistent with the X-ray diffraction results and with the series of observations by Volkov *et al.* (see the discussion of [84VIT] in this appendix). Thermodynamic (solubility product) data for these non-stoichiometric solids are not accepted in this review. If a stable Na_(2x-1)NpO₂(CO₃)_x(s) solid phase with $x < 1$ is formed, it would be transformed into a hydrated NaNpO₂CO₃(s) phase when the free carbonate concentration is increased. One would then expect a correlation between the error ($[\text{Np}]_{\text{measured}} - [\text{Np}]_{\text{calculated}}$) and $[\text{CO}_3^{2-}]$ which was not detected in data analysed in the present review. This confirmed that the scatter of the data was due to kinetic problems (slow crystallisation and possible variation of the number of water molecules in the hydrated solid [93LEM/BOY]), and the influence of the ion exchange equilibrium in the solid phase, if any, was less important.

At higher carbonate concentrations for which batch experiments were used, four weeks were needed to achieve equilibrium (two weeks were insufficient). This indicates that probably all the other previously published values based on the solubility of hydrated NaNpO₂CO₃(s) at room temperature are based on experiments that had not reached equilibrium; this kinetic problem has not usually been mentioned. In 0.1 M carbonate ($I = 3$ M NaClO₄) solution, the expected solubility was greater than was measured. This was evidence of the formation of a new solid phase. The authors identified a hydrated Na₃NpO₂(CO₃)₂(s) solid phase by its X-ray diffraction pattern.

Table A.21: Determination of the stoichiometry of a hydrated $\text{Na}_{(2x-1)}\text{NpO}_2(\text{CO}_3)_x(\text{s})$ solid phase from solubility data [84VIT, 85CÔM, 85KIM, 86GRE/ROB, 90RIG]. x and $K_{s,x}$ were calculated by linear regression (see text). Np(V) was first precipitated (“Precipitation 1”), then dissolved (“Dissolution 1”), precipitated again (“Precipitation 2”) and so on. . . by varying the pH by addition of HClO_4 or NaHCO_3 to a cell through which $\text{CO}_2(\text{g})$ was bubbled.

n°	data used	x	$\log_{10} K_{s,x}$	$\log_{10} K_{s,1}$
1	Precipitation 1	0.53	-8.18	$-(10.30 \pm 0.47)$
2	Dissolution 1	(0.89 ± 0.06)	$-(10.43 \pm 0.46)$	$-(10.42 \pm 0.26)$
3	Precipitation 2	(0.98 ± 0.09)	$-(11.33 \pm 0.59)$	$-(10.53 \pm 0.10)$
4	Dissolution 2	(0.94 ± 0.07)	$-(11.10 \pm 0.51)$	$-(10.61 \pm 0.09)$
5	Precipitation 3	(0.95 ± 0.09)	$-(11.22 \pm 0.65)$	$-(10.67 \pm 0.31)$
6	3 + 4 + 5	(1.04 ± 0.07)	$-(11.78 \pm 0.32)$	$-(10.63 \pm 0.27)$
7	2 + 3 + 4 + 5	(1.02 ± 0.07)	$-(11.60 \pm 0.30)$	$-(10.57 \pm 0.32)$

The same observation was also made for some of the experiments in 0.025 M CO_3^{2-} aqueous solution. Some of these values are the same (within the uncertainties) as those previously measured by Simakin who used a hydrated $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ solid phase as starting material and proposed the following equilibrium



This review followed Simakin’s interpretation (see the discussion of [77SIM] in this appendix). However, some of the solubilities in 0.1 M CO_3^{2-} solution reported here [90RIG] are lower still, indicating yet another new solid phase was forming slowly. This could have been a better crystallised $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ hydrated compound, that also may have been hydrated to a different extent. It could also have been a Na-Np(V)- CO_3 hydrated compound with a $\text{CO}_3:\text{Np(V)}$ ratio greater than 2.0.

To minimise systematic errors due to variation in the solid phase, stepwise formation constants, $K_i = \beta_i/\beta_{i-1}$, were used for comparison with equilibrium constants measured by other techniques. There is only one later set of publications [91KIM/KLE, 94NEC/KIM, 94NEC/RUN, 95NEC/RUN] relating to the determination of Np(V) carbonate complexation at the same ionic strength but, as discussed elsewhere in this appendix, comparison is not very useful because of calibration problems leading to uncertainties in the carbonate concentrations in the later work. Constants determined by Vitorge *et al.* at $I = 3$ M [84VIT, 85CÔM, 85KIM, 86GRE/ROB] are in fair agreement with other reliable data at lower ionic strength and with the spectrophotometric results in this work [90RIG], and the values were used to extrapolate the complexation constants to zero ionic strength. The $\text{NaNpO}_2\text{CO}_3(\text{s})$ solubility product measured here [86GRE/ROB, 90RIG] is lower than those measured at room temperature by Maya [83MAY] or by Kim’s group, while it is slightly greater than a determination at 30°C [93LEM/BOY]. The maximum difference between all these values was

about an order of magnitude. It seems that the time taken to prepare the solid compound was longer in this work [86GRE/ROB, 90RIG], and that the X-ray diffraction pattern [98VIT/CAP] of the final solid was different (as discussed elsewhere in this appendix for [91KIM/KLE, 93LEM/BOY]). There are probably two or more hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ solid phases, and different researchers may well have been working with different compounds. Therefore a linear regression to zero ionic strength (Appendix B) was not used to derive a unique equilibrium constant (*e.g.*, solubility product) involving $\text{NaNpO}_2\text{CO}_3(\text{s})$ solid.

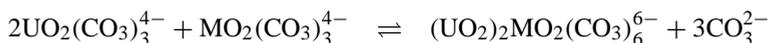
c) Np(VI) and Pu(VI) trinuclear complexes

This thesis also describes a spectrophotometric study of the dissociation of the Np(VI) carbonate limiting complex, previously published, in part, by Grenthe, Riglet and Vitorge [86GRE/RIG]. Dissociation of the limiting Np(VI) carbonate complex in 3 M NaClO_4 was studied in aqueous solution at $t = (22 \pm 1)^\circ\text{C}$. A combination glass electrode with zero junction potential was properly calibrated in concentration units ($-\log_{10}[\text{H}^+]$). From the isosbestic points and a quantitative graphical analysis the author concluded that the assumption of two species was sufficient for interpretation of the data. For constant total metal concentration, the measured molar absorptivity was plotted on a single curve as a function of $[\text{CO}_3^{2-}]$, regardless of the carbon dioxide gas partial pressure used ($0.1 < p_{\text{CO}_2} < 1$ atm). This qualitative conclusion was checked in the present review (see below). The author then concluded that the major dissociated complex contains only CO_3^{2-} ligand. The stability of the dissociated complex increases with the total metal concentration, providing direct experimental evidence that a polynuclear complex was formed. This was confirmed by the sensitivity analysis performed by the author [90RIG] (and also checked in the present review, see below).

Straightforward slope analysis (see below) showed that the dissociation equilibrium is



The experimental data ($\log_{10}[\text{CO}_3^{2-}]$, \log_{10} (molar absorptivity)) were graphically compared with theoretical curves calculated for constant total metal concentration, assuming that there was only one major soluble dissociated complex with different possible stoichiometries. This method allows the determination of the constant of the above equilibrium. In the same way for $\text{M} = \text{Np}$ or Pu



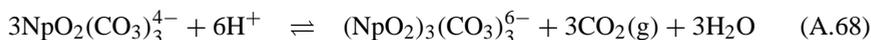
mixed equilibria were studied under the same conditions using the same experimental procedures. The corresponding equilibrium constants were determined by using the same graphical method. These values were previously accepted in the uranium volume [92GRE/FUG] of this series of reviews. This review accepts the same values for the mixed complexes.

This work also reports qualitative experimental observations useful to understanding the methodology used, and in interpreting other publications on similar subjects:

- The precipitation of $\text{NpO}_2\text{CO}_3(\text{s})$ is slow, taking several hours instead of a few seconds as for the U and Pu analogues.
- Colour changes and spectrophotometric observations before and during the precipitation suggest the formation of polymeric or colloidal species.

In carrying out the present review the graphical slope analysis as explained by the author [90RIG] was reproduced. This confirmed her results and interpretation (as described in detail by Vitorge and Capdevila [98VIT/CAP]). This slope analysis is similar to the one performed in the present review to test different interpretations of Maya's potentiometric titration data for similar conditions. Also in the course of the present review, a sensitivity analysis was carried out to try to fit the data using other possible chemical species: this always gave very poor curve-fitting results, and confirmed the interpretation originally proposed. In addition, the equilibrium constant was calculated from each experimental datum and the possibility of systematic deviations as a function of the key chemical parameters was examined. For this sensitivity analysis, maximum weight was given to the data near the half reaction point where the theoretical error in the equilibrium constants is minimized. The weighting procedure practically eliminated the data corresponding to less than 25% of one of the two complexes. It seems that the data at the lowest carbon dioxide gas partial pressure could be shifted by up to 0.4 \log_{10} unit toward higher stability of the dissociated complex, but this is still within the uncertainty of the corresponding series of measurements. In addition a few of the data at 1 atm are similarly shifted. The influence of $-\log_{10}[\text{H}^+]$ leads to the same observations and comments. Conversely, no systematic deviation with the total metal concentration was observed. The fitted values of the molar absorptivity coefficients have little influence on the $\log_{10} K$ value [98VIT/CAP]. The above observations are consistent with the formation of a trinuclear hydroxo-carbonate complex as a minor species. Such a species, $(\text{UO}_2)_3\text{O}(\text{OH})_2\text{HCO}_3^+$, is indeed stable for U(VI) [92GRE/FUG]. Spectrophotometry gives very reliable results for determining the major species, but is not particularly appropriate for generating quantitative data on minor species by curve-fitting techniques. Therefore, this interpretation of the data is not explored further here.

To determine the stoichiometry of the dissociated complex, the author used a wide range of chemical conditions. Once this stoichiometry is established, only the best measurements should be retained, or at least the data should be weighted as a function of the theoretical errors. This was done intrinsically by the author, since she only used a graphical determination. She proposed $\log_{10} K(\text{A.68}) = (42.8 \pm 0.1)$, and this indeed corresponds exactly to the fitting result performed in the present review based on the best series of experimental data (highest p_{CO_2} and $[\text{Np(VI)}]_{\text{total}}$): $\log_{10} K(\text{A.68}) = (42.79 \pm 0.19)$. As noted previously, the fitting results of the author agree within the experimental uncertainties. The weighting procedures are quite arbitrary since many experimental sources of inaccuracy could be taken into account, however they all give very similar results (for example, another procedure leads to $\log_{10} K(\text{A.68}) = (42.88 \pm 0.27)$ [98VIT/CAP]). The values accepted in the present review are for:



$\log_{10} K((A.68), I = 3 \text{ M})$	$= 42.79 \pm 0.19$	recalculated from [90RIG]
$\log_{10} K((A.68), I = 1 \text{ M})$	$= 42.84 \pm 1.06$	calculated in the present review from [84MAY]

Thus for: $\beta_{6,3}/\beta_3^3 = K(A.67)$

$\log_{10} K(A.67, I = 3 \text{ M})$	$= -(10.06 \pm 0.57)$	recalculated from [90RIG]
$\log_{10} K(A.67, I = 1 \text{ M})$	$= -(8.81 \pm 1.08)$	calculated in the present review from [84MAY]

d) Normal potential of the Np(V)/Np(VI) redox couple in bicarbonate media

The redox potential of the Np(VI)/Np(V) couple measured by Riglet [90RIG, pg. 104] in 0.1 M Na_2CO_3 + 3 M NaClO_4 , is accepted in the present review since the methodology used was checked using the corresponding uranium system and gave reliable data consistent with those selected by the uranium review [92GRE/FUG]. It is also in good agreement with the previous value measured by Simakin [77SIM] and selected by this review.

[90RÖS/HUN]

Electromigration measurements were carried out for Np(V) solutions at 298.1 K, $I = 0.1 \text{ M}$ (perchlorate) in the presence of a holding reductant (NO_2^- or N_2H_4 , $1 \times 10^{-3} \text{ M}$). The mobilities began to drop at pH values near 9, and reverse direction near a pH value of 11, indicating the formation of an anionic species at high pH. The values $\log_{10}^* \beta_1 = -(10.45 \pm 0.25)$ and $\log_{10}^* \beta_2 = -(21.95 \pm 0.35)$ were reported, but these are probably mixed constants, and are identical to those reported in [87RÖS/MIL] (and probably from the same experiments). See the discussion for [87RÖS/MIL].

[90SAW/CHA]

This seems to be a partial summary, or a preliminary publication, of Sawant, Chaudhuri and Patil [90SAW/CHA2]. See comments there.

[90SAW/CHA2]

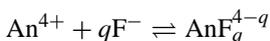
This is a comprehensive study on the fluoride complexation of Th(IV), U(IV), Np(IV) and Pu(IV), using a fluoride-selective electrode. Preliminary summaries of this study were also published separately by Sawant and Chaudhuri [89SAW/CHA, 90SAW/CHA]. The experiments were carried out at $I = 1 \text{ M}$ (Na, H)ClO₄ and $(23 \pm 1)^\circ\text{C}$ ("room temperature"). The constants were determined by titrating the corresponding metal perchlorate solution with a NaF solution. Correction for the liquid junction potential was made at each point of the titration curve according

to the free H^+ concentration, which was between 0.3 and 1 M. In the evaluation, the authors included only points recorded well before the onset of precipitation, which they assumed to be associated with the appearance of instability of the electrode potential after the addition of a certain amount of NaF solution.

The authors reported that the best fit was obtained by using a model with four complexes, assuming that higher complexes were not likely to be formed. However, they gave no indication on the goodness-of-fit nor a comparison with results of fits with less than four complexes. K_4 is larger than K_3 in the case of Th(IV), Np(IV) and Pu(IV). The authors have no explanation for this unexpected result.

The reported constants are summarised in Table A.22. The relevant equilibria in the experimental system ($\text{pH} < 1$) obviously involve HF(aq) rather than F^- . The authors did not indicate the value of the protonation constant of fluoride ion they used for these experimental conditions ($I = 1$ M, perchloric acid). However, we may assume that the protonation constant of $\log_{10} \beta_1(1 \text{ M HClO}_4) = 2.95$ for HF(aq) as reported by them in [90SAW/CHA] was used in the present study as well. We therefore transform the reported constants back to represent the corresponding equilibria with HF(aq). The resulting constants are listed in Table A.23. The uncertainties are estimated to be larger than indicated by the authors. Obviously, the errors estimated by the authors are a result of their fitting exercise; they have therefore a statistical background and probably reflect the shape of the minima in the fitting of the constants. Unfortunately, the authors did not indicate the exact meaning of their uncertainties. We have to assume that the reported uncertainties reflect only the precision of the measurements, and that the real uncertainties must be considerably larger. We therefore multiply the uncertainties given by the authors by a factor of 5, cf. Table A.23. A correction of the first complexation constant of Np(IV) to 25°C using the enthalpy selected in this review, results in an insignificant change (by -0.01): $\log_{10} {}^*\beta_1(298.15 \text{ K}) = 5.21$.

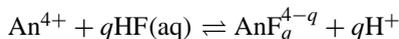
Table A.22: Formation constants of fluoride complexes of tetravalent actinides as reported by Sawant, Chaudhuri and Patil [90SAW/CHA2]. $I = 1$ M (Na, H)ClO₄, 23°C.



Metal ion (An ⁴⁺)	$\log_{10} \beta_1$	$\log_{10} \beta_2$	$\log_{10} \beta_3$	$\log_{10} \beta_4$
Th ⁴⁺	(7.61 ± 0.01)	(13.42 ± 0.05)	(17.65 ± 0.20)	(23.67 ± 0.11)
U ⁴⁺	(8.48 ± 0.01)	(14.66 ± 0.01)	(19.51 ± 0.03)	(23.92 ± 0.06)
Np ⁴⁺	(8.17 ± 0.04)	(14.52 ± 0.13)	(20.05 ± 0.13)	(25.95 ± 0.18)
Pu ⁴⁺	(7.61 ± 0.12)	(14.77 ± 0.10)	(20.11 ± 0.37)	(26.07 ± 0.16)

It should be mentioned that this publication was not available for consideration in the uranium book of this series [92GRE/FUG]. To check the compatibility of the study of Sawant, Chaudhuri and Patil [90SAW/CHA2] with the selected uranium value,

Table A.23: Formation constants of fluoride complexes of tetravalent actinides [90SAW/CHA2] after correction for the protonation constant of fluoride. The uncertainties are estimated in this review. $I = 1$ M (Na, H)ClO₄, 23°C.



Metal ion (An ⁴⁺)	log ₁₀ *β ₁	log ₁₀ *β ₂	log ₁₀ *β ₃	log ₁₀ *β ₄
Th ⁴⁺	(4.66 ± 0.05)	(7.52 ± 0.25)	(8.80 ± 1.00)	(11.87 ± 0.55)
U ⁴⁺	(5.53 ± 0.05)	(8.76 ± 0.05)	(10.66 ± 0.15)	(12.12 ± 0.30)
Np ⁴⁺	(5.22 ± 0.20)	(8.62 ± 0.65)	(11.20 ± 0.65)	(14.15 ± 0.90)
Pu ⁴⁺	(4.66 ± 0.60)	(8.87 ± 0.50)	(11.26 ± 1.85)	(14.27 ± 0.80)

we correct the constants reported here [90SAW/CHA2] to $I = 0$, after conversion to molal units and by using the same ion interaction coefficients as used by Grenthe *et al.* [92GRE/FUG]. A temperature correction is not considered necessary. The resulting log₁₀ β_q^o values are compared with those of the uranium book in Table A.24 below. Surprisingly, the first constant is inconsistently high, while the other constants are in agreement with those of other studies and the ones selected in the uranium review [92GRE/FUG]. Partial hydrolysis of U⁴⁺ is negligible under the conditions of the present experiment.

Table A.24: Comparison of the formation constants of the U(IV) fluoride complexes of [90SAW/CHA2] with those selected in the TDB uranium review [92GRE/FUG].

Reference	log ₁₀ β ₁ ^o	log ₁₀ β ₂ ^o	log ₁₀ β ₃ ^o	log ₁₀ β ₄ ^o
[90SAW/CHA2] (see text)	(10.21 ± 0.11)	(16.58 ± 0.14)	(21.6 ± 0.2)	(26.3 ± 0.3)
[92GRE/FUG] (critical review)	(9.28 ± 0.09)	(16.23 ± 0.15)	(21.6 ± 1.0)	(25.6 ± 1.0)

In addition to values for U(IV), the log₁₀ β₁ values for the Np(IV) and Pu(IV) systems also differ significantly from the other values reported in earlier studies for similar conditions, see Sections 9.2.1.2 and 18.2.1.2. Sawant, Chaudhuri and Patil [90SAW/CHA, 90SAW/CHA2] did not discuss any conceivable reasons for these discrepancies. An open question is certainly the irregularity in the stepwise constants ($K_4 > K_3$). It is not clear to what extent an error in K_4 and K_3 may have an impact on the values of K_2 and K_1 in the statistical treatment used by the authors. In the Np(IV) system, K_1 can be considered as an outlier, the same can be said about K_2 in the Pu(IV) system. Although there is no obvious reason to discard the results of this study, we suspect that the computer evaluation of the experimental data sets was fragile. It was not

reported how the minimisation of least squares was done in a multicomplex system, *i.e.*, how exactly the program was directed to find the minima for the four constants in the system. Depending on the experimental errors, it is conceivable that different combinations of stability constants can fit the experimental data set equally well. In view of these open questions and the discrepancies with the results of other studies, the constants reported by Sawant, Chaudhuri and Patil [90SAW/CHA2] are not included in the evaluation of the selected constants in this review.

[91CHO/MAT]

No new experimental values were reported in this paper for any actinide species other than those of uranium(VI).

[91GOU/JEM]

The enthalpies of reaction of the neptunates with 1 M HCl are used with auxiliary data consistent with the present review to calculate the accepted values for the enthalpies of formation of Li_2NpO_4 , $\alpha\text{-Na}_2\text{NpO}_4$, $\beta\text{-Na}_2\text{NpO}_4$, K_2NpO_4 and Cs_2NpO_4 . These auxiliary data include the CODATA [89COX/WAG] values for $\Delta_f H_m^\circ(\text{M}^+, \text{aq}, 298.15 \text{ K})$ and $\Delta_f H_m^\circ(\text{Cl}^-, \text{aq}, 298.15 \text{ K})$, and the heats of solution, $\Delta_{\text{sol}} H_m^\circ$, of $\text{MCl}(\text{cr})$ in $\text{H}_2\text{O}(\text{l})$ based on those reported in Annex II of the CODATA review [89COX/WAG] (-34.265 ± 0.04 $\text{kJ}\cdot\text{mol}^{-1}$ for LiCl; 4.46 ± 0.40 $\text{kJ}\cdot\text{mol}^{-1}$ for NaCl; 18.01 ± 0.04 $\text{kJ}\cdot\text{mol}^{-1}$ for KCl; 16.925 ± 0.045 $\text{kJ}\cdot\text{mol}^{-1}$ for CsCl; the same values discussed in [92GRE/FUG] in the Appendix A entries for the references labelled as [74OHA/HOE2] and [74OHA/HOE4] in that volume).

[91KIM/KLE]

The work presented in this report is an important detailed study of the $\text{Np}(\text{V})/\text{OH}^-/\text{CO}_3^{2-}/\text{HCO}_3^-/\text{CO}_2/\text{H}_2\text{O}$ system at 25°C . Much of the work was subsequently published [92NEC/KIM, 94NEC/RUN], and the data were used in a further series of publications [94MEI, 94NEC/KIM, 95FAN/NEC, 95NEC/FAN, 95NEC/RUN, 96RUN/NEU], in which equilibrium constants and activity coefficients were proposed for $\text{Np}(\text{V})$ aqueous solution species. $\text{Np}(\text{V})$ solubility was measured in aqueous solutions of constant ionic strength (0.1, 1 and 3 M NaClO_4) and the results were tabulated (additional measurements in 5 M NaClO_4 media were tabulated in a later report [94NEC/KIM]). Similar, but less extensive, measurements were previously reported by Vitorge *et al.* [84VIT, 86GRE/ROB, 90RIG] (also [85CÔM, 85KIM]).

The authors reported (*pp.* 30 to 33) that $\text{NaNpO}_2\text{CO}_3(\text{s})$ was transformed slowly (over 10 days) into $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ in 1 and 3 M Na^+ media. Solid transformations can decrease the accuracy of solubility measurements as discussed for other entries in this appendix [84VIT, 86GRE/ROB, 93LEM/BOY]. However, evidence of solid phase transformation was reported and was discussed [91KIM/KLE] and the evolution of the solids does seem to have been followed in many of these, or related, experiments [95NEC/RUN]. Careful examination of the original solubility data indicates scattering

of the data in the $\text{NpO}_2\text{CO}_3^-$ predominance domain, but less than reported by Vitorge [84VIT] and Lemire, Boyer and Campbell [93LEM/BOY], while no scattering at all was reported for the conditions used to determine the solubility product, $K_{s,1}$, and the second complexation constant, β_2 .

Earlier work from the same laboratory required correction for liquid junction effects on the calibration of their glass electrodes (*cf. p. 281* in [95SIL/BID]). In this work a different method was used for pH calibration, but there are also problems with the revised method. An incorrect definition of pH was used involving the mean activity coefficient of HClO_4 (instead of the H^+ activity coefficient in NaClO_4 aqueous solutions). Under other circumstances this might be a useful approximation, but when the SIT is applied the $\varepsilon_{(\text{H}^+, \text{ClO}_4^-)}$ and $\varepsilon_{(\text{Na}^+, \text{ClO}_4^-)}$ values are not the same, nor is this type of approximation valid when using a third order virial expansion [95NEC/RUN]. It is also not clear which molality to molarity conversion factor they used. The calibration procedure used may have been self-consistent in that the measured values of the water ionic product are in accord with published data, and with the SIT as used by this review. However, the same was not true for the values of the carbonic acid deprotonation constants. This is apparently not the result of experimental problems in controlling carbonate speciation, as the error increased with ionic strength (the deviation in pK changes from 0.03 to 0.38). To allow for this, the uncertainty assigned in this review to systematic error in $\log_{10}[\text{CO}_3^{2-}]$ for these results has been increased. Information given in a later paper [94NEC/RUN] indicates the junction potential corrections could be quite important. There is no way to predict these since they strongly depend on the experimental set up. In the course of the present review, an attempt was made to derive junction potentials from the ΔpH values in Table 1 of Neck *et al.* [94NEC/RUN], using SIT values for the activity coefficients of H^+ and OH^- . However, this led to different results for acidic and basic media. Further, as a 3 M NaCl liquid junction was used the junction potential correction might be expected to be at a minimum for solutions having an ionic strength near 3 M, which was not the case. Thus, there seems to have been a problem, but is not clear whether its source was chemical (carbonate equilibration), the junction potential corrections or the incorrect definition of pH. However, most of these problems would remain the same during solubility measurements and be cancelled out. For this reason, this review accepts and uses the measurements from this paper as extrapolated to zero ionic strength.

To recalculate the stability constants proposed by Kim *et al.* [91KIM/KLE] and Neck *et al.* [94NEC/RUN, 95NEC/FAN, 95NEC/RUN], this review used the experimental solubility measurements tabulated in the reports [91KIM/KLE, 94NEC/KIM] and scanned those for 5 M NaCl aqueous solutions as reported in Figure 3d of Neck *et al.* [95NEC/RUN]. The possibility of different solid phases was also considered in the reanalysis of the data. Only the set of solubility measurements extrapolated to $I = 0$ was used to select thermodynamic data. It was also found that ionic strength corrections for the solubility products were not consistent in the original papers (see the discussion of [94NEC/RUN] in this appendix). Therefore, independently determined parameters were used to estimate the corresponding ionic strength corrections. The reported parameters [91KIM/KLE, 94NEC/RUN] were also not consistent with those in a later paper [95FAN/NEC] from this group.

I (M)	$\log_{10} K_{s,1}$	$\log_{10} K_{s,2}$	$\log_{10} \beta_1$	$\log_{10} \beta_2$	$\log_{10} \beta_3$	$1.96 \Sigma / \sqrt{n}$ (k)
0.1	$-10.28 \pm 0.04^{(a)}$		$4.58 \pm 0.04^{(a)}$	$6.60 \pm 0.07^{(a)}$	$6.70^{(a,f)}$	0.110
0.1	$-10.28 \pm 0.22^{(a,d)}$		$4.59 \pm 0.30^{(a,d)}$	$6.59 \pm 0.40^{(a,d)}$	$6.70^{(a,d,f)}$	0.109
0.1	$-10.29 \pm 0.13^{(a,e)}$		$4.51 \pm 0.19^{(a,e)}$	$6.59 \pm 0.38^{(a,e)}$	$6.70^{(a,e,f)}$	0.146
1	$-10.10 \pm 0.03^{(a)}$	$-12.23 \pm 0.15^{(a,g)}$	$4.50 \pm 0.04^{(a)}$	$6.96 \pm 0.06^{(a)}$	$8.67 \pm 0.09^{(a)}$	0.048
1	$-10.10 \pm 0.10^{(a,d)}$		$4.52 \pm 0.10^{(a,d)}$	$6.97 \pm 0.13^{(a,d)}$	$8.68 \pm 0.10^{(a,d)}$	0.042
1	$-10.10 \pm 0.10^{(a,e)}$	$-12.25 \pm 0.33^{(a,e)}$	$4.48 \pm 0.10^{(a,e)}$	$6.97 \pm 0.10^{(a,e)}$	$8.68 \pm 0.10^{(a,e)}$	0.056
1	$-10.14 \pm 0.04^{(b)}$		$4.49 \pm 0.06^{(b)}$	$7.03 \pm 0.24^{(b)}$	$8.52 \pm 0.41^{(b)}$	0.104
1	$-10.12 \pm 0.35^{(b,e)}$		$4.57 \pm 0.35^{(b,e)}$	$7.11 \pm 0.07^{(b,e)}$	$8.53 \pm 0.09^{(b,e)}$	0.097
1	$-10.11 \pm 0.09^{(a,b,d)}$		$4.54 \pm 0.14^{(a,b,d)}$	$6.98 \pm 0.37^{(a,b,d)}$	$8.65 \pm 0.27^{(a,b,d)}$	0.082
1	$-10.10 \pm 0.10^{(a,b,e)}$		$4.49 \pm 0.15^{(a,b,e)}$	$6.95 \pm 0.32^{(a,b,e)}$	$8.66 \pm 0.26^{(a,b,e)}$	0.096
3	$-10.45 \pm 0.04^{(a)}$	$-12.59 \pm 0.10^{(a)}$	$4.76 \pm 0.04^{(a)}$	$7.69 \pm 0.07^{(a)}$	$10.30 \pm 0.09^{(a)}$	0.444
3	$-10.45 \pm 0.10^{(a,d)}$		$4.77 \pm 0.10^{(a,d)}$	$7.70 \pm 0.11^{(a,d)}$	$10.29 \pm 0.10^{(a,d)}$	0.444
3	$-10.65 \pm 0.33^{(c,e)}$	$-12.91 \pm 0.48^{(c,e)}$	$5.25 \pm 0.29^{(c,e)}$	$8.15 \pm 0.46^{(c,e)}$	$10.64 \pm 0.37^{(c,e)}$	0.114
3	$-10.65 \pm 0.51^{(a,c,d)}$		$4.9 \pm 0.9^{(a,c,d)}$	$8.3 \pm 0.5^{(a,c,d)}$	$10.6 \pm 0.55^{(a,c,d)}$	0.437
5	$-11.06^{(a)}$	$-13.57 \pm 0.11^{(a)}$	$5.00^{(a)}$	$8.29^{(a)}$	$11.47^{(a)}$	0.185
5	$-11.07 \pm 0.14^{(a,d)}$		$5.04 \pm 0.22^{(a,d)}$	$7.77 \pm 0.23^{(a,d)}$	$11.62 \pm 0.21^{(a,d)}$	0.142

(Continued on next page)

5	$-10.63 \pm 0.11^{(g)}$	$-12.48 \pm 0.23^{(g)}$	$0.14 \pm 0.15^{(h,i)}$	$-1.64 \pm 0.34^{(h,j)}$
5				

- (a) [91KIM/KLE, 94NEC/KIM].
- (b) [83MAY].
- (c) [86GRE/ROB].
- (d) Best fit calculated in the present review.
- (e) Minimum solubility (and not mean or fitted values) assuming that the scatter of the data was due to solid transformation (see text and the discussion of [86GRE/ROB]).
- (f) A β_3 fixed value was added by this review.
- (g) [95NEC/RUN], 5 M NaCl.
- (h) Graphically estimated by this review from Figure 3d of [95NEC/RUN] and using the same correction as in that paper for chloride complexation.
- (i) Value of $\log_{10}(K_{s,1} \times \beta_3)$;
- (j) Value of $\log_{10}(K_{s,2}/K_{s,1})$;
- (k) Uncertainties, 1.96 standard deviations of a weighted mean of the corresponding equilibrium constant (not increased for systematic error (see text) in this table to allow statistical comparison), and $1.96 \Sigma/\sqrt{n}$ values (n is the number of measurements) are calculated in the present review.

The value of the solubility product for hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$, as measured by Kim *et al.* [91KIM/KLE] and Neck *et al.* [94NEC/RUN] and extrapolated to zero ionic strength in the present review, was slightly greater than found in other reliable solubility studies [83MAY, 86GRE/ROB, 93LEM/BOY]. The solubility values in 1 M NaClO_4 aqueous solutions were the same as those of Maya [83MAY], although different values were used for the protonation constants for carbonate ion. For 3 M NaClO_4 aqueous solutions the results are clearly different from the results of Grenthe, Robouch and Vitorge [86GRE/ROB]. The difference is too large to have resulted from the pH electrode calibration problems discussed above, but might have resulted from different solid phases being present in the two studies. This discrepancy is reflected mainly in the value of β_1 at $I = 3$ M, which would affect the accuracy of β_1^0 and have a dramatic effect on extrapolation to zero ionic strength (*i.e.*, on the value of $\varepsilon_{(\text{NpO}_2\text{CO}_3^-, \text{Na}^+)}$). The stepwise constants, K_2 and K_3 , are in agreement with the values selected by this review, even up to $I = 5$ M. This was quite surprising as the SIT approximation is usually not valid at such high ionic strengths and there was the possibility of systematic deviation at high ionic strength. In conclusion, except for the value of $\log_{10} \beta_1$ none of the complexation constants at high ionic strength deviate by more than a factor of $10^{0.3}$ from other published works as reinterpreted in the present review. The origin of the deviation in $\log_{10} \beta_1$ is not understood.

The spectra of Np(V) carbonate complexes were also reported and were used later [94NEC/RUN] to calculate the formation constants for two Np(V) carbonate complexes. The spectra were in accord with those reported previously [90RIG]. The reported value of β_1 is in quite reasonable agreement (within 0.2 in $\log_{10} \beta$) with the value measured by the solubility technique, and the same was true for the β_2 values reported in [94NEC/RUN]. The formation constants are inconsistent only within the rather optimistic estimates of the uncertainties by the authors. It is also interesting to note that the stepwise constant, $k_2 = \beta_2/\beta_1$, measured by each technique, was the same.

[91OKA/REE]

This study reported the use of absorption spectroscopy and laser photoacoustic spectroscopy (LPAS) to investigate the hydrolysis of $^{242}\text{Pu}(\text{VI})$. A value of the first hydrolysis constant, $\log_{10}^* \beta_{1,1} = -(5.2 \pm 0.2)$ was reported for $(21 \pm 1)^\circ\text{C}$ and a medium of 0.1 M NaClO_4 . The value was based on a least-squares fit to LPAS data and was dependent on the assumption that PuO_2OH^+ is the sole major hydrolysis species for the Pu(VI) at a concentration of 2.6×10^{-4} M for pH values below 5.3. It appears the reported hydrogen ion concentrations are really $10^{-\text{pH}}$. The authors later [93OKA/REE] included polymeric hydrolysis species in their data analysis, and recinded their proposed value for $\log_{10}^* \beta_{1,1}$. Therefore, this value for $\log_{10}^* \beta$ is not credited in the present review.

[91POS/ROV]

The adsorption of Np(IV) on stainless steel in nitric acid solutions (no supporting electrolyte) of concentration 0.1 – 6 M has been investigated at an unspecified temperature. The Np concentration used is not reported, but from the figures it must have

been approximately 1 mM. From the decrease of the sorption of Np(IV) and Np(VI) on stainless steel with the increase of nitric acid concentration, the authors obtained $\beta(\text{NpNO}_3^{3+}) = (1.95 \pm 0.16)$ and $\beta(\text{NpO}_2\text{NO}_3^+) = (0.13 \pm 0.20)$. The uncertainty in the radiometric Np analysis was reported as 10%. No inert atmosphere was used in work with Np(IV), as oxidation was assumed slow during the first few hours. Assumptions of the authors that the constants do not change in the ionic strength interval 0.5 – 2 M, and that only Np^{4+} is sorbed may not be correct, and no evidence is reported to support them. For these reasons the results of this study are not accepted in the present review.

[91SUL/CHO]

This is a report of what appears to be a well designed experiment to obtain the enthalpy of the first hydrolysis step for NpO_2^+ . Unfortunately, not all the original data have been reported (nor were they preserved), and at least one piece of the reported data is inconsistent. The final pH of the solution titrated (Table 1) is reported as 7.5. It is not clear what volume of base addition would result in this “final pH”, the titration to $n = 0.26$ in the table or to $n = 0.6$ (as in Figure 1 and implied by the text). In either case, “ $\log_{10} \beta_{1,0,1}$ ” must be markedly greater than 4.68 (at least 6.0) for the final pH value to be as low as 7.5. This is inconsistent with the selected value for this value for the hydrolysis constant (there is also a relevant discussion of the source reference ([83MAY]) in this appendix), and with essentially all values reported in the literature. The hydrolysis constant used by the authors would suggest a final pH value of approximately 8.7. It would appear there was some impurity in the solutions used (possibly partially substituted alkylammonium ions), and the problem casts doubt on the reliability of the calorimetric results. This also causes doubt as to whether the authors arguments are correct as to the consistent value for β_1 (based on Figure 2). On the basis of several other studies (see Sections 8.1.3 and 8.2.4.2), addition of base to an acidic solution of 0.04 M neptunium(V) would be expected to result in precipitation prior to hydrolysis. Because of the lack of details, the values from this study are not accepted in the present review.

[91VIT/OLI]

This report includes an English translation of a part of Riglet’s thesis (see the discussion of [90RIG] in this appendix).

[91YAM/PRA]

The solubility of $\text{NpO}_2\text{OH(am)}$ was measured in solutions having pH values between 6.5 and 13 ($T=?$). The solubility measurements at the four lowest values of pH are anomalously low when compared to all other reported measurements (see Figure 8.3, Section 8.2.4.2). The lack of variation in the solubility for solutions with pH values between 6.5 and 8 is also not in agreement with the hydrolysis scheme used by the authors [91YAM/PRA] or that selected in the present review. Conversely, the rest of the

data in this paper are consistent (below pH values of 11) with, among others, those of Ewart *et al.* [86EWA/HOW] and Lierse *et al.* [85LIE/TRE]. The reported experimental procedure suggests the initial neptunium concentrations in the low pH solutions may have been too low to cause precipitation. The solubilities for the four lowest pH values are rejected in the present review.

[92BEN/HOF]

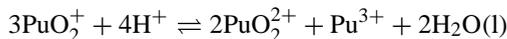
This is a recapitulation of the work described in [90BEN]. For the reasons previously discussed (see entry for [90BEN] in this appendix), the reported stability of the first hydrolysis product is taken only as an upper bound and the first carbonate complex is accepted (with some revision of interaction coefficients) for the purpose of this review.

[92CAP]

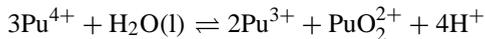
Portions of the experimental work described in this thesis were used in various other reports and papers [89RIG/ROB, 90CAP/VIT, 92CAP/VIT, 94GIF/VIT, 95CAP/VIT, 96CAP/VIT, 97CAP/VIT].

a) Standard potentials of Pu redox couples in non-complexing media

Capdevila determined the disproportionation constant of PuO_2^+ by studying the equilibrium (Equation 16.11, Section 16.4)



using spectrophotometry, at five different ionic strengths ($I = 0.1, 0.5, 1, 2, 3 \text{ M}$). From an SIT treatment, she derived the equilibrium constant at standard state $\log_{10} K_V = (2.6 \pm 0.5)$ and $\Delta\varepsilon = (0.09 \pm 0.1) \text{ kg}\cdot\text{mol}^{-1}$. K_V is the nomenclature used in the thesis for $K(16.11)$. She also measured the extent of the disproportionation equilibrium (Equation 16.5, Section 16.2)



by mixing solutions of PuO_2^{2+} and Pu^{3+} having the same acidity (1 M HClO_4) and following the change of the different oxidation states spectrophotometrically. From the data, $\log_{10} K_{IV}(1 \text{ M}) = -(2.09 \pm 0.5)$ (K_{IV} is the nomenclature used in the thesis for $K(16.5)$) was determined. This part of the work formed the basis of a paper [92CAP/VIT] and was used later (with corrections) by Capdevila and Vitorge [97CAP/VIT].

Furthermore, the redox potentials of $\text{Pu}^{4+}/\text{Pu}^{3+}$ and $\text{PuO}_2^{2+}/\text{PuO}_2^+$ were determined by cyclic voltammetry in 1 M HClO_4 at 298.15 K and at several different ionic strengths ($I = 0.5, 1, 2, 3 \text{ M}$) and temperatures between 5°C and 65°C in five-degree steps. SIT treatment of the data yielded the standard potentials, temperature and ion interaction coefficients. The results are summarised in Table A.26.

For the $\text{Pu}^{4+}/\text{Pu}^{3+}$ couple, the formal potential $E^{\circ'} = (0.978 \pm 0.007) \text{ V}$ agrees with the formal potentials $E^{\circ'} = (0.982 \pm 0.002) \text{ V}$ of Connick and

Table A.26: Temperature dependence of redox couples [92CAP].

Couple	<i>I</i> (M)	<i>E</i> (V vs. SHE)	(<i>dE/dT</i>) _{isotherm} (V·K ⁻¹)	Δ <i>ε</i> (kg·mol ⁻¹)
Pu ⁴⁺ /Pu ³⁺	1	(0.978±0.007) ±0.005 ^(a)	(0.00184±0.00010) (0.00147±0.00011) ^(a)	
	0	(1.044±0.010)	(0.00168±0.0003) (0.00167±0.00014) ^(a)	(0.35±0.10) ±0.05 ^(a)
PuO ₂ ²⁺ /PuO ₂ ⁺	1	(0.912±0.007) (0.913±0.005) ^(a)	(0.00039±0.00010) (0.00016±0.00004) ^(a)	—
	0	(0.938±0.010)	(0.00019±0.00030) (0.00034±0.00004) ^(a)	(0.22±0.10) ±0.03 ^(a)

^(a) Values reported in [95CAP/VIT] from the same set of experimental data, recalculated using a second order polynomial regression versus temperature. Simple linear regression was used in [92CAP].

McVey [51CON/MCV] and $E^{of} = (0.9821 \pm 0.0005)$ V of Rabideau and Lemons [51RAB/LEM]. The difference between the standard potential and the formal potential,

$$E^{\circ} - E^{of} = (0.064 \pm 0.012) \text{ V}$$

agrees with the (0.064 ± 0.011) V reported for the analogous Np⁴⁺/Np³⁺ system by Riglet, Robouch and Vitorge [89RIG/ROB]. The results of this cyclic voltammetry study (including temperature effects) were cited in [92CAP/VIT] (which was written before the thesis was completed) and reported in [95CAP/VIT].

Using the constants K_V and K_{IV} for the disproportionation equilibrium of PuO₂⁺ or Pu⁴⁺, respectively, and the corresponding data for the reversible redox couples, Capdevila calculated the values in Table A.27 for the irreversible plutonium couples.

b) Standard potential of the Pu(VI)/Pu(V) redox couple in carbonate media

This report also gives results of an apparently very thorough study on Pu(V) in acidic and basic carbonate media. Pu(V) was prepared electrolytically, and characterized spectrophotometrically. The data from cyclic voltammetric experiments (25°C, 1 M sodium carbonate) and previously determined stability constants of PuO₂(CO₃)₃⁴⁻ [87ROB/VIT] were used to calculate a value for the formation of the PuO₂(CO₃)₃⁵⁻ at $I = 0$ using SIT and interaction coefficients determined experimentally of $\log_{10} \beta_3^{\circ} = (4.9 \pm 0.8)$. All data was presented to permit re-evaluation of errors.

The value of $\log_{10} \beta_3$ is similar to (or a little smaller than) the value of the corresponding Np(V) tricarbonato complex ($\log_{10} \beta_3 = 5.50 \pm 0.15$) selected in this review

Table A.27: Values of the potentials for the irreversible plutonium couples as calculated by Capdevila [92CAP].

	<i>I</i> (M)	<i>E</i> (VI/IV) (V vs. SHE)	<i>E</i> (VI/III) (V vs. SHE)	<i>E</i> (V/IV) (V vs. SHE)	<i>E</i> (V/III) (V vs. SHE)
Using K_V	0	(0.965 ± 0.035)	(0.988 ± 0.020)	(0.991 ± 0.060)	(1.014 ± 0.025)
	1	(1.022 ± 0.035) ± 0.030	(1.006 ± 0.020)	(1.134 ± 0.060) ± 0.050	(1.053 ± 0.022)
Using K_{IV}	0	-	-	-	-
	1	(1.033 ± 0.022)	(1.013 ± 0.017)	(1.154 ± 0.050)	(1.063 ± 0.030)

Values in italics are those reported in [92CAP/VIT].

12.1.2.1, and can be compared to the value of $\log_{10} \beta_1^\circ = (5.12 \pm 0.14)$ from Bennett *et al.* [92BEN/HOF]. Both these determinations result in values for the equilibrium quotients of K_2° and K_3° that are equal to or less than unity. Such values for consecutive association quotients are unusual, since consecutive values of association quotients usually vary by at least a factor of ~ 10 . The results may be rationalized by postulating that the reduction of $\text{PuO}_2(\text{CO}_3)_3^{4-}$ at the electrode produces $\text{PuO}_2(\text{CO}_3)_3^{5-}$ which is a reactive intermediate (not the thermodynamically stable product of the reduction) and this species rearranges to the thermodynamically stable mono- or bis- carbonatoplutonium(V) which precipitates from the solution. The results of [74SIM/VOL] provide evidence consistent with this hypothesis.

c) Pu(IV) in carbonate media

The results of the spectrophotometric study of the reaction:



are not consistent with an earlier study reported by Eiswirth, Kim and Lierse [85EIS/KIM] (and [86LIE/KIM]) who concluded that over the same pH range the spectral changes required three carbonate complexes rather than the two hypothesized in this study. There are three significant differences between the experimental protocols in these studies: (i) the Pu(IV) was prepared by reduction by Capdevila [92CAP]; (ii) Capdevila [92CAP] did not state that any filtration was carried out to remove possible colloids prior to the spectrophotometric observations as was done by Eiswirth, Kim and Lierse [85EIS/KIM] (in spite of this difference in experimental procedure the reported spectra are qualitatively the same); and (iii) Capdevila's initial solution at pH = 10.2 was acidified by bubbling $\text{CO}_2(\text{g})$ into the solutions in contrast to the other study [85EIS/KIM] in which perchloric acid was added. There is no specific evidence presented in this report concerning the stoichiometry of the limiting Pu(IV) carbonate species in solution. The results are consistent with any one carbonate

addition. However, based on the results of Lierse and Kim [86LIE/KIM] which clearly indicate that complexes with $\text{CO}_3^{2-}/\text{Pu(IV)}$ ratios higher than 3 are formed in solution, and by analogy to the U(IV) carbonate complexes [92GRE/FUG], this assignment of pentacarbonato stoichiometry seems eminently reasonable.

[92CAP/VIT]

This is the publication of a part of Capdevila's thesis [92CAP] in a refereed journal.

[92EWA/SMI]

This presents modelling results in conjunction with experimental results that are, in essence, those presented in earlier publications [85EWA/GOR, 86EWA/HOW]. More experimental details are given, but these do not, in some cases, agree with those in the earlier papers, even though experimental points plotted appear to be from many of the same experiments. The authors contended the method used to prepare the $\text{Pu(OH)}_4(\text{am})$ for the solubility measurements made it likely the plutonium in solution was Pu(IV), but there was no experimental confirmation (*e.g.*, by extraction). Other work [94NEU/HOF, 94PER/DAV] suggests Pu(V) or Pu(VI) may have formed.

[92HAS]

This paper describes a qualitative study of the corrosion products of Pu metal in aqueous solution. The final product was identified as PuO_2 , and indications were found for several intermediate phases. The product after termination of the reaction at a stage when 0.5 mole of $\text{H}_2(\text{g})$ had been evolved per initial mole of Pu was identified as $\text{PuOH}(\text{s})$, the monoxide hydride. A phase $\text{Pu}_7\text{O}_9\text{H}_3$ was produced by limited oxidation of $\text{PuOH}(\text{s})$. Thermal decomposition of $\text{PuOH}(\text{s})$ produced a metastable solid (violently reactive with $\text{O}_2(\text{g})$), with properties consistent with those expected for $\text{PuO}(\text{s})$. Selected lattice parameter information from XRD data is presented.

[92ITA/NAK]

This paper reported solubility measurements for $\text{NpO}_2\text{OH}(\text{s})$ precipitated using NaOH. The shapes of the solubility curves for more basic solutions are similar to those described by Neck, Kim and Kanellakopoulos [92NEC/KIM]. However, between pH values of 6 and approximately 9.5, the solubilities measured in the lower ionic strength solutions ($I = 0.012 \text{ M}$ and $I = 0.10 \text{ M}$) were essentially constant, having a total solution concentration of neptunium near $10^{-3.6} \text{ M}$. The authors could not find a satisfactory explanation for this observation. It would appear the amorphous solid formed under these conditions must have been metastable, even compared to the less stable of the two hydroxide forms discussed by Neck, Kim and Kanellakopoulos [92NEC/KIM], or else unfilterable colloidal material formed in the experiments. The solutions appear to have been allowed sufficient time for equilibrium to be attained (longer than in other similar studies), and X-ray diffraction measurements on the final solids did not indicate crystallinity. It should be emphasised that even quite low concentrations of carbonate

could have caused spurious solubility results for the high pH solutions. The pH measurements were corrected for junction potential differences in the different media. However, the actual procedure of “measuring pH buffer solutions containing NaClO₄” may or may not have been adequate, depending on the (unreported) nature of the solutes in the buffer solutions. The corrections (albeit using different electrodes) are somewhat greater than those of Neck, Kim and Kanellakopoulos [92NEC/KIM] in similar media. The solubilities are lower in the higher ionic strength solutions, and this type of behaviour has been attributed by Neck, Kim and Kanellakopoulos [92NEC/KIM] to changes in the nature of the solid. The solid is probably not the same in the solutions at different ionic strengths. If this is the case, it would be futile to attempt to derive a single solubility product from the entire set of data. The experimental solubilities for $I = 0.8$ are very close to those of Neck, Kim and Kanellakopoulos [92NEC/KIM] for their aged solid at $I = 1.0$, although the scatter in the data means the location of the solubility minimum (and hence the values of the hydrolysis constants) is not well defined. The experimental solubility values are not supplied except as points on a graph, and no recalculation of the hydrolysis constants has been done in this review. The reported values of $\log_{10} {}^*\beta$ for ($I = 0$) are accepted, but with the uncertainties increased to ± 0.7 .

[92NEC/KIM]

This reports the extension of an earlier study [85LIE/TRE]. The solubility of NpO₂OH(s) was measured in aqueous sodium perchlorate solutions (0.1, 1.0 and 3.0 M). The work appears to have been done carefully, and junction potential corrections have been applied to the pH measurements (however, also see the discussion for [91KIM/KLE]). Two different solids were assumed, one being found in contact with 0.1 M NaClO₄ solutions or with 1 M NaClO₄ solutions that had not aged more than a few days. The second, more stable solid was formed in contact with 3 M NaClO₄ solutions or after 20-30 days in contact with 1 M NaClO₄. The equilibration periods are somewhat shorter than those used in several other studies (*e.g.* [92ITA/NAK, 95PAN/CAM]). The solids were not analysed for possible incorporation of sodium ions, however the parallel solubility curves obtained for the two solids strongly suggests they have similar stoichiometries. The solubility product and hydrolysis constants were analysed using the SIT. The value of $\Delta\varepsilon$ derived by the authors (their “A parameter”) for the solubility product and first hydrolysis constant differ (by 0.06 kg·mol⁻¹) from the value calculated using the values tabulated in Appendix B of the present review. For the sake of consistency, the solubility product values were refitted with the constraint that the $A = 0.29$. This results in $\log_{10} {}^*\beta_1^\circ = -11.34$, $\log_{10} {}^*\beta_2^\circ = -23.65$, $\log_{10} {}^*K_{s,0}^\circ = 5.30$ for the “fresh” solid, $\log_{10} {}^*K_{s,0}^\circ = 4.71$ for the “aged” solid, and $\varepsilon_{(\text{Na}^+, \text{NpO}_2(\text{OH})_2^-)} = -(0.01 \pm 0.07)$ kg·mol⁻¹.

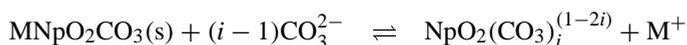
[93GIF/VIT2]

This report is a republication of [94GIF/VIT] with supplementary materials including an explanation on obtaining thermodynamic functions ($\Delta_f G$, $\Delta_f H$, $S...$) consistent

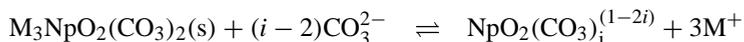
with thermodynamic conventions (and standard states) for the electron “e[−]” (as used by electrochemists in half-cell reactions).

[93LEM/BOY]

Lemire, Boyer and Campbell studied $\text{NaNpO}_2\text{CO}_3(\text{s})$ and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ equilibration with $\text{HCO}_3^-/\text{CO}_3^{2-}$, 1 M Na^+ (NaClO_4) solutions at 30, 50, and 75°C, and 0.5 M Na^+ aqueous solutions at 75°C, and $\text{KNpO}_2\text{CO}_3(\text{s})$ equilibration with KCl solutions at 30 and 75°C. The glass electrode was calibrated in concentration ($-\log_{10}[\text{H}^+]$) and not activity (pH) units at each temperature. Measurements of $-\log_{10}[\text{H}^+]$ at different temperatures were used to calculate $[\text{CO}_3^{2-}]$ from the known total carbonate molarities. Uncertainties mainly came from solid phase transformations and lack of buffering effect at low $[\text{CO}_3^{2-}]$. Previous work [74VIS/VOL, 77SIM, 77VOL/VIS, 79VOL/VIS2, 81VOL/VIS2, 83MAY, 84VIT] on Np(V) solubility and soluble complexes [85BID/TAN, 85INO/TOC] in carbonate media were well documented and used to guide and interpret the experiments. It was assumed that the reactions



or the equilibria



controlled the solubility. As discussed elsewhere in this appendix [90RIG], it is clear that hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ is not very well crystallised at low $[\text{CO}_3^{2-}]$ and temperature. Its solubility was not very reproducible despite the 2-4 week equilibration times used in this work [93LEM/BOY] (or longer — successive equilibration periods with the same solid samples meant some solid samples were in contact with solutions for over two months). Grenthe, Robouch and Vitorge [86GRE/ROB] had predicted that the hydrated $\text{NaNpO}_2\text{CO}_3(\text{s})$ compound would be transformed into $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$, when $[\text{CO}_3^{2-}]$ became greater than 1 mM in $[\text{Na}^+]=3$ M solution (and thus if greater than 9 and 18 mM in $[\text{Na}^+] = 1.0$ and 0.5 M solutions, respectively), and this was confirmed by later work [91KIM/KLE, 95NEC/RUN]. The kinetics of this transformation are very slow at 25°C and were found here to be somewhat more rapid at higher temperatures. It was difficult to deduce solubility products and formation constants from curve fitting, because NpO_2CO_3 was transformed to $\text{NpO}_2(\text{CO}_3)_2^{3-}$ in the $[\text{CO}_3^{2-}]$ domain where a solid phase transformation occurs, and this leads to strongly correlated fitting parameters.

To estimate equilibrium constants, this review accepted the qualitative interpretation in [93LEM/BOY] but used a classical graphical procedure to reanalyse the data. The results are shown in Table A.28. At 30°C, Lemire, Boyer and Campbell found approximately the same solubility as Maya [83MAY] had at 25°C for $[\text{CO}_3^{2-}] < 1$ mM. Values of $K_{s,1}$ and β_i were estimated graphically for $i = 0, 1$ and 2, assuming that some of the data shown of the Figure 1a ([93LEM/BOY]) corresponded to supersaturated solutions. For this reason, the values estimated in the present review were smaller

than those from the least-squares curve fitting results. At higher carbonate concentrations, the initial $\text{NaNpO}_2\text{CO}_3(\text{s})$ solid phase was slowly transformed into a thermodynamically more stable phase. This explains the X-ray diffraction pattern observations. No thermodynamic data were estimated from those results. The Np(V) solubility using a $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ solid phase as starting material was in accord with these observations (Figure 1b of [93LEM/BOY]) and allowed graphical estimation of $K_{s,2}$ β_i for $i = 2$ and 3 and of very approximate values for the other equilibrium constants (Table A.28). Some solubility measurements could not be explained by the above interpretation. A few (at 0.2 to 10 mM $[\text{CO}_3^{2-}]$) might suggest the final $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ phase was not really controlling the solubility at the beginning of the experiment (possibly there were changes in the extent of hydration of the solid phase; dehydration might have occurred between 22 – 25°C and 30°C). Regardless, there is still at least one solubility measurement (at about 0.15 M $[\text{CO}_3^{2-}]$) that remains an outlier.

data are in 1 M Na⁺ media, except as noted $\beta_i = [\text{NpO}_2(\text{CO}_3)_i^{(1-2i)}]/([\text{NpO}_2^+][\text{CO}_3^{2-}]^i)$, $K_{s,j} = [\text{M}^{+}]^{(1-2j)}[\text{NpO}_2^+][\text{CO}_3^{2-}]^j$ is the solubility product of a $\text{M}_{(1-2j)}\text{NpO}_2(\text{CO}_3)_j$ hydrated solid phase.

t (°C)	$\log_{10} \beta_1$	$\log_{10} \beta_2$	$\log_{10} \beta_3$	$\log_{10} K_{s,1}$	$\log_{10} K_{s,2}$	References
25	(4.6±0.1)	(7.1±0.1)	(8.5±0.1)	-(10.12±0.04)		[83MAY] ^(a)
25	(4.57±0.35)	(7.03±0.24)	(8.52±0.41)	-(10.12±0.35)		[83MAY] ^(b)
30	(4.7±0.1)	(7.0±0.1)		-(10.7±0.1)		[93LEM/BOY]
30	(4.77±0.51)	(7.47±0.54)	(8.97±0.58)	-(10.77±0.5)	-(13.47±0.55)	[93LEM/BOY] ^(b,c)
30	(4.77±0.51)	(7.47±0.54)	(8.97±0.58)	-(10.77±0.5)	-(12.97±0.62)	[93LEM/BOY] ^(b,c)
50	(5.6±0.2)	(6.9±0.3)	(8.6±0.3)	-(11.0±0.1)	-(12.90±0.22)	[93LEM/BOY]
50	(5.7±0.54)	(8.80±0.57)	(10.30±0.66)	-(11.1±0.2)	-(14.8±0.55)	[93LEM/BOY] ^(b)
75	(5.80±0.58)	(8.80±1.62)	(10.10±1.42)	-(10.94±0.29)	-(14.40±1.15)	[93LEM/BOY] ^(d)
75	(5.2±0.54)	(7.30±0.61)	(8.90±0.61)	-(10.5±0.5)	-(13.4±0.57)	[93LEM/BOY] ^(b)
75	(4.8±0.28)	(7.20±0.36)	(8.55±0.56)	-(9.80±0.2)	-(13.25±0.47)	[93LEM/BOY] ^(b,e)

(a) As recalculated in [93LEM/BOY].

(b) As recalculated in the present review.

(c) Two $K_{s,2}$ values were proposed at 30°C, because at this temperature, the $\text{NaNpO}_2\text{CO}_3(\text{s})$ hydrated solid phase is assumed to be transformed into a less hydrated one.

(d) Calculated in this review from some of the constants in [93LEM/BOY].

(e) For 0.5 M Na⁺; also recalculated for 1 M KCl solutions: $\log_{10} K_{s,1} \beta_1 = -(6.7 \pm 0.2)$; $\log_{10} K_{s,1} \beta_2 = -(4.5 \pm 0.5)$; $\log_{10} K_{s,1} \beta_3 = -(2.0 \pm 0.6)$; $\log_{10} K_{s,2}/K_{s,1} = -(2.7 \pm 0.6)$.

The same solid phase transformations may explain the solubility measurements at 50°C ([93LEM/BOY], Figure 2). Values of $K_{s,1} \beta_i$ for $i = 0$ and 1, and $K_{s,2} \beta_i$ for $i = 1, 2$ and 3 were estimated graphically. Again, for the recalculations, the minimum solubility was used for chemical conditions where solid phase transformation was suspected. As at 30°C, this interpretation can be valid only if it is assumed that in the early cycles of an equilibration experiment the solid in equilibrium with the aqueous solution was not the same as the final $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ phase found after equilibration with several successive batches of solution. Similar recalculations were carried out from the solubility measurements at 75°C ([93LEM/BOY], Figure 3) in 0.5 and 1 M sodium aqueous solutions. In the course of the present review, the recalculated stepwise formation constants, taken in pairs of temperatures were used in a (futile) attempt to estimate stepwise reaction enthalpies. Values for 40, 62.5 and 52.5°C were (87 ± 70) , $-(43 \pm 66)$ and (19 ± 34) $\text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_1 H$, (37 ± 27) , $-(86 \pm 29)$ and $-(27 \pm 17)$ $\text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_2 H$ and (0 ± 38) , (9 ± 38) and (4 ± 16) $\text{kJ}\cdot\text{mol}^{-1}$ for $\Delta_3 H$. Obviously the values are much too scattered to be used, and are also undoubtedly badly correlated.

For the five solubility measurements in K^+ aqueous solutions at 75°C the final solution concentrations of neptunium were markedly lower than those in the corresponding Na^+ aqueous system. It may be that in K^+ media the value of $\log_{10}(K_{s,1}\beta_1)$ is smaller by about 1.4 compared to the value in Na^+ media, but much smaller differences were found between the values of the $\log_{10}(K_{s,2}\beta_3)$ constants in both media. Since ionic strength effects should nearly cancel between the two media, this would indicate that the $\text{KNpO}_2\text{CO}_3(\text{s})$ solid phase is more stable than the $\text{NaNpO}_2\text{CO}_3(\text{s})$, while the $\text{K}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ and $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ solid phases may have similar stabilities.

Solid phase transformations lowered solubility while complexation increased it, resulting in practically constant Np(V) solubility over a wide range of carbonate concentrations, especially for temperatures above 30°C. Classical curve fitting cannot distinguish between these two effects that resulted in flat solubility curves. Solid phases with similar M:Np:CO_3 ratios, but hydrated to a different extent may exist, and (probably metastable) phases with intermediate stoichiometry $(\text{Na}_{2x-1}\text{NpO}_2(\text{CO}_3)_x(\text{s}))$ where $1 < x < 2$ may form [76VOL/VIS]. In accordance with the conclusions of the authors, the solubility product tabulated above should not be compared with similar values from other works (at other temperatures), since at least some do not correspond to the same solid phase even when X-ray characterisation was claimed. Lemire, Boyer and Campbell, in agreement with Vitorge [84VIT] and Riglet [90RIG], clearly demonstrated that there are problems with this type of characterisation. Other authors have mainly used or shown X-ray diffraction characterisation of initial solid phases.

In the present review the qualitative results from this work are accepted, but none of the thermodynamic data.

[93LEM/CAM]

See the discussion of [96LEM/CAM].

[93LI/KAT]

The potential of the Np(VI/V) couple was studied in 1 M HClO₄ and 1 M Na₂CO₃ aqueous solutions and was found to be reversible. The formal potential of the equilibrium was found to be

$$E_{\text{Np(VI)/Np(V)}} \text{ in 1 M HClO}_4 = 0.93 \text{ V/S.S.C.}$$

The potential of the S.S.C. reference electrode, 0.24 ± 0.01 V was measured at $(23 \pm 2)^\circ\text{C}$, therefore,

$$E_{\text{Np(VI)/Np(V)}} \text{ in 1 M HClO}_4 = 1.07 \text{ V/SHE}$$

while the value selected in the present review is 1.137 ± 0.001 V/SHE. In the same way

$$E_{\text{Np(VI)/Np(V)}} \text{ in 1 M Na}_2\text{CO}_3 = 0.25 \text{ V/S.S.C.}$$

and

$$E_{\text{Np(VI)/Np(V)}} \text{ in 1 M Na}_2\text{CO}_3 = 0.49 \text{ V/SHE}$$

The Np(VI)/Np(V) potential shift from acidic to carbonate media was calculated by the authors to be

$$E_{\text{Np(VI)/Np(V)}} \text{ in 1 M Na}_2\text{CO}_3 - E_{\text{Np(VI)/Np(V)}} \text{ in 1 M HClO}_4 = 0.68 \text{ V}$$

As it is known that the two limiting complexes are NpO₂(CO₃)₃⁴⁻ and NpO₂(CO₃)₃⁵⁻, this corresponds to

$$\log_{10} (\beta_{3\text{Np(VI)}}/\beta_{3\text{Np(V)}})_{0.2 \text{ to } 3 \text{ M K}_2\text{CO}_3} = 11.5$$

This is similar to the value selected in the present review (but based on other experimental data). No indication was given of the size of the junction potential or on the uncertainties, so the result obtained by Li, Kato and Yoshida [93LI/KAT] is not used in the assessment in the present review. However, the reported value of the difference in potentials is in agreement with Simakin's work [77SIM] and the other selected data [90RIG, 95OFF/CAP].

The electrolytic synthesis of Np(IV) was carried out in 1 M Na₂CO₃ solutions. The Np(V)/ Np(IV) couple is reasonably reversible and has been studied by several other groups. The preparation of Np(IV) is possible [79FED/PER, 81WES/SUL, 84VAR/HOB, 96DEL/VIT], but Li, Kato and Yoshida did not succeed, probably because the potential was not sufficiently negative, because they did not use an appropriate electrode. Therefore the redox study is not very useful, nor is it not very precise since there is no indication as to the junction potential. The Np(IV) carbonate complex was then obtained by mixing an acidic Np⁴⁺ solution with a Na₂CO₃ solution. The spectrum of the solution is the well known [71MOS2, 77SAI/UEN, 81WES/SUL, 84VAR/HOB] spectrum of the limiting

carbonate complex of Np(IV); but for the first time, spectrophotometric evidence is shown of the dissociation of the Np(IV) limiting complex when the pH was decreased. These spectra have later been confirmed [95VIT, 95VIT/CAP, 96DEL/VIT]. This phenomenon occurs under similar conditions as for U [92GRE/FUG] and Pu [92CAP]. This suggests the same interpretation as for these actinides(IV):



We estimate that the published spectrum probably corresponds to the above reaction proceeding to less than 50% (and possibly less than 10%) of completion (*cf.* Section 12.1.2.1.4)

[93OKA/REE]

In this study, the hydrolysis of plutonium(VI) in aqueous solution ($I = 0.1 \text{ M}$, NaClO_4) was investigated using absorption spectroscopy and laser photoacoustic spectroscopy. Both ^{242}Pu and ^{239}Pu were used, and radiolytic reduction of the plutonium stock solutions was minimised by restricting the time between solution preparation and measurements. The reported value for $\log_{10}^*\beta_{2,2}^{mix} (-7.3 \pm 0.2)$ is reasonable, as is the conclusion the first monomeric hydrolysis complex is weak.

The data from this paper were reanalysed. The three data points from spectra obtained using 0.028 M Pu(VI) do not appear to be consistent with the other data. In particular, they seem to be inconsistent with the absorption spectroscopic data for 0.0128 M Pu(VI). Nevertheless, there was no apparent reason to exclude the data obtained using the most concentrated plutonium stock solution, and indeed, the absorbance data from this solution should actually be more reliable than those from the more dilute solution.

The activity coefficients from the ion-interaction treatment were calculated, and $\log_{10}^*\beta_{2,2}^\circ = -(7.73 \pm 0.08)$ at 25°C was determined by fitting the absorption (visible) spectroscopy data using a non-linear least squares algorithm. The uncertainties in the absorbances were all ± 0.002 , as in the original paper. The laser photoacoustic spectroscopy data were similarly analysed, and resulted in the value $\log_{10}^*\beta_{2,2}^\circ = -(7.33 \pm 0.09)$. The data analyses only included absorbances for those solutions which were reported to have no detectable absorbance at 638 nm, and were based on $(\text{PuO}_2)_2(\text{OH})_2^{2+}$ being the only major species from hydrolysis of PuO_2^{2+} for these conditions. This assumption may not be correct (the 1:1 complex is more likely). The experimental and calculated absorbances show systematic differences.

A slight decrease in $\log_{10}^*\beta_{2,2}^{mix}$ with increasing temperature was reported. This is not consistent with experimental evidence (calorimetric [68ARN/SCH] and potentiometric [62BAE/MEY]) for the temperature dependence of the corresponding uranium(VI) species, $(\text{UO}_2)_2(\text{OH})_2^{2+}$ in higher ionic strength media. Further work on the temperature dependence would be useful.

[93PAS/KIM]

The results of this spectrophotometric study show a variation in the spectra of basic Pu(VI) solutions upon the addition of NaClO. The data that form the basis of identification of the bands at 852 nm and 862 nm as characteristic of the mono- and bis-hypochlorite complexes, respectively, are not presented. In addition, the values calculated for the association quotients are based on questionable assumptions. It has not been clearly demonstrated that the hydrolysed species is solely the dihydroxide species, and the values used for the calculation of the solubility product are not reliable. The values presented for the formation of the Pu(VI) hypochlorite complexes can therefore not be accepted in this review.

[93PAS/KIM2]

This paper presents a careful spectrophotometric and potentiometric study of $^{242}\text{Pu(VI)}$ hydrolysis, with emphasis on the kinetics of the formation of polymeric hydrolysis species. Little of the original experimental data has been supplied, so recalculation of the results is difficult. The β_1 values for 20°C apparently were calculated using 25°C values for the ion product for water, corrected for ionic strength, but not for the difference in temperature (the ion product of water at 20°C is $10^{-14.17}$ [59ROB/STO] — the D value as used in the SIT apparently was corrected for temperature). In a later paper from the same group [95PAS/KIM], the large values of β_{12} in this paper [93PAS/KIM2] were explained as probably resulting from polymer formation in the oversaturated solutions of Pu(VI) near neutral pH. When the reported average value for $\beta_{1,1}$ is adjusted using the ion product for water at 20°C, the value $\log_{10} \beta_{1,1} = 8.82$ is obtained, resulting in $\log_{10} \beta_{1,1}^\circ = 9.40$ (using the SIT). Thus, $\log_{10} \beta_{1,1}^* = -4.76$ at 20°C. This value is also much less negative than the value found in the later study by Pashalidis *et al.* [95PAS/KIM] and, further, is markedly less negative than values from studies selected by the authors for comparison [49KRA/DAM2, 72CAS/MAG, 84KIM/BER, 91OKA/REE].

[93PRA]

This thesis has also been published as a series of papers [89PRA/MOR, 90PRA/MOR, 91PRA/YAM, 93PRA/MOR, 93PRA/YAM].

[93PRA/MOR]

The work (also reported as part of Prapoto's thesis [93PRA]) was similar to that described in a later paper by the same authors [95MOR/PRA].

Total $^{237}\text{Np(VI)}$ solubilities were measured in aqueous solutions prepared by adding NaHCO_3 to 0.1 M NaClO_4 solutions so that the total carbonate concentrations were 25.3 to 167 mM. It is not clear whether the NaHCO_3 used for these additions was the solid or was in concentrated aqueous solution. In neither case is it likely the procedure would provide accurate knowledge of the volumetric concentrations, especially of Na^+ . The total carbonate concentration is at least of the same order

of magnitude as the NaClO_4 concentration. Therefore, the ionic medium was not constant over the series of solubility measurements, and the concentration of Na^+ varied from 0.15 to 0.43 M (at least as recalculated in the present review—see below). The pH measurements reported by the authors (9.61 to 10.5) are, for some samples, considerably greater than the theoretical values calculated assuming the above procedure. The authors also may have added a strong base (possibly NaOH) to vary the pH. It is not possible to accurately calculate the amount of NaOH that might have been added for pH adjustment, as equilibration with air during the pH adjustment would have also added an acidic reactant (carbon dioxide gas). Thus, the concentrations of Na^+ and the ionic strength corrections to the equilibrium constants for the carbonate protonation reactions cannot be estimated with good accuracy (and the ones used by the authors are then probably in error).

The authors reported the absorption spectrum of the solution most concentrated in Np(VI) and total carbonate. Although of poor quality compared with the previously published spectra [81WES/SUL, 86GRE/RIG] cited by the authors, the spectrum (contrary to the contention of the authors) still clearly corresponds to the spectrum of the pure limiting complex, $\text{NpO}_2(\text{CO}_3)_3^{4-}$. The analysis of the absorbance measurements strongly relies on the values of the molar absorbances for the pure species. Such values were not proposed by the authors, nor can the values be deduced because there was no evidence for a second absorbing species.

The authors plotted their experimental solubility data as a function of the logarithm of the aqueous concentration of CO_3^{2-} , and proposed a slope analysis. In the present review it is concluded that the range of experimental conditions was too small, the chemical conditions too poorly defined, and the scatter of the experimental results too large, to obtain any useful result from such an analysis. The authors' proposed initial complex, final complex, and the number of OH ligands they claim were exchanged are completely in error.

[93PRA/YAM]

See [91YAM/PRA].

[93SAW/MAH]

The authors carried out potentiometric titrations using a fluoride electrode at $(23 \pm 1)^\circ\text{C}$ ("room temperature") and $I = 1 \text{ M}$ (NaClO_4). This method is well established and has a high precision. This study supersedes the one published earlier by the same group [86MAH/SAW], in which $\log_{10} \beta_1(A.69, q = 1, I = 1 \text{ M}) = (3.07 \pm 0.04)$ was reported. This earlier result was called into question by these authors [93SAW/MAH], because higher complexes had not been considered in the evaluation in [86MAH/SAW].

Pure starting solutions of Pu(III) were obtained by adding an excess of quinhydrone to a Pu stock solution before each experiment. The remaining quinhydrone served as a holding reductant for Pu(III). The absorption spectra were recorded before each experiment to ensure absence of Pu(IV). The liquid junction potential was carefully evaluated at each titration point as a function of the free proton concentration. The data

were evaluated using a chemical model that included the formation of three Pu(III) fluoride complexes according to the equilibria



The following constants were reported at $I = 1 \text{ M}$ (NaClO_4): $\log_{10} \beta_1$ (A.69, $q = 1$) = (3.58 ± 0.08) , $\log_{10} \beta_2$ (A.69, $q = 2$) = (6.40 ± 1.13) , and $\log_{10} \beta_3$ (A.69, $q = 3$) = (12.61 ± 0.15) . The authors reported that β_2 could be omitted without reducing significantly the goodness-of-fit, and they concluded that $K_3 > K_2$, where K_q is the stepwise formation constant according to the equilibria



However, the result of the fitting exercise suggests not only $K_3 > K_2$, but also $K_3 > K_1$: $\log_{10} K_1$ (A.70, $q = 1$) = 3.58, $\log_{10} K_2$ (A.70, $q = 2$) = 2.82, and $\log_{10} K_3$ (A.70, $q = 3$) = 6.21. As a comparison, we use the constants selected in the americium review [95SIL/BID] for the corresponding Am(III) system (where values have been selected for the formation of the 1:1 and 1:2 complexes only), and we calculate the speciation at the highest fluoride concentration used by the authors: We find that under these conditions only 6.5% of Pu(III) was complexed with fluoride, the rest was present as the free aqua ion, Pu^{3+} . Certainly, it cannot be *a priori* excluded that a metal-ligand system behaves such that the 1:3 complex is drastically more stable than both the 1:1 and the 1:2 complex. But it is striking that the authors found very much the same behaviour of Sm(III) and Bi(III), with very high stabilities of the 1:3 complexes, and comparatively low stabilities for the 1:1 and 1:2 complexes. This is in contradiction to the lanthanide(III) and actinide(III) fluoride complexation behaviour found in other studies, e.g. [61PAU/GAL, 86CHO, 92FUG/KHO, 92MIL]. On this basis it is not possible to accept the results of this study unless they are verified by independent measurements.

[93STA/LAR]

This paper describes a study of the reaction of water vapour (at 0.02 Pa) with plutonium metal (also see the entry for [92HAS] in this appendix). A non-equilibrium surface layer is formed, and the composition of the outermost 5 nm was found (using X-ray photoelectron spectroscopy (XPS)) to have a composition near $\text{PuO}_{2.2}$. The higher oxide can apparently be formed from water adsorbed on PuO_2 , and loses oxygen to form PuO_2 at temperatures above 350°C.

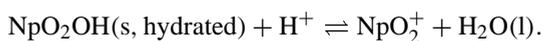
[93WEG/OKA]

This was a qualitative spectrophotometric study of the Pu(VI) phosphate system. No data on complexes or solubility of a specific solid were reported, and complications due to colloid formation arose during absorbance measurements. The authors have measured the shift of their reported 833 nm band of Pu(VI) in solutions of varying phosphate concentrations and for pH values of 2.7 to 11.9. It was proposed that the

bands at 842, 846 and 849 nm correspond to H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} complexes of Pu(VI), based only on the predominant phosphoric acid anion at the pH of the solutions where the bands were recorded. There is no convincing evidence for the simultaneous existence of the three species at pH = 2.7. The high Pu(VI) solubilities measured in the filtered solutions have been explained by the authors as resulting from the formation of stable and unstable colloids.

[94CAM/LEM]

Values are reported for the enthalpy of solution of hydrated dioxoneptunium(V) hydroxide based on twelve samples from two different batches of the solid, $\text{NpO}_2\text{OH} \cdot x\text{H}_2\text{O}(\text{s})$. The apparent hydration number, x , was 1.52 for the first batch and 1.28 for the second. Unexpectedly, the experimental enthalpies of solution are more exothermic for the less hydrated sample, although the results do agree marginally within the 95% confidence limits. The radiochemical analyses for neptunium gave systematically lower results than gravimetric analyses (by almost 10%), and one set or the other must be assumed to be in error. The gravimetric analyses could overestimate the amount of neptunium in the samples if these contained an inert impurity that remained as part of the solid at 500°C. This is not likely considering the method of synthesis, and it is more probable the radiochemical analyses were systematically in error. In this review the results based on the gravimetric results are accepted. The difference in the enthalpies of solution for the slightly differently hydrated solids is not considered to be proven, and the difference in the enthalpy effect corresponding to the transfer of the NpO_2^+ ion from 1.0 mol·kg⁻¹ HClO₄ to infinite dilution is assumed to be negligible. An average value of $-(43.7 \pm 4.4)$ kJ·mol⁻¹ is accepted from this work for the reaction



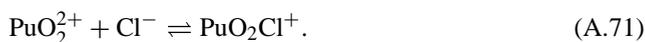
[94CLA/EKB]

The results of photoacoustic spectroscopic studies were reported for basic carbonate solutions of Pu(IV). The results are consistent with those of Capdevila [92CAP]; there was a reversible spectral change in the relative spectral intensity of the 486 and 492 nm peaks. The authors concluded that a single carbonate-containing species is dominant in 1 M total carbonate solution from pH = 8.4 to 12.0. Other species with peaks at 500, 492 and 513 nm were described but no stoichiometry was assigned. Although supportive of other spectrometric studies, no new thermodynamic data were presented that is useful for this review.

[94GIF]

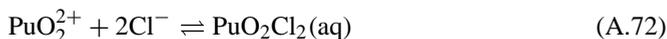
Giffaut investigated the influence of chloride ions on the visible absorption spectrum of PuO_2^{2+} in 1 M HClO₄ solution. He observed, by adding increasing quantities of a 11.6 M HCl solution to this starting solution, the appearance of a second absorption peak at $[\text{Cl}^-]_t > 0.1$ M, and of a third peak above a $[\text{Cl}^-]_t$ concentration of about

2-2.5 M. At chloride concentrations higher than about 4.5 M, an additional absorption band can be identified, indicating the existence of a third chloride complex of PuO_2^{2+} . In order to allow a quantitative evaluation of these absorption spectra, Giffaut [94GIF] carried out two measurements at constant ionic strength, 2.2 m and 3.5 m (HCl, HClO_4), respectively. By measuring the absorption at 831 nm and 838 nm, *i.e.*, at the absorption peaks due to PuO_2^{2+} and PuO_2Cl^+ , respectively, he obtained no evidence for the formation of the 1:2 complex, $\text{PuO}_2\text{Cl}_2(\text{aq})$, except at the highest chloride concentration used (2.11 M). Unfortunately, Giffaut did not record the absorption at a wavelength of 844 nm, *i.e.*, at the absorption peak of $\text{PuO}_2\text{Cl}_2(\text{aq})$. This would have provided a clearer picture about the existence of the 1:2 complex under these conditions. Hence, Giffaut evaluated the absorption measurements at $I = 2.2$ m and 3.5 m, respectively, in terms of the reaction



He obtained $\log_{10} \beta_1(\text{A.71}, I = 2.2 \text{ m}, 298.15 \text{ K}) = -(0.07 \pm 0.09)$ and $\log_{10} \beta_1(\text{A.71}, I = 3.5 \text{ m}, 298.15 \text{ K}) = -(0.06 \pm 0.07)$, respectively. These values are in fair agreement with the other studies available on this system. Giffaut [94GIF] demonstrated the absence of polynuclear complexes below a total Pu concentration of 2.8×10^{-4} M. By linear extrapolation to $I = 0$ according to the specific ion interaction equation, *cf.* Appendix B, he obtained $\log_{10} \beta_1^0(\text{A.71}, 298.15 \text{ K}) = (0.70 \pm 0.13)$ and $\Delta\varepsilon(\text{A.71}) = -(0.08 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$. This constant seems reliable and is selected in the present review (with a slight increase of its uncertainty).

Giffaut [94GIF] evaluated the formation constant of the 1:2 complex according to the reaction



from his measurements at variable ionic strength and chloride concentrations between 1.18 M and 4.75 M. Knowing the formation constant and its ionic strength dependence for the 1:1 complex from the measurements at constant ionic strength, he calculated the corresponding $\log_{10} \beta_1$ values for each ionic strength used, and thus obtained $\log_{10} \beta_2$ values over an ionic strength range varying from 2.4 M to 5.2 M (chloride concentration varying from 1.5 to 4.2 M). The extrapolation of these $\log_{10} \beta_2(I)$ values to $I = 0$ according to the specific ion interaction equation, *cf.* Appendix B, resulted in $\log_{10} \beta_2^0(\text{A.72}, 298.15 \text{ K}) = -(0.6 \pm 0.2)$ and $\Delta\varepsilon(\text{A.72}, \text{HCl}) = -(0.43 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}$. The points used in the extrapolation of $\log_{10} \beta_2 + 6D$ vs. I_m lie on a well-defined straight line, see ([94GIF, p. 108], Fig. III.12). It should be mentioned that the $\log_{10} \beta_2(I)$ values in Table III/III [94GIF, p. 126] for $I = 2, 3$ and 4 M (HCl), respectively, are in error (probably an error in sign, *i.e.*, +0.6 instead of -0.6 used for $\log_{10} \beta_2^0$). Our calculation results in $\log_{10} \beta_2(I = 2 \text{ M}, \text{HCl}) = -1.10$ (Giffaut: 0.08), $\log_{10} \beta_2(I = 3 \text{ M}, \text{HCl}) = -0.71$ (Giffaut: 0.46), and $\log_{10} \beta_2(I = 4 \text{ M}, \text{HCl}) = -0.27$ (Giffaut: 0.89). These values are more or less in agreement with other literature data. The existence of $\text{PuO}_2\text{Cl}_2(\text{aq})$ has been shown spectroscopically by a distinct peak at 844 nm ([94GIF, p. 99], Fig. III.2) leading to an isobestic point. However, we do not consider the existence of $\text{PuO}_2\text{Cl}_3^-$ proven by

the slight changes in absorption near 851 nm in that figure. Giffaut [94GIF] also studied the chloride complexes of Pu^{4+} by spectrophotometry. He observed the formation of PuCl^{3+} , PuCl_2^{2+} , PuCl_3^+ and $\text{PuCl}_4(\text{aq})$. For the stepwise constants, Giffaut obtained $\log_{10} K_1(I = 3 \text{ M}) = (0.20 \pm 0.08)$, $\log_{10} K_2(I = 3 \text{ M}) = -(0.56 \pm 0.16)$, $\log_{10} K_1(I = 4 \text{ M}) = (0.25 \pm 0.08)$, $\log_{10} K_2(I = 4 \text{ M}) = -(0.61 \pm 0.18)$, and, at variable ionic strength, the approximative values of $-0.7 \leq \log_{10} K_3 \leq -1$ and $\log_{10} K_4 < -1$. Large discrepancies are observed among different literature values for the second formation constant, *cf.* Table 18.4. We use the first constants reported for $I = 3 \text{ M}$ and $I = 4 \text{ M}$ in our regression analysis and assign them an uncertainty of ± 0.2 .

As to the chloride complexes of neptunium, Giffaut [94GIF] observed practically no changes in the absorption spectrum of $\text{Np}(\text{V})$ in 4 M NaCl solution with respect to 1 M HClO_4 solution. For the chloride complexation of Np^{4+} and NpO_2^{2+} , Giffaut evaluated the available literature and corrected the measured constants to $I = 0$ by using ion interaction coefficients that he had compiled or estimated. He obtained $\log_{10} \beta_1^\circ(\text{NpCl}^{3+}) = (1.45 \pm 0.25)$, $\log_{10} \beta_2^\circ(\text{NpCl}_2^{2+}) = (2.4 \pm 0.3)$, and $\log_{10} \beta_1^\circ(\text{NpO}_2\text{Cl}^+) = (0.7 \pm 0.4)$. However, his recalculations of these values to ionic strengths of 2, 3 and 4 M ([94GIF, *p.* 126], Table III/III) in many cases resulted in $\log_{10} \beta$ values that are higher than the available experimental determinations.

[94GIF/VIT]

In this paper Giffaut, Vitorge and Capdevila derived formulas for calculating the temperature dependence of the enthalpy, entropy and heat capacity of a reaction in an aqueous ionic medium, when using the SIT (Appendix B) to account for activity coefficient and ionic strength effects.

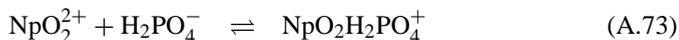
[94HOB/PAL]

The results obtained in a series of spectrophotometric $\text{Pu}(\text{IV})/\text{carbonate}$ complexation studies over wavelengths from 400 to 700 nm were summarized. The pH was varied by controlling p_{CO_2} ($\text{pH} = 7.17$ to 9.67 ; $p_{\text{CO}_2} = 0.3$ to 100%). The authors concluded that the results indicated there are three important species over this range of conditions. The results were found to be consistent with two independent but simultaneous equilibria, the addition of one CO_3^{2-} and the addition of one OH^- and perhaps an additional carbonate to an initial species in neutral solution. The results of a computer analysis listed equilibrium constants for a number of possible stoichiometric models. However, as the initial species in near-neutral solution remain unidentified, no definitive assignment of equilibrium constants can be made.

[94MAT/CHO]

Mathur and Choppin studied phosphate complexes of dioxoneptunium(VI) at 1 M NaClO_4 and 25°C by solvent extraction using either HDNNS (dinonylnaphthalenesulphonic acid) or a mixture of DBM (dibenzoylmethane) and

TOPO(tri-*n*-octylphosphine oxide) as the organic phase extractant. Potassium permanganate was used as a holding oxidant. In the experiments performed at pH = 2.5 the sodium form of HDNNS was used as the extractant, and the data were explained in terms of formation of the complex $\text{NpO}_2\text{H}_2\text{PO}_4^+$,

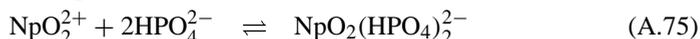


$$\log_{10} \beta(\text{A.73}, 1 \text{ M NaClO}_4, 298.15 \text{ K}) = (2.52 \pm 0.07)$$

Since the data were obtained at constant pH, no information about the proton content of the species formed can be obtained. Analogy with the dioxouranium(VI) phosphate system at acidic pH would suggest the formation of H_3PO_4 and mixed $\text{H}_3\text{PO}_4 - \text{H}_2\text{PO}_4^-$ complexes, which the authors have not considered at pH = 2.5 (although they did considered HPO_4^- species). The concentrations of the various phosphate ions reported in their Table 1 differ from the ones calculated with the values of the constants reported at the bottom of the same table. For these reasons, the constant corresponding to Equation A.73 has been accepted only with a substantially increased uncertainty. In view of the analogies between uranium(VI) and neptunium(VI) systems, a correction to infinite dilution similar to that used for Equation V.134 in [92GRE/FUG] was applied. This, together with the corresponding correction of K_1 for phosphoric acid, yields:

$$\log_{10} \beta^\circ(\text{A.73}, 298.15 \text{ K}) = (3.32 \pm 0.50)$$

For the experiments performed at pH = 5.14, TOPO was used as the extractant, and the extraction mechanism was verified - a slope of 2 was obtained in the plot of $\log_{10} 1/D$ vs. $\log_{10}[\text{DBM}]$. The data have been explained with the equilibria:



with the constants: $\log_{10} \beta(\text{A.74}, 1 \text{ M NaClO}_4, 298.15 \text{ K}) = (4.54 \pm 0.13)$ and $\log_{10} \beta(\text{A.75}, 1 \text{ M NaClO}_4, 298.15 \text{ K}) = (7.49 \pm 0.13)$.

No details of the pH electrode calibration are reported, and the influence of an activity scale calibration to the calculated concentrations is apparently more important at pH = 5.14. Distribution coefficients much higher than those reported in Fig. 1 of [94MAT/CHO] seems to have been used in the same system according to Fig. 3 of the reference. Thus, D_0 values of the order of 500 can be estimated from Fig. 3, while in Fig. 1 the D_0 values vary between 0.03 and 1. The model function (Equation 9 in [94MAT/CHO]) used to obtain the formation constants for HPO_4^{2-} complexes contains a linear term in HPO_4^{2-} multiplied by the constant for the H_2PO_4^- complex, thus propagating its error here. No allowance has been made for the hydrolysis of the dioxoneptunium(VI) ion at pH 5.14, and there is not enough information to permit recalculation of the data.

Hence, the values reported have been selected with substantially increased uncertainty limits:

$$\log_{10} \beta(\text{A.74}, 1 \text{ M NaClO}_4, 298.15 \text{ K}) = (4.54 \pm 0.70)$$

$$\log_{10} \beta(\text{A.75}, 1 \text{ M NaClO}_4, 298.15 \text{ K}) = (7.5 \pm 1.0)$$

By using interaction coefficients from Appendix B, as well as $\varepsilon_{(\text{Na}^+, \text{NpO}_2\text{HPO}_4(\text{aq}))} = 0 \text{ kJ}\cdot\text{mol}^{-1}$ and an estimated $\varepsilon_{(\text{Na}^+, \text{NpO}_2(\text{HPO}_4)_2^-)} \approx -0.1 \text{ kJ}\cdot\text{mol}^{-1}$ yields:

$$\log_{10} \beta^\circ(\text{A.74}, 298.15 \text{ K}) = (6.2 \pm 0.7)$$

$$\log_{10} \beta^\circ(\text{A.75}, 298.15 \text{ K}) = (9.5 \pm 1.0)$$

[94MEI]

Meinrath prepared a $\text{NaNpO}_2\text{CO}_3(\text{s})$ compound by precipitation from a 0.02 M NpO_2^+ acidic solution with 0.05 M Na_2CO_3 . After three weeks of equilibration, he measured the solubility of the solid at 25°C on bubbling the solution with a 1% $\text{CO}_2(\text{g})$ (in $\text{N}_2(\text{g})$) mixture. In calibrating his glass electrode he determined the value $\log_{10} K_{\text{p},2} = (17.62 \pm 0.07)$ for the carbon dioxide gas/carbonate equilibrium constant [91MEI]. He compared this to a value of (17.65 ± 0.07) reported by Kim *et al.* [92RUN/MEI]. The value calculated with the auxiliary thermodynamic data selected by this review is $\log_{10} K_{\text{p},2} = (17.53 \pm 0.04)$. Meinrath determined values for the solubility product, $K_{\text{s},1}$, and the first carbonate complexing constant, β_1 , that are the same (within the uncertainties) as those published earlier by Kim *et al.* [91KIM/KLE]. The actual solubility values from the measurements under 0.03% $\text{CO}_2(\text{g})$ were given in that earlier report [91KIM/KLE], but not in the later [94MEI] publication. However, the new results for the solubility measurements under 1.0% $\text{CO}_2(\text{g})$, [94MEI], appear only as points on graphs. Meinrath indicated the X-ray diffraction pattern for his sodium neptunium carbonate solid differed somewhat from patterns reported by Volkov, Visyashcheva and Kapshukov [77VOL/VIS]; also, the pattern is not completely consistent with later work [94NEC/RUN, 95NEC/RUN]. Because of this, no attempt was made to re-evaluate Meinrath's results in the present review. However, the values are consistent with the earlier study [91KIM/KLE] and, within the uncertainties, consistent with the values selected in the present review.

[94MER/FUG]

The authors measured the enthalpy of solution of $\text{Np}_2\text{O}_5(\text{cr})$ in 6 M HCl to be $-(80.3 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$ (where the uncertainty has been expanded slightly, and it has been assumed the errors are random with respect to all four batches of solid). The selected value for $\Delta_f H_m^\circ(\text{NpO}_2^+, \text{aq})$ is assumed equal to the value in 6 M HCl, and using $-286.63 \text{ kJ}\cdot\text{mol}^{-1}$ for the enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ in the medium $\Delta_f H_m^\circ(\text{Np}_2\text{O}_5(\text{cr})) = -(2162.7 \pm 9.5) \text{ kJ}\cdot\text{mol}^{-1}$ is calculated.

Values are also reported for the enthalpy of solution (in 1 M HCl) of hydrated dioxoneptunium(V) hydroxide based on ten samples from three different batches of the solid, $\text{NpO}_2\text{OH}\cdot x\text{H}_2\text{O}(\text{s})$, with an apparent hydration number ranging from $x = 2.17$ to $x = 2.54$. An average enthalpy of solution of $-(38.8 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$ can be calculated from the data assuming $x = 2.50$. If instead, the analyses are assumed to indicate slightly variable hydration, and the molar masses are adjusted accordingly, the enthalpy of reaction is $-(38.5 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$.

This value is used in the present review and, as in the original paper, the difference in the enthalpy effect corresponding to the transfer of the NpO_2^+ ion from 1.0 M HCl to infinite dilution is assumed to be negligible.

[94NEC/KIM]

This review used the Np(V) solubility measurements tabulated in this report, with other data published by the same group of authors (as discussed in this appendix [91KIM/KLE, 94NEC/RUN]). Experimental data of Np(V) liquid-liquid extraction by NaDNNS from 0.2 to 5 M $\text{Na}(\text{ClO}_4, \text{Cl})$ aqueous solutions were also tabulated in this report. These were used by Neck, Kim and Kanellakopoulos to estimate Np(V) activity coefficients, however there are difficulties with the interpretation of the authors as explained in the discussion of [94NEC/RUN] (work based on the same experimental data from the same group). In the present review we have interpreted interactions between NpO_2^+ and Cl^- solely in terms of the selected interaction coefficients rather than invoke a model involving the formation of weak chloro-complexes (also see [96RUN/NEU]). The interpretation of the liquid-liquid extraction study neglected activity coefficient corrections for the organic phase. These corrections might be important compared to activity coefficient corrections. The corresponding uncertainty could not be deduced from statistical analysis since some of the possible errors were systematic (not random). The necessary activity coefficient corrections (especially for chloride media, cf. Section 12.1.2.1.3.c) increased the uncertainty in the interpretation of the data. Therefore these extraction measurements were not used in the present review to estimate the stability constants of Np(V) carbonate complexes (see also the discussions of [91KIM/KLE, 94NEC/RUN] in this appendix).

[94NEC/RUN]

This paper incorporates and discusses the solubility and spectroscopic results described in an earlier report [91KIM/KLE]. New activity coefficient values are also proposed. In this paper the SIT, as used in the present review, was used by Neck *et al.*, while in a later paper [95FAN/NEC] the authors used a simplified Pitzer equation. The junction potential was measured (and not set to zero by using the same ionic medium for the reference electrode and working solutions). The interpretation of the liquid-liquid extraction study [94NEC/KIM, 95NEC/FAN] neglected activity coefficient corrections for the organic phase. These corrections might be important compared to activity coefficient corrections. The corresponding uncertainty could not be deduced from statistical analysis since some of the possible errors were systematic (not random). In addition, possible chemical systematic error (discussed above) could be even more important. For these reasons, the activity coefficients proposed in this work [94NEC/RUN] are not accepted in the present review. However, as mentioned elsewhere in this appendix (see discussions of [91KIM/KLE, 94NEC/KIM]), some of the systematic errors, if they exist, will cancel, especially for the values of equilibrium constants extrapolated to zero ionic strength. The $\Delta\varepsilon$ value of the solubility products can be calculated from ε values used by this review (see Appendix B) that were determined from isopiestic

(for $\varepsilon_{(\text{Na}^+, \text{ClO}_4^-)}$), equilibrium constant (for $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})}$) and redox (for $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$) measurements. For this last value an analogy between NpO_2^{2+} and UO_2^{2+} was also assumed since the experimental determinations of the values of the $\text{MO}_2^{2+}/\text{MO}_2^+$ redox couples were found to be the same for $M = \text{U}, \text{Np}, \text{Pu}$ [87RIG/VIT, 89RIG/ROB, 90RIG, 94CAP/VIT]. The $\Delta\varepsilon$ value of the two solubility product reactions as determined by Kim *et al.* and Neck *et al.* [91KIM/KLE, 95NEC/RUN] are not consistent with the value calculated in the present review (Table A.29). The two $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$ values calculated from those $\Delta\varepsilon$ values are also not consistent with later determinations by the same group [95NEC/FAN]. A simplified Pitzer equation was used from which this review determined $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = 0.20 \pm 0.03 \text{ kg}\cdot\text{mol}^{-1}$, a value which is in accord with the value 0.25 ± 0.05 accepted in the present review (Table A.29).

Table A.29: Values of $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$ recalculated in this review from the measurements of [91KIM/KLE, 94NEC/KIM, 95NEC/FAN, 95NEC/RUN]^(a) and auxiliary values from Appendix B. Similar values using auxiliary values calculated in this review from experimental data published in these references are reported in Table 12.5.

	ε ^(h)	ε ^(e)	ε ^(f)	$\log_{10} K_{s,1}^\circ$
this review ^(b)	(0.25±0.05)			
[91KIM/KLE]	(0.36±0.04)			
[95NEC/RUN]	(0.34±0.04)	(0.37±0.09)	(0.42±0.09)	
0.1 to 3 M ^(c)	(0.38±0.07)			−(10.95 ± 0.11)
0.1 to 5 M ^(c)	(0.38±0.04)			−(10.95 ± 0.07)
[95NEC/FAN] ^(d)	(0.20±0.05)			
[94NEC/KIM] ^(g)	(0.18±0.03)			

- (a) Unless noted otherwise, ε is $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)}$ from $\Delta\varepsilon_{s,i} = i\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})} + \varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} + (2i - 1)\varepsilon_{(\text{Na}^+, \text{ClO}_4^-)} + x_i r$ as determined by SIT linear regression from the values determined at different ionic strength for $K_{s,i}$, the $\text{Na}_{(2i-1)}\text{NpO}_2(\text{CO}_3) \cdot x_i \text{H}_2\text{O}(\text{s})$ solubility product, where r is $a_{\text{H}_2\text{O}}/m_{\text{NaClO}_4}$ mean value, $x_1 = 3.5$ and x_2 is unknown; $i=1$ in column 2; $i=2$ in columns 3 and 4.
- (b) ε values calculated with the auxiliary values used by this review.
- (c) Calculated in the present review from the data reported in [91KIM/KLE].
- (d) Calculated in the present review from the Pitzer set of parameters proposed in [95NEC/FAN]. The uncertainty has been estimated in this review as the difference ($\varepsilon(3 \text{ M}) - \varepsilon(0.5 \text{ M})$) where the ε values were calculated from the mean activity coefficients.
- (e) Calculated from $K_{s,2}$ using the arbitrary x_2 value $x_2 = 0$ in the solid phase.
- (f) Calculated from $K_{s,2}$ using the arbitrary x_2 value $x_2 = 3.5$.
- (g) From liquid-liquid extraction data also published in [95NEC/FAN]
- (h) Calculated using $K_{s,1}$ (unless otherwise noted)

Thus, the ionic strength corrections from this and related work [95NEC/RUN, 96RUN/NEU] are not self consistent, and the $\Delta\varepsilon$ values from the solubility products are not consistent with currently accepted ε values. These two inconsistencies could

result from several causes: including the small systematic errors noted in this appendix, incorrect theoretical methodology (*i.e.*, problems with the SIT or the currently accepted ε values), chemical problems with the solid phases or other experimental difficulties.

[94RIZ/RAO]

The paper presents results of a calorimetric study at 25°C of the titration of $^{242}\text{Pu(VI)}$ in initially acidic aqueous solution with CO_3^{2-} -free NaOH. It provides estimates of the enthalpies of hydrolysis of PuO_2^{2+} to form the monohydroxydioxoplutonium(VI) ($\Delta_r H_m = (28.0 \pm 5.0) \text{ kJ}\cdot\text{mol}^{-1}$) and the dihydroxydioxoplutonium(VI) complexes ($\Delta_r H_m = (42.6 \pm 7.0) \text{ kJ}\cdot\text{mol}^{-1}$).



The raw data are not available for recalculation, and this is unfortunate because the partition of the enthalpy change between the reactions to form different hydrolysis species is dependent on the selected hydrolysis constants, or at least on their relative values. The hydrolysis constant values actually used were from Pashalidis *et al.* [93PAS/KIM2]. Recalculation as discussed in Appendix A of the present review, suggests only slightly different values, $\log_{10}^* \beta_{11} = -5.14$ and $\log_{10}^* \beta_{12} = -10.03$ in 1 M NaClO_4 at 20°C, but these (particularly $^* \beta_{12}$) may be in error [95PAS/KIM]. However, if the entropies of reaction as reported are correct, it appears that regardless of other problems, the $\log_{10}^* \beta_{1i}$ values can be considered to be independent of temperature between 20 and 25°C. If the results from Pashalidis *et al.* [95PAS/KIM] are considered, it would appear the enthalpy changes observed by Rizkalla *et al.* should be attributed to the first hydrolysis reaction, and (probably) to some undesired polymerisation reaction(s), at least for the pH ranges shown in Table 2. The suggested value of $28 \text{ kJ}\cdot\text{mol}^{-1}$ is accepted here for the first hydrolysis step, but with the uncertainty increased to $\pm 15 \text{ kJ}\cdot\text{mol}^{-1}$. It is not clear which hydrolysis reaction should be properly associated with the second enthalpy, and it is not accepted in the present review.

[94VEI/SMI]

This is a qualitative study of Pu(IV) nitrate complexation using a variety of spectroscopic methods at an unspecified temperature and at 2.34 molal ionic strength, probably perchloric acid (this is not clearly stated, if the total molar concentration was constant, the molality changes in the mixtures). The major finding from the absorption spectroscopy measurements is the presence of two near-isobestic points at 471.2 and 472.3 nm. This is interpreted as proof of the existence of three species, that is, the aqueous ion and its two complexes with one and two nitrates. Furthermore, the two nitrate complexes have identical maximum molar absorptivity at 476 nm. This review does not consider the observed effect as sufficient proof of the formation of the dinitrate complex. Preliminary EXAFS measurements were also been reported, but a more complete discussion was carried out in [96ALL/VEI].

[94YAM/SAK]

This paper reports solubility experiments with a poorly characterized Pu(IV), and perhaps changing, solid phase in 0.1 M K(Cl, CO₃, OH) solutions. NaNO₂ was added to prevent Pu(IV) oxidation. The plutonium valence state and pH were verified at the end of every experiment. The procedure used to determine carbonate concentration might lead to underestimation at high solute and solid concentrations. There are additional unexplained discrepancies in the solution compositions and reports of ionic strength. The results of these experiments were interpreted as the consequence of formation of two mixed hydroxycarbonate species: Pu(OH)₂(CO₃)₂²⁻ at pH 9.4 – 10.1 and Pu(OH)₄(CO₃)₂⁴⁻ at pH 12 - 13. This is not consistent with other reports. The assignment of these stoichiometries is vitally dependent on the nature and constancy of the solid phase used and therefore the results reported must be regarded with scepticism. Under conditions of increasing pH and CO₃²⁻ concentration, the solid phase will tend to change from the initial, very amorphous and soluble, Pu(IV) hydroxide at near-neutral pH, to a more stable Pu(IV) hydroxide from pH 8 to 10 (see for example, [86LIE/KIM]), to a potassium salt, perhaps K₄Pu(CO₃)₄·nH₂O(s) at higher pH and carbonate concentrations (see [58GEL/ZAI, 95CLA/HOB] and the text). The carbonate solid phase would not need to be present in large amounts to affect the equilibrium concentrations of Pu(IV) in solution. This progression of phases would help to explain the observed anomaly of higher apparent Pu(IV) solubilities in near-neutral HCO₃⁻ solutions as compared to the basic CO₃²⁻ solutions.

Due to the poor control over, and perhaps changing, solid-phase composition, the results of this paper, which are at odds with other results suggesting that mixed hydroxycarbonate complexes are unimportant in this system, are given no weight in the present review.

[95CAP/VIT]

This paper contains some of the data of [92CAP], but more calculations are presented for the temperature dependence of the redox potentials and heat capacities. Literature data for the plutonium couples are discussed and evaluated. Data for the Pu(VI)/Pu(V) and the Pu(IV)/Pu(III) couples previously published from the same laboratory [89RIG/ROB] are rejected. The average heat capacity of reaction for the redox couple reaction (5 to 65°C) is calculated to be approximately -400 J·K⁻¹·mol⁻¹, and this value is too negative to be compatible with apparent molar heat capacity values estimated by analogy from experimental results for the uranium [89HOV/NGU, 96LEM/CAM] and neptunium [93LEM/CAM, 96LEM/CAM] systems. This suggests the uncertainty for the entropy of reaction proposed in this paper has been underestimated by the authors. The values of C_{p,m}(T) for the ionic species vary strongly with temperature and ionic strength, and it is probable the same is true of Δ_rC_{p,m}(T). Although the experimental work appears to be well done, the results of this study are too sparse and not sufficiently accurate to generate reliable heat capacity values. New values were proposed for Δε for the Pu(VI/V) and Pu(IV/III) couples; the differences in

the interaction coefficients are very similar for An = U, Np and Pu: $\Delta\varepsilon(\text{IV/III}) = \varepsilon_{(\text{An}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{An}^{3+}, \text{ClO}_4^-)} = (0.35 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$, $(0.35 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ and $(0.33 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ respectively, and $\Delta\varepsilon(\text{VI/V}) = \varepsilon_{(\text{AnO}_2^{2+}, \text{ClO}_4^-)} - \varepsilon_{(\text{AnO}_2^+, \text{ClO}_4^-)} = (0.20 \pm 0.06)$, (0.21 ± 0.03) and $(0.22 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ respectively. For plutonium the uncertainty in $\Delta\varepsilon(\text{IV/III})$ was reported as $\pm 0.05 \text{ kg}\cdot\text{mol}^{-1}$ in Table 4, but as $\pm 0.03 \text{ kg}\cdot\text{mol}^{-1}$ in the abstract and in Table 2. The authors increased their uncertainties for systematic errors (considering variation of the junction potential with temperature, ionic strength and temperature corrections to the standard potential of the reference electrode, and use of the SIT approximation). Re-evaluation carried out in conjunction with the present review led to $\Delta\varepsilon(\text{IV/III}) = 0.22 \text{ kg}\cdot\text{mol}^{-1}$ with an uncertainty of ≤ 0.03 , regardless of whether only the 25°C or the data for all temperatures, smoothed to 25°C, were used. Previous $\Delta\varepsilon$ values for the plutonium couples [89RIG/ROB] were rejected because interference between the two redox couples during the measurement of $E^{\circ'}$ was suspected. Published $E^{\circ'}$ and E° data were discussed, and possible explanations of outliers were given. The $E^{\circ'}$ and E° values [95CAP/VIT] are in accord with the ones selected in this review. This review selects and uses the $\Delta\varepsilon$ values reported in this paper in preference to the SIT coefficients for Np and Pu species that had been derived from [89RIG/ROB] and used previously [92GRE/FUG, 95SIL/BID].

The influence of changes in temperature on interaction coefficients of reaction, $\Delta\varepsilon$, and the ionic strength correction applicable to the enthalpies and entropies of reactions are also calculated in this work from the temperature and ionic strength dependence of the formal potentials of the plutonium reversible redox couples in acidic media.

[95FAN/NEC]

In this report a set of Pitzer coefficients is derived for Np(V) hydrolysis species and carbonate complexes for perchlorate and chloride media (based on data reported in earlier publications). See the discussions of [91KIM/KLE, 94MEI, 94NEC/KIM, 94NEC/RUN] in this appendix.

[95MOR/PRA]

Pratopo's data (also in [93PRA/MOR]) were obtained from experiments in which equilibrium was probably not attained. Although equilibrium constants based on these data were proposed in Pratopo's thesis [93PRA], equilibrium constants for soluble species based on these data are not accepted in the present review. All the published Np(VI) solubility measurements for these conditions ($[\text{CO}_3^{2-}] > 10 \mu\text{M}$) are quite scattered. Some values plotted in \log_{10} - \log_{10} representation are parallel to those for $\text{UO}_2\text{CO}_3(\text{s})$ solubility curves over small domains; but extracting numbers from this type of observation leads to contradictions with other published solubility work. The slow transformation of one solid phase ($\text{NpO}_2\text{CO}_3(\text{s})$) to another ($\text{Na}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$) could explain these scattered results for a single series of measurements, since soluble species generally attain equilibrium faster than transformation can occur within the bulk of the solid phase. Also see the comments in this appendix, for [93PRA/MOR, 98VIT/CAP].

[95NEC/FAN]

The investigation of the interaction between NpO_2^+ and Cl^- by absorption spectroscopy and solvent extraction, and the derivation of Pitzer coefficients for NpO_2^+ in chloride and perchlorate media were reported in this paper. Much of the same material was provided in an earlier report [94NEC/KIM]. Also see the discussions of [94NEC/KIM, 96RUN/NEU] in this appendix.

[95NEC/RUN]

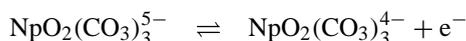
In this publication Neck *et al.* reported some additional solubility measurements (in 5 M NaCl-carbonate aqueous solutions). The solubility measurements were carried out in a similar fashion to those that had been described in previous reports from the same group of authors, and that are examined elsewhere (see the discussions of [91KIM/KLE, 94NEC/KIM] in this appendix). The presentation of the new experimental results also included figures showing the transformation of the initial hydrated phase, $\text{NaNpO}_2\text{CO}_3(\text{s})$ into a $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ phase. Np(V) concentrations were measured during this solid phase transformation. The shape and the scatter about the experimental curves in 5 M NaCl media might suggest solid phase transformation possibly between different hydrated forms of $\text{Na}_3\text{NpO}_2(\text{CO}_3)_2(\text{s})$ as previously suggested for 3 M NaClO_4 media [93LEM/BOY], or to a new solid phase with intermediate stoichiometry (see the discussions of [74VIS/VOL, 90RIG] in this appendix). However, the authors also suggest that trace activities of anions do not depend simply on the nature of the primary cation in the solution. Anion-anion interactions, not considered in the current version of the SIT, may be important for carbonate and for the Np(V) carbonate complexes. This is correct, but there seems to be direct experimental evidence of this effect only for the first Np(V) carbonate complex (and surprisingly not for the other two carbonate complexes). Another possible (but no more probable) interpretation could involve formation of a mixed carbonatochloro Np(V) complex such as $\text{NpO}_2\text{ClCO}_3^{2-}$.

Pitzer coefficients for the various species were proposed to extend modelling of the neptunium complexation and hydrolysis reactions to 5 M NaClO_4 and NaCl aqueous media.

[95OFF/CAP]

This was the publication of Offerlé's pre-thesis experimental work as an open literature report. The original experimental results were tabulated and discussed. Using cyclic voltammetry, the redox potential of the Np(VI)/Np(V) couple *versus* an Ag/AgCl reference electrode was measured. Typically the initial Np(V) concentrations were 0.6 mM in 0.22 to 2 M Na_2CO_3 aqueous solutions at 5 to 60°C. For each Na_2CO_3 concentration, a new working solution and a new reference electrode were prepared. Measurements were usually made at several temperatures in a single day. Therefore, in most cases, there are several measurements for each set of experimental conditions ($[\text{Na}_2\text{CO}_3]$, t) corresponding to measurements following increase and decrease of temperature. The reference electrode was checked twice daily. A remark in the original

publication [95OFF/CAP] said that it was not clear whether only the stability of the electrode was checked, or whether its junction potential was also measured. A later publication [98VIT/CAP] gave indications that lead this review to assume the values (less than 1 mV) tabulated in the original publication [95OFF/CAP] were junction potential measurements. The peak intensity was proportional to the square root of the scanning speed, and the potential shift between the oxidation and reduction peaks was a little more than the theoretical value, but the mean value, $E_{1/2}$, remained independent of the scanning speed. This confirms that, as for other reversible and quasi-reversible systems studied in this laboratory [87RIG/VIT, 89RIG/ROB, 89ROB, 90CAP/VIT, 90RIG, 92CAP, 95CAP/VIT], $E_{1/2}$ is a good approximation to the thermodynamic potential of the studied redox equilibrium. For the treatment of the data, it was assumed that the potential was controlled by the redox equilibrium



Corrections for the dissociation of the Np(V) limiting complex, were calculated to be about 5 mV for the less concentrated (0.22 M Na_2CO_3) solution at 25°C, which is within the uncertainty; but was taken into account in this review. Extrapolation to zero ionic strength was performed at each temperature using the SIT with the same procedure and physical parameters as recommended in the present review. A second order polynomial regression about the value for 25°C was used for the treatment of the data as a function of temperature. The first order term is related to the entropy of reaction, and the second order term to heat capacity changes corresponding to the above equilibrium. A similar treatment was applied to the specific interaction coefficients. Hence, a value for E° was determined. The numerical values of the thermodynamic quantities ($\Delta_r S_m^\circ$, $\Delta_r C_{p,m}^\circ$), $\Delta\varepsilon^\circ$ and its first and second derivatives as a function of T , were found to be similar to those selected for uranium [92GRE/FUG] or published for uranium and plutonium by one of the authors [92CAP].

The original data (V/S.S.C.) were recalculated (V/SHE) taking into account small errors pointed out in [95OFF/CAP] and in [98VIT/CAP]. The mean values of E° and associated statistical uncertainties are shown in Table 1 in [98VIT/CAP]. The measured junction potential (± 0.6 to 1.2 mV) are considerably less than the estimated uncertainties in the measurements (2.6 to 6.5 mV) and therefore have been neglected in the present review. Extrapolation of the data to $I = 0$ by several different procedures results in values of $E^\circ(T)$ and $\Delta\varepsilon(T)$ which agree with Offerlé's original calculations within the uncertainty limits (see Tables 2 and 3 in [98VIT/CAP]). Retaining or omitting the data for 60°C (for which data are lacking at the lower ionic strengths) has little effect, except for the values extrapolated to zero ionic strength, and even those differences are within the selected uncertainties. Two (small) corrections were disregarded by the authors, and also in the present review because they are small at 25°C, and have unknown values at other temperatures. The first is the difference between the diffusion coefficients of the two limiting complexes (that were the major electroactive species) [90RIG]. The other is the extent of dissociation of the Np(V) limiting complex [98VIT/CAP]. This correction changes the final results E° and $\Delta\varepsilon$, by -3.1 mV and -0.020 kg·mol⁻¹ respectively, at 25°C. These differences are less than the uncertainties. (The potentials measured at 25°C were consistent with other data [77SIM, 90RIG]

selected by this review. For this comparison, the original data were corrected for dissociation of the Np(V) limiting complex (see Table 7 in [98VIT/CAP]).

Both the original $E(T, I)$ values, and the $E(T, 0)$ and $\Delta\varepsilon(T)$ values resulting from the SIT regressions, were fitted to second order polynomial functions about a reference temperature T° . The first order ($E'(T^\circ, I)$ or $\Delta\varepsilon'(T^\circ)$) term, and the second order ($E''(T^\circ, I)/2$ or $\Delta\varepsilon''(T^\circ)/2$) term were related to the corresponding entropy and heat capacity of reaction by using classical thermodynamic equations (with $T^\circ = 298.15$ K). This approximation assumes that the effect on the other parameters of the value of heat capacity of reaction is negligible. To check this assumption, three different ways of using this type of approximation were used:

$$FE(T, I) \approx FE(T^\circ, I) + (T - T^\circ)\Delta_r S_m(T^\circ, I) - (T - T^\circ - T \ln(T/T^\circ))\Delta_r C_{p,m}(T^\circ, I)$$

$$FE(T, I) \approx FE(T^\circ, I) + (T - T^\circ)\Delta_r S_m(T^\circ, I) + (T - T^\circ)^2 \Delta_r C_{p,m}(T^\circ, I)/(2T^\circ)$$

$$FE(T, I)/T \approx FE(T^\circ, I)/T - (1/T - 1/T^\circ)\Delta_r H_m(T^\circ, I) + (1/T - 1/T^\circ)^2 T^{\circ 2} \Delta_r C_{p,m}(T^\circ, I)/2$$

The first is obtained assuming constant $\Delta_r C_{p,m}$. The second and third are second order Taylor-series expansions neglecting the variation of $\Delta_r C_{p,m}$ with temperature. Consistent values for the thermodynamic quantities were found whatever the equation used. The plot of the experimental data E as a function of T or $1/T$ yields lines that are close to being straight lines. This means that the variation with temperature of the corresponding entropy change, $\Delta_r S_m$ (or of $\Delta_r H_m$) is small. Hence, the effect of $\Delta_r C_{p,m}$ on E or E/T is small (but $\Delta_r C_{p,m}$ is not necessarily constant; its influence on E in the temperature range studied is merely difficult to detect, and only an overall mean value can be estimated). Even setting C_p to zero leads to changes in the values of E (or E/T) and $\Delta_r S_m$ (or $\Delta_r H_m$) that are within the experimental uncertainties.

In the present review $\Delta_r G_m$, $\Delta_r H_m$, $\Delta_r S_m$ and $\Delta_r C_{p,m}$ at 25°C were calculated using a second order polynomial regression of E as a function of $(t - 25^\circ\text{C})$. The results found in this review are consistent with those initially calculated by Offerlé, Capdevila and Vitorge [95OFF/CAP] (the value of $\Delta_r C_{p,m}$ at zero ionic strength is different by approximately 400 J·K⁻¹·mol⁻¹; but this is still within the selected uncertainties). The variation of $\Delta\varepsilon$ with temperature was also fitted to a second order polynomial expression. As was the case above, the second order term could not be determined with a high degree of accuracy.

All these calculations show that consistent results are found for the (relatively narrow) temperature domain studied over a wide range of ionic strength conditions. To summarize:

- Second order terms, $\Delta_r C_{p,m}$ and $\Delta\varepsilon''_T$, have nearly negligible influence

- Different data treatments using the approximation of constant $\Delta_r C_{p,m}$, give consistent results
- Within the calculated uncertainties, the order of application of regression on temperature and regression on ionic strength has no effect on the calculated thermodynamic quantities
- The values proposed originally by Offerlé agree well with those calculated in the present review.

[95PAN/CAM]

The solubility of $\text{Np}_2\text{O}_5(\text{cr})$ was measured under carefully controlled conditions in an inert atmosphere for solutions with (measured) pH values between 6.54 and 12.61, with initial total ionic strengths of 0.1 and 0.02 M. The final total ionic strengths, after allowing for evaporation losses from the solution, were 0.10 to 0.21 $\text{mol}\cdot\text{kg}^{-1}$ and 0.023 to 0.055 $\text{mol}\cdot\text{kg}^{-1}$. The total solution concentrations of neptunium parallel those of Lierse *et al.* [85LIE/TRE] and Neck *et al.* [92NEC/KIM] for pH values between 6.5 and 8.5, but level out near $10^{-4.5}$ M at higher pH values. There is no indication of an increase in solubility at high pH attributed by others [92ITA/NAK, 92NEC/KIM] to formation of $\text{NpO}_2(\text{OH})_2^-$. Values of $\log_{10} {}^*\beta_1^\circ = -(8.4 \pm 0.3)$ and $\log_{10} {}^*K_{s,0}^\circ = (3.90 \pm 0.01)$ are recalculated from the experimental data. The comparatively large value of ${}^*\beta_1^\circ$ is also incompatible with a number of studies on carbonate complexation of $\text{Np}(\text{V})$ *e.g.* [83MAY, 85BID/TAN]. In the recalculations using the SIT, all anions in the solutions are treated as perchlorate. This is not correct, especially for the most basic solutions; however, because the ionic strengths of the solutions were low the calculated values of the constants (especially $\log_{10} {}^*K_{s,0}^\circ$) are not sensitive to this approximation.

The solid was carefully characterised before and after the experiments that lasted several months. Evidence was found that the crystalline solid gradually ripened, suggesting $\text{Np}_2\text{O}_5(\text{cr})$ is probably the stable solid under the experimental conditions (rather than amorphous $\text{NpO}_2\text{OH}(\text{am})$). This is also consistent with the solubility results for pH values below 8.

The solutions were prepared to constant ionic strength by addition of NaOH (0.1 m and 0.5 m [96PAN]) and HClO_4 . It is possible the stock sodium hydroxide solutions may have contained sufficient carbonate (as an impurity from the original NaOH(s)) to increase the neptunium concentrations for pH values above 8 (conversely, the fact that the solubilities are similar in the solutions of two different ionic strengths indicates this may not have been a problem). Otherwise, the study appears to have been done carefully, and although the results for pH values above 8 are not credited in the present review, it is possible they are correct. Radiolytic reactions may also need to be considered. Further experiments are necessary to confirm or refute this set of results.

The work described in this report was the basis of a later publication [98PAN/CAM].

[95PAS/KIM]

The paper reports on a spectroscopic (UV/VIS) study of the hydrolysis of $^{242}\text{Pu(VI)}$ at 22°C . The Pu(VI) was generated at low concentrations in solutions with pH values between 4.5 and 9.5 by dissolution of $\text{PuO}_2\text{CO}_3(\text{s})$ (that was converted gradually to $\text{PuO}_2(\text{OH})_2(\text{s})$ under the experimental conditions, however the length of time the solid was left in contact with the solution prior to the spectroscopic measurements was not stated), and the authors believed metastable polymeric hydrolysis species were not generated under these conditions. The β_1 values for 22°C apparently were calculated using 25°C values for the ion product for water, corrected for ionic strength, but not for the difference in temperature (the ion product of water at 22°C is approximately $10^{-14.10}$ [59ROB/STO]). The D parameter in the SIT is also temperature dependent ($D = 0.507$ at 22°C), and although changed correctly in an earlier paper [93PAS/KIM2], it is not clear that the minor change was made here. The correction of $\beta_{1,2}$ to $\beta_{1,2}^\circ$ also appears to have been done incorrectly. We calculate $\log_{10} K_{s,0} = -(21.3 \pm 0.1)$, $\log_{10} \beta_1 = (8.20 \pm 0.15)$, $\log_{10} \beta_2 = (14.45 \pm 0.18)$ and thus, $\log_{10} {}^*K_{s,0}^\circ = (6.3 \pm 0.1)$, $\log_{10} {}^*\beta_1^\circ = -(5.48 \pm 0.15)$ and $\log_{10} {}^*\beta_2^\circ = -(13.15 \pm 0.18)$ at 22°C .

[95VIT]

This report was originally prepared as a first draft of the Np(IV) carbonate section of the present review, but with more details, calculations, figures and tables. The solubility of Np(IV) in various bicarbonate and carbonate media was calculated and compared with the scattered published measurements [89MOR/PRA, 90PRA/MOR]. New experimental data on the Np(IV) and Np(VI) carbonate systems were made available here prior to final data treatment and publication [96DEL/VIT, 95OFF/CAP]. Spectra attributed to $\text{Np}(\text{CO}_3)_4^{4-}$ and $\text{Np}(\text{CO}_3)_5^{6-}$ were presented, and compared to most published spectra of Np(IV) in bicarbonate or carbonate media [71MOS2, 77SAI/UEN, 81WES/SUL, 84VAR/HOB, 93LI/KAT]. Speciation in different bicarbonate and carbonate media were calculated using various approximations, as were formation constants and values of $\Delta\varepsilon$. These numbers were used in the review of carbonato-neptunium chemistry.

[96ALL/VEI]

The paper reports structures of aqueous nitrate complexes.

[96CAP/VIT]

This is an article, based on some of the data reported in [92CAP], in which the implications of spectrophotometric measurements made on solutions of Pu(IV) and $\text{Na}(\text{Na}, \text{H})\text{CO}_3$ under various partial pressures of $\text{CO}_2(\text{g})$ are discussed. All potential sources of error are accounted for, and SIT calculations were done using interaction coefficients from the americium review [95SIL/BID]. The observations here, as in [92CAP], confirm that the limiting complexes at high ionic strength are $\text{Pu}(\text{CO}_3)_4^{4-}$ and $\text{Pu}(\text{CO}_3)_5^{6-}$ and that there is no simultaneous change in OH^- complexing. The

equilibrium constant for the stepwise addition of CO_3^{2-} to the penultimate complex is given as $\log_{10} K_5(3 \text{ M}) = (2.25 \pm 0.29)$ and $\log_{10} K_5^\circ = -(1.36 \pm 0.09)$ with $\Delta\varepsilon = -(0.11 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$. The $\log_{10} \beta_5(3 \text{ M})$ was found to be (35.8 ± 1.3) , but insufficient independent evidence is available to extrapolate this value to the standard state. The constants in this paper supersede constants reported in [92CAP].

[96CLA/CON]

This is mostly a review paper that was based primarily on experimental observations of the authors and a literature comparison that they published previously. Nevertheless, Clark *et al.* reported new results from their experimental study of the temperature influence on the $\text{NpO}_2\text{CO}_3^-$ and $\text{NpO}_2(\text{CO}_3)_2^{3-}$ formation constants. Values of β_1 and β_2 were measured in 0.1 M tetrabutylammonium nitrate aqueous solution by spectrophotometry, possibly using the same methods described by Neck *et al.* [94NEC/RUN]. (However, the spectrophotometric results of that publication were not particularly accurate and were not used in the final data assessment in the present review. See the discussions of [91KIM/KLE] and [94NEC/RUN] in this appendix). Clark *et al.* found that $\log_{10}\beta_1$ and $\log_{10}\beta_2$ increased by about 0.4 units from 30 to 70°C, while they estimated an uncertainty of ± 0.2 in the $\log_{10}\beta_1$ value. The influence of temperature was therefore not much greater than the experimental accuracy. Values of $\log_{10}\beta_1$, $\log_{10}\beta_2$ and $\log_{10}K_2$ ($K_2 = \beta_2/\beta_1$) were plotted as a function of $1/T$ and straight lines were found with slopes 829 ± 27 , 811 and 18 respectively, from which $\Delta H_1 = -(15.9 \pm 0.5)$, $\Delta H_2 = -(15.5 \pm 0.5)$ and thus $\Delta H_2 - \Delta H_1 = -(0.3 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$ respectively. These results were not accepted in the present review since the information needed to check them (*e.g.*, method of pH electrode calibration at temperature, values used for carbonate protonation constants at temperatures other than 25°C, spectral changes with temperature for the key species) was not reported in this publication [96CLA/CON]. An as yet unpublished later paper, cited in this reference [96CLA/CON] as “submitted”, may contain details that will allow later reviewers to make good use of these results.

[96CLA/CON2]

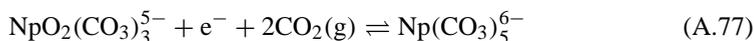
This is an interesting paper that proposes values for bond lengths in $\text{NpO}_2(\text{CO}_3)_i^{(1-2i)}$ aqueous complexes from EXAFS studies, assuming reasonable geometry of these species. Tetrabutylammonium cations instead of the more usual alkali metal cations, were used in the supporting electrolyte when fixing the aqueous speciation (a classical way to avoid precipitation of the Np(V) solids containing alkali metal cations). No information from this publication was used in assessments in the present review.

[96DEL/VIT]

a) Preparation of Np(IV) in carbonate media

Np(IV) was prepared in 0.3, 0.6, 1.0 and 1.5 M Na_2CO_3 aqueous solutions, by reduction of Np(V) at -1.6 V/SHE . During this process water was reduced, and probably

Np(III) was also formed since the Np(IV)/Np(III) reduction potential in 1.0 M Na₂CO₃ aqueous solutions is -1.32 V/SHE [79FED/PER]. It seems the main goal of this work was to understand this preparation. Varlashkin *et al.* [84VAR/HOB] had reported difficulty in reproducing results of Fedoseev, Peretrukhin and Krot [79FED/PER] (who also indicated they were unable to stabilise the redox potential of their Np(V)/Np(IV) mixture). Delmau, Vitorge and Capdevila obtained more stable potentials, and found that in the course of their electrochemical reduction Np(V), water reduction produced OH⁻. They attributed the difficulties of the previous authors to this pH increase and to poor buffering, which could result in a as much as a three order of magnitude change in the CO₂ partial pressure, p_{CO_2} . The work of Varlashkin *et al.* and Fedoseev, Peretrukhin and Krot as well as their own observations were interpreted in terms of the following equilibrium



This interpretation is also used in the present review.

b) Formal potential of the Np(V)/Np(IV) redox couple in carbonate media

Initially, for each solution, a stable potential was obtained after 1 to 3 days, and then the potential remained stable for the duration of the experiment (about one month). In one of the experiments, at 21.5°C, the potential varied by less than 15 mV over 25 days and by less than 10 mV for the 10 last days. The temperature was usually changed each day from 5 to 60°C and back to 5°C in 5°C steps. The reference electrode (with low junction potential obtained by using same ionic strength on both sides of the junction) varied by 10 mV in this temperature cycle, and their data, as reported, were corrected for this variation. Usually, the pH was measured only prior to electrolysis, which is not particularly useful because electrochemical reduction of water would increase the pH, while uptake of CO₂(g) from the air (especially when the solution was stirred during electrolysis) would decrease it. Only for the 1.0 M Na₂CO₃ aqueous solution was the pH measured after electrolysis. Hence, pH values given in this part are not reliable.

The molarities of Np(V) and Np(IV) were measured by spectrophotometry, but in some cases the values were not properly controlled. Hence the [Np(V)]/[Np(IV)] ratio values are not reliable. Nevertheless, these data are the best that are currently available, and from the measured redox potentials, the following possible formal potentials can be calculated:

$$\begin{aligned} E_0' &= E - 2 \times 0.05916 \times (-3.5) \\ E_1' &= E_0' - 0.05916 \log_{10}([\text{Np}(\text{V})]/[\text{Np}(\text{IV})]) \\ E_2' &= E - 2 \times 0.05916 \log_{10} p_{\text{CO}_2} \\ E_3' &= E_2' - 0.05916 \log_{10}([\text{Np}(\text{V})]/[\text{Np}(\text{IV})]) \end{aligned}$$

These values are calculated either by assuming equilibrium was maintained with the air (*i.e.*, $\log_{10} p_{\text{CO}_2} = -3.5$ for E_0' and E_1'), or calculating p_{CO_2} from pH measurements (for E_2' and E_3'), with or without correction for the ([Np(V)]/[Np(IV)]) ratio. See

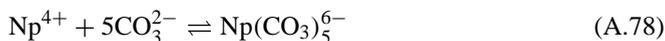
Table A.30: Formal potentials for the Np(V)/Np(IV) couple in Na₂CO₃(aq) solutions as calculated from values in [96DEL/VIT].

[Na ₂ CO ₃] (mol·dm ⁻³)	E'_0	E'_1	E'_2	E'_3
0.3	0.661	0.641	0.693	0.673
0.6	0.648	0.694	0.651	0.696
1.0	0.658	0.641	0.552	0.535 ^(a)
1.5	0.642	0.620	0.819	0.798
0	(0.538 ± 0.020)	(0.553 ± 0.058)	(0.480 ± 0.266)	(0.494 ± 0.268)
1.0 ^(b)	0.514 ^(b)			
$\Delta\varepsilon$ (A.77) (kg·mol ⁻¹)	(0.361 ± 0.176)	(0.535 ± 0.501) ^(a)	-(0.472 ± 2.296)	-(0.298 ± 2.317)
$\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_5^{6-})}$ (kg·mol ⁻¹)	-(0.173 ± 0.223)	(0.001 ± 0.519)	-(1.006 ± 2.301)	-(0.832 ± 2.321)

(a) used in this review

(b) [79FED/PER]

Table A.30. From these various possible formal potentials, the standard potential of the NpO₂⁺/Np⁴⁺ redox couple, the values corrected to the aqueous media for the formation constant of the Np(V) limiting complex, and the value of the $p\text{CO}_2/[\text{CO}_3^{2-}]$ equilibrium constant selected in this review, values of the formation constant of the Np(IV) limiting complex



$$\beta_{5(\text{IV})}(\text{A.78}) = \frac{[\text{Np}(\text{CO}_3)_5^{6-}]}{a_{\text{Np}^{4+}}[\text{CO}_3^{2-}]^5}$$

were calculated (where $a_{\text{Np}^{4+}}$ is in molal units, while the concentrations are in molar units). Extrapolation to zero ionic strength was done by linear regression.

The influence of the [Np(V)]/[Np(IV)] ratio is usually smaller than the uncertainty. As expected, using the measured pH values does not remove the scatter in the data, especially if the sole value measured following electrolysis is used along with values measured before electrolysis. For this reason, the only reliable ionic strength corrections are those calculated assuming equilibrium with the air. The standard potential is (88 ± 58) mV lower than the formal potential in 1.0 M Na₂CO₃, from which it is deduced (corresponding to (2.98 ± 1.02) in log₁₀ β_{5(IV)}). From the Δε value derived from this extrapolation to zero ionic strength, $\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_5^{6-})} = (0.00 \pm 0.52)\text{kg}\cdot\text{mol}^{-1}$ is calculated. Assuming equilibrium with the air, recalculation results in the value log₁₀ β_{5(IV)}(1.0 M Na₂CO₃, A.78) = 43.93, while 42.13 is calculated using the (only) solution for which the pH was measured at the end of the electrolysis. This last value is consistent with Fedoseev, Peretrukhin and Krot's value, 41.79, recal-

culated assuming equilibrium with the air (again no pH measurement was provided), from which $\log_{10} \beta_{5(\text{IV})}(1.0 \text{ M Na}_2\text{CO}_3, \text{A.78}) = (38.98 \pm 1.97)$ is calculated.

c) Temperature influence on the formal potential of the Np(V)/Np(IV) redox couple in carbonate media

The main source of uncertainty (lack of pH measurement) cancels in the study of the temperature dependence of the potential measured for a single solution. The potentials measured in each solution varied linearly as a function of temperature, and these changes were reproducible within less than 10 mV. From linear regression, the authors calculated temperature coefficient values of -2.058, -2.168 and -2.241 $\text{mV}\cdot\text{K}^{-1}$ for the 0.6, 1.0 and 1.5 M Na_2CO_3 aqueous solutions, respectively. If the heat capacity of reaction is assumed to be negligible, these temperature coefficients can be used to calculate $\Delta_r H(\text{A.77}) = -82.40, -85.86$ and $-89.91 \text{ kJ}\cdot\text{mol}^{-1}$ in 0.6, 1.0 and 1.5 M Na_2CO_3 aqueous solutions, respectively. From linear regression of $(\Delta_r H(\text{A.77}) - 11\Delta z^2 T^2 (\partial \Delta \varepsilon / \partial T) R \ln 10) \text{ vs. } m_{\text{Na}^+}$, the reviewer calculated $\Delta_r H(\text{A.77}) = -(84.39 \pm 4.38) \text{ kJ}\cdot\text{mol}^{-1}$ and $T^\circ (\partial \Delta \varepsilon / \partial T)(\text{A.77}) = -(0.50 \pm 0.34) \text{ kg}\cdot\text{mol}^{-1}$ (values of $(\partial D / \partial T)$ were calculated from the Debye Hückel A and B values given in Appendix B assuming no variation of a_j with T, and that $Ba_j = 1.5$ at 25°C). This value of $\Delta_r H(\text{A.77})$ is virtually the same as the mean of the three values for the different media, $-(85.06 \pm 4.63) \text{ kJ}\cdot\text{mol}^{-1}$.

d) Dissociation of the Np(IV) limiting complex in bicarbonate media

To study the dissociation of the Np(IV) carbonate limiting complex, Np(IV) was prepared as above by electrolysing 0.2, 0.3, 0.4, 0.5, 0.6 and 1.5 M Na_2CO_3 aqueous solutions of Np(V). Carbon dioxide gas, preequilibrated with NaCl solutions of the same ionic strength, was then bubbled through these carbonate solutions. During these titrations, pH was measured and spectra were recorded from 600 to 1100 nm. No spectral change was observed in the 1.5 M Na_2CO_3 solution from pH 12.64 to 10.34, although precipitation (attributed to $\text{NaHCO}_3(\text{s})$ formation) was observed. The authors interpreted their experimental observations, including molar absorbances at 823, 990 and 1013 nm, in terms of dissociation of the Np(IV) limiting carbonate complex according to the following equilibrium



involving the loss of only one CO_3^{2-} . Ionic strength varied during each titration as a result of the reaction



In their data analysis, Delmau, Vitorge and Capdevila used the data at the half dissociation point for the mean at the three wavelengths. Using the data given page 57 of the report [96DEL/VIT], $\log_{10} K_5^0(\text{A.79}) = -(1.071 \pm 0.136)$ and $\Delta \varepsilon = (0.377 \pm 0.184) \text{ kg}\cdot\text{mol}^{-1}$ are calculated. From

this $\Delta\varepsilon$ value, $\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_5^{6-})} = (0.00 \pm 0.52)\text{kg}\cdot\text{mol}^{-1}$ as calculated above, and $\varepsilon_{(\text{Na}^+, \text{CO}_3^{2-})} = -(0.08 \pm 0.03)\text{kg}\cdot\text{mol}^{-1}$ (Appendix B), the value $\varepsilon_{(\text{Na}^+, \text{Np}(\text{CO}_3)_4^{4-})} = -(0.30 \pm 0.55)\text{kg}\cdot\text{mol}^{-1}$ is calculated. In the present review the uncertainty in $\log_{10} K_5$ is increased to 0.3 because the pH calibration was only done after the measurements, and because of spectral baseline drift during the measurements.

[96FAN/NEC]

This paper came to the attention of the reviewer after the present review was essentially complete. The paper contains supplementary information on the calibration procedure used by these authors for their glass electrode, and aids interpretation of data published previously (*e.g.* [95NEC/RUN]). The authors said that using acidic and alkaline calibration solutions for a single electrode, they found a slope of 58.0 to 58.8 mV/ $\log_{10} a_{\text{H}^+}$ at 25°C media instead of the theoretical Nernstian slope (59.16 mV/ $\log_{10} a_{\text{H}^+}$ at 25°C). The problem might have been due response of the glass electrode to alkali metal ions, but this is usually important only at higher pH values than used in this work. The reported K_w results are in agreement with the thermodynamic data selected by this review and those cited in a previous paper from the same laboratory [94NEC/RUN]. The reported carbonic acid acidity constants are also in accord with previous determinations from the same laboratory [94NEC/RUN], and again deviate from published values at high ionic strength. The authors attributed the problem to the possible non-Nernstian slope of glass electrodes in previous work by others, and improper use of trace activity coefficients in different media. They empirically corrected for this type of systematic deviation in their [96FAN/NEC] work, and assumed that other authors should have used the same empirical procedure. Their empirical correction also includes effects from the variation of the liquid junction potential between their working solutions and the buffer solutions they use. Use of an experimental set-up designed to minimize the junction potentials in the working solutions, and evidence of more redundant calibration measurement checking would have been useful.

It is possible (but unlikely) such errors went undetected in most other laboratories experienced in using proper techniques. However the work indicates that minimally more checking should be done for the type of glass electrode used in this work [96FAN/NEC], and direct comparisons should be made with other glass electrodes, along with interlaboratory comparisons, paying particular attention to other details such as minimizing junction potentials. Many of such deviations should be quite small and certainly should cancel at low ionic strength. The results also indicate that more attention may need to be paid to interactions between ions of like charge.

[96KAT/KIM]

This paper describes the synthesis of $\text{NpO}_2\text{CO}_3(\text{s})$ and a hydrated Np(VI) oxide. The oxide was prepared by equilibrating a solution of Np(VI) in aqueous NaClO_4 (0.1 M) for a minimum of two weeks while purging the solution with ozone (in air). No ele-

mental analyses were reported for the solid (written by the authors as $\text{NpO}_3 \cdot \text{H}_2\text{O}(\text{s})$), which has an X-ray diffraction pattern that differs from those reported by Bagnall and Laidler [64BAG/LAI] for hydrated Np(VI) oxides. FT-IR photoacoustic spectroscopy did not show a sharp band near 3450 cm^{-1} , from which the authors concluded the solid was a hydrated oxide, not a true hydroxide. This also contrasts [75BEL/IL'] with the IR spectrum as described by Bagnall and Laidler for their $\text{NpO}_3 \cdot \text{H}_2\text{O}(\text{s})$, and that reported by Chaikhorskii, Matuzenko and Leikina [75CHA/MAT] for $\text{NpO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$. Furthermore, the synthesis procedure was similar to that reported [75CHA/MAT] to yield an amorphous tetrahydrate.

The pH measurements were done using electrodes calibrated against standard buffers (not concentration standards), and hydrolysis species were not included in the data analysis, although the authors indicated there was some spectroscopic evidence of a small amount of hydrolysis. Reanalysis using $\log_{10} \beta_{1,1} = -5.28$, $\log_{10} \beta_{2,2} = -6.48$, and $\log_{10} \beta_{5,3} = -17.76$ (as calculated for a 0.1 M NaClO_4 medium using parameters from the present review), results in a value of $\log_{10} K_{s,0}^\circ = 5.47$ ($\log_{10} K_{s,0}^\circ = -22.53$). However, when this analysis is done, the calculated solubilities at lower pH values are generally greater than the experimental values (by as much as a factor of 1.4), and the calculated solubilities at higher pH tend to be lower than those measured. Only adjusting the first hydrolysis constant to unrealistically large values improved the fit. This suggests a problem with the selected hydrolysis constants (or more likely, their ionic strength dependence) or minor experimental problems. Therefore, an increased uncertainty of ± 0.4 is assigned in this review to the recalculated value of $\log_{10} K_{s,0}$.

The solubility measurements for the carbonates $\text{NpO}_2\text{CO}_3(\text{s})$ and $\text{UO}_2\text{CO}_3(\text{s})$ were made in 0.1 M NaClO_4 aqueous solution, but it is not clear from the described procedures that constant ionic strength was maintained. The text states (perhaps in error) that values of the carbonic acid deprotonation constants from pH measurements taken at $I = 1 \text{ M}$ were used, whereas values for 0.1 M should have been used.

The solubility product of $\text{UO}_2\text{CO}_3(\text{s})$ proposed by the authors from solubility measurements in 0.1 M HClO_4 , $-(14.10 \pm 0.14)$, does not agree well with the value $-(13.66 \pm 0.04)$ calculated from the standard solubility product selected in the thorough TDB review [92GRE/FUG, 95GRE/PUJ]. However, values for the solubility product as measured in 0.1 M NaClO_4 aqueous solution, and published since the review was carried out (approximately 1990), have not been particularly consistent, ranging from -13.29 to -14.18 [96KAT/KIM].

If the difference between the experimentally measured value [96KAT/KIM] and the TDB value for the solubility product of the uranium compound, 0.44, is assumed to apply equally to the $\text{NpO}_2\text{CO}_3(\text{s})$ solubility product (i.e., assuming the difference can be attributed to problems in the calibration of the glass electrode and/or the procedure to calculate $[\text{CO}_3^{2-}]$ from pH measurements), a value of $-(14.18 \pm 0.56)$ is estimated for the solubility product of $\text{NpO}_2\text{CO}_3(\text{s})$ in the present review based on the results of this study [96KAT/KIM]. The estimated uncertainty is increased by the same amount as the "correction" applied to the solubility product.

The authors drew conclusions concerning the relative values of the solubility products for $\text{MO}_2\text{CO}_3(\text{s})$ ($M = \text{U}, \text{Np}, \text{Pu}$), but any apparent variation within the

actinide series is probably within the current uncertainties (also, *cf.* Section 21.1.2.2.1).

[96LEM/CAM]

This paper is a continuation of an earlier study [93LEM/CAM], and presents a rather sparse set of results for the apparent molar heat capacities and volumes of NpO_2ClO_4 in mixed electrolyte solutions (with HClO_4) from 18 to 100°C. The values are quite scattered, but uncertainties at each temperature probably do not exceed $\pm 25 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. The ionic strength dependence is not well defined because the maximum ionic strength for the measurements was 0.22 m. It is unfortunate no oxidation state analyses were carried out on the (presumed) neptunium(V) solutions. Nevertheless, the apparent molar heat capacity values are reasonable and, even with the large uncertainties, could be used with reliable 25°C Gibbs energy and entropy of reaction values to calculate tenable equilibrium constants for temperatures to 200 or 300°C. Use is made of results for $\text{UO}_2(\text{ClO}_4)_2$ ([89HOV/NGU] and this paper) to estimate the temperature dependence of the dioxoactinide(VI/V) couples.

[96MOR/KIM]

This describes an absorption spectroscopic study of phosphate complexation of Np(V) carried out at $(22 \pm 2)^\circ\text{C}$ for an aqueous 0.1 M NaClO_4 medium with a range in pH values from 6.4 to 10.04. The absorption spectra in the interval 980-1010 nm at constant total phosphate and Np(V) , but varying pH, have been interpreted as resulting from formation of the species $\text{NpO}_2\text{HPO}_4^-$ and $\text{NpO}_2\text{PO}_4^{2-}$:



with corresponding constants:

$$\log_{10} \beta(\text{A.80}, 0.1 \text{ M NaClO}_4, 295 \text{ K}) = (2.54 \pm 0.02)$$

$$\log_{10} \beta(\text{A.81}, 0.1 \text{ M NaClO}_4, 295 \text{ K}) = (6.33 \pm 0.08)$$

The authors obtained practically unit slopes by plotting $\log_{10}([\text{NpO}_2\text{H}_m\text{PO}_4^{m-2}]/[\text{NpO}_2^+])$ vs. $\log_{10}[\text{H}_m\text{PO}_4^{m-3}]$, presenting this as confirmation of the chemical model adopted. There is general agreement about the formation of the species $\text{NpO}_2\text{HPO}_4^-$ in Np(V) phosphate systems, hence the value reported in this work has been used further in the selection of a value for the formation constant. Extrapolation of this value to $I = 0$ with the SIT equations and interaction coefficients from Appendix B ($\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = 0.25$ (Table B.3), $\varepsilon_{(\text{Na}^+, \text{HPO}_4^{2-})} = -0.30$ (Table B.5)) results in:

$$\log_{10} \beta^\circ(\text{A.80}, I = 0, 298.15 \text{ K}) = (2.98 \pm 0.1)$$

where the increased uncertainty allows for the fact that the measurements were carried out at a temperature slightly less than 25°C. There is not the same agreement among

different studies as to the species formed at higher pH in Np(V) phosphate systems (see Section 11.2.3). For these reasons the value of the $\text{NpO}_2\text{PO}_4^{2-}$ formation constant has not been considered further.

If the $\text{NpO}_2\text{PO}_4^{2-}$ species proposed in [96MOR/KIM] is accepted, then the agreement between the values calculated for the $\text{NpO}_2\text{HPO}_4^-$ formation constant from the various different studies becomes much worse. Furthermore, the $\text{NpO}_2\text{PO}_4^{2-}$ species proposed in [96MOR/KIM] should then have been the predominant species in at least two titrations reported in [85INO/TOC2]. However, the pH dependence of their data shows only the existence of H_2PO_4^- and HPO_4^{2-} complexes.

[96NIT/SIL]

This paper, primarily a description of a spectroscopic study of acetate and carbonate complexation of Pu(IV), also included results of a measurement of the first hydrolysis constant, done using ^{242}Pu (1.3×10^{-4} M). The authors reported $^*K_1 = (0.267 \pm 0.0021)$, *i.e.*, $\log_{10}^*K_1 = -(1.57 \pm 0.04)$, in 0.5 M perchlorate at $(22 \pm 2)^\circ\text{C}$. The measured “pH” values were traceable to HClO_4 concentration standards.

The original molar acid concentrations and integrated absorbances were made available to the reviewers [97NIT/SIL], and are as follows:

0.032 M	477.758	0.063 M	540.208	0.182 M	590.692
0.043 M	511.692	0.100 M	559.765	0.500 M	611.394

Recalculation indicated strong correlation between the values of the integrated molar absorbance of PuOH^{3+} and the hydrolysis constant as determined from fitting the appropriate function to the data. The values recalculated in the present review are (623 ± 6) and (170 ± 145) for the integrated molar absorbances of Pu^{4+} and PuOH^{3+} , respectively, and $^*K_1 = -(0.0145 \pm 0.0070)$. On conversion to a molal constant, the recalculated value, $\log_{10}^*K_1 = -(1.83 \pm 0.20)$ was used with the results from other experimental studies to determine the accepted value for the first hydrolysis constant for Pu^{4+} at $I = 0$.

[96ROB/SIL]

This paper was received after the main portion of the review section on the solubility of $\text{NpO}_2\text{OH}(\text{am})$ had been prepared. The study reports a solubility product of $\log_{10}^*K_{s,0}^\circ = (5.21 \pm 0.12)$ from experiments in chloride media at 21°C , and appears to deal with at least some of the same measurements reported by Novak and Roberts [95NOV/ROB]. Although the solid contacted the solutions for 37 days, the calculated solubility product is similar to that for the “freshly precipitated” solid of Neck, Kim and Kanellakopoulos [92NEC/KIM] (perchlorate media) rather than their “aged” solid. The value $\varepsilon_{(\text{NpO}_2^+, \text{Cl}^-)} = (0.08 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ derived by the authors is also reasonable.

[96RUN/NEU]

This paper reported new Np(V)-CO₃ solubility product and complexation constants for 0.1 and 3 M NaCl aqueous solutions. These again appear to be good values from well-designed experiments. Because of difficulties in deriving a consistent set of SIT interaction coefficients from the data obtained using aqueous NaCl solutions (Section 12.1.2.1.3.d), and the possible effects of formation of weak chloride complexation (such interactions are treated in the present review as activity coefficient effects), this review has only tabulated the stepwise carbonate complexing constants, and did not use them directly in determining selected ε values. Runde, Neu and Clark proposed some new Pitzer parameters to calculate the mean activity coefficients, γ_{\pm} , of Np(V) species with ClO₄⁻, Cl⁻ or Na⁺ counterions. These are compared to an earlier [95NEC/RUN, 95NOV/ROB] sets of parameters (based on fewer results in chloride media). The numerical values proposed [96RUN/NEU] to calculate γ_{\pm} for NpO₂ClO₄ and NpO₂Cl are slightly different from the set of values determined earlier [95NEC/FAN], and in the present review the SIT coefficients $\varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.20 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ and $(0.18 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ have been calculated from the Pitzer parameters of these two publications [95NEC/FAN, 96RUN/NEU]. These values are in reasonable agreement with the value $(0.25 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ recommended in the present review (see the discussion of [94NEC/RUN] in this appendix). This procedure was tested previously ([95OFF/CAP], pages 27-38) for 1-1 electrolytes, and during the present review for the Pitzer parameters tabulated in this paper [96RUN/NEU]. As was the case for previous work [95NEC/FAN], the problem is not in the use of the Pitzer equation (the parameters could be readily converted into the corresponding SIT ε coefficients), but in finding a completely self-consistent approach to handling the complexation and hydrolysis data from perchlorate and chloride media.

Use of the Pitzer equations can provide a better fit to the experimental results, but there are a fair number of highly correlated coefficients to be derived from the experimental data. Thus, the physical significance of the Pitzer coefficients (and SIT ε values derived from these) may be lost.

[97NEC/FAN]

This paper was published after the main part of the present review was completed. It reports the same type of study done earlier by Riglet [90RIG], with the same interpretation for the stoichiometries of mixed carbonato-hydroxo complexes from dissociation of the limiting carbonate complex of Np(V) in alkaline media



Neck, Fanghänel and Kim clearly indicate in their discussion only one new complex could be identified, however they provide formation constants for three new complexes, NpO₂OH(CO₃)₂⁴⁻, NpO₂(OH)₂CO₃³⁻ and NpO₂OHCO₃²⁻. The formation constant for NpO₂OHCO₃²⁻ was an estimate, there being no direct experimental evidence for its formation. Neck, Fanghänel and Kim also showed a graphical slope analysis of the

stoichiometry of the reactions from which (Figure 4 of [97NEC/FAN]) it is clear the complex $\text{NpO}_2\text{OH}(\text{CO}_3)_2^{4-}$ was formed.

The qualitative experimental observations suggest difficulties in the treatment of the data, and indicate uncertainties were probably greater than estimated by the authors. Procedures for determination of $[\text{OH}^-]$ were not explained. Reanalysis was limited to those data presented in Figure 3 of Neck, Fanghänel and Kim. These corresponded to values from similar experiments previously performed by Riglet [90RIG]. However, slope analysis performed in [97NEC/FAN] used data at two characteristic wavelengths. Results are similar to those reported at the Migration'91 Conference and later discussed by Vitorge and Capdevila [98VIT/CAP]. These authors used data for only one wavelength in their analysis of the data. It is not clear which method is more accurate because using the data from the second wavelength also requires estimation of a additional molar absorptivity value. The values reported by Neck, Fanghänel and Kim for the mixed hydroxocarbonato complexes of Np(V) are not selected because they were not available in time for a full quantitative reanalysis, but their data are important, and have been used in the discussion in Section 12.1.2.1.3.d of the present review.

[97PAS/CZE]

In this paper the stability of $\text{PuO}_2(\text{CO}_3)_n^{2-2n}$ complexes was evaluated based on the observed solubility of $\text{PuO}_2\text{CO}_3(\text{s})$ in 0.1 M NaClO_4 at $(22 \pm 2)^\circ\text{C}$ [93PAS/RUN]. The results of these experiments and the reported stability constants are not inconsistent with earlier experiments discussed in Section 21.1.2.1.1. However, this paper uses a different solubility constant for $\text{PuO}_2\text{CO}_3(\text{s})$ than is recommended in this review, uses the Pitzer procedure for extrapolation to zero ionic strength, and uses virial constants determined from the analogous U system at the basis for this extrapolation. Readers are advised to use caution in using the results of [97PAS/CZE] in conjunction with the constants determined in the present review unless corrections are made for the discrepancies in the assumptions and extrapolation procedure. These results will be evaluated in a future volume of this series.

[98VIT/CAP]

This report was prepared as a draft of the Np(V) and Np(VI) carbonate sections of the present review, with more details, calculations, figures and tables, and included a section with supplementary experimental data on the solubility of $\text{NpO}_2\text{CO}_3(\text{cr})$.

The main problem with this work, as pointed out by the authors, is that it was not always possible to reach equilibrium. The authors took this problem into account in the interpretation of their data and uncertainty estimation, and the formation constants determined in this work [98VIT/CAP] are accepted in the present review. When the concentration of CO_3^{2-} exceeded $10 \mu\text{M}$, a slow transformation of the solid phase occurred, possibly to $\text{Na}_4\text{NpO}_2(\text{CO}_3)_3(\text{s})$. The solubility product of this solid was estimated. Most values of equilibrium constants for reactions involving actinide(VI) species (An = U, Np, Pu), show small monotonous shifts over this partial actinide series.

The equilibrium constants extracted from the Np(VI) solubility work are consistent with those for the corresponding U and Pu complexes. Regular trends are observed in speciation predicted by using these values (Figure VI.3 in [98VIT/CAP]). The calculations confirm that the trinuclear carbonate species is most stable for uranium [92GRE/FUG] (the formation constants vary according to $U > Np > Pu$), and the trimeric species was observed only in supersaturated solutions for plutonium and even for neptunium. As a consequence, the trinuclear species of Np(VI) or Pu(VI) are calculated to be stable only in oversaturated conditions (even though they were observed experimentally).

Some of the numbers given in this report are different from those finally selected in the present review, typically the result of (small) errors in the molal to molar conversion formula for Np(V), which changes values for Np(IV) and Np(VI) (through the thermodynamic cycles). Nevertheless these changes are usually within the uncertainties.

Supplementary materials related to Np(V) complexation with carbonate include the material as presented at the Migration'91 Conference, solubility and X-ray diffraction spectra used in [84VIT, 85CÔM, 85KIM, 86GRE/ROB, 90RIG] tabulated with more details and figures for sensitivity analysis, and comparison of the X-ray spectra with published spectra. There are original experimental data on a spectrophotometric study of the formation of a mixed hydroxide-carbonato complex (with a tentative interpretation). The report also lists experimental data taken (or scanned) from the publications reviewed in this appendix, with graphical comparison of measurements and their calculated values as reinterpreted, linear extrapolations to $I = 0$ (as in Appendix B of the present review) and graphical comparison of all published solubility results. The same type of information is also provided for Np(VI).

[99RAI/HES]

This paper was received after the review was essentially complete. Rai *et al.* measured Np(IV) solubility in aqueous solutions by equilibration of NpO₂(am) in sealed tubes. In their quantitative interpretation, the authors selected samples with concentration ranges of (a) 1.78 m K₂CO₃ + (0.0123 to 1.514) m KOH (series 1); (b) 6.3 10⁻⁴ to 2.34 m K₂CO₃ + 0.01 M KOH (series 2); and (c) 0.0123 to 0.537m KHCO₃ (series 3). Solutions 0.001 or 0.05 M in Na₂S₂O₄ were used to maintain neptunium in the +4 oxidation state for up to 8 days; after this period Np(V) was detected in some of the samples. The authors selected samples equilibrated for 3 days (series 1, undersaturation), 7 or 8 days (series 2, oversaturation) or 8 days (series 3, undersaturation). Samples obtained with other procedures were rejected because of possible Np(IV) oxidation. This also confirmed the scattered solubility measurements of Prapoto *et al.* [89MOR/PRA, 90PRA/MOR] should be rejected for the same reason.

The authors interpreted the solubility results in 1.78 m K₂CO₃ (series 1) in terms of the equilibrium



Figure 1C of [99RAI/HES] shows a slope -4 for a plot of $\log_{10}m_{\text{Np}}$ vs. $\log_{10}m_{\text{KOH}}$ for data of series 1 where the ionic strength was approximately constant ($I = 5.44 \pm$

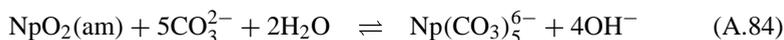
0.12) mol·kg⁻¹). For the series 2 solutions the solubilities calculated by Rai *et al.* fit the experimental results for $m_{\text{K}_2\text{CO}_3} > 1$ m, but at lower concentrations the calculated solubilities were too low. This was interpreted in terms of the formation of a new complex, $\text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$, from dissociation of $\text{Np}(\text{CO}_3)_5^{6-}$ as the carbonate concentration was decreased.

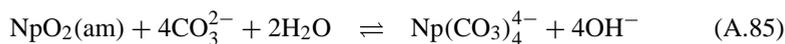
Inclusion of this new complex in their models did not markedly improve the fit to the series 2 experimental data. Rai *et al.* interpreted solubility at variable KHCO_3 concentration (series 3), in terms of the same species. The calculated solubilities are higher than, and not parallel to, the experimental results. It is not possible to determine whether the observed differences between calculated and observed solubilities result from the assumptions made in the data analysis as to what species were present, or if the differences are the result of ionic strength effects.

The interpretation used in this review (Figure A.8) is based on the same number of complexes as in the original paper, but the relative stability of the complex $\text{Np}(\text{CO}_3)_4^{4-}$, was deduced from independent spectrophotometric data (Section 12.1.2.1.4.b). The interpretation used in this review then involved calculation of one equilibrium constant, while Rai *et al.* fitted two equilibrium constants. However, the equilibrium constant and activity coefficients for the highly charged limiting complex are highly correlated. This review determined one ϵ coefficient from the data, whereas Rai *et al.* did not determine any ion pair interaction parameters from the neptunium solubility data. Instead, they used a simplified Pitzer formula to calculate the activity coefficient of the pentacarbonato complexes using parameters determined previously from work on similar systems. Thus, they interpreted similar solubility experimental data for several actinide(IV) systems using the same values for the Pitzer parameters and stoichiometric coefficients [87RYA/RAI, 95RAI/FEL, 97FEL/RAI, 98RAI/FEL, 99RAI/HES, 99RAI/HES2]. Although the model adopted in this review is simpler for standard conditions, it is not clear which model is simpler for reproducing the experimental data (some of which were measured at high ionic strength). The complex $\text{Np}(\text{CO}_3)_2(\text{OH})_2^{2-}$ proposed by Rai *et al.*, or other carbonate or mixed hydroxocarbonate Np(IV) complexes not selected in this review may very well be stable. However, it is not possible to obtain more than two reliable fitted parameters from the experimental solubilities. Consequently the formation constant value selected in this review for $\text{Np}(\text{CO}_3)_4^{4-}$ may be overestimated. Despite this difficulty in interpretation, the value is certainly within the estimated uncertainties.

In the present review data from other sources have been analysed in terms of the species $\text{Np}(\text{CO}_3)_5^{6-}$ and $\text{Np}(\text{CO}_3)_4^{4-}$, and the solubility values obtained by scanning Figures 1, 2 and 3 from a copy of [99RAI/HES] (a copy of the version accepted for publication was supplied by the authors) were re-analysed in the same manner.

The value selected for K_5° (12.25) in the present review was fixed for the sake of consistency and to avoid invoking too many fitting constants. The re-analysis using data from all three series results in $\log_{10} K_{s,4}^\circ$ (A.85) = $-(17.79 \pm 0.22)$ and $\Delta\epsilon$ (A.84) = $-(0.45 \pm 0.25)$ kg·mol⁻¹

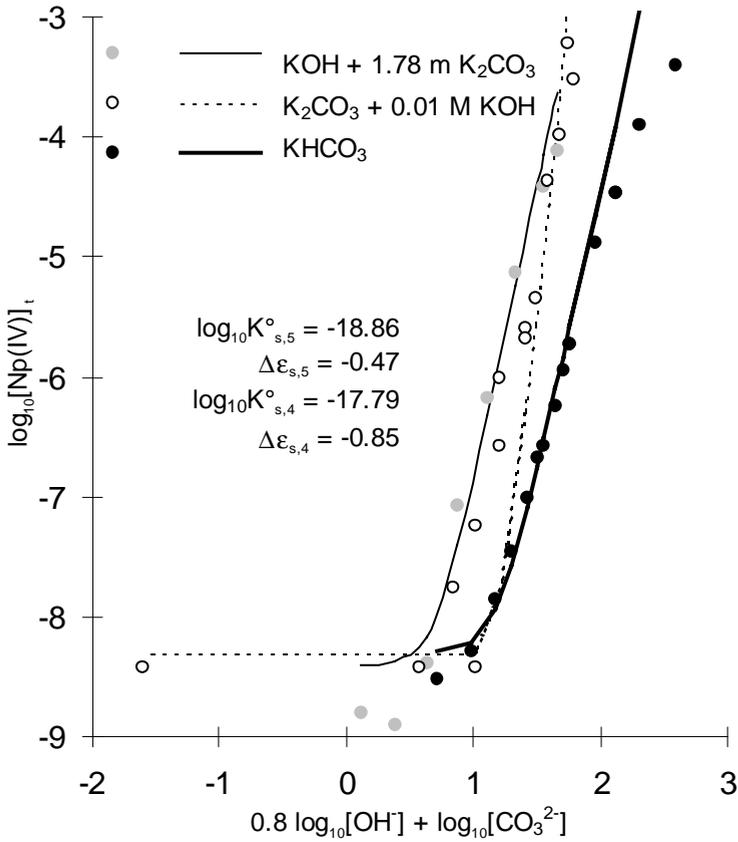




From this last value and the very rough approximation $\Delta\varepsilon(12.25) = (0.38 \pm 0.18) \text{ kg}\cdot\text{mol}^{-1}$ (assuming the same value for $\Delta\varepsilon(12.25)$ in aqueous Na^+ and K^+ media), $\Delta\varepsilon(\text{A.85}) = -(0.83 \pm 0.31) \text{ kg}\cdot\text{mol}^{-1}$ was calculated. From $\log_{10} K_{s,4}^\circ(\text{A.85}) = -(17.79 \pm 0.22)$ and $\log_{10} K_5^\circ(12.25) = -(1.07 \pm 0.30)$ the value $\log_{10} K_{s,5}^\circ(\text{A.84}) = -(18.86 \pm 0.37)$ is calculated. From these values, $\log_{10} K_{s,0} = -(54.48 \pm 1.00)$, essentially the same value as was used in Section 8.2.5.2, and also used in [99RAI/HES], $\varepsilon_{(\text{CO}_3^{2-}, \text{K}^+)} = (0.02 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ and $\varepsilon_{(\text{OH}^-, \text{K}^+)} = (0.09 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$, the values $\log_{10} \beta_5^\circ(12.23) = (35.62 \pm 1.07)$, $\log_{10} \beta_4^\circ(12.27) = (36.69 \pm 1.03)$, and $\varepsilon_{(\text{Np}(\text{CO}_3)_5^{6-}, \text{K}^+)} = -(0.73 \pm 0.68) \text{ kg}\cdot\text{mol}^{-1}$ are also calculated. These recalculated values of β_5° and $K_{s,5}^\circ$ are more than two orders of magnitude greater than the values from the analysis in [99RAI/HES]; the differences probably result, at least in part, from the different assumptions used for extrapolation to $I = 0$.

The authors concluded from X-ray absorption spectroscopic data that $\text{Np}(\text{CO}_3)_5^{6-}$ is the major solution species when $\text{NpO}_2(\text{am})$ is equilibrated with 0.93 m KHCO_3 or 5.4 m K_2CO_3 aqueous solutions. This is consistent with the stoichiometry for the limiting complex assumed in the present review. However, according to the thermodynamic data used by the authors, less than 1 % of the limiting complex was dissociated in the 0.93 m KHCO_3 sample, while $(45 \pm 26)\%$ dissociation is calculated using the spectrophotometric data accepted in the present review. The reason for this discrepancy is not known.

Figure A.8: Comparison of experimental data from [99RAI/HES] with values calculated from the model used in the present review to interpret their data ($[\text{Np(IV)}]$, $[\text{OH}^-]$, $[\text{CO}_3^{2-}]$ are molalities).



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 2.3.1. According to this definition, the standard state for a solute B in a solution is a hypothetical solution, at the standard state pressure, in which $m_B = m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$, and in which the activity coefficient 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 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 [73PIT] 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 the equilibrium reactions. Earlier, this approach has been used extensively in marine chemistry, *cf.* Refs. [79JOH/PYT, 79MIL, 79PYT, 79WHI2].

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

[†]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. The main differences between this Appendix and the one in Grenthe *et al.* [92GRE/FUG] are: Table B.1, Eq. (B.11), Example B.3 and Sections B.1.2 and B.1.4. The contents of Tables B.3 and B.4 have also been revised.

interaction methods or the Davies equation [62DAV]. However, the Davies equation should in general not be used at ionic strengths larger than $0.1 \text{ mol} \cdot \text{kg}^{-1}$. The method preferred in the NEA Thermochemical Data Base review is a medium-dependent expression for the activity coefficients, which is the specific ion interaction theory in the form of the Brønsted-Guggenheim-Scatchard approach. Other forms of specific ion interaction methods (the Pitzer and Brewer “B-method” [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 may be extensively hydrolysed, one cannot perform experiments at low ionic strengths. Hence, it is impossible to estimate the extrapolation error. This is true for all methods used to estimate activity corrections. Systematic model errors of this type are not included in the uncertainties assigned to the selected data in this review.

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 $1 \text{ kJ} \cdot \text{mol}^{-1}$ in derived $\Delta_f G_m^\circ$ 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 [22BRØ2, 22BRØ], 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).

$$\log_{10} \gamma_j = -z_j^2 D + \sum_k \varepsilon_{(j,k,I_m)} m_k \quad (\text{B.1})$$

D is the Debye-Hückel term:

$$D = \frac{A\sqrt{I_m}}{1 + Ba_j\sqrt{I_m}} \quad (\text{B.2})$$

where I_m is the molal ionic strength:

$$I_m = \frac{1}{2} \sum_i m_i z_i^2$$

A and B are constants which are temperature and pressure dependent, and a_j is an ion size parameter (“distance of closest approach”) for the hydrated ion j . The Debye-Hückel limiting slope, A , has a value of $(0.509 \pm 0.001) \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ 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 $Ba_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ 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 $I_m = 0.5 \text{ m}$ and $I_m = 3.5 \text{ m}$. 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 $Ba_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$.

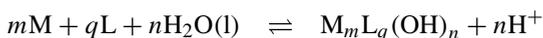
The summation in Eq. (B.1) extends over all ions k present in solution. Their molality is denoted m_k , and the specific ion interaction parameters, $\varepsilon_{(j,k,I_m)}$, in general depend only slightly on the ionic strength. The concentrations of the ions of the ionic medium is often very much 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 few data of this type are currently available.

The way in which the activity coefficient corrections are performed in this review according to the specific ion interaction theory is illustrated below for a general case of a complex formation reaction. Charges are omitted for brevity.



The formation constant of $M_mL_q(OH)_n$, ${}^*\beta_{q,n,m}$, determined in an ionic medium (1:1 salt NX) of the ionic strength I_m , is related to the corresponding value at zero ionic strength, ${}^*\beta_{q,n,m}^\circ$, by Eq. (B.3).

$$\log_{10} {}^*\beta_{q,n,m} = \log_{10} {}^*\beta_{q,n,m}^\circ + m \log_{10} \gamma_M + q \log_{10} \gamma_L + n \log_{10} a_{H_2O} - \log_{10} \gamma_{q,n,m} - n \log_{10} \gamma_{H^+} \quad (B.3)$$

The subscript (q,n,m) denotes the complex ion $M_mL_q(OH)_n$. If the concentrations of N and X are much greater than the concentrations of M, L, $M_mL_q(OH)_n$ and H^+ , only the molalities m_N and m_X have to be taken into account for the calculation of the term $\sum_k \varepsilon_{(j,k,I_m)} m_k$ in Eq. (B.1). For example, for the activity coefficient of the metal cation M, γ_M , Eq. (B.4) is obtained at 25°C and 1 bar.

$$\log_{10} \gamma_M = \frac{-z_M^2 0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} + \varepsilon_{(M,X,I_m)} m_X \quad (B.4)$$

Under these conditions, $I_m \approx m_X = m_N$. Substituting the $\log_{10} \gamma_j$ values in Eq. (B.3) with the corresponding forms of Eq. (B.4) and rearranging leads to

$$\log_{10}^* \beta_{q,n,m} - \Delta z^2 D - n \log_{10} a_{H_2O} = \log_{10}^* \beta_{q,n,m}^\circ - \Delta \varepsilon I_m \quad (\text{B.5})$$

where, at 25°C and 1 bar:

$$\Delta z^2 = (mz_M - qz_L - n)^2 + n - mz_M^2 - qz_L^2 \quad (\text{B.6})$$

$$D = \frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \quad (\text{B.7})$$

$$\Delta \varepsilon = \varepsilon_{(q,n,m,N \text{ or } X)} + n\varepsilon_{(H,X)} - q\varepsilon_{(N,L)} - m\varepsilon_{(M,X)} \quad (\text{B.8})$$

Here $(mz_M - qz_L - n)$, z_M and z_L are the charges of the complex $M_mL_q(OH)_n$, the metal ion M and the ligand L, respectively.

Equilibria involving $H_2O(l)$ as a reactant or product require a correction for the activity of water, a_{H_2O} . The activity of water in an electrolyte mixture can be calculated as

$$\log_{10} a_{H_2O} = \frac{-\phi \sum_k m_k}{\ln(10) \times 55.51} \quad (\text{B.9})$$

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 $I_m \approx m_{NX}$, Eq. (B.9) becomes

$$\log_{10} a_{H_2O} = \frac{-2m_{NX}\phi}{\ln(10) \times 55.51} \quad (\text{B.10})$$

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 $N_{\nu_+}X_{\nu_-}$ of a concentration much larger than those of the reacting ions, the osmotic coefficient can be calculated according to Eq. (B.11) (*cf.* Eqs. (23-39), (23-40) and (A4-2) in [61LEW/RAN]).

$$1 - \phi = \frac{A \ln(10) |z_+ z_-|}{I_m (Ba_j)^3} \left[1 + Ba_j \sqrt{I_m} - 2 \log_{10} (1 + Ba_j \sqrt{I_m}) - \frac{1}{1 + Ba_j \sqrt{I_m}} \right] - \ln(10) \varepsilon_{(N,X)} m_{NX} \left(\frac{\nu_+ \nu_-}{\nu_+ + \nu_-} \right) \quad (\text{B.11})$$

where ν_+ and ν_- are the number of cations and anions in the salt formula ($\nu_+ z_+ = \nu_- z_-$), and in this case

$$I_m = \frac{1}{2} |z_+ z_-| m_{NX} (\nu_+ + \nu_-)$$

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 may be necessary to use Pitzer's equation to calculate the activity of water. On the other hand, $a_{\text{H}_2\text{O}}$ is near constant in most experimental studies of equilibria in dilute aqueous solutions, where an ionic medium is used in large excess with respect to the reactants. The medium electrolyte thus determines the osmotic coefficient of the solvent.

In natural waters the situation is similar; the ionic strength of most surface waters is so low that the activity of $\text{H}_2\text{O}(\text{l})$ can be set equal to unity. A correction may be necessary in the case of seawater, where a sufficiently good approximation for the osmotic coefficient may be obtained by considering NaCl as the dominant electrolyte.

In more complex solutions of high ionic strengths with more than one electrolyte at significant concentrations, *e.g.*, $(\text{Na}^+, \text{Mg}^{2+}, \text{Ca}^{2+})(\text{Cl}^-, \text{SO}_4^{2-})$, Pitzer's equation (*cf.* [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 $\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2} \text{H}_2(\text{g})$ is necessary (*cf.* Example B.3).

B.1.2 Ionic strength corrections at temperatures other than 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 $t \geq 100^\circ\text{C}$. 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/KIR, 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 $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ 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 $1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$. 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 $t \leq 100^\circ\text{C}$ and $I < 6 \text{ m}$, and less than ± 0.006 at $t \leq 50^\circ\text{C}$ and $I \leq 4 \text{ m}$).

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 $t \geq 100^\circ\text{C}$. 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 $(\text{kg} \cdot \text{mol}^{-1})^{\frac{1}{2}}$	$B \times 10^{-10}$ $(\text{kg}^{\frac{1}{2}} \cdot \text{mol}^{-\frac{1}{2}} \cdot \text{m}^{-1})$
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: $a_j(T) = a_j(298.15 \text{ K}, 1 \text{ bar}) + |z_j|g(T, p)$ [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 $Ba_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ 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 [97GRE/PLY]. The absolute values for the reported ion interaction parameters differ in these studies due to the fact that the Debye-Hückel term used by these authors is not exactly the same. Nevertheless, common to all these studies is the fact that values

of $(\partial\varepsilon/\partial T)_p$ are usually $\leq 0.005 \text{ kg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ for temperatures below 200°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 $t \neq 25^\circ$, studies on the variation of $\varepsilon_{(j,k,I_m)}$ -values with temperature should be undertaken.

B.1.3 Estimation of ion interaction coefficients

B.1.3.1 Estimation from mean activity coefficient data

Example B.1:

The ion interaction coefficient $\varepsilon_{(\text{H}^+, \text{Cl}^-)}$ can be obtained from published values of $\gamma_{\pm, \text{HCl}}$ vs. m_{HCl} .

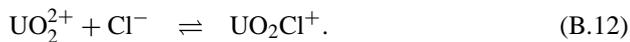
$$\begin{aligned} 2 \log_{10} \gamma_{\pm, \text{HCl}} &= \log_{10} \gamma_{\text{H}^+} + \log_{10} \gamma_{\text{Cl}^-} \\ &= -D + \varepsilon_{(\text{H}^+, \text{Cl}^-)} m_{\text{Cl}^-} - D + \varepsilon_{(\text{Cl}^-, \text{H}^+)} m_{\text{H}^+} \\ \log_{10} \gamma_{\pm, \text{HCl}} &= -D + \varepsilon_{(\text{H}^+, \text{Cl}^-)} m_{\text{HCl}} \end{aligned}$$

By plotting $\log_{10} \gamma_{\pm, \text{HCl}} + D$ vs. m_{HCl} a straight line with the slope $\varepsilon_{(\text{H}^+, \text{Cl}^-)}$ is obtained. The degree of linearity should in itself indicate the range of validity of the specific ion interaction approach. Osmotic coefficient data can be treated in an analogous way.

B.1.3.2 Estimations based on experimental values of equilibrium constants at different ionic strengths

Example B.2:

Equilibrium constants are given in Table B.2 for the reaction



The following formula is deduced from Eq. (B.5) for the extrapolation to $I = 0$:

$$\log_{10} \beta_1 + 4D = \log_{10} \beta_1^\circ - \Delta\varepsilon I_m \quad (\text{B.13})$$

The linear regression is done as described in Appendix C. The following results are obtained:

$$\begin{aligned} \log_{10} \beta_1^\circ &= 0.170 \pm 0.021 \\ \Delta\varepsilon(\text{B.12}) &= -(0.248 \pm 0.022) \text{ kg} \cdot \text{mol}^{-1} \end{aligned}$$

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 $I \neq 0$.

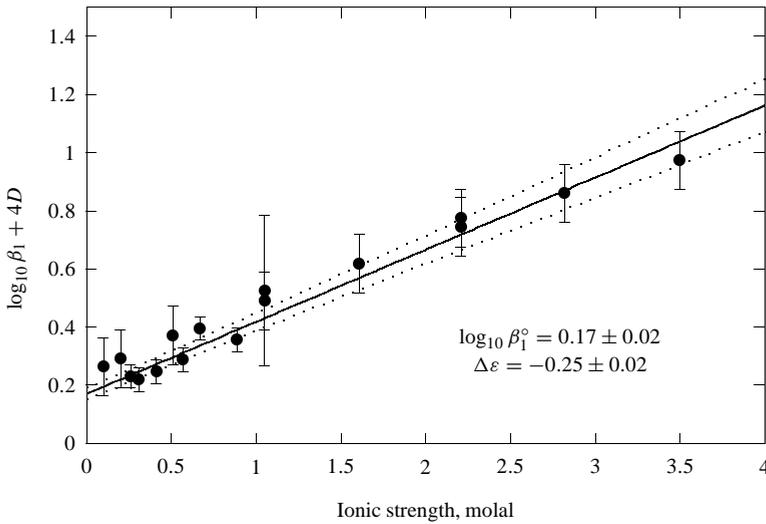
Table B.2: The preparation of the experimental equilibrium constants for the extrapolation to $I = 0$ with the specific ion interaction method at 25°C and 1 bar, according to Reaction (B.12). The linear regression of this set of data is shown in Figure B.1.

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.

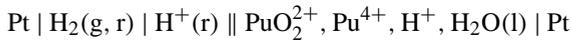
^(b) Equilibrium constants corrected from molarity to molality units, as described in Section 2.2.

Figure B.1: Plot of $\log_{10} \beta_1 + 4D$ vs. I_m for Reaction (B.12), $\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$ at 25°C and 1 bar. The straight line shows the result of the weighted linear regression, and the dotted lines represent the uncertainty range obtained by propagating the resulting uncertainties at $I = 0$ back to $I = 4$ m.

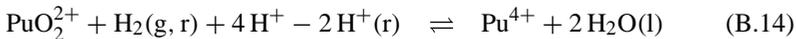


Example B.3:

When using the specific ion interaction theory, the relationship between the redox potential of the couple $\text{PuO}_2^{2+}/\text{Pu}^{4+}$ in a medium of ionic strength I_m and the corresponding quantity at $I = 0$ should be calculated in the following way. The reaction in the galvanic cell



is



where the “r” is used to indicate that $\text{H}_2(\text{g})$ and H^+ are at the chemical conditions in the reference electrode compartment, *i.e.*, standard conditions when the reference electrode is the SHE. However, H^+ , $\text{H}_2\text{O}(\text{l})$ and the $\text{PuO}_2^{2+}/\text{Pu}^{4+}$ are the conditions of the experimental measurements (*i.e.*, non-standard conditions, usually high ionic strength to improve the accuracy of the measurement).

For Reaction B.14

$$\log_{10} K^\circ = \log_{10} \left(\frac{a_{\text{Pu}^{4+}} \times a_{\text{H}_2\text{O}}^2 \times a_{\text{H}^+(\text{r})}^2}{a_{\text{PuO}_2^{2+}} \times a_{\text{H}^+}^4 \times f_{\text{H}_2}(\text{r})} \right)$$

Since by definition of the SHE $f_{\text{H}_2(r)} = 1$ and $\gamma_{\text{H}^+(r)} = 1$

$$\begin{aligned}\log_{10} K^\circ &= \log_{10} K + \log_{10} \gamma_{\text{Pu}^{4+}} - \log_{10} \gamma_{\text{PuO}_2^{2+}} - 4 \log_{10} \gamma_{\text{H}^+} \\ &\quad + 2 \log_{10} a_{\text{H}_2\text{O}},\end{aligned}$$

and

$$\begin{aligned}\log_{10} \gamma_{\text{Pu}^{4+}} &= -16D + \varepsilon_{(\text{Pu}^{4+}, \text{ClO}_4^-)} m_{\text{ClO}_4^-} \\ \log_{10} \gamma_{\text{PuO}_2^{2+}} &= -4D + \varepsilon_{(\text{PuO}_2^{2+}, \text{ClO}_4^-)} m_{\text{ClO}_4^-} \\ \log_{10} \gamma_{\text{H}^+} &= -D + \varepsilon_{(\text{H}^+, \text{ClO}_4^-)} m_{\text{ClO}_4^-}\end{aligned}$$

Hence,

$$\begin{aligned}\log_{10} K^\circ &= \log_{10} K - 8D \\ &\quad + \left(\varepsilon_{(\text{Pu}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{PuO}_2^{2+}, \text{ClO}_4^-)} - 4\varepsilon_{(\text{H}^+, \text{ClO}_4^-)} \right) m_{\text{ClO}_4^-} \\ &\quad + 2 \log_{10} a_{\text{H}_2\text{O}}\end{aligned}\tag{B.15}$$

The relationship between the equilibrium constant and the redox potential is

$$\ln K = \frac{nF}{RT} E^{\circ'}\tag{B.16}$$

$$\ln K^\circ = \frac{nF}{RT} E^\circ.\tag{B.17}$$

$E^{\circ'}$ 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).

$$\begin{aligned}E^{\circ'} - (8D - 2 \log_{10} a_{\text{H}_2\text{O}}) \left(\frac{RT \ln(10)}{nF} \right) &= \\ E^\circ - \Delta \varepsilon m_{\text{ClO}_4^-} \left(\frac{RT \ln(10)}{nF} \right)\end{aligned}\tag{B.18}$$

For $n = 2$ in the present example and $T = 298.15$ K, Eq. (B.18) becomes

$$E^{\circ'}[\text{mV}] - 236.6D + 59.16 \log_{10} a_{\text{H}_2\text{O}} = E^\circ[\text{mV}] - 29.58 \Delta \varepsilon m_{\text{ClO}_4^-}$$

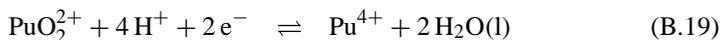
where

$$\Delta \varepsilon = \left(\varepsilon_{(\text{Pu}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{PuO}_2^{2+}, \text{ClO}_4^-)} - 4\varepsilon_{(\text{H}^+, \text{ClO}_4^-)} \right)$$

The value of $a_{(\text{H}_2\text{O})}$ can be taken from experimental data or calculated from equations (B.10) and (B.11).

In general, formal potentials are reported with reference to the standard hydrogen electrode, *cf.* Section 2.1.6.5, as exemplified in Tables V.2 and V.3 of the uranium

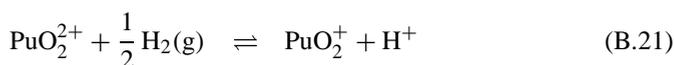
NEA review [92GRE/FUG]. In that case, the H^+ appearing in the reduction reaction is already at standard conditions. For example, experimental data are available on the formal potentials for reactions



and



While Reaction (B.19) corresponds to (B.14), Reaction (B.20) is equivalent to



where the designator “(r)” has been omitted, since in these equations only the H^+ in the reference compartment is relevant.

The cations in Reaction (B.14) represent aqueous species in the ionic media used during the experiments. 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). Reaction B.20 and B.21 are equivalent, as are Reactions B.14 and B.19, as can be seen in any of these equations are combined with Reaction 2.26. Hence Equation B.18 can be obtained more simply by using Equation 2.33 for Reaction B.19.

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.

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,

$$\varepsilon_{(ML, N \text{ or } X)} \approx (\varepsilon_{(M,X)} + \varepsilon_{(L,N)})/2 \quad (B.22)$$

$$\varepsilon_{(ML_2, N, \text{ or } X)} \approx (\varepsilon_{(M,X)} + 2\varepsilon_{(L,N)})/3 \quad (B.23)$$

Ciavatta obtained [90CIA] an average deviation of $\pm 0.05 \text{ kg} \cdot \text{mol}^{-1}$ 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 $\varepsilon_{(M^{n+}, ClO_4^-)}$ as a substitute for $\varepsilon_{(M^{n+}, Cl^-)}$ and $\varepsilon_{(M^{n+}, NO_3^-)}$. 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 $kg \cdot mol^{-1}$ and are valid for 298.15 K and 1 bar. The species are ordered by charge and appear, within each charge class, in standard order of arrangement, *cf.* Section 2.1.8.

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 $\pm 0.03 kg \cdot mol^{-1}$ 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 comparisons of ion interaction coefficients, or when estimates are made by analogy, this aspect must be taken into account.

Table B.3: Ion interaction coefficients $\varepsilon_{j,k}$ for cations j with $k = \text{Cl}^-$, ClO_4^- and NO_3^- , taken from Ciavatta [80CIA, 88CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B.5. The coefficients $\varepsilon_{(\text{M}^{n+}, \text{Cl}^-)}$ and $\varepsilon_{(\text{M}^{n+}, \text{NO}_3^-)}$ reported by Ciavatta [80CIA] were evaluated without taking chloride and nitrate complexation into account, as discussed in Section B.2.

$j \quad k \rightarrow$ ↓	Cl^-	ClO_4^-	NO_3^-
H^+	(0.12 ± 0.01)	(0.14 ± 0.02)	(0.07 ± 0.01)
NH_4^+	$-(0.01 \pm 0.01)$	$-(0.08 \pm 0.04)^\dagger$	$-(0.06 \pm 0.03)^\dagger$
H_2gly^+	$-(0.06 \pm 0.02)$		
Tl^+		$-(0.21 \pm 0.06)^\dagger$	
ZnHCO_3^+	$0.2^{(a)}$		
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)	
Ag^+			$-(0.12 \pm 0.05)^\dagger$
YCO_3^+		$(0.17 \pm 0.04)^{(b)}$	
$\text{Am}(\text{OH})_2^+$		$(0.17 \pm 0.04)^{(c)}$	
AmF_2^+		$(0.17 \pm 0.04)^{(c)}$	
AmSO_4^+		$(0.22 \pm 0.08)^{(d)}$	
AmCO_3^+		$(0.17 \pm 0.04)^{(c)}$	
PuO_2^+		$(0.24 \pm 0.05)^{(e)}$	
PuO_2F^+		$(0.29 \pm 0.11)^{(f)}$	
PuO_2Cl^+		$(0.50 \pm 0.09)^{(g)}$	

(Continued on next page)

(a) Taken from Ferri *et al.* [85FER/GRE].

(b) Taken from Spahiu [83SPA].

(c) Estimated in the NEA-TDB review on americium thermodynamics [95SIL/BID].

(d) Evaluated in the NEA-TDB review on americium thermodynamics [95SIL/BID].

(e) Derived from $\Delta\varepsilon = \varepsilon_{(\text{PuO}_2^{2+}, \text{ClO}_4^-)} - \varepsilon_{(\text{PuO}_2^+, \text{ClO}_4^-)} = (0.22 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ [95CAP/VIT].

In [92GRE/FUG] $\varepsilon = \varepsilon_{(\text{PuO}_2^+, \text{ClO}_4^-)} = (0.17 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ was tabulated based on [89ROB, 89RIG/ROB, 90RIG]. Capdevila and Vitorge's data [92CAP, 94CAP/VIT, 95CAP/VIT] were not available at that time.

(f) Estimated in this review by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) reaction.

Table B.3: (continued)

$j \quad k \rightarrow$ ↓	Cl^-	ClO_4^-	NO_3^-
NpO_2^+	(0.09 ± 0.05)	$(0.25 \pm 0.05)^{\text{(h)}}$	
NpO_2OH^+		$-(0.06 \pm 0.40)^{\text{(i)}}$	
$(\text{NpO}_2)_3(\text{OH})_5^+$		$-(0.45 \pm 0.20)^{\text{(i)}}$	
NpO_2F^+		$(0.29 \pm 0.12)^{\text{(j)}}$	
NpO_2Cl^+		$(0.50 \pm 0.14)^{\text{(k)}}$	
$\text{NpO}_2\text{IO}_3^+$		$(0.33 \pm 0.04)^{\text{(l)}}$	
$\text{Np}(\text{SCN})_3^+$		$(0.17 \pm 0.04)^{\text{(m)}}$	
UO_2^+		$(0.26 \pm 0.03)^{\text{(n)}}$	
UO_2OH^+		$-(0.06 \pm 0.40)^{\text{(n)}}$	$(0.51 \pm 1.4)^{\text{(n)}}$
$(\text{UO}_2)_3(\text{OH})_5^+$	$(0.81 \pm 0.17)^{\text{(n)}}$	$(0.45 \pm 0.15)^{\text{(n)}}$	$(0.41 \pm 0.22)^{\text{(n)}}$
UF_3^+	$(0.1 \pm 0.1)^{\text{(o)}}$	$(0.1 \pm 0.1)^{\text{(o)}}$	
UO_2F^+	$(0.04 \pm 0.07)^{\text{(p)}}$	$(0.29 \pm 0.05)^{\text{(n)}}$	
UO_2Cl^+		$(0.33 \pm 0.04)^{\text{(n)}}$	
$\text{UO}_2\text{ClO}_3^+$		$(0.33 \pm 0.04)^{\text{(o)}}$	
UO_2Br^+		$(0.24 \pm 0.04)^{\text{(o)}}$	
$\text{UO}_2\text{BrO}_3^+$		$(0.33 \pm 0.04)^{\text{(o)}}$	
UO_2IO_3^+		$(0.33 \pm 0.04)^{\text{(o)}}$	
UO_2N_3^+		$(0.3 \pm 0.1)^{\text{(o)}}$	
UO_2NO_3^+		$(0.33 \pm 0.04)^{\text{(o)}}$	

(Continued on next page)

(g) From $\Delta\varepsilon$ evaluated by Giffaut [94GIF].

(h) As in [92GRE/FUG], derived from $\Delta\varepsilon = \varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} - \varepsilon_{(\text{NpO}_2^+, \text{ClO}_4^-)} = (0.21 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ [87RIG/VIT, 89RIG/ROB, 90RIG].

(i) Estimated in the present review.

(j) Estimated in this review by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction.

(k) Estimated in this review by analogy with $\Delta\varepsilon$ of the corresponding P(VI) reaction.

(l) Estimated in this review by assuming $\varepsilon_{(\text{NpO}_2\text{IO}_3^+, \text{ClO}_4^-)} \approx \varepsilon_{(\text{UO}_2\text{IO}_3^+, \text{ClO}_4^-)}$.

(m) Estimated in this review by assuming $\varepsilon_{(\text{Np}(\text{SCN})_3^+, \text{ClO}_4^-)} \approx \varepsilon_{(\text{AmF}_2^+, \text{ClO}_4^-)}$.

(n) Evaluated in the uranium review [92GRE/FUG], using $\varepsilon_{(\text{UO}_2^{2+}, X)} = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$, where $X = \text{Cl}^-, \text{ClO}_4^-$ and NO_3^- , cf. Section B.2.

(o) Estimated in the uranium review [92GRE/FUG].

(p) Taken from Riglet, Robouch and Vitorge [89RIG/ROB], where the following assumptions were made: $\varepsilon_{(\text{Np}^{3+}, \text{ClO}_4^-)} \approx \varepsilon_{(\text{Pu}^{3+}, \text{ClO}_4^-)} = 0.49 \text{ kg} \cdot \text{mol}^{-1}$ as for other $(\text{M}^{3+}, \text{ClO}_4^-)$ interactions, and

$$\varepsilon_{(\text{NpO}_2^{2+}, \text{ClO}_4^-)} \approx \varepsilon_{(\text{PuO}_2^{2+}, \text{ClO}_4^-)} \approx \varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)} = 0.46 \text{ kg} \cdot \text{mol}^{-1}.$$

Table B.3: (continued)

$j \quad k \rightarrow$ \downarrow	Cl^-	ClO_4^-	NO_3^-
UO_2SCN^+		$(0.22 \pm 0.04)^{(o)}$	
Pb^{2+}		(0.15 ± 0.02)	$-(0.20 \pm 0.12)^\dagger$
AlOH^{2+}	$0.09^{(q)}$	$0.31^{(q)}$	
$\text{Al}_2\text{CO}_3(\text{OH})_2^{2+}$	$0.26^{(q)}$		
Zn^{2+}		(0.33 ± 0.03)	(0.16 ± 0.02)
ZnCO_3^{2+}	$(0.35 \pm 0.05)^{(a)}$		
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+}		$0.38^{(b)}$	
FeSCN^{2+}		$0.45^{(b)}$	
Mn^{2+}	(0.13 ± 0.01)		
YHCO_3^{2+}		$(0.39 \pm 0.04)^{(b)}$	
AmOH^{2+}		$(0.39 \pm 0.04)^{(c)}$	
AmF^{2+}		$(0.39 \pm 0.04)^{(c)}$	
AmCl^{2+}		$(0.39 \pm 0.04)^{(c)}$	
AmN_3^{2+}		$(0.39 \pm 0.04)^{(c)}$	
AmNO_2^{2+}		$(0.39 \pm 0.04)^{(c)}$	
AmNO_3^{2+}		$(0.39 \pm 0.04)^{(c)}$	
$\text{AmH}_2\text{PO}_4^{2+}$		$(0.39 \pm 0.04)^{(c)}$	
AmSCN^{2+}		$(0.39 \pm 0.04)^{(c)}$	
PuO_2^{2+}		$(0.46 \pm 0.05)^{(r)}$	
PuF_2^{2+}		$(0.36 \pm 0.17)^{(j)}$	
PuCl^{2+}		$(0.39 \pm 0.16)^{(s)}$	
PuI^{2+}		$(0.39 \pm 0.04)^{(t)}$	
NpO_2^{2+}		$(0.46 \pm 0.05)^{(u)}$	

(Continued on next page)

^(q) Taken from Hedlund [88HED].^(r) By analogy with $\varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)}$ as derived from isopiestic measurements in [92GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.^(s) Estimated in this review by analogy with $\Delta\varepsilon$ of the corresponding Am(III) reaction.

Table B.3: (continued)

$j \quad k \rightarrow$ \downarrow	Cl^-	ClO_4^-	NO_3^-
$(\text{NpO}_2)_2(\text{OH})_2^{2+}$		$-(0.57 \pm 0.10)^{(i)}$	
NpF_2^{2+}		$(0.38 \pm 0.17)^{(j)}$	
NpSO_4^{2+}		(0.48 ± 0.11)	
$\text{Np}(\text{SCN})_2^{2+}$		$(0.38 \pm 0.20)^{(j)}$	
UO_2^{2+}	$(0.21 \pm 0.02)^{(v)}$	(0.46 ± 0.03)	$(0.24 \pm 0.03)^{(v)}$
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	$(0.69 \pm 0.07)^{(n)}$	$(0.57 \pm 0.07)^{(n)}$	$(0.49 \pm 0.09)^{(n)}$
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	$(0.50 \pm 0.18)^{(n)}$	$(0.89 \pm 0.23)^{(n)}$	$(0.72 \pm 1.0)^{(n)}$
UF_2^{2+}		$(0.3 \pm 0.1)^{(o)}$	
USO_4^{2+}		$(0.3 \pm 0.1)^{(o)}$	
$\text{U}(\text{NO}_3)_2^{2+}$		$(0.49 \pm 0.14)^{(w)}$	
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)	$-(0.28 \pm 0.03)$
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)	
$\text{La}^{3+} \rightarrow \text{Lu}^{3+}$		$0.47 \rightarrow 0.52^{(b)}$	
Am^{3+}		$(0.49 \pm 0.03)^{(c)}$	
Pu^{3+}		$(0.49 \pm 0.05)^{(x)}$	
PuOH^{3+}		$(0.50 \pm 0.05)^{(i)}$	
PuF^{3+}		$(0.56 \pm 0.11)^{(y)}$	
PuCl^{3+}		$(0.85 \pm 0.09)^{(z)}$	

(Continued on next page)

(i) Estimated in this review by assuming $\varepsilon_{(\text{Pu}^{2+}, \text{ClO}_4^-)} \approx \varepsilon_{(\text{AmSCN}^{2+}, \text{ClO}_4^-)}$ and $\varepsilon_{(\text{I}^-, \text{NH}_4^+)} \approx \varepsilon_{(\text{SCN}^-, \text{Na}^+)}$.

(u) By analogy with $\varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)}$ as derived from isopiestic measurements in [92GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.

(v) These coefficients were not used in the NEA-TDB uranium review [92GRE/FUG] because they were evaluated by Ciavatta [80CIA] without taking chloride and nitrate complexation into account. Instead, Grenthe *et al.* used $\varepsilon_{(\text{UO}_2^{2+}, X)} = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$, for $X = \text{Cl}^-, \text{ClO}_4^-$ and NO_3^- .

(w) Evaluated in the uranium review [92GRE/FUG] using $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} = (0.76 \pm 0.06) \text{ kg} \cdot \text{mol}^{-1}$.

(x) Estimated by analogy with $\varepsilon_{(\text{Ho}^{3+}, \text{ClO}_4^-)}$ [83SPA] as in previous books in this series [92GRE/FUG, 95SIL/BID]. The uncertainty is increased because the value is estimated by analogy.

(y) Estimated in this review by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) reaction.

Table B.3: (continued)

$j \quad k \rightarrow$ \downarrow	Cl^-	ClO_4^-	NO_3^-
PuBr^{3+}		$(0.58 \pm 0.16)^{\text{A}}$	
PuSCN^{3+}		$(0.39 \pm 0.04)^{\text{B}}$	
Np^{3+}		$(0.49 \pm 0.05)^{\text{(x)}}$	
NpOH^{3+}		$(0.50 \pm 0.05)^{\text{(i)}}$	
NpF^{3+}		$(0.58 \pm 0.07)^{\text{C}}$	
NpCl^{3+}		$(0.81 \pm 0.19)^{\text{D}}$	
NpI^{3+}		$(0.77 \pm 0.26)^{\text{E}}$	
NpSCN^{3+}		$(0.76 \pm 0.12)^{\text{(j)}}$	
U^{3+}		$(0.49 \pm 0.05)^{\text{(w)}}$	
UOH^{3+}		$(0.48 \pm 0.08)^{\text{(w)}}$	
UF^{3+}		$(0.48 \pm 0.08)^{\text{(o)}}$	
UCl^{3+}		$(0.59 \pm 0.10)^{\text{(w)}}$	
UBr^{3+}		$(0.52 \pm 0.10)^{\text{(o)}}$	
UI^{3+}		$(0.55 \pm 0.10)^{\text{(o)}}$	
UNO_3^{3+}		$(0.62 \pm 0.08)^{\text{(w)}}$	
$\text{Be}_2\text{OH}^{3+}$		$(0.50 \pm 0.05)^{\text{F}}$	
$\text{Be}_3(\text{OH})_3^{3+}$	$(0.30 \pm 0.05)^{\text{F}}$	$(0.51 \pm 0.05)^{\text{(w)}}$	$(0.29 \pm 0.05)^{\text{F}}$
$\text{Al}_3\text{CO}_3(\text{OH})_4^{4+}$	$0.41^{\text{(q)}}$		
$\text{Fe}_2(\text{OH})_2^{4+}$		$0.82^{\text{(b)}}$	
$\text{Y}_2\text{CO}_3^{4+}$		$(0.80 \pm 0.04)^{\text{(b)}}$	
Pu^{4+}		$(0.82 \pm 0.06)^{\text{G}}$	
Np^{4+}		$(0.84 \pm 0.06)^{\text{H}}$	

(Continued on next page)

^(z) Derived from the $\Delta\varepsilon$ evaluated in the present review.^A Estimated in this review by analogy with $\Delta\varepsilon$ of the corresponding U(IV) reaction, and by assuming $\varepsilon(\text{Br}^-, \text{H}^+) \approx \varepsilon(\text{Br}^-, \text{Na}^+)$.^B Estimated in this review by assuming $\varepsilon(\text{PuSCN}^{2+}, \text{ClO}_4^-) \approx \varepsilon(\text{AmSCN}^{2+}, \text{ClO}_4^-)$.^C Evaluated in the present review.^D Derived from the $\Delta\varepsilon$ selected in the present review, cf. text.^E Estimated in this review by analogy with $\Delta\varepsilon$ of the corresponding Np(IV) chloride reaction, and by assuming $\varepsilon(\text{I}^-, \text{H}^+) \approx \varepsilon(\text{I}^-, \text{Na}^+)$.^F Taken from Bruno [86BRU], where the following assumptions were made: $\varepsilon(\text{Be}^{2+}, \text{ClO}_4^-) = 0.30 \text{ kg} \cdot \text{mol}^{-1}$ as for other $\varepsilon_{(\text{M}^{2+}, \text{ClO}_4^-)}$, $\varepsilon(\text{Be}^{2+}, \text{Cl}^-) = 0.17 \text{ kg} \cdot \text{mol}^{-1}$ as for other $\varepsilon_{(\text{M}^{2+}, \text{Cl}^-)}$, and $\varepsilon(\text{Be}^{2+}, \text{NO}_3^-) = 0.17 \text{ kg} \cdot \text{mol}^{-1}$ as for other $\varepsilon_{(\text{M}^{2+}, \text{NO}_3^-)}$.

Table B.3: (continued)

$j \quad k \rightarrow$ \downarrow	Cl^-	ClO_4^-	NO_3^-
U^{4+} Th^{4+}	(0.25 ± 0.03)	$(0.76 \pm 0.06)^{\text{I(o)}}$	(0.11 ± 0.02)
$\text{Al}_3(\text{OH})_4^{5+}$	$0.66^{\text{(q)}}$	$1.30^{\text{(q)}}$	

^G Derived from $\Delta\varepsilon = \varepsilon_{(\text{Pu}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{Pu}^{3+}, \text{ClO}_4^-)} = (0.33 \pm 0.035) \text{ kg}\cdot\text{mol}^{-1}$ [95CAP/VIT]. Uncertainty estimated in this review (see Appendix A). In the first book of this series [92GRE/FUG], $\varepsilon_{(\text{Pu}^{3+}, \text{ClO}_4^-)} = (1.03 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ was tabulated based on references [89ROB, 89RIG/ROB, 90RIG]. Capdevila and Vitorge's data [92CAP, 94CAP/VIT, 95CAP/VIT] were not available at that time.

^H Derived from $\Delta\varepsilon = \varepsilon_{(\text{Np}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{Np}^{3+}, \text{ClO}_4^-)} = (0.35 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ [89ROB, 89RIG/ROB, 90RIG].

^I Using the measured value of $\Delta\varepsilon = \varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} - \varepsilon_{(\text{U}^{3+}, \text{ClO}_4^-)} = (0.35 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ page 89 [90RIG], where the uncertainty is recalculated in the present review from the data given in this thesis, and $\varepsilon_{(\text{U}^{3+}, \text{ClO}_4^-)} = (0.49 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ (see footnote (w)), a value for $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)}$ can be calculated in the same way as is done for $\varepsilon_{(\text{Np}^{4+}, \text{ClO}_4^-)}$ and $\varepsilon_{(\text{Pu}^{4+}, \text{ClO}_4^-)}$. This value, $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} = (0.84 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$, is consistent with the tabulated $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)} = (0.76 \pm 0.06)$ since the uncertainties overlap. The authors of the present work do not believe that a change in the previously selected value for $\varepsilon_{(\text{U}^{4+}, \text{ClO}_4^-)}$ is justified at present.

Table B.4: Ion interaction coefficients $\varepsilon_{j,k}$ for anions j with $k = \text{Li}^+, \text{Na}^+$ and K^+ , taken from Ciavatta [80CIA, 88CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table B.5.

$j \quad k \rightarrow$ ↓	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^-		$-(0.01 \pm 0.02)$	
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^-		$-(0.06 \pm 0.02)$	
$\text{I}^- \text{ (p)}$	(0.16 ± 0.01)	(0.08 ± 0.02)	(0.02 ± 0.01)
IO_3^-		$-(0.06 \pm 0.02)^{(b)}$	
HSO_4^-		$-(0.01 \pm 0.02)$	
N_3^-		$(0.0 \pm 0.1)^{(b)}$	
NO_2^-	$(0.06 \pm 0.04)^\dagger$	(0.00 ± 0.02)	$-(0.04 \pm 0.02)$
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^-		$(0.00 \pm 0.02)^{(d)}$	$-(0.06 \pm 0.05)^{(i)}$
SCN^-		(0.05 ± 0.01)	$-(0.01 \pm 0.01)$
HCOO^-		(0.03 ± 0.01)	
CH_3COO^-	(0.05 ± 0.01)	(0.08 ± 0.01)	(0.09 ± 0.01)
$\text{SiO}(\text{OH})_3^-$		$-(0.08 \pm 0.03)^{(a)}$	
$\text{Si}_2\text{O}_2(\text{OH})_5^-$		$-(0.08 \pm 0.04)^{(b)}$	
$\text{B}(\text{OH})_4^-$		$-(0.07 \pm 0.05)^\dagger$	
$\text{Am}(\text{SO}_4)_2^-$		$-(0.05 \pm 0.05)^{(c)}$	
$\text{Am}(\text{CO}_3)_2^-$		$-(0.05 \pm 0.05)^{(c)}$	
$\text{PuO}_2\text{CO}_3^-$		$-(0.18 \pm 0.18)^{(o)}$	
$\text{NpO}_2(\text{OH})_2^-$		$-(0.01 \pm 0.07)^{(q)}$	
$\text{NpO}_2\text{CO}_3^-$		$-(0.18 \pm 0.15)^{(f)}$	
$(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$		$(0.00 \pm 0.05)^{(k)}$	
$\text{UO}_2(\text{OH})_3^-$		$-(0.09 \pm 0.05)^{(b)}$	
UO_2F_3^-		$(0.00 \pm 0.05)^{(b)}$	
$\text{UO}_2(\text{N}_3)_3^-$		$(0.0 \pm 0.1)^{(b)}$	

(Continued on next page)

Table B.4: (continued)

$j \quad k \rightarrow$ \downarrow	Li^+	Na^+	K^+
$(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$		$(0.00 \pm 0.05)^{(b)}$	
SO_3^{2-}		$-(0.08 \pm 0.05)^\dagger$	
SO_4^{2-}	$-(0.03 \pm 0.04)^\dagger$	$-(0.12 \pm 0.06)^\dagger$	$-(0.06 \pm 0.02)$
$\text{S}_2\text{O}_3^{2-}$		$-(0.08 \pm 0.05)^\dagger$	
HPO_4^{2-}		$-(0.15 \pm 0.06)^\dagger$	$-(0.10 \pm 0.06)^\dagger$
CO_3^{2-}		$-(0.08 \pm 0.03)^{(d)}$	(0.02 ± 0.01)
$\text{SiO}_2(\text{OH})_2^{2-}$		$-(0.10 \pm 0.07)^{(a)}$	
$\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$		$-(0.15 \pm 0.06)^{(b)}$	
CrO_4^{2-}		$-(0.06 \pm 0.04)^\dagger$	$-(0.08 \pm 0.04)^\dagger$
$\text{NpO}_2(\text{HPO}_4)_2^{2-}$		$-(0.1 \pm 0.1)$	
$\text{NpO}_2(\text{CO}_3)_2^{2-}$		$-(0.02 \pm 0.14)^{(k)}$	
$\text{UO}_2\text{F}_4^{2-}$		$-(0.08 \pm 0.06)^{(b)}$	
$\text{UO}_2(\text{SO}_4)_2^{2-}$		$-(0.12 \pm 0.06)^{(b)}$	
$\text{UO}_2(\text{N}_3)_4^{2-}$		$-(0.1 \pm 0.1)^{(b)}$	
$\text{UO}_2(\text{CO}_3)_2^{2-}$		$-(0.02 \pm 0.09)^{(d)}$	
PO_4^{3-}		$-(0.25 \pm 0.03)^\dagger$	$-(0.09 \pm 0.02)$
$\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$		$-(0.25 \pm 0.03)^{(b)}$	
$\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$		$-(0.25 \pm 0.03)^{(b)}$	
$\text{Si}_4\text{O}_7(\text{OH})_5^{3-}$		$-(0.25 \pm 0.03)^{(b)}$	
$\text{Am}(\text{CO}_3)_3^{3-}$		$-(0.15 \pm 0.05)^{(c)}$	
$\text{Np}(\text{CO}_3)_3^{3-}$			$-(0.15 \pm 0.07)^{(n)}$
$\text{NpO}_2(\text{CO}_3)_2^{3-}$		$-(0.33 \pm 0.17)^{(f)}$	
$\text{P}_2\text{O}_7^{4-}$		$-(0.26 \pm 0.05)$	$-(0.15 \pm 0.05)$
$\text{Fe}(\text{CN})_6^{4-}$			$-(0.17 \pm 0.03)$
$\text{NpO}_2(\text{CO}_3)_3^{4-}$		$-(0.40 \pm 0.19)^{(e)}$	$-(0.62 \pm 0.42)^{(g)(h)}$
$\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}$		$-(0.40 \pm 0.19)^{(m)}$	
$\text{U}(\text{CO}_3)_4^{4-}$		$-(0.09 \pm 0.10)^{(b)(d)}$	
$\text{UO}_2(\text{CO}_3)_3^{4-}$		$-(0.01 \pm 0.11)^{(d)}$	
$\text{NpO}_2(\text{CO}_3)_3^{5-}$		$-(0.53 \pm 0.19)^{(f)}$	
$\text{UO}_2(\text{CO}_3)_3^{5-}$		$-(0.62 \pm 0.15)^{(d)}$	

(Continued on next page)

Table B.4: (continued)

$j \quad k \rightarrow$ \downarrow	Li^+	Na^+	K^+
$\text{Np}(\text{CO}_3)_5^{6-}$			$-(0.73 \pm 0.68)^{(i)}$
$(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$		$-(0.46 \pm 0.73)^{(e)}$	
$\text{U}(\text{CO}_3)_5^{6-}$		$-(0.30 \pm 0.15)^{(d)}$	$(0.70 \pm 0.31)^{(i)}$
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$		$(0.37 \pm 0.11)^{(d)}$	
$(\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^{6-}$		$(0.09 \pm 0.71)^{(l)}$	

(a) Evaluated in the NEA-TDB uranium review [92GRE/FUG].

(b) Estimated in the NEA-TDB uranium review [92GRE/FUG].

(c) Estimated in the NEA-TDB americium review [95SIL/BID].

(d) These values differ from those reported in the NEA-TDB uranium review. See the discussion in [95GRE/PUI]. Values for CO_3^{2-} and HCO_3^- are based on [80CIA].

(e) Calculated in this review (Section 12.1.2.1.2)

(f) Calculated in this review (Section 12.1.2.1.3)

(g) Calculated in this review (Section 12.1.2.2.1)

(h) $\varepsilon_{(\text{NpO}_2(\text{CO}_3)_3^{4-}, \text{NH}_4^+)} = -(0.78 \pm 0.25) \text{ kg}\cdot\text{mol}^{-1}$ is calculated in this review (Section 12.1.2.2.1)

(i) Calculated in this review from Pitzer coefficients [98RAI/FEL]

(j) Calculated in this review (Section 12.1.2.1.4)

(k) Estimated by analogy in this review (Section 12.1.2.1.2)

(l) Estimated by analogy in this review (Section 12.1.2.2.1)

(m) Estimated in this review by analogy with $\text{NpO}_2(\text{CO}_3)_3^{4-}$

(n) Estimated by analogy in this review (Section 12.1.2.1.5).

(o) Estimated in this review by analogy with $\varepsilon_{(\text{NpO}_2\text{CO}_3^-, \text{Na}^+)}$

(p) $\varepsilon_{(\text{I}^-, \text{NH}_4^+)} \approx \varepsilon_{(\text{SCN}^-, \text{Na}^+)} = (0.05 \pm 0.01)$.

(q) Estimated in this review (Section 8.1.3).

The uncertainties represent the 95% confidence level.

$j \ k \rightarrow$ ↓	Cl^-		ClO_4^-		NO_3^-	
	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
NH_4^+			-0.088 ± 0.002	0.095 ± 0.012	-0.075 ± 0.001	0.057 ± 0.004
Tl^+			-0.18 ± 0.02	0.09 ± 0.02		
Ag^+					-0.1432 ± 0.0002	0.0971 ± 0.0009
Pb^{2+}					-0.329 ± 0.007	0.288 ± 0.018
Hg^{2+}					-0.145 ± 0.001	0.194 ± 0.002
Hg_2^{2+}					-0.2300 ± 0.0004	0.194 ± 0.002
$j \ k \rightarrow$ ↓	Li^+		Na^+		K^+	
	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
OH^-	-0.039 ± 0.002	0.072 ± 0.006				
NO_2^-	0.02 ± 0.01	0.11 ± 0.01				
NO_3^-			-0.049 ± 0.001	0.044 ± 0.002	-0.131 ± 0.002	0.082 ± 0.006
H_2PO_4^-			-0.109 ± 0.001	0.095 ± 0.003	-0.1473 ± 0.0008	0.121 ± 0.004
$\text{B}(\text{OH})_4^-$			-0.092 ± 0.002	0.103 ± 0.005		
SO_3^{2-}			-0.125 ± 0.008	0.106 ± 0.009		
SO_4^{2-}	-0.068 ± 0.003	0.093 ± 0.007	-0.184 ± 0.002	0.139 ± 0.006		
$\text{S}_2\text{O}_3^{2-}$			-0.125 ± 0.008	0.106 ± 0.009		
HPO_4^{2-}			-0.19 ± 0.01	0.11 ± 0.03	-0.152 ± 0.007	0.123 ± 0.016
CrO_4^{2-}			-0.090 ± 0.005	0.07 ± 0.01	-0.123 ± 0.003	0.106 ± 0.007
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 the average \bar{X} :

$$s_X = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (X_i - \bar{X})^2} \quad (\text{C.1})$$

The standard deviation s_X is thus calculated from the dispersion of the equally weighted data points X_i around the average \bar{X} , and the probability is 95% that an X_i is within

[†]This Appendix contains essentially the text of the TDB-3 guideline, 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 3, 4 and 5, the text is reproduced here with minor revisions.

$\bar{X} \pm 1.96 s_X$, 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.

$$\sigma_{\bar{X}} = \sqrt{s_X^2 + \sum_j (s_j^2)} \quad (\text{C.2})$$

The estimation of the systematic errors s_j (which, of course, have to relate to \bar{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 \bar{X} and its uncertainty $\sigma_{\bar{X}}$ are then calculated according to Eqs. (C.3) and (C.4).

$$\bar{X} \equiv \frac{\sum_{i=1}^N \left(\frac{X_i}{\sigma_i^2} \right)}{\sum_{i=1}^N \left(\frac{1}{\sigma_i^2} \right)} \quad (\text{C.3})$$

$$\sigma_{\bar{X}} = \sqrt{\frac{1}{\sum_{i=1}^N \left(\frac{1}{\sigma_i^2} \right)}} \quad (\text{C.4})$$

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 $\sigma_{\bar{X}}$ 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 $\sigma_{\bar{X}}$ 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).

$$\bar{X} = \frac{1}{N} \sum_{i=1}^N X_i \quad (\text{C.5})$$

$$\sigma_{\bar{X}} = \frac{\sigma}{\sqrt{N}} \quad (\text{C.6})$$

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:

$$\bar{X} = (25.3 \pm 0.2)$$

The calculated uncertainty $\sigma_{\bar{X}} = 0.2$ appears relatively small but is statistically correct, for the values are assumed to follow a Gaussian distribution. As a consequence of Eq. (C.4), $\sigma_{\bar{X}}$ will always come out smaller than the smallest σ_i . Assuming $\sigma_4 = 0.10$ instead of 0.25 would yield $\bar{X} = (25.0 \pm 0.1)$, and $\sigma_4 = 0.60$ would result in $\bar{X} = (25.6 \pm 0.2)$. In fact, the values ($X_i \pm \sigma_i$) in this example are at the limit of consistency, 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 $\bar{X} = (25.3 \pm 0.3)$.

- ii. If reconsideration of the previous assessments gives no evidence for reassigning the X_i and σ_i (95% confidence level) values listed above, the statistical conclusion will be that all the X_i do not belong to the same parent distribution and cannot therefore be treated in the same group (*cf.* item iii below for a non-statistical explanation). The values for $i = 1, 4$ and 5 might be considered as belonging to Group A and the values for $i = 2$ and 3 to Group B. The weighted average of the values in Group A is $X_A(i = 1, 4, 5) = (24.95 \pm 0.21)$ 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 $\sigma_{\bar{X}}$ is chosen in such a way that it covers the complete ranges of expectancy of X_A and X_B . The selected value is then $\bar{X} = (25.5 \pm 0.9)$.
- iii. Another explanation could be that unidentified systematic errors are associated with some values. If this seems likely to be the case, there is no reason for splitting the values up into two groups. The correct way of proceeding would be to calculate the unweighted average of all the five points and assign an uncertainty that covers the whole range of expectancy of the five values. The resulting value is then $\bar{X} = (25.45 \pm 1.05)$, which is rounded according to the rules in Section C.4.3 to $\bar{X} = (25.4 \pm 1.1)$.

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 $\sigma_{\bar{X}}$ assigned to the selected mean \bar{X} has to cover the range of expectation of both source data X_1, X_2 , as shown in Eq. (C.7),

$$\sigma_{\bar{X}} = |X_i - \bar{X}| + \sigma_{\max}, \quad (\text{C.7})$$

where $i = 1, 2$, and σ_{\max} is the larger of the two uncertainties σ_i , see Example C.1.ii and Example C.2.

Example C.2:

The following credible source data are given:

$$X_1 = (4.5 \pm 0.3)$$

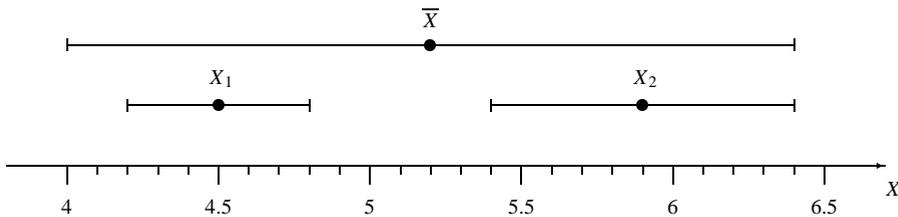
$$X_2 = (5.9 \pm 0.5)$$

The uncertainties have been assigned by the reviewer. Both experimental methods are satisfactory, and there is no justification to discard one of the data. The selected value is then:

$$\bar{X} = (5.2 \pm 1.2)$$

Case II. Outliers: This problem can often be solved by either discarding the outlying

Figure C.1: Illustration for Example C.2



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:

$$\bar{X} = (5.0 \pm 0.9)$$

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 $I = 0$, \bar{X}° , and $\Delta\varepsilon$. The first step is the conversion of the ionic strength from the frequently used molar ($\text{mol} \cdot \text{dm}^{-3}$, M) to the molal ($\text{mol} \cdot \text{kg}^{-1}$, m) scale, as described in Section 2.2. 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 \bar{X}° and the slope $-\Delta\varepsilon$:

$$\bar{X}^\circ = \frac{1}{\Delta} \left(\sum_{i=1}^N \frac{m_{k,i}^2}{\sigma_i^2} \sum_{i=1}^N \frac{X_i}{\sigma_i^2} - \sum_{i=1}^N \frac{m_{k,i}}{\sigma_i^2} \sum_{i=1}^N \frac{m_{k,i} X_i}{\sigma_i^2} \right) \quad (\text{C.8})$$

$$-\Delta\varepsilon = \frac{1}{\Delta} \left(\sum_{i=1}^N \frac{1}{\sigma_i^2} \sum_{i=1}^N \frac{m_{k,i} X_i}{\sigma_i^2} - \sum_{i=1}^N \frac{m_{k,i}}{\sigma_i^2} \sum_{i=1}^N \frac{X_i}{\sigma_i^2} \right) \quad (\text{C.9})$$

$$\sigma_{\bar{X}^\circ} = \sqrt{\frac{1}{\Delta} \sum_{i=1}^N \frac{m_{k,i}^2}{\sigma_i^2}} \quad (\text{C.10})$$

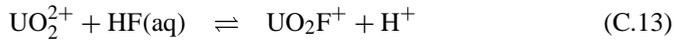
$$\sigma_{\Delta\varepsilon} = \sqrt{\frac{1}{\Delta} \sum_{i=1}^N \frac{1}{\sigma_i^2}}, \quad (\text{C.11})$$

$$\text{where } \Delta = \sum_{i=1}^N \frac{1}{\sigma_i^2} \sum_{i=1}^N \frac{m_{k,i}^2}{\sigma_i^2} - \left(\sum_{i=1}^N \frac{m_{k,i}}{\sigma_i^2} \right)^2. \quad (\text{C.12})$$

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 $\sigma_{\bar{X}^\circ}$ and $\sigma_{\Delta\varepsilon}$ in Eqs. (C.10) and (C.11). If the σ_i represent the 95% confidence level, $\sigma_{\bar{X}^\circ}$ and $\sigma_{\Delta\varepsilon}$ will also do so. In other words, the uncertainties of the intercept and the slope do not depend on the dispersion of the data points around the straight line but rather directly on their absolute uncertainties σ_i .

Example C.4:

Ten independent determinations of the equilibrium constant $\log_{10}^*\beta$ for the reaction



are available in $\text{HClO}_4/\text{NaClO}_4$ media at different ionic strengths. Uncertainties that represent the 95% confidence level have been assigned by the reviewer. A weighted linear regression, $(\log_{10}^*\beta + 2D)$ vs. m_k , according to the formula $\log_{10}^*\beta(\text{C.13}) + 2D = \log_{10}^*\beta^\circ(\text{C.13}) - \Delta\varepsilon m_k$, 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	$m_{\text{ClO}_4^-,i}$	$\log_{10}^*\beta_i + 2D$	σ_i
1	0.05	1.88	0.10
2	0.25	1.86	0.10
3	0.51	1.73	0.10
4	1.05	1.84	0.10
5	2.21	1.88	0.10
6	0.52	1.89	0.11
7	1.09	1.93	0.11
8	2.32	1.78	0.11
9	2.21	2.03	0.10
10	4.95	2.00	0.32

The results of the linear regression are:

$$\begin{aligned} \text{intercept} &= (1.837 \pm 0.054) = \log_{10}^*\beta^\circ(\text{C.13}) \\ \text{slope} &= (0.029 \pm 0.036) = -\Delta\varepsilon \end{aligned}$$

Calculation of the ion interaction coefficient $\varepsilon_{(\text{UO}_2\text{F}^+, \text{ClO}_4^-)} = \Delta\varepsilon + \varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)} - \varepsilon_{(\text{H}^+, \text{ClO}_4^-)}$: From $\varepsilon_{(\text{UO}_2^{2+}, \text{ClO}_4^-)} = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$, $\varepsilon_{(\text{H}^+, \text{ClO}_4^-)} = (0.14 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$ (see Appendix B) and the slope of the linear regression, $\Delta\varepsilon = -(0.03 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$, it follows that $\varepsilon_{(\text{UO}_2\text{F}^+, \text{ClO}_4^-)} = (0.29 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$.

Note that the uncertainty (± 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

$$\begin{aligned} \log_{10}^* \beta^\circ (\text{C.13}) &= (1.84 \pm 0.05) \\ \varepsilon_{(\text{UO}_2\text{F}^+, \text{ClO}_4^-)} &= (0.29 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1} \end{aligned}$$

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



are available in different electrolyte media:

$$I_c = 0.1 \text{ M (KNO}_3\text{)}: \quad \log_{10} \beta(\text{C.14}) = (1.19 \pm 0.03)$$

$$I_c = 0.33 \text{ M (KNO}_3\text{)}: \quad \log_{10} \beta(\text{C.14}) = (0.90 \pm 0.10)$$

$$I_c = 1.0 \text{ M (NaClO}_4\text{)}: \quad \log_{10} \beta(\text{C.14}) = (0.75 \pm 0.03)$$

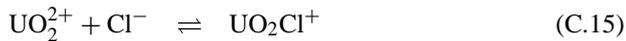
$$I_c = 1.0 \text{ M (NaClO}_4\text{)}: \quad \log_{10} \beta(\text{C.14}) = (0.76 \pm 0.03)$$

$$I_c = 1.0 \text{ M (NaClO}_4\text{)}: \quad \log_{10} \beta(\text{C.14}) = (0.93 \pm 0.03)$$

$$I_c = 2.5 \text{ M (NaNO}_3\text{)}: \quad \log_{10} \beta(\text{C.14}) = (0.72 \pm 0.03)$$

The uncertainties are assumed to represent the 95% confidence level. From the values at $I_c = 1 \text{ M}$, it can be seen that there is a lack of consistency in the data, and that a linear regression 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



The value of $\Delta\varepsilon(\text{C.15}) = -(0.25 \pm 0.02)$ was obtained from a linear regression using 16 experimental data between $I_c = 0.1 \text{ M}$ and $I_c = 3 \text{ M Na(Cl,ClO}_4\text{)}$ [92GRE/FUG]. It is thus assumed that

$$\Delta\varepsilon(\text{C.14}) = \Delta\varepsilon(\text{C.15}) = -(0.25 \pm 0.02)$$

The correction of $\log_{10} \beta(\text{C.14})$ to $I_c = 0$ is done using the specific ion interaction equation, *cf.* TDB-2, which uses molal units:

$$\log_{10} \beta + 4D = \log_{10} \beta^\circ - \Delta\varepsilon I_m \quad (\text{C.16})$$

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±0.03 ^(a)
0.335	KNO ₃	(0.90 ± 0.10)	0.617	−0.084	1.65±0.10 ^(a)
1.050	NaClO ₄	(0.75 ± 0.03)	0.822	−0.263	1.31±0.04
1.050	NaClO ₄	(0.76 ± 0.03)	0.822	−0.263	1.32±0.04
1.050	NaClO ₄	(0.93 ± 0.03)	0.822	−0.263	1.49±0.04
2.714	NaNO ₃	(0.72 ± 0.03)	0.968	−0.679	1.82±0.13 ^(a)

^(a) These values were corrected for the formation of the nitrate complex UO_2NO_3^+ by using $\log_{10} K(\text{UO}_2\text{NO}_3^+) = (0.30 \pm 0.15)$ [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

$$\log_{10} \beta^\circ = (1.56 \pm 0.39)$$

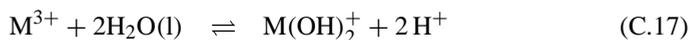
C.4 Procedures for data handling

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 dm³ of solution (molar, M) and has to be converted to moles per kg H₂O (molal, m), as the model requires. Conversion factors for the most common inert salts are given in Table 2.5.

Example C.6:

For the equilibrium constant of the reaction



only one credible determination in 3 M NaClO₄ solution is known, $\log_{10}^*\beta(\text{C.17}) = -6.31$, to which an uncertainty of ± 0.12 has been assigned. The ion interaction coefficients are as follows:

$$\begin{aligned}\varepsilon_{(\text{M}^{3+}, \text{ClO}_4^-)} &= (0.56 \pm 0.03) \text{kg}\cdot\text{mol}^{-1} \\ \varepsilon_{(\text{M}(\text{OH})_2^+, \text{ClO}_4^-)} &= (0.26 \pm 0.11) \text{kg}\cdot\text{mol}^{-1} \\ \varepsilon_{(\text{H}^+, \text{ClO}_4^-)} &= (0.14 \pm 0.02) \text{kg}\cdot\text{mol}^{-1}\end{aligned}$$

The values of $\Delta\varepsilon$ and $\sigma_{\Delta\varepsilon}$ can be obtained readily (*cf.* Eq. C.19):

$$\begin{aligned}\Delta\varepsilon &= \varepsilon_{(\text{M}(\text{OH})_2^+, \text{ClO}_4^-)} + 2\varepsilon_{(\text{H}^+, \text{ClO}_4^-)} - \varepsilon_{(\text{M}^{3+}, \text{ClO}_4^-)} = -0.02 \text{kg}\cdot\text{mol}^{-1} \\ \sigma_{\Delta\varepsilon} &= \sqrt{(0.11)^2 + (2 \times 0.02)^2 + (0.03)^2} = 0.12 \text{kg}\cdot\text{mol}^{-1}\end{aligned}$$

The two variables are thus:

$$\begin{aligned}\log_{10}^*\beta(\text{C.17}) &= -(6.31 \pm 0.12) \\ \Delta\varepsilon &= -(0.02 \pm 0.13) \text{kg}\cdot\text{mol}^{-1}\end{aligned}$$

According to the specific ion interaction model the following equation is used to correct for ionic strength for the reaction considered here:

$$\log_{10}^*\beta(\text{C.17}) + 6D = \log_{10}^*\beta^\circ(\text{C.17}) - \Delta\varepsilon m_{\text{ClO}_4^-}$$

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 $m_{\text{ClO}_4^-}$ ($I_m \approx m_{\text{ClO}_4^-}$) have to be expressed in molal units, 3 M NaClO₄ corresponding to 3.5 m NaClO₄ (see Section 2.2), giving $D = 0.25$. This results in

$$\log_{10}^*\beta^\circ(\text{C.17}) = -4.88$$

The uncertainty in $\log_{10}^*\beta^\circ$ is calculated from the uncertainties in $\log_{10}^*\beta$ and $\Delta\varepsilon$ (*cf.* Eq. C.19):

$$\sigma_{\log_{10}^*\beta^\circ} = \sqrt{\sigma_{\log_{10}^*\beta}^2 + (m_{\text{ClO}_4^-} \sigma_{\Delta\varepsilon})^2} = \sqrt{(0.12)^2 + (3.5 \times 0.12)^2} = 0.44.$$

The selected, rounded value is

$$\log_{10}^*\beta^\circ(\text{C.17}) = -(4.9 \pm 0.4)$$

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, \dots, Y_N .

$$\sigma_X^2 = \sum_{i=1}^N \left(\frac{\partial X}{\partial Y_i} \sigma_{Y_i} \right)^2 \quad (\text{C.18})$$

Eq. (C.18) can be used only if the variables Y_1, Y_2, \dots, 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.

$$X = c_1 Y_1 \pm c_2 Y_2 : \quad \sigma_X^2 = (c_1 \sigma_{Y_1})^2 + (c_2 \sigma_{Y_2})^2 \quad (\text{C.19})$$

$$X = \pm c Y_1 Y_2 \quad \text{and} \quad X = \pm \frac{c Y_1}{Y_2} : \quad \left(\frac{\sigma_X}{X} \right)^2 = \left(\frac{\sigma_{Y_1}}{Y_1} \right)^2 + \left(\frac{\sigma_{Y_2}}{Y_2} \right)^2 \quad (\text{C.20})$$

$$X = c_1 Y^{\pm c_2} : \quad \frac{\sigma_X}{X} = c_2 \frac{\sigma_Y}{Y} \quad (\text{C.21})$$

$$X = c_1 e^{\pm c_2 Y} : \quad \frac{\sigma_X}{X} = c_2 \sigma_Y \quad (\text{C.22})$$

$$X = c_1 \ln(\pm c_2 Y) : \quad \sigma_X = c_1 \frac{\sigma_Y}{Y} \quad (\text{C.23})$$

Example C.7:

A few simple calculations illustrate how these formulas are used. The values have not been rounded.

$$\begin{aligned} \text{Eq. (C.19)} : \quad \Delta_r G_m &= 2[-(277.4 \pm 4.9)] \text{ kJ} \cdot \text{mol}^{-1} - [-(467.3 \pm 6.2)] \text{ kJ} \cdot \text{mol}^{-1} \\ &= -(87.5 \pm 11.6) \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\text{Eq. (C.20)} : \quad K = \frac{(0.038 \pm 0.002)}{(0.0047 \pm 0.0005)} = (8.09 \pm 0.92)$$

$$\text{Eq. (C.21)} : \quad K = 4(3.75 \pm 0.12)^3 = (210.9 \pm 20.3)$$

$$\begin{aligned} \text{Eq. (C.22)} : \quad K^\circ &= e^{\frac{-\Delta_r G_m^\circ}{RT}}; & \Delta_r G_m^\circ &= -(2.7 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1} \\ & & R &= 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ & & T &= 298.15 \text{ K} \end{aligned}$$

$$K^\circ = (2.97 \pm 0.36)$$

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.*,

$$\log_{10} K = (2.45 \pm 0.10); \quad K = 10^{\log_{10} K} = e^{(\ln(10) \log_{10} K)} = (282 \pm 65).$$

$$\text{Eq. (C.23): } \begin{aligned} \Delta_r G_m^\circ &= -RT \ln K^\circ; & K^\circ &= (8.2 \pm 1.2) \times 10^6 \\ R &= 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ T &= 298.15 \text{ K} \end{aligned}$$

$$\begin{aligned} \Delta_r G_m^\circ &= -(39.46 \pm 0.36) \text{ kJ} \cdot \text{mol}^{-1} \\ \ln K^\circ &= 15.92 \pm 0.15 \\ \log_{10} K^\circ &= \ln K^\circ / \ln(10) = (6.91 \pm 0.06) \end{aligned}$$

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.

$$\begin{aligned} \text{Example: } & 3.478 \pm 0.008 \\ & 3.48 \pm 0.01 \\ & 2.8 \pm 0.4 \end{aligned}$$

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.

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