

**CHEMICAL THERMODYNAMICS  
OF COMPOUNDS AND COMPLEXES OF  
U, Np, Pu, Am, Tc, Se, Ni and Zr  
WITH SELECTED ORGANIC LIGANDS**

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# Preface

This book is the ninth of the series “Chemical Thermodynamics” edited by the OECD Nuclear Energy Agency (NEA), and it is the first review in this series focused on organic ligands.

This *Organics Review* was initiated by the Management Board of the NEA Thermochemical Database Project Phase II (NEA TDB II). Originally Wolfgang Hummel (PSI, Switzerland), Giorgio Anderegg (ETH Zürich, Switzerland), Ignasi Puigdomènech (SKB, Sweden), Osamu Tochiyama (Tohoku University, Sendai, Japan), Josef Havel and Přemek Lubal (Masaryk University, Brno, Czech Republic) participated in the Organics Review. In August 2003 time constraints and the pressure of other commitments forced Josef Havel and Přemek Lubal to resign from the Review Team. In December 2003 Linfeng Rao (LBNL, Berkeley, USA) joined the Review Team.

The first meeting of the Organics Review Group was held in August 1998 at the NEA Headquarters at Issy-les-Moulineaux (France) and six plenary meetings followed in October 1999 (Brno, Czech Republic), April 2000 (Sendai, Japan), November 2000 (PSI, Switzerland), September 2001 (Bregenz, Austria), October 2002 (PSI, Switzerland) and January 2004 (OECD, Paris, France). The Executive Group of the Management Board provided scientific assistance and Hans Wanner, as the designated member of the Executive Group, participated in some of the Review Group meetings and maintained close contact with the chairman of the Organics Review Team.

At the NEA Data Bank the responsibility for the overall co-ordination of the Project was placed with Eric Östhols (from its initiation in 1998 to February 2000), with Stina Lundberg (from March 2000 to September 2000) and with Federico Mompean (since September 2000). Federico Mompean was in charge of the preparation of the successive drafts, updating the NEA thermodynamic database and editing the book to its present final form, with assistance from Myriam Illemassène and Jane Perrone.

All the members of the Review Team contributed fully to the main text and the discussions, and the excellent internal communication of the team has to be noted here. However, the workload was distributed according to the expertise of each member. Wolfgang Hummel was the principal author of the sections about oxalic acid, protonation and Na and K interactions of oxalate, while Josef Havel and Přemek Lubal were initially involved in reviewing the compounds and complexes of oxalate. Ignasi Puigdomènech reviewed citric acid and ethylenediaminetetraacetic acid, as well as protonation and Na and K interactions of citrate and edta. Osamu Tochiyama was the principal author of all sections concerning metal citrate complexes, whereas Giorgio Anderegg carried out the review of edta complexes with the editorial help of Wolfgang

Hummel. After the resignation of Josef Havel and Přemek Lubal their remaining tasks were reassigned: Linfeng Rao reviewed uranium oxalate compounds and complexes, Wolfgang Hummel Ca and Mg oxalates, Osamu Tochiyama Zr and Am oxalates and Ignasi Puigdomènech Ni, Tc, Se, Np and Pu oxalates. The chapter on iso-saccharinic acid and compounds and complexes of isa is a joint review of Linfeng Rao and Wolfgang Hummel.

Villigen, Switzerland, March 2005

Wolfgang Hummel, Chairman



# Acknowledgements

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ANSTO, Australia  
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IPSN (now IRSN), France  
FZK, Germany  
JNC, Japan  
ENRESA, Spain  
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At the NEA Data Bank, Pierre Nagel and Eric Lacroix have provided excellent software and advice, which have eased the editorial and database work. Cynthia Picot, Solange Quarneau and Amanda Costa from NEA Publications have provided considerable help in editing the present series. Their contributions and the support of many NEA staff members are highly appreciated.

Jan Rosdahl (Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden) helped through literature searches in preparing several figures showing molecular structures of complexes. His contribution is gratefully recognized.

Ingmar Grenthe (Inorganic Chemistry, Royal Institute of Technology, Stockholm, Sweden) reviewed early versions of Chapters VII and VIII. His contributions are gratefully acknowledged.

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 Guideline, available from the NEA. The peer reviewers have seen and approved the modifications made by the authors in response to their comments. The peer review comment records may be obtained on request from the OECD Nuclear Energy Agency. The peer reviewers were:

Prof. Gregory R. Choppin, Florida State University, Tallahassee, Florida, USA

Prof. Pier G. Daniele, University of Turin, Turin, Italy

Prof. Alfredo Mederos, University of La Laguna, Tenerife, Spain

Their contributions are gratefully acknowledged.

# **Note from the Chairman of the NEA TDB Project Phase II**

The need to make available a comprehensive, internationally recognised and quality-assured chemical thermodynamic database that meets the modelling requirements for the safety assessment of radioactive waste disposal systems prompted the Radioactive Waste Management Committee (RWMC) of the OECD Nuclear Energy Agency (NEA) to launch in 1984 the Thermochemical Database Project (NEA TDB) and to foster its continuation as a semi-autonomous project known as NEA TDB Phase II in 1998.

The RWMC assigned a high priority to the critical review of relevant chemical thermodynamic data of inorganic species and compounds of the actinides uranium, neptunium, plutonium and americium, as well as the fission product technetium. The first four books in this series on the chemical thermodynamics of uranium, americium, neptunium and plutonium, and technetium originated from this initiative.

The organisation of Phase II of the TDB Project reflects the interest in many OECD/NEA member countries for a timely compilation of the thermochemical data that would meet the specific requirements of their developing national waste disposal programmes.

The NEA TDB Phase II Review Teams, comprising internationally recognised experts in the field of chemical thermodynamics, exercise their scientific judgement in an independent way during the preparation of the review reports. The work of these Review Teams has also been subjected to further independent peer review.

Phase II of the TDB Project consisted of: (i) updating the existing, CODATA-compatible database for inorganic species and compounds of uranium, neptunium, plutonium, americium and technetium, (ii) extending it to include selected data on inorganic species and compounds of nickel, selenium and zirconium, (iii) and further adding data on organic complexes of citrate, oxalate, edta and iso-saccharinic acid (isa) with uranium, neptunium, plutonium, americium, technetium, nickel, selenium, zirconium and some other competing cations.

The NEA TDB Phase II objectives were formulated by the 17 participating organisations coming from the fields of radioactive waste management and nuclear regulation. The TDB Management Board is assisted for technical matters by an Executive Group of experts in chemical thermodynamics. In this second phase of the Project, the

NEA acts as coordinator, ensuring the application of the Project Guidelines and liaising with the Review Teams.

The present volume is the fifth one published within the scope of NEA TDB Phase II. It contains a database for organic complexes of citrate, oxalate, edta and iso-saccharinic acid (isa) with uranium, neptunium, plutonium, americium, technetium, nickel, selenium, zirconium and some other competing cations. We trust that the efforts of the reviewers, the peer reviewers and the NEA Data Bank staff merit the same high recognition from the broader scientific community as received for previous volumes of this series.

Mehdi Askarieh

United Kingdom Nirex limited

Chairman of TDB Project Phase II Management Board

On behalf of the NEA TDB Project Phase II Participating Organisations:

ANSTO, Australia

ONDRAF/NIRAS, Belgium

RAWRA, Czech Republic

POSIVA, Finland

ANDRA, France

IPSN (now IRSN), France

FZK, Germany

JNC, Japan

ENRESA, Spain

SKB, Sweden

SKI, Sweden

HSK, Switzerland

NAGRA, Switzerland

PSI, Switzerland

BNFL, UK

Nirex, UK

DoE, USA

## Editor's note

This is the ninth volume of a series of expert reviews of the chemical thermodynamics of key chemical elements in nuclear technology and waste management. This volume is devoted to organic compounds and complexes of citrate, oxalate, edta and iso-saccharinic acid (isa) with uranium, neptunium, plutonium, americium, technetium, selenium, nickel, zirconium and some other competing cations. The tables contained in Chapters III and IV list the currently selected thermodynamic values within the NEA TDB Project. The database system developed at the NEA Data Bank, see Section II.6, assures consistency among all the selected and auxiliary data sets.

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

**How to contact the NEA TDB Project**

Information on the NEA and the TDB Project, on-line access to selected data and computer programs, as well as many documents in electronic format are available at

[www.nea.fr](http://www.nea.fr).

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

TDB project coordinator  
OECD Nuclear Energy Agency, Data Bank  
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F-92130 Issy-les-Moulineaux  
FRANCE

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 and PHRQPITZ, 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.

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# **Part I**

## **Introductory material**





# Chapter I

## Introduction

### I.1 Background

The modelling of the behaviour of hazardous materials under environmental conditions is among the most important applications of natural and technical sciences for the protection of the environment. In order to assess, for example, the safety of a waste deposit, it is essential to be able to predict the eventual dispersion of its hazardous components in the environment (geosphere, biosphere). For hazardous materials stored in the ground or in geological formations, the most probable transport medium is the aqueous phase. An important 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, in addition to lesser amounts from other sources such as waste from medicine, industry and research facilities. The scientific literature on thermodynamic data, mainly on equilibrium constants and redox potentials in aqueous solution, has been contradictory in a number of cases, especially in actinide chemistry. A critical and comprehensive review of the available literature is necessary in order to establish a reliable thermochemical database that fulfils the requirements for rigorous 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 volumes, 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 recognised the need for an internationally acknowledged, high-quality thermochemical database for application in the safety assessment of radioactive waste disposal, and undertook the development of the NEA Thermochemical Data Base (TDB) project [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. The first four books in this series on the chemical thermodynamics of uranium [92GRE/FUG], americium [95SIL/BID], technetium [99RAR/RAN] and neptunium and plutonium [2001LEM/FUG] originated from this initiative. Simultaneously with the NEA TDB project, other reviews on the physical and chemical properties of actinides 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 review series mentioned above.

In 1998, Phase II of the TDB Project (TDB-II) was started to provide for the further needs of the radioactive waste management programs by updating the existing database and applying the TDB review methodology to other elements (nickel, selenium, zirconium) and to simple organic compounds and complexes. In TDB-II the overall objectives are set by a Management Board, integrated by the representatives of 17 organisations from the field of radioactive waste management. These participating organisations, together with the NEA, provide financial support for TDB-II. The TDB-II Management Board is assisted in technical matters by a group of experts in chemical thermodynamics (the Executive Group). The NEA acts in this phase as Project Coordinator ensuring the implementation of the Project Guidelines and liaising with the Review Teams. After the update on the chemical thermodynamics of uranium, neptunium, plutonium, americium and technetium [2003GUI/FAN], and the books on chemical thermodynamics of nickel [2005GAM/BUG], selenium [2005OLI/NOL] and zirconium [2005BRO/CUR], the present volume is the fifth to be published within this second phase of the TDB project.

## I.2 Focus of the review

This NEA TDB organics review is within the scope and the spirit of the previous reviews aimed at helping to model the chemical behaviour of actinides and fission and activation products in the near and far field of a radioactive waste repository using consistent data. The present critical review deals with compounds and complexes of U, Np, Pu, Am, Tc, Se, Ni, Zr as well as H, Na, K, Mg, Ca with oxalate, citrate, ethylenediaminetetraacetate (edta) and iso-saccharinate (isa).

A prerequisite for a successful widely recognized critical evaluation of thermodynamic data is the sensible decision which organic ligands the evaluation should comprise. This decision has two aspects, namely the importance of the ligands in radioactive waste problems, and the availability of experimental data. The “Agreement of the OECD/NEA Thermochemical Data Base Project (Phase II)” states in Annex I that the evaluation of organic ligands should be limited to oxalate, citrate, edta and isa.

From the viewpoint of importance for radioactive waste problems this set of ligands is very well posed. Oxalate is, with respect to its complexation strength, the major product of radiolytic degradation of bitumen, sometimes used for waste conditioning, and ion exchange resins used in decontamination procedures. In addition, oxalate is one of the strong complexing natural organic ligands (besides humic substances). Citrate and edta are used in decontamination processes and thus, they become part of the radioactive waste inventory. In terms of complexation strength, oxalate, citrate and edta cover a wide range of complex stability, and they may be used in model calculations as representatives of dicarboxylic acids (oxalate), hydroxy-polycarboxylic acids (citrate) and polyamino-polycarboxylic acids (edta). Finally, from the viewpoint of complexation strength, isa is the most important product of alkaline degradation of cellulose in cement pore waters. Thus, isa is of major concern in many performance assessments of planned radioactive waste repositories.

Regarding the availability of experimental data, the situation is less clear. In the case of oxalate, citrate and edta a large body of experimental studies has been published and this review provides, based on the critical discussion of several hundreds of publications, a considerable set of selected thermodynamic values. However, in the case of isa the number of experimental studies is very limited and, despite of the importance of isa for performance assessments, only a few thermodynamic values could be selected. The critical review of experimental studies concerning isa mainly is a status report pointing out gaps in our present knowledge and further research needs.

As the task of the present review on organic ligands is to complement the other reviews of the NEA TDB project, which are restricted to inorganic compounds and complexes of actinides and fission and activation products, a natural choice of elements comprises U, Np, Pu, Am, Tc, Se, Ni and Zr. However, this review cannot be restricted to these elements as it aims at a thermodynamic data set useful for practical application. In addition to the above mentioned actinides and fission and activation products this

review considers also the major constituents of ground and surface waters which may interact with the selected organic ligands, *i.e.*, H, Na, K, Mg and Ca. Any geochemical model including organic ligands should take into account these competing interactions and therefore, the present review provides a selected consistent set of these auxiliary constants.

The protonation equilibria (complexation with  $H^+$ ) of the organic ligands belong to the basic data of these systems and have been, in general, very well studied. They are considered in the present review as the main auxiliary data for the critical evaluation of metal – ligand complexation in the review itself, and as the most important auxiliary data for practical application.

The situation is more complicated for Na and K interactions. Here, we are in the realm of ambiguity characterised by the question: “Weak complexation or strong specific ion interaction?”. As discussed in Chapters V, VI, VII and VIII the answer is different for different ligands. In the case of oxalate, Na and K interactions are treated solely as specific ion interactions. In the case of edta, Na and K complexation constants had to be included in the speciation models. Na and K interactions with citrate are in between these two extremes. In the course of the review process both variants have been evaluated and compared, and finally the review team decided to treat the effects of Na and K on citrate solely as rather strong specific ion interactions.

The elements Ca and Mg are included in the present review because complexation of the organic ligands with these competing cations is of importance in geochemical models concerning the complexation of actinides and fission products in common ground and surface waters.

Further auxiliary data are taken both from the publication of CODATA key values [\[89COX/WAG\]](#) and from the evaluation of additional auxiliary data in this series of NEA TDB reviews [\[92GRE/FUG\]](#), [\[99RAR/RAN\]](#), [\[2003GUI/FAN\]](#), [\[2005GAM/BUG\]](#) and [\[2005OLI/NOL\]](#) and their use is recommended by this review.

Care has been taken that all the selected thermodynamic data at standard state and conditions (*cf.* Section II.3) and 298.15 K are internally consistent. For this purpose, special software within the NEA TDB database system has been used; *cf.* Section II.6. In order to maintain consistency in the application of the values selected by this review, it is essential to use the NEA TDB selected and auxiliary data when calculating equilibrium constants involving actinide and fission product compounds and complexes.

### I.3 Review procedure and results

The literature has been surveyed up to the end of 2001 for all ligands. For oxalate a few more recent references are included, and for *isa* the aim had been to consider all relevant literature up to the end of 2004. Experimental measurements published in the scientific

literature are the main source for the selection of recommended data. Previous reviews are not neglected. They have been primarily used as sources for original scientific literature, but they also form a valuable source of critical information on the quality of primary publications.

In the realm of metal – organic complexes a plethora of experimental studies is found in the literature dealing with mixed complexes, *i.e.*, complexes containing a common metal ion and two or more different ligands. In this review mixed complexes, in general, were considered if they contain combinations of oxalate, citrate, edta and isa with or without additional inorganic ligands. Mixed complexes comprising other organic ligands are mentioned occasionally for qualitative comparison only. From the viewpoint of application, by far the most important class of mixed complexed are ternary metal – hydroxide – organic ligand complexes. These hydrolysed organic complexes may predominate in alkaline ground and surface waters and in high pH cement pore waters and thus, they are important in assessing the influence of organic ligands on radionuclide complexation in cementitious repositories. The relevant literature about such complexes is discussed in the present review, but only in a few cases reliable thermodynamic constants could be selected. Also of importance in many ground and surface waters would be the class of metal – carbonate – organic ligand complexes. However, this review can only state the almost complete lack of such data.

The detailed discussion of organic compounds has been restricted in this review to the so-called “sparingly soluble” solids. These are mainly metal oxalates, which are considered in several sections of Chapter VI. The generally rather soluble citrate and edta compounds are discussed in qualitative terms only in Chapters VII and VIII. From the viewpoint of model application in performance assessments the most important solid is calcium oxalate, because the possible precipitation of this solid in many ground and surface waters can limit the concentration of dissolved oxalate to rather low levels.

When necessary, experimental source data are re-evaluated by using chemical models that are either found to be more realistic than those used by the original author, or are consistent with side-reactions discussed in another section of the review (for example, data on metal complex formation might need to be re-interpreted to take into account consistent values for ligand protonation reactions). Re-evaluation of literature values might also be necessary to correct for known systematic effects (for example, if metal – chloride complexation has been neglected in the original literature) 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 [\[2000OST/WAN\]](#), [\[2000GRE/WAN\]](#), [\[2000WAN/OST\]](#), [\[99WAN\]](#), [\[99WAN/OST\]](#).

Some of these procedures are also outlined in this volume, *cf.* Chapter II, Appendix B and Appendix C. Particular problems encountered in this review on organic ligands are discussed in detail in Chapter V.

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 judgments 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 persons having technical expertise in the subject matter to be reviewed, to a degree at least equivalent to that needed for the original review.

The thermodynamic data selected in the present review (see Chapters III and IV) refer to the reference temperature of 298.15 K and to standard conditions, *cf.* Section II.3. For the modelling of real systems it is, in general, necessary to recalculate the standard thermodynamic data to non-standard 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. 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 on which they are based. The quality aspect includes both the numerical values of the thermodynamic data used in the model and the “completeness” of the chemical model used, *e.g.*, the inclusion of all 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 III and IV) is certainly not “complete” with respect to all the conceivable systems and conditions; there are gaps in the information. The gaps are pointed out in the various sections of Chapters VI, VII, VIII and IX, and this information may be used as a basis for the assignment of research priorities.

## Chapter II

# Standards, Conventions and Contents of the Tables

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

### II.1 Symbols, terminology and nomenclature

#### II.1.1 Abbreviations

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

Table II-1: Abbreviations for experimental methods.

aix	Anion exchange
AES	Atomic Emission Spectroscopy
cal	Calorimetry
chr	Chromatography
cix	Cation exchange
col	Colorimetry
con	Conductivity
cou	Coulometry
cry	Cryoscopy
dis	Distribution between two phases
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
EDS	Energy Dispersive Spectroscopy
em	Electromigration
emf	Electromotive force, not specified

(Continued on next page)

Table II-1: (continued)

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

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



## II.1.2 Symbols and terminology

The symbols for physical and chemical quantities used in the TDB review follow the recommendations of the International Union of Pure and Applied Chemistry, IUPAC [79WHI], [93MIL/CVI]. They are summarised in Table II-2.

Table II-2: Symbols and terminology.

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

(Continued next page)

Table II-2 (Continued)

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

- (a) ratio of the average mass per formula unit of a substance to  $\frac{1}{12}$  of the mass of an atom of nuclide  $^{12}\text{C}$ .
- (b) cf. sections 1.2 and 3.6 of the IUPAC manual [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  $N_v X_v$  which dissociates into  $\nu_{\pm}$  ( $= \nu_+ + \nu_-$ ) ions, in an aqueous solution with molality  $m$ , the individual cationic molality and activity coefficient are  $m_+ (= \nu_+ m)$  and  $\gamma_+ (= a_+ / m_+)$ . A similar definition is used for the anionic symbols. Electrical neutrality requires that  $\nu_+ z_+ = \nu_- z_-$ .
- (f) Special notations for equilibrium constants are outlined in Section II.1.6. 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 II.3.1.

### II.1.3 Chemical formulae and nomenclature

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

- The formulae of coordination compounds and complexes are not enclosed in square brackets [71JEN] (Rule 7.21). Exceptions are made in cases where square brackets are required to distinguish between coordinated and uncoordinated ligands.
- The prefixes “oxy–” and “hydroxy–” are retained if used in a general way, *e.g.*, “gaseous uranium oxyfluorides”. For specific formula names, however, the IUPAC recommended citation [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:  $\text{H}_3\text{edta}^-$ ,  $\text{Am}(\text{Hedta})(\text{s})$  (where edta stands for ethylenediaminetetraacetate).

### II.1.4 Phase designators

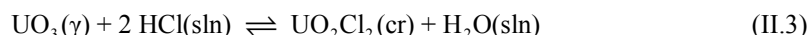
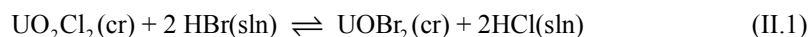
Chemical formulae may refer to different chemical species and are often required to be specified more clearly in order to avoid ambiguities. For example,  $\text{UF}_4$  occurs as a gas, a solid, and an aqueous complex. The distinction between the different phases is made by phase designators that immediately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

- The designator (l) is used for pure liquid substances, *e.g.*,  $\text{H}_2\text{O}(\text{l})$ .
- 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  $\text{H}_2\text{O}$  (*e.g.*,  $\text{D}_2\text{O}$ , 90% ethanol/10%

H<sub>2</sub>O), then (aq) is replaced by a more explicit designator, *e.g.*, “(in D<sub>2</sub>O)” or “(sln)”. In the case of (sln), the composition of the solution is described in the text.

- The designator (sln) is used for substances in solution without specifying the actual equilibrium composition of the substance in the solution. Note the difference in the designation of H<sub>2</sub>O in Eqs.(II.2) and (II.3). H<sub>2</sub>O(l) in Reaction (II.2) indicates that H<sub>2</sub>O is present as a pure liquid, *i.e.*, no solutes are present, whereas Reaction (II.3) involves an HCl solution, in which the thermodynamic properties of H<sub>2</sub>O(sln) may not be the same as those of the pure liquid H<sub>2</sub>O(l). In dilute solutions, however, this difference in the thermodynamic properties of H<sub>2</sub>O can be neglected, and H<sub>2</sub>O(sln) may be regarded as pure H<sub>2</sub>O(l).

Example:



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

Phase designators are also used in conjunction with thermodynamic symbols to define the state of aggregation of a compound to which a thermodynamic quantity refers. The notation is in this case the same as outlined above. In an extended notation (*cf.* [82LAF]) the reference temperature is usually given in addition to the state of aggregation of the composition of a mixture.

Example:

$\Delta_f G_m^\circ(\text{Na}^+, 298.15 \text{ K})$	standard molar Gibbs energy of formation of aqueous Na <sup>+</sup> 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 <sub>2</sub> (SO <sub>4</sub> ) · 2.5H <sub>2</sub> O(cr) at 298.15 K

$C_{p,m}^{\circ}(\text{UO}_3, \alpha, 298.15 \text{ K})$	standard molar heat capacity of $\alpha - \text{UO}_3$ at 298.15 K
$\Delta_f H_m(\text{HF, sln, HF} \cdot 7.8\text{H}_2\text{O})$	enthalpy of formation of HF diluted 1:7.8 with water.

### II.1.5 Processes

Chemical processes are denoted by the operator  $\Delta$ , written before the symbol for a property, as recommended by IUPAC [82LAF]. An exception to this rule is the equilibrium constant, *cf.* Section II.1.6. The nature of the process is denoted by annotation of the  $\Delta$ , *e.g.*, the Gibbs energy of formation,  $\Delta_f G_m$ , the enthalpy of sublimation,  $\Delta_{\text{sub}} H_m$ , *etc.* The abbreviations of chemical processes are summarised in Table II-3.

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

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

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

### II.1.6 Equilibrium constants

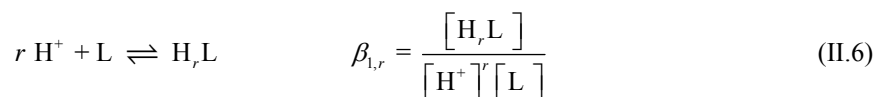
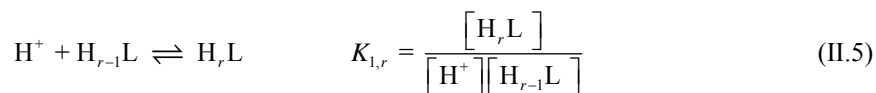
The IUPAC has not explicitly defined the symbols and terminology for equilibrium constants of reactions in aqueous solution. The NEA has therefore adopted the conventions that have been used in the work *Stability Constants of Metal Ion Complexes* by Sillén and Martell [64SIL/MAR], [71SIL/MAR]. An outline 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 to which the data refer, especially in cases where several ligands are discussed that might be confused. For example, for the equilibrium:



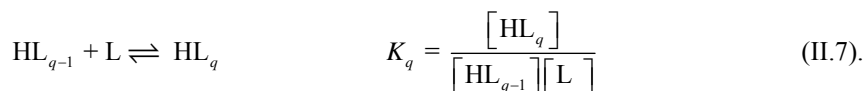
both  $\beta_{q,m}$  and  $\beta$  (II.4) would be appropriate, and  $\beta_{q,m}$  (II.4) is accepted, too. Note that, in general,  $K$  is used for the consecutive or stepwise formation constant, and  $\beta$  is used for the cumulative or overall formation constant. In the following outline, charges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

### II.1.6.1 Protonation of a ligand

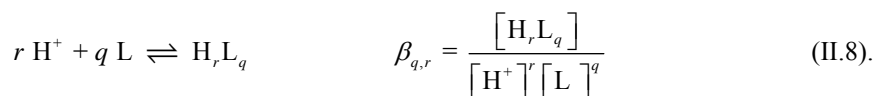


This notation has been proposed and used by Sillén and Martell [64SIL/MAR], but it has been simplified later by the same authors [71SIL/MAR] from  $K_{1,r}$  to  $K_r$ .

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

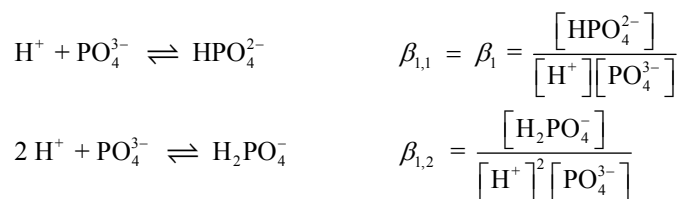


Eq.(II.8) refers to the overall formation constant of the species  $\text{H}_r\text{L}_q$ .

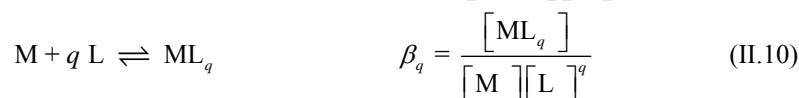
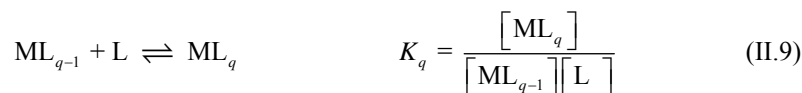


In Eqs.(II.5), (II.6) and (II.8), the second subscript  $r$  can be omitted if  $r = 1$ , as shown in Eq.(II.7).

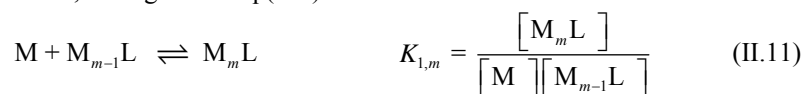
Example:



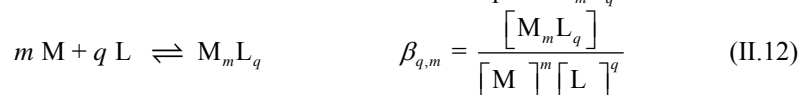
## II.1.6.2 Formation of metal complexes



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

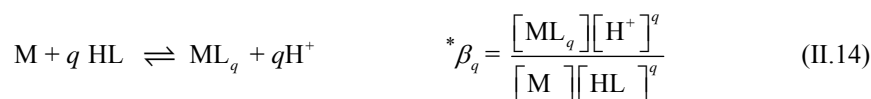


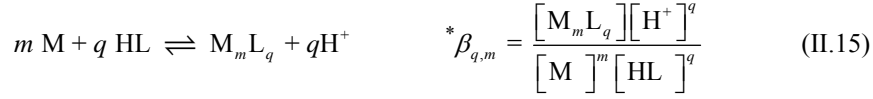
Eq.(II.12) refers to the overall formation constant of a complex  $\text{M}_m\text{L}_q$ .



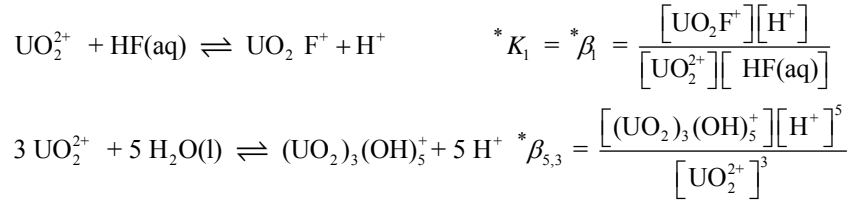
The second index can be omitted if it is equal to 1, *i.e.*,  $\beta_{q,m}$  becomes  $\beta_q$  if  $m = 1$ . The formation constants of mixed ligand complexes are not indexed. In this case, it is necessary to list the chemical reactions considered and to refer the constants to the corresponding reaction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

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





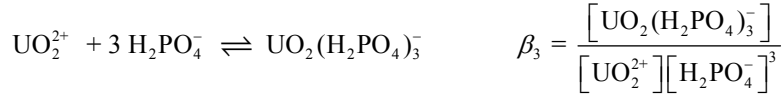
Example:



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



Example:

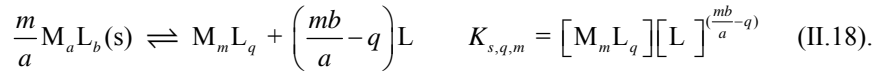


### II.1.6.3 Solubility constants

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



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



Example:



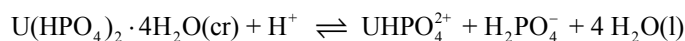


Similarly, an asterisk is added to the solubility constant if it simultaneously involves a protonation equilibrium:

$$\frac{m}{a} M_a L_b(s) + \left( \frac{mb}{a} - q \right) H^+ \rightleftharpoons M_m L_q + \left( \frac{mb}{a} - q \right) HL$$

$$^* K_{s,q,m} = \frac{[M_m L_q][HL]^{\left(\frac{mb}{a}-q\right)}}{[H^+]^{\left(\frac{mb}{a}-q\right)}} \quad (\text{II.19})$$

Example:



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

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

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

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

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

Example:

$$\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{aq}) \quad K_{\text{p}} = \frac{[\text{CO}_2(\text{aq})]}{p_{\text{CO}_2}}$$

$$3\text{UO}_2^{2+} + 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightleftharpoons (\text{UO}_2)_3(\text{CO}_3)_6^{6-} + 12\text{H}^+$$

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

$$\text{UO}_2\text{CO}_3(\text{cr}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{UO}_2(\text{CO}_3)_2^{2-} + 2\text{H}^+$$

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

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

#### II.1.6.5 Redox equilibria

Redox reactions are usually quantified in terms of their electrode (half cell) potential,  $E$ , which is identical to the electromotive force (emf) of a galvanic cell in which the elec-

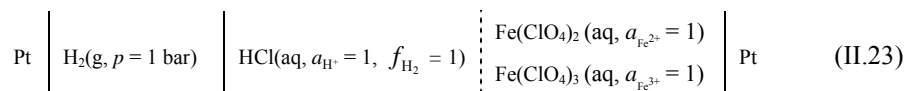
trode on the left is the standard hydrogen electrode, SHE<sup>1</sup>, in accordance with the “1953 Stockholm Convention” [93MIL/CVI]. Therefore, electrode potentials are given as reduction potentials relative to the standard hydrogen electrode, which acts as an electron donor. In the standard hydrogen electrode, H<sub>2</sub>(g) is at unit fugacity (an ideal gas at unit pressure, 0.1 MPa), and H<sup>+</sup> is at unit activity. The sign of the electrode potential,  $E$ , is that of the observed sign of its polarity when coupled with the standard hydrogen electrode. The standard electrode potential,  $E^\circ$ , *i.e.*, the potential of a standard galvanic cell relative to the standard hydrogen electrode (all components in their standard state, *cf.* Section II.3.1, and with no liquid junction potential) is related to the standard Gibbs energy change  $\Delta_r G_m^\circ$  and the standard (or thermodynamic) equilibrium constant  $K^\circ$  as outlined in Eq.(II.21):

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

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

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

For example, for the hypothetical galvanic cell:



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



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



The terminology is useful, although it must be emphasised “e<sup>-</sup>” here does not represent the hydrated electron.

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

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

---

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

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

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

This equation is used to calculate a numerical value of  $a_{e^-}$  from 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:

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

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

In addition,  $\Delta_r G_m^\circ(\text{II.26}) = 0$ ,  $\Delta_r H_m^\circ(\text{II.26}) = 0$ ,  $\Delta_r S_m^\circ(\text{II.26}) = 0$  by definition, at all temperatures, and therefore  $\Delta_r G_m^\circ(\text{II.25}) = \Delta_r G_m^\circ(\text{II.24})$ . From  $\Delta_r G_m^\circ(\text{II.26})$  and the values given at 298.15 K in selected auxiliary data for  $\text{H}_2(\text{g})$  and  $\text{H}^+$ , the corresponding values for  $e^-$  can be calculated to be used in thermodynamic cycles involving half cell reactions. The following equations describe the change in the redox potential of Reaction (II.24), if  $p_{\text{H}_2}$  and  $a_{\text{H}^+}$  are equal to unity (*cf.* Eq.(II.22)):

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

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

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

and from Eq.(II.27):

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

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

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

The splitting of redox reactions into two half cell reactions by introducing the symbol “ $e^-$ ”, which according to Eq.(II.27) is related to the standard electrode potential, is arbitrary, but useful (this  $e^-$  notation does not in any way refer to solvated electrons). When calculating the equilibrium composition of a chemical system, both “ $e^-$ ”, and  $\text{H}^+$  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  $\text{H}^+$

represents the hydrated proton in aqueous solution, the above equations use only the activity of “ $e^-$ ”, and never the concentration of “ $e^-$ ”. Concentration to activity conversions (or activity coefficients) are never needed for the electron (*cf.* Appendix B, Example B.3).

In the literature on geochemical modelling of natural waters, it is customary to represent the “electron activity” of an aqueous solution with the symbol “pe” or “p $\epsilon$ ” ( $= -\log_{10} a_{e^-}$ ) by analogy with pH ( $= -\log_{10} a_{H^+}$ ), and the redox potential of an aqueous solution relative to the standard hydrogen electrode is usually denoted by either “Eh” or “ $E_H$ ” (see for example [81STU/MOR], [82DRE], [84HOS], [86NOR/MUN]).

In this review, the symbol  $E'^o$  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  $E'^o$  parallels that of “concentration quotients” for equilibria). Therefore, from

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

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

$$E'^o = E^o - \frac{RT}{nF} \sum v_i \ln \varrho \gamma_i = -\frac{\Delta_r G_m}{nF} \quad (\text{II.35})$$

where the  $\gamma_i$  are the molality activity coefficients and  $\varrho$  is ( $\frac{m_i}{c_i}$ ), the ratio of molality to molarity (*cf.* Section II.2). The medium must be specified.

### II.1.7 pH

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

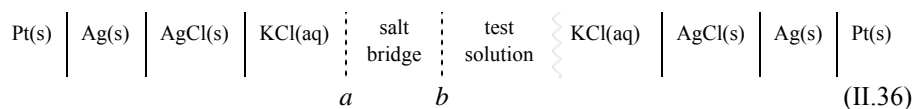
The acidity of aqueous solutions is often expressed in a logarithmic scale of the hydrogen ion activity. The definition of pH as:

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

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

The determination of pH is often performed by emf measurements of galvanic cells involving liquid junctions [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  $\text{---}$  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 liquid junction potential. The purpose of the salt bridge is to minimise the junction potential in junction “*b*”, while keeping constant the junction potential for junction “*a*”. Two methods are most often used to reduce and control the value of  $E_j$ . An electrolyte solution of *high* concentration (the “salt bridge”) is a requirement of both methods. In the first method, the salt bridge is a saturated (or nearly saturated) solution of potassium chloride. A problem with a bridge of high potassium concentration is that potassium perchlorate might precipitate<sup>1</sup> inside the liquid junction when the test solution contains a high concentration of perchlorate ions.

In the other method the salt bridge contains the same *high* concentration of the same inert electrolyte as the test solution (for example, 3 M NaClO<sub>4</sub>). However, if the concentration of the background electrolyte in the salt bridge and test solutions is reduced, the values of  $E_j$  are dramatically increased. For example, if both the bridge and the test solution have [ClO<sub>4</sub><sup>−</sup>] = 0.1 M as background electrolyte, the dependence of the liquid junction at “*b*” on acidity is  $E_j \approx -440 \times [\text{H}^+] \text{ mV} \cdot \text{dm}^3 \cdot \text{mol}^{-1}$  at 25°C [69ROS] (p.110), which corresponds to an error at pH = 2 of  $\geq 0.07$  pH units.

Because of the problems in eliminating the liquid junction potentials and in defining individual ionic activity coefficients, an “operational” definition of pH is given by IUPAC [93MIL/CVI]. This definition involves the measurement of pH differences between the test solution and standard solutions of known pH and similar ionic strength (in this way similar values of  $\gamma_{\text{H}^+}$  and  $E_j$  cancel each other when emf values are subtracted).

The measurement and use of pH in equilibrium analytical investigations creates many problems that have not always been taken into account by the investigators, as discussed in many reviews in Appendix A. In order to deduce the stoichiometry and equilibrium constants of complex formation reactions and other equilibria, it is necessary to vary the concentrations of reactants and products over fairly large concentration ranges under conditions where the activity coefficients of the species are either known,

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

or constant. Only in this manner is it possible to use the mass balance equations for the various components together with the measurement of one or more free concentrations to obtain the information desired [61ROS/ROS], [90BEC/NAG], [97ALL/BAN], p. 326-327. For equilibria involving hydrogen ions, it is necessary to use concentration units, rather than hydrogen ion activity. For experiments in an ionic medium, where the concentration of an “inert” electrolyte is much larger than the concentration of reactants and products we can ensure that, as a first approximation, their trace activity coefficients remain constant even for moderate variations of the corresponding total concentrations. Under these conditions of fixed ionic strength the free proton concentration may be measured directly, thereby defining it in terms of  $-\log_{10}[\text{H}^+]$  (also often referred to as pcH) rather than on the activity scale as pH, and the value of  $-\log_{10}[\text{H}^+]$  and pH will differ by a constant term, *i.e.*,  $\log_{10}\gamma_{\text{H}^+}$ . Equilibrium constants deduced from measurements in such ionic media are therefore *conditional* constants, because they refer to the given medium, not to the standard state. In order to compare the magnitude of equilibrium constants obtained in different ionic media it is necessary to have a method for estimating activity coefficients of ionic species in mixed electrolyte systems to a *common* standard state. Such procedures are discussed in Appendix B.

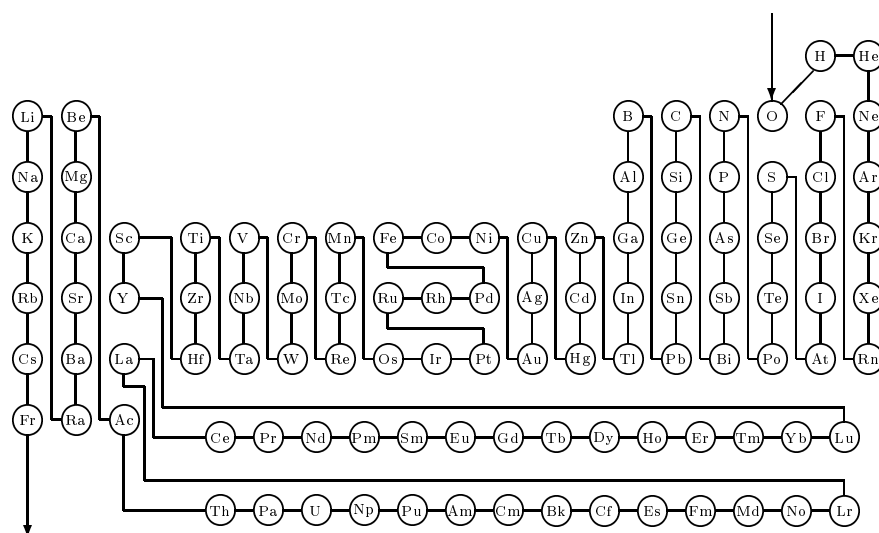
Note that the precision of the measurement of  $-\log_{10}[\text{H}^+]$  and pH is virtually the same, in very good experiments,  $\pm 0.001$ . However, the accuracy is generally considerably poorer, depending in the case of glass electrodes largely on the response of the electrode (linearity, age, pH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

### II.1.8 Order of formulae

To be consistent with CODATA, the data tables are given in “*Standard Order of Arrangement*” [82WAG/EVA]. This scheme is presented in Figure II-1 below, and shows the sequence of the ranks of the elements in this convention. The order follows the ranks of the elements.

For example, for uranium, this means that, after elemental uranium and its monoatomic ions (*e.g.*,  $\text{U}^{4+}$ ), 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  $\text{UOF}_2(\text{cr})$ ,  $\text{UOF}_4(\text{cr})$ ,  $\text{UOF}_4(\text{g})$ ,  $\text{UO}_2\text{F}(\text{aq})$ ,  $\text{UO}_2\text{F}^+$ ,  $\text{UO}_2\text{F}_2(\text{aq})$ ,  $\text{UO}_2\text{F}_2(\text{cr})$ ,  $\text{UO}_2\text{F}_2(\text{g})$ ,  $\text{UO}_2\text{F}_3^-$ ,  $\text{UO}_2\text{F}_4^{2-}$ ,  $\text{U}_2\text{O}_3\text{F}_6(\text{cr})$ , *etc.* [92GRE/FUG]. Formulae with identical stoichiometry are in alphabetical order of their designators.

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



### II.1.9 Reference codes

The references cited in the review are ordered chronologically and alphabetically by the first two authors within each year, as described by CODATA [87GAR/PAR]. A reference code is made up of the final two digits of the year of appearance (if the publication is not from the 20th century, the year will be put in full). The year is followed by the first three letters of the surnames of the first two authors, separated by a slash.

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

## II.2 Units and conversion factors

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

Table II-4: Unit conversion factors.

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

Since a large part of the NEA TDB project deals with the thermodynamics of aqueous solutions, the units describing the amount of dissolved substance are used very frequently. For convenience, this review uses “M” as an abbreviation of “ $\text{mol} \cdot \text{dm}^{-3}$ ” for molarity,  $c$ , and, in Appendices B and C, “m” as an abbreviation of “ $\text{mol} \cdot \text{kg}^{-1}$ ” for molality,  $m$ . It is often necessary to convert concentration data from molarity to molality and vice versa. This conversion is used for the correction and extrapolation of equilibrium data to zero ionic strength by the specific ion interaction theory, which works in molality units (*cf.* Appendix B). This conversion is made in the following way. Molality is defined as  $m_B$  moles of substance B dissolved in 1 kilogram of pure water. Molarity is defined as  $c_B$  moles of substance B dissolved in  $(\rho - c_B M)$  kilogram of pure water, where  $\rho$  is the density of the solution in  $\text{kg} \cdot \text{dm}^{-3}$  and  $M$  the molar weight of the solute in  $\text{kg} \cdot \text{mol}^{-1}$ . From this it follows that:

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

Baes and Mesmer [76BAE/MES], (p.439) give a table with conversion factors (from molarity to molality) for nine electrolytes and various ionic strengths. Conversion factors at 298.15 K for twenty one electrolytes, calculated using the density equations reported by Söhnle and Novotný [85SOH/NOV], are reported in Table II-5.

Example:

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

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,  $0 = \sum_B \nu_B B$ , the equilibrium constants can be expressed either in molarity or molality units,  $K_c$  or  $K_m$ , respectively:

$$\begin{aligned} \log_{10} K_c &= \sum_B \nu_B \log_{10} c_B \\ \log_{10} K_m &= \sum_B \nu_B \log_{10} m_B \end{aligned}$$



With  $(m_B/c_B) = \varrho$ , or  $(\log_{10} m_B - \log_{10} c_B) = \log_{10} \varrho$ , the relationship between  $K_c$  and  $K_m$  becomes very simple, as shown in Eq.(II.37).

$$\log_{10} K_m = \log_{10} K_c + \sum_B \nu_B \log_{10} \varrho \quad (\text{II.37})$$

$\sum_B \nu_B$  is the sum of the stoichiometric coefficients of the reaction, *cf.* Eq. (II.53) and the values of  $\varrho$  are the factors for the conversion of molarity to molality as tabulated in Table II-5 for several electrolyte media at 298.15 K. The differences between the values in Table II-5 and the values listed in the uranium NEA TDB review [92GRE/FUG] (p.23) are found at the highest concentrations, and are no larger than  $\pm 0.003 \text{ dm}^3 \cdot \text{kg}^{-1}$ , reflecting the accuracy expected in this type of conversion. The uncertainty introduced by the use of Eq.(II.37) in the values of  $\log_{10} K_m$  will be no larger than  $\pm 0.001 \sum_B \nu_B$ .

Table II-5: Factors  $\varrho$  for the conversion of molarity,  $c_B$ , to molality,  $m_B$ , of a substance B, in various media at 298.15 K (calculated from densities in [85SOH/NOV]).

$c \text{ (M)}$	$\varrho = m_B / c_B \text{ (dm}^3 \text{ of solution per kg of H}_2\text{O)}$							
	HClO <sub>4</sub>	NaClO <sub>4</sub>	LiClO <sub>4</sub>	NH <sub>4</sub> ClO <sub>4</sub>	Ba(ClO <sub>4</sub> ) <sub>2</sub>	HCl	NaCl	LiCl
0.10	1.0077	1.0075	1.0074	1.0091	1.0108	1.0048	1.0046	1.0049
0.25	1.0147	1.0145	1.0141	1.0186	1.0231	1.0076	1.0072	1.0078
0.50	1.0266	1.0265	1.0256	1.0351	1.0450	1.0123	1.0118	1.0127
0.75	1.0386	1.0388	1.0374	1.0523	1.0685	1.0172	1.0165	1.0177
1.00	1.0508	1.0515	1.0496	1.0703	1.0936	1.0222	1.0215	1.0228
1.50	1.0759	1.0780	1.0750	1.1086	1.1491	1.0324	1.0319	1.0333
2.00	1.1019	1.1062	1.1019		1.2125	1.0430	1.0429	1.0441
3.00	1.1571	1.1678	1.1605		1.3689	1.0654	1.0668	1.0666
4.00	1.2171	1.2374	1.2264			1.0893	1.0930	1.0904
5.00	1.2826	1.3167				1.1147	1.1218	1.1156
6.00	1.3547	1.4077				1.1418		1.1423
$c \text{ (M)}$	KCl	NH <sub>4</sub> Cl	MgCl <sub>2</sub>	CaCl <sub>2</sub>	NaBr	HNO <sub>3</sub>	NaNO <sub>3</sub>	LiNO <sub>3</sub>
0.10	1.0057	1.0066	1.0049	1.0044	1.0054	1.0056	1.0058	1.0059
0.25	1.0099	1.0123	1.0080	1.0069	1.0090	1.0097	1.0102	1.0103
0.50	1.0172	1.0219	1.0135	1.0119	1.0154	1.0169	1.0177	1.0178
0.75	1.0248	1.0318	1.0195	1.0176	1.0220	1.0242	1.0256	1.0256
1.00	1.0326	1.0420	1.0258	1.0239	1.0287	1.0319	1.0338	1.0335
1.50	1.0489	1.0632	1.0393	1.0382	1.0428	1.0478	1.0510	1.0497
2.00	1.0662	1.0855	1.0540	1.0546	1.0576	1.0647	1.0692	1.0667
3.00	1.1037	1.1339	1.0867	1.0934	1.0893	1.1012	1.1090	1.1028
4.00	1.1453	1.1877	1.1241	1.1406	1.1240	1.1417	1.1534	1.1420
5.00		1.2477		1.1974	1.1619	1.1865	1.2030	1.1846
6.00					1.2033	1.2361	1.2585	1.2309

(Continued on next page)

Table II-5 (continued)

$\varrho = m_B / c_B$ (dm <sup>3</sup> of solution per kg of H <sub>2</sub> O)								
$c$ (M)	NH <sub>4</sub> NO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	H <sub>3</sub> PO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	NaSCN
0.10	1.0077	1.0064	1.0044	1.0082	1.0074	1.0027	1.0042	1.0069
0.25	1.0151	1.0116	1.0071	1.0166	1.0143	1.0030	1.0068	1.0130
0.50	1.0276	1.0209	1.0127	1.0319	1.0261	1.0043	1.0121	1.0234
0.75	1.0405	1.0305	1.0194	1.0486	1.0383	1.0065	1.0185	1.0342
1.00	1.0539	1.0406	1.0268	1.0665	1.0509	1.0094	1.0259	1.0453
1.50	1.0818	1.0619	1.0441	1.1062	1.0773	1.0170	1.0430	1.0686
2.00	1.1116	1.0848		1.1514	1.1055	1.0268	1.0632	1.0934
3.00	1.1769	1.1355		1.2610	1.1675		1.1130	1.1474
4.00	1.2512	1.1935		1.4037	1.2383		1.1764	1.2083
5.00	1.3365	1.2600			1.3194		1.2560	1.2773
6.00	1.4351	1.3365			1.4131			1.3557

## II.3 Standard and reference conditions

### II.3.1 Standard state

A precise definition of the term “standard state” has been given by IUPAC [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,  $p^\circ = 0.1$  MPa (1 bar), has therefore also been adopted, *cf.* Section II.3.2. The application of the standard state principle to pure substances and mixtures is summarised below. It should be noted that the standard state is always linked to a reference temperature, *cf.* Section II.3.3.

- The standard state for a gaseous substance, whether pure or in a gaseous mixture, is the pure substance at the standard state pressure and in a (hypothetical) state in which it exhibits ideal gas behaviour.
- The standard state for a pure liquid substance is (ordinarily) the pure liquid at the standard state pressure.
- The standard state for a pure solid substance is (ordinarily) the pure solid at the standard state pressure.
- The standard state for a solute B in a solution is a hypothetical liquid solution, at the standard state pressure, in which  $m_B = m^\circ = 1$  mol·kg<sup>-1</sup>, and in which the activity coefficient  $\gamma_B$  is unity.

It should be emphasised that the use of superscript <sup>°</sup>, *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 II.3.3) are listed in Table II-6.

Table II-6: Reference states for some elements at the reference temperature of 298.15 K and standard pressure of 0.1 MPa [\[82WAG/EVA\]](#), [\[89COX/WAG\]](#), [\[91DIN\]](#), [\[2005GAM/BUG\]](#), [\[2005OLI/NOL\]](#).

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

### II.3.2 Standard state pressure

The standard state pressure chosen for all selected data is 0.1 MPa (1 bar) as recommended by the International Union of Pure and Applied Chemistry IUPAC [\[82LAF\]](#).

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:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = V(1 - \alpha T) \quad (\text{II.38})$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \quad (\text{II.39})$$

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

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad (\text{II.41})$$

$$\text{where } \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad (\text{II.42})$$

For ideal gases,  $V = RT/p$  and  $\alpha = R/pV = 1/T$ . The conversion equations listed below (Eqs. (II.43) to (II.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 <sup>(atm)</sup>, and those that refer to the new standard state pressure of 1 bar are assigned the superscript <sup>(bar)</sup>.

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

$$\Delta_f H^{(\text{bar})}(T) - \Delta_f H^{(\text{atm})}(T) = 0 \quad (\text{II.43})$$

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

For gaseous substances, the entropy difference is:

$$\begin{aligned} S^{(\text{bar})}(T) - S^{(\text{atm})}(T) &= R \ln \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) = R \ln 1.01325 \\ &= 0.1094 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \end{aligned} \quad (\text{II.45})$$

This is exactly true for ideal gases, as follows from Eq.(II.40) with  $\alpha = R/pV$ . The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

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

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

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

$$\begin{aligned}\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})} &= -\delta \cdot RT \ln \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) \\ &= -\delta \times 0.03263 \text{ kJ}\cdot\text{mol}^{-1} \text{ at } 298.15 \text{ K.}\end{aligned}\quad (\text{II.47})$$

Eq.(II.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:

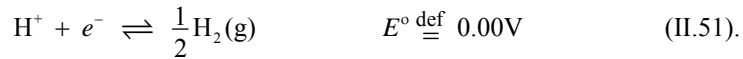
$$\Delta_f G^{(\text{bar})} - \Delta_f G^{(\text{atm})} = -\delta \times 0.03263 \text{ kJ}\cdot\text{mol}^{-1} \text{ at } 298.15 \text{ K.} \quad (\text{II.48})$$

The changes in the equilibrium constants and cell potentials with the change in the standard state pressure follows from the expression for Gibbs energy changes, Eq.(II.47),

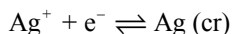
$$\begin{aligned}\log_{10} K^{(\text{bar})} - \log_{10} K^{(\text{atm})} &= -\frac{\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})}}{RT \ln 10} \\ &= \delta \cdot \frac{\ln \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right)}{\ln 10} = \delta \cdot \log_{10} \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right) \\ &= \delta \times 0.005717\end{aligned}\quad (\text{II.49})$$

$$\begin{aligned}E^{(\text{bar})} - E^{(\text{atm})} &= -\frac{\Delta_r G^{(\text{bar})} - \Delta_r G^{(\text{atm})}}{nF} \\ &= \delta \cdot \frac{RT \ln \left( \frac{p^{(\text{atm})}}{p^{(\text{bar})}} \right)}{nF} \\ &= \delta \cdot \frac{0.0003382}{n} \text{ V at } 298.15 \text{ K}\end{aligned}\quad (\text{II.50})$$

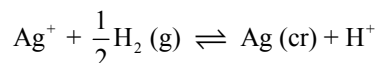
It should be noted that the standard potential of the hydrogen electrode is equal to 0.00 V exactly, by definition.



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:

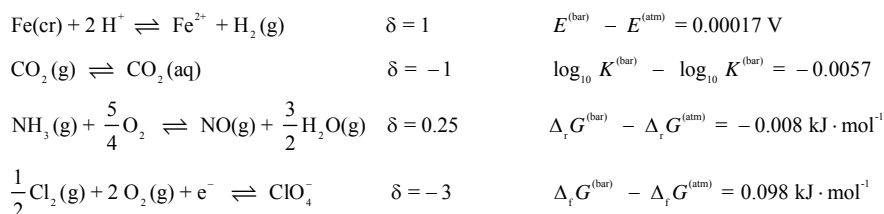


should thus be calculated from the balanced reaction that includes the hydrogen electrode,



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

Example:



### II.3.3 Reference temperature

The definitions of standard states given in Section II.3 make no reference to fixed temperature. Hence, it is theoretically possible to have an infinite number of standard states of a substance as the temperature varies. It is, however, convenient to complete the definition of the standard state in a particular context by choosing a reference temperature. As recommended by IUPAC [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  $t = (T - T_o)$  where  $T_o = 273.15 \text{ K}$ .

## II.4 Fundamental physical constants

To ensure the consistency with other NEA TDB Reviews, the fundamental physical constants are taken from a publication by CODATA [86COD]. Those relevant to this review are listed in Table II-7. Note that updated values of the fundamental constants can be obtained from CODATA, notably through its Internet site. In most cases, recalculation of the NEA TDB database entries with the updated values of the fundamental constants will not introduce significant (with respect to their quoted uncertainties) excursions from the current NEA TDB selections.

Table II-7: Fundamental physical constants. These values have been taken from CODATA [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	m·s <sup>-1</sup>
permeability of vacuum	$\mu_0$	$4\pi \times 10^{-7} = 12.566\,370\,614\dots$	10 <sup>-7</sup> N·A <sup>-2</sup>
permittivity of vacuum	$\epsilon_0$	$1/\mu_0 c^2 = 8.854\,187\,817\dots$	10 <sup>-12</sup> C <sup>2</sup> ·J <sup>-1</sup> ·m <sup>-1</sup>
Planck constant	h	6.626 0755(40)	10 <sup>-34</sup> J·s
elementary charge	e	1.602 177 33(49)	10 <sup>-19</sup> C
Avogadro constant	N <sub>A</sub>	6.022 1367(36)	10 <sup>23</sup> mol <sup>-1</sup>
Faraday constant	F	96 485.309(29)	C·mol <sup>-1</sup>
molar gas constant	R	8.314 510(70)	J·K <sup>-1</sup> ·mol <sup>-1</sup>
Boltzmann constant, R/N <sub>A</sub>	k	1.380 658(12)	10 <sup>-23</sup> J·K <sup>-1</sup>
Non-SI units used with SI:			
electron volt, (e/C) J	eV	1.602 177 33(49)	10 <sup>-19</sup> J
atomic mass unit,	u	1.660 5402(10)	10 <sup>-27</sup> kg
$1\text{u} = m_{\text{u}} = \frac{1}{12} m(^{12}\text{C})$			

## II.5 Uncertainty estimates

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

## II.6 The NEA-TDB system

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

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

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

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

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

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

$$\begin{aligned}X(T) &= a_x + b_x \cdot T + c_x \cdot T^2 + d_x \cdot T^{-1} + e_x \cdot T^{-2} + f_x \cdot \ln T + g_x \cdot T \ln T \\ &\quad + h_x \cdot \sqrt{T} + \frac{i_x}{\sqrt{T}} + j_x \cdot T^3 + k_x \cdot T^{-3}.\end{aligned}\quad (\text{II.52})$$

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

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

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

The pressure dependence of thermodynamic data has not been the subject of critical analysis in the present compilation. The reader interested in higher temperatures and pressures, or the pressure dependency of thermodynamic functions for geochemical applications, is referred to the specialised literature in this area, *e.g.*, [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 database. A chemical reaction “ $r$ ”, involving reactants and products ‘B’, can be abbreviated as:

$$0 = \sum_B \nu_B^r B \quad (\text{II.53})$$

where the stoichiometric coefficients  $\nu_B^r$  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 ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\Delta_r H_m^\circ$	the molar enthalpy of reaction ( $\text{kJ}\cdot\text{mol}^{-1}$ )
$\Delta_r S_m^\circ$	the molar entropy of reaction ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )
$\Delta_r C_{p,m}^\circ$	the molar heat capacity of reaction ( $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ).

The temperature functions of these data, if available, are stored according to Eq.(II.52).

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

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

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

$$\log_{10} K_r^\circ = -\frac{1}{RT \ln(10)} \sum_B \nu_B^r \Delta_f G_m^\circ(B) \quad (\text{II.54})$$

## II.7 Presentation of the selected data

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

Chapter III contains tables of selected thermodynamic data for individual compounds and complexes of oxalate, citrate and edta (Table III–1, Table III–3 and Table III–5, respectively), tables of selected reaction data (Table III–2, Table III–4, Table III–6 and Table III–7) for reactions concerning oxalate, citrate, edta and isa species, respectively. The selection of these data is discussed in Chapters VI to IX.

Chapter IV contains, for auxiliary compounds and complexes, a table of the thermodynamic data for individual species (Table IV–1) and a table of reaction data

(Table IV–2). Most of these values are the CODATA Key Values [89COX/WAG]. The selection of the remaining auxiliary data is discussed in [92GRE/FUG], [99RAR/RAN], [2001LEM/FUG], [2005GAM/BUG] and [2005OLI/NOL].

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

It is important to note that Table III–2, Table III–4, Table III–6, Table III–7 and Table IV–2 include only those species for which the primary selected data are reaction data. The formation data derived there from and listed in Table III–1, Table III–3, Table III–5 and Table IV–1, are obtained using auxiliary data, and their uncertainties are propagated accordingly. In order to maintain the uncertainties originally assigned to the selected data in this review, the user is advised to make direct use of the reaction data presented in that Table III–2, Table III–4, Table III–6, Table III–7 and Table IV–2, rather than taking the derived values in Table III–1, Table III–3, Table III–5 and Table IV–1 to calculate the reaction data with Eq.(II.54). The later approach would imply a twofold propagation of the uncertainties and result in reaction data whose uncertainties would be considerably larger than those originally assigned.

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

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

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

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

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

In the case of aqueous species, for which enthalpies of reaction are selected or can be calculated from the selected enthalpies of formation, but for which there are no selected heat capacities, it is in most cases possible to recalculate equilibrium constants to temperatures up to 100 to 150°C, with an additional uncertainty of perhaps about 1 to 2 logarithmic units, due to neglecting 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 *et al.* [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  $K^\circ$  at  $I = 0$  using activity coefficients  $\gamma$ , is explained in Appendix B. The corresponding Gibbs energy of dilution is:

$$\Delta_{\text{dil}} G_{\text{m}} = \Delta_{\text{r}} G_{\text{m}}^\circ - \Delta_{\text{r}} G_{\text{m}} \quad (\text{II.55})$$

$$= - R T \Delta_{\text{r}} \ln \gamma_{\pm} \quad (\text{II.56})$$

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

$$\Delta_{\text{dil}} H_{\text{m}} = R T^2 \frac{\partial}{\partial T} (\Delta_{\text{r}} \ln \gamma_{\pm})_p \quad (\text{II.57})$$

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



## **Part II**

### **Tables of selected data**



## Chapter III

# Selected data for organic compounds and complexes

This chapter presents the chemical thermodynamic data set for compounds and complexes of U, Np, Pu, Am and Ni as well as H, Na, K, Mg and Ca with oxalate, citrate, ethylenediaminetetraacetate (edta) and iso-saccharinate (isa) that has been selected in this review. Table III-1, Table III-3 and Table III-5 contain the recommended thermodynamic data of the compounds and species complexed with oxalate, citrate and edta, respectively. Table III-2, Table III-4, Table III-6 and Table III-7 contain the recommended thermodynamic data of chemical equilibrium reactions by which the oxalate, citrate, edta and isa compounds and complexes are formed, respectively.

The species and reactions in the tables appear in standard order of arrangement. Table III-2, Table III-4, Table III-6 and Table III-7 contain information only on those reactions for which primary data selections are made in Chapter VI, VII, VIII and IX of this review, respectively. These selected reaction data are used, together with data for species and auxiliary data selected in the NEA TDB Project, to derive the corresponding formation data in Table III-1, Table III-3 and Table III-5. The uncertainties associated with values for the species and the auxiliary data are in some cases substantial, leading to comparatively large uncertainties in the formation quantities derived in this manner.

The values of  $\Delta_f G_m^\circ$  for many reactions are known more accurately than would be calculated directly from the uncertainties of the  $\Delta_f G_m^\circ$  values in Table III-1, Table III-3, Table III-5 and auxiliary data. The inclusion of tables for reaction data (Table III-2, Table III-4, Table III-6 and Table III-7) in this report allows the use of equilibrium constants with total uncertainties that are based directly on the experimental accuracies. This is the main reason for including both the table for reaction data (Table III-2, Table III-4, Table III-6 and Table III-7) and the tables of  $\Delta_f G_m^\circ$ ,  $\Delta_f H_m^\circ$  and  $S_m^\circ$  values (Table III-1, Table III-3 and Table III-5).

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

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



Table III-1: Selected thermodynamic data for compounds and complexes with oxalate. 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 computer media from the OECD Nuclear Energy Agency.

Compound	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
ox <sup>2-</sup>	- 680.134 <sup>(b)</sup> ±1.830	- 830.660 <sup>(b)</sup> ±1.592	47.597 <sup>(d)</sup> ±3.020	
Hox <sup>-</sup>	- 704.393 <sup>(d)</sup> ±1.831	- 823.360 <sup>(b)</sup> ±1.588	153.447 <sup>(d)</sup> ±3.045	
α-H <sub>2</sub> ox	- 698.549 <sup>(a)</sup> ±1.502	- 828.800 ±1.500	115.600 ±0.200	105.900 ±0.200
H <sub>2</sub> ox(aq)	- 712.384 <sup>(d)</sup> ±1.839	- 820.060 <sup>(b)</sup> ±1.508	191.318 <sup>(d)</sup> ±3.523	
β-H <sub>2</sub> ox		- 827.500 ±1.500		
H <sub>2</sub> ox · 2H <sub>2</sub> O(cr)		- 1427.000 ±1.500		
Ni(ox)(aq)	- 755.531 <sup>(b)</sup> ±1.998	- 885.672 <sup>(b)</sup> ±1.843	15.159 <sup>(b)</sup> ±3.561	
Ni(ox) <sub>2</sub> <sup>2-</sup>	- 1449.650 <sup>(b)</sup> ±3.761	- 1724.132 <sup>(b)</sup> ±3.317	83.499 <sup>(b)</sup> ±6.423	
Am(ox) <sup>+</sup>	- 1315.991 <sup>(b)</sup> ±5.166			
Am(ox) <sub>2</sub> <sup>-</sup>	- 2020.099 <sup>(b)</sup> ±6.107			
Am(ox) <sub>3</sub> <sup>3-</sup>	- 2713.304 <sup>(b)</sup> ±9.237			
NpO <sub>2</sub> ox <sup>-</sup>	- 1610.160 <sup>(b)</sup> ±5.945			
NpO <sub>2</sub> (ox) <sub>2</sub> <sup>3-</sup>	- 2301.140 <sup>(b)</sup> ±6.809			

(Continued on next page)

Table III-1 (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
UO <sub>2</sub> ox(aq)	-1673.383 <sup>(b)</sup> ±2.690	-1824.300 <sup>(d)</sup> ±18.300	170.958 <sup>(a)</sup> ±62.039	
UO <sub>2</sub> ox · 3H <sub>2</sub> O(cr)	-2395.078 <sup>(b)</sup> ±3.103	-2702.000 ±18.000	347.517 <sup>(b)</sup> ±63.351	
UO <sub>2</sub> (ox) <sub>2</sub> <sup>2-</sup>	-2379.317 <sup>(b)</sup> ±4.145			
UO <sub>2</sub> (ox) <sub>3</sub> <sup>4-</sup>	-3071.723 <sup>(b)</sup> ±10.320			
Mg(ox)(aq)	-1155.830 <sup>(b)</sup> ±2.277			
Mg(ox) <sub>2</sub> <sup>2-</sup>	-1845.154 <sup>(b)</sup> ±3.922			
Ca(ox) · H <sub>2</sub> O(cr)	-1519.912 <sup>(b)</sup> ±2.138	-1680.990 <sup>(b)</sup> ±1.945	156.370 ±2.000	153.340 ±2.000
Ca(ox) · 2H <sub>2</sub> O(cr)	-1754.598 <sup>(b)</sup> ±2.139	-1970.520 <sup>(b)</sup> ±2.180	205.678 <sup>(b)</sup> ±5.006	
Ca(ox) · 3H <sub>2</sub> O(cr)	-1991.110 <sup>(b)</sup> ±2.126	-2260.850 <sup>(b)</sup> ±2.289	258.429 <sup>(b)</sup> ±5.452	
Ca(ox)(aq)	-1251.149 <sup>(b)</sup> ±2.138			
Ca(ox) <sub>2</sub> <sup>2-</sup>	-1936.020 <sup>(b)</sup> ±3.016			

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

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

(d) Value calculated internally from reaction data for a different key species.

Table III-2: Selected thermodynamic data for reactions involving oxalate 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 computer media from the OECD Nuclear Energy Agency.

Species	Reaction	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$	$\Delta_r H_m^{\circ}$	$\Delta_r S_m^{\circ}$
			(kJ · mol <sup>-1</sup> )	(kJ · mol <sup>-1</sup> )	(J · K <sup>-1</sup> · mol <sup>-1</sup> )
ox <sup>2-</sup>	Hox <sup>-</sup> $\rightleftharpoons$ H <sup>+</sup> + ox <sup>2-</sup>				
		- 4.250	24.259	- 7.300	- 105.850 <sup>(a)</sup>
		±0.010	±0.057	±0.100	±0.386
Hox <sup>-</sup>	H <sub>2</sub> ox(aq) $\rightleftharpoons$ H <sup>+</sup> + Hox <sup>-</sup>				
		- 1.400	7.991	- 3.300	- 37.871 <sup>(a)</sup>
		±0.030	±0.171	±0.500	±1.773
H <sub>2</sub> ox(aq)	H <sub>2</sub> ox · 2H <sub>2</sub> O(cr) $\rightleftharpoons$ 2H <sub>2</sub> O(l) + H <sub>2</sub> ox(aq)				
				35.280 ±0.130	
Ni(ox)(aq)	Ni <sup>2+</sup> + ox <sup>2-</sup> $\rightleftharpoons$ Ni(ox)(aq)				
		5.190	- 29.625	0.000	99.362 <sup>(a)</sup>
		±0.040	±0.228	±0.300	±1.264
Ni(ox) <sub>2</sub> <sup>2-</sup>	Ni <sup>2+</sup> + 2 ox <sup>2-</sup> $\rightleftharpoons$ Ni(ox) <sub>2</sub> <sup>2-</sup>				
		7.640	- 43.609	- 7.800	120.105 <sup>(a)</sup>
		±0.070	±0.400	±0.300	±1.676
Am(ox) <sup>+</sup>	Am <sup>3+</sup> + ox <sup>2-</sup> $\rightleftharpoons$ Am(ox) <sup>+</sup>				
		6.510	- 37.159		
		±0.150	±0.856		
Am(ox) <sub>2</sub> <sup>-</sup>	Am <sup>3+</sup> + 2 ox <sup>2-</sup> $\rightleftharpoons$ Am(ox) <sub>2</sub> <sup>-</sup>				
		10.710	- 61.133		
		±0.200	±1.142		
Am(ox) <sub>3</sub> <sup>3-</sup>	Am <sup>3+</sup> + 3 ox <sup>2-</sup> $\rightleftharpoons$ Am(ox) <sub>3</sub> <sup>3-</sup>				
		13.000	- 74.205		
		±1.000	±5.708		
NpO <sub>2</sub> ox <sup>-</sup>	NpO <sub>2</sub> <sup>+</sup> + ox <sup>2-</sup> $\rightleftharpoons$ NpO <sub>2</sub> ox <sup>-</sup>				
		3.900	- 22.261		
		±0.100	±0.571		

(Continued on next page)

Table III-2 (continued)

Species	Reaction	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$	$\Delta_r H_m^{\circ}$	$\Delta_r S_m^{\circ}$
			(kJ · mol <sup>-1</sup> )	(kJ · mol <sup>-1</sup> )	(J · K <sup>-1</sup> · mol <sup>-1</sup> )
NpO <sub>2</sub> (ox) <sub>2</sub> <sup>3-</sup>	NpO <sub>2</sub> <sup>+</sup> + 2 ox <sup>2-</sup> ⇌ NpO <sub>2</sub> (ox) <sub>2</sub> <sup>3-</sup>	5.800	- 33.107		
		±0.200	±1.142		
UO <sub>2</sub> ox(aq)	UO <sub>2</sub> <sup>2+</sup> + ox <sup>2-</sup> ⇌ UO <sub>2</sub> ox(aq)	7.130	- 40.698		
		±0.160	±0.913		
UO <sub>2</sub> ox · 3H <sub>2</sub> O(cr)	UO <sub>2</sub> ox(aq) + 3H <sub>2</sub> O(l) ⇌ UO <sub>2</sub> ox · 3H <sub>2</sub> O(cr)	1.800	- 10.274	- 20.200	- 33.290 <sup>(a)</sup>
		±0.270	±1.541	±3.500	±12.827
UO <sub>2</sub> (ox) <sub>2</sub> <sup>2-</sup>	UO <sub>2</sub> <sup>2+</sup> + 2 ox <sup>2-</sup> ⇌ UO <sub>2</sub> (ox) <sub>2</sub> <sup>2-</sup>	11.650	- 66.499		
		±0.150	±0.856		
UO <sub>2</sub> (ox) <sub>3</sub> <sup>4-</sup>	UO <sub>2</sub> <sup>2+</sup> + 3 ox <sup>2-</sup> ⇌ UO <sub>2</sub> (ox) <sub>3</sub> <sup>4-</sup>	13.800	- 78.771		
		±1.500	±8.562		
Mg(ox)(aq)	Mg <sup>2+</sup> + ox <sup>2-</sup> ⇌ Mg(ox)(aq)	3.560	- 20.321		
		±0.040	±0.228		
Mg(ox) <sub>2</sub> <sup>2-</sup>	Mg <sup>2+</sup> + 2 ox <sup>2-</sup> ⇌ Mg(ox) <sub>2</sub> <sup>2-</sup>	5.170	- 29.511		
		±0.080	±0.457		
Ca(ox) · H <sub>2</sub> O(cr)	Ca <sup>2+</sup> + H <sub>2</sub> O(l) + ox <sup>2-</sup> ⇌ Ca(ox) · H <sub>2</sub> O(cr)	8.730	- 49.831	- 21.500	95.023 <sup>(a)</sup>
		±0.060	±0.342	±0.500	±2.033
Ca(ox) · 2H <sub>2</sub> O(cr)	Ca <sup>2+</sup> + 2H <sub>2</sub> O(l) + ox <sup>2-</sup> ⇌ Ca(ox) · 2H <sub>2</sub> O(cr)	8.300	- 47.377	- 25.200	74.381 <sup>(a)</sup>
		±0.060	±0.342	±1.100	±3.864
Ca(ox) · 3H <sub>2</sub> O(cr)	Ca <sup>2+</sup> + 3H <sub>2</sub> O(l) + ox <sup>2-</sup> ⇌ Ca(ox) · 3H <sub>2</sub> O(cr)	8.190	- 46.749	- 29.700	57.182 <sup>(a)</sup>
		±0.040	±0.228	±1.300	±4.427
Ca(ox)(aq)	Ca <sup>2+</sup> + ox <sup>2-</sup> ⇌ Ca(ox)(aq)	3.190	- 18.209		
		±0.060	±0.342		
Ca(ox) <sub>2</sub> <sup>2-</sup>	Ca(ox)(aq) + ox <sup>2-</sup> ⇌ Ca(ox) <sub>2</sub> <sup>2-</sup>	0.830	- 4.738		
		±0.190	±1.085		

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

Table III–3: Selected thermodynamic data for compounds and complexes with citrate. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ( $I = 0$ ). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnote (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 computer media from the OECD Nuclear Energy Agency.

Compound	$\Delta_f G_m^\circ$ (kJ · mol <sup>–1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>–1</sup> )	$S_m^\circ$ (J · K <sup>–1</sup> · mol <sup>–1</sup> )	$C_{p,m}^\circ$ (J · K <sup>–1</sup> · mol <sup>–1</sup> )
cit <sup>3–</sup>	– 1162.258 <sup>(b)</sup> ±2.014	– 1519.920 <sup>(b)</sup> ±2.070	75.587 <sup>(b)</sup> ±1.855	
Hcit <sup>2–</sup>	– 1198.561 <sup>(b)</sup> ±2.011	– 1516.620 <sup>(b)</sup> ±2.048	208.417 <sup>(b)</sup> ±1.510	
H <sub>2</sub> cit <sup>–</sup>	– 1225.845 <sup>(b)</sup> ±2.010	– 1519.020 <sup>(b)</sup> ±2.026	291.879 <sup>(b)</sup> ±1.110	
H <sub>3</sub> cit(cr)	– 1236.695 ±2.019	– 1541.730 <sup>(b)</sup> ±2.010	252.100 ±0.200	225.400 ±0.200
H <sub>3</sub> cit(aq)	– 1243.712 <sup>(b)</sup> ±2.009	– 1523.520 <sup>(b)</sup> ±2.003	336.710 <sup>(b)</sup> ±0.428	
H <sub>3</sub> cit · H <sub>2</sub> O(cr)	– 1473.272 ±2.009	– 1838.460 ±2.000	283.600 ±0.200	268.050 ±0.100
Ni(cit) <sup>–</sup>	– 1246.617 <sup>(b)</sup> ±2.204			
Ni(cit) <sub>2</sub> <sup>4–</sup>	– 2418.807 <sup>(b)</sup> ±4.694			
Ni(Hcit)(aq)	– 1268.079 <sup>(b)</sup> ±2.228			
Ni(H <sub>2</sub> cit) <sup>+</sup>	– 1283.320 <sup>(b)</sup> ±2.583			
Am(cit)(aq)	– 1809.759 <sup>(b)</sup> ±5.288			
Am(cit) <sub>2</sub> <sup>3–</sup>	– 3002.555 <sup>(b)</sup> ±8.451			
Am(Hcit) <sup>+</sup>	– 1834.361 <sup>(b)</sup> ±7.696			

(Continued on next page)

Table III-3 (continued)

Compound	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
Am(Hcit) <sub>2</sub> <sup>-</sup>	- 3057.466 <sup>(b)</sup> ±8.448			
NpO <sub>2</sub> cit <sup>2-</sup>	- 2091.029 <sup>(b)</sup> ±5.984			
UO <sub>2</sub> cit <sup>-</sup>	- 2165.953 <sup>(b)</sup> ±2.838			
(UO <sub>2</sub> ) <sub>2</sub> (cit) <sub>2</sub> <sup>2-</sup>	- 4351.198 <sup>(b)</sup> ±6.049			
UO <sub>2</sub> (Hcit)(aq)	- 2179.652 <sup>(b)</sup> ±6.299			
Mg(cit) <sup>-</sup>	- 1645.089 <sup>(b)</sup> ±2.423			
Mg(Hcit)(aq)	- 1668.777 <sup>(b)</sup> ±2.447			
Mg(H <sub>2</sub> cit) <sup>+</sup>	- 1688.698 <sup>(b)</sup> ±2.580			
Ca(cit) <sup>-</sup>	- 1742.463 <sup>(b)</sup> ±2.278	- 2062.920 <sup>(b)</sup> ±6.425	111.282 <sup>(b)</sup> ±20.242	
Ca(Hcit)(aq)	- 1768.035 <sup>(b)</sup> ±2.304			
Ca(H <sub>2</sub> cit) <sup>+</sup>	- 1787.385 <sup>(b)</sup> ±2.445			
Ca <sub>3</sub> (cit) <sub>2</sub> · 4H <sub>2</sub> O(cr)	- 5033.670 <sup>(b)</sup> ±5.149			

(b) Value calculated internally from reaction data (see Table III-4).

Table III–4: Selected thermodynamic data for reactions involving citrate 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 computer media from the OECD Nuclear Energy Agency.

Species	Reaction			
	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_r H_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_r S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
cit <sup>3-</sup>	Hcit <sup>2-</sup> $\rightleftharpoons$ H <sup>+</sup> + cit <sup>3-</sup>			
	- 6.360	36.303	- 3.300	- 132.830 <sup>(a)</sup>
	$\pm 0.020$	$\pm 0.114$	$\pm 0.300$	$\pm 1.077$
Hcit <sup>2-</sup>	H <sub>2</sub> cit <sup>-</sup> $\rightleftharpoons$ H <sup>+</sup> + Hcit <sup>2-</sup>			
	- 4.780	27.284	2.400	- 83.463 <sup>(a)</sup>
	$\pm 0.010$	$\pm 0.057$	$\pm 0.300$	$\pm 1.024$
H <sub>2</sub> cit <sup>-</sup>	H <sub>3</sub> cit(aq) $\rightleftharpoons$ H <sup>+</sup> + H <sub>2</sub> cit <sup>-</sup>			
	- 3.130	17.866	4.500	- 44.830 <sup>(a)</sup>
	$\pm 0.010$	$\pm 0.057$	$\pm 0.300$	$\pm 1.024$
H <sub>3</sub> cit(cr)	H <sub>3</sub> cit · H <sub>2</sub> O(cr) $\rightleftharpoons$ H <sub>3</sub> cit(cr) + H <sub>2</sub> O(l)			
			10.900	
			$\pm 0.200$	
H <sub>3</sub> cit(aq)	H <sub>3</sub> cit · H <sub>2</sub> O(cr) $\rightleftharpoons$ H <sub>3</sub> cit(aq) + H <sub>2</sub> O(l)			
	1.328	- 7.580	29.110	123.060 <sup>(a)</sup>
	$\pm 0.004$	$\pm 0.023$	$\pm 0.110$	$\pm 0.377$
Ni(cit) <sup>-</sup>	Ni <sup>2+</sup> + cit <sup>3-</sup> $\rightleftharpoons$ Ni(cit) <sup>-</sup>			
	6.760	- 38.586		
	$\pm 0.080$	$\pm 0.457$		
Ni(cit) <sub>2</sub> <sup>4-</sup>	Ni <sup>2+</sup> + 2 cit <sup>3-</sup> $\rightleftharpoons$ Ni(cit) <sub>2</sub> <sup>4-</sup>			
	8.500	- 48.518		
	$\pm 0.400$	$\pm 2.283$		
Ni(Hcit)(aq)	Ni <sup>2+</sup> + Hcit <sup>2-</sup> $\rightleftharpoons$ Ni(Hcit)(aq)			
	4.160	- 23.745		
	$\pm 0.100$	$\pm 0.571$		

(Continued on next page)

Table III-4 (continued)

Species	Reaction	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$	$\Delta_r H_m^{\circ}$	$\Delta_r S_m^{\circ}$
			(kJ · mol <sup>-1</sup> )	(kJ · mol <sup>-1</sup> )	(J · K <sup>-1</sup> · mol <sup>-1</sup> )
Ni(H <sub>2</sub> cit) <sup>+</sup>	Ni <sup>2+</sup> + H <sub>2</sub> cit <sup>-</sup> ⇌ Ni(H <sub>2</sub> cit) <sup>+</sup>	2.050 ±0.250	- 11.701 ±1.427		
Am(cit)(aq)	Am <sup>3+</sup> + cit <sup>3-</sup> ⇌ Am(cit)(aq)	8.550 ±0.200	- 48.804 ±1.142		
Am(cit) <sub>2</sub> <sup>3-</sup>	Am <sup>3+</sup> + 2 cit <sup>3-</sup> ⇌ Am(cit) <sub>2</sub> <sup>3-</sup>	13.900 ±1.000	- 79.342 ±5.708		
Am(Hcit) <sup>+</sup>	Am <sup>3+</sup> + Hcit <sup>2-</sup> ⇌ Am(Hcit) <sup>+</sup>	6.500 ±1.000	- 37.102 ±5.708		
Am(Hcit) <sub>2</sub> <sup>-</sup>	Am <sup>3+</sup> + 2 Hcit <sup>2-</sup> ⇌ Am(Hcit) <sub>2</sub> <sup>-</sup>	10.800 ±1.000	- 61.647 ±5.708		
NpO <sub>2</sub> cit <sup>2-</sup>	NpO <sub>2</sub> <sup>+</sup> + cit <sup>3-</sup> ⇌ NpO <sub>2</sub> cit <sup>2-</sup>	3.680 ±0.050	- 21.006 ±0.285		
UO <sub>2</sub> cit <sup>-</sup>	UO <sub>2</sub> <sup>2+</sup> + cit <sup>3-</sup> ⇌ UO <sub>2</sub> cit <sup>-</sup>	8.960 ±0.170	- 51.144 ±0.970		
(UO <sub>2</sub> ) <sub>2</sub> (cit) <sub>2</sub> <sup>2-</sup>	2UO <sub>2</sub> <sup>2+</sup> + 2 cit <sup>3-</sup> ⇌ (UO <sub>2</sub> ) <sub>2</sub> (cit) <sub>2</sub> <sup>2-</sup>	21.300 ±0.500	- 121.581 ±2.854		
UO <sub>2</sub> (Hcit)(aq)	UO <sub>2</sub> <sup>2+</sup> + Hcit <sup>2-</sup> ⇌ UO <sub>2</sub> (Hcit)(aq)	5.000 ±1.000	- 28.540 ±5.708		
Mg(cit) <sup>-</sup>	Mg <sup>2+</sup> + cit <sup>3-</sup> ⇌ Mg(cit) <sup>-</sup>	4.810 ±0.030	- 27.456 ±0.171		
Mg(Hcit)(aq)	Mg <sup>2+</sup> + Hcit <sup>2-</sup> ⇌ Mg(Hcit)(aq)	2.600 ±0.070	- 14.841 ±0.400		

(Continued on next page)



Table III-4 (continued)

Species	Reaction	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$	$\Delta_r H_m^{\circ}$	$\Delta_r S_m^{\circ}$
			(kJ · mol <sup>-1</sup> )	(kJ · mol <sup>-1</sup> )	(J · K <sup>-1</sup> · mol <sup>-1</sup> )
Mg(H <sub>2</sub> cit) <sup>+</sup>	Mg <sup>2+</sup> + H <sub>2</sub> cit <sup>-</sup> ⇌ Mg(H <sub>2</sub> cit) <sup>+</sup>	1.310	- 7.478		
		±0.160	±0.913		
Ca(cit) <sup>-</sup>	Ca <sup>2+</sup> + cit <sup>3-</sup> ⇌ Ca(cit) <sup>-</sup>	4.800	- 27.399	0.000	91.895 <sup>(a)</sup>
		±0.030	±0.171	±6.000	±20.132
Ca(Hcit)(aq)	Ca <sup>2+</sup> + Hcit <sup>2-</sup> ⇌ Ca(Hcit)(aq)	2.920	- 16.667		
		±0.070	±0.400		
Ca(H <sub>2</sub> cit) <sup>+</sup>	Ca <sup>2+</sup> + H <sub>2</sub> cit <sup>-</sup> ⇌ Ca(H <sub>2</sub> cit) <sup>+</sup>	1.530	- 8.733		
		±0.160	±0.913		
Ca <sub>3</sub> (cit) <sub>2</sub> · 4H <sub>2</sub> O(cr)	3Ca <sup>2+</sup> + 4H <sub>2</sub> O(l) + 2 cit <sup>3-</sup> ⇌ Ca <sub>3</sub> (cit) <sub>2</sub> · 4H <sub>2</sub> O(cr)	17.900	- 102.174		
		±0.100	±0.571		

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

Table III–5: Selected thermodynamic data for compounds and complexes with edta. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to the reference temperature of 298.15 K and to the standard state, *i.e.*, a pressure of 0.1 MPa and, for aqueous species, infinite dilution ( $I = 0$ ). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnote (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 computer media from the OECD Nuclear Energy Agency.

Compound	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
edta <sup>4-</sup>		- 1704.800 <sup>(b)</sup> ±3.751		
Hedta <sup>3-</sup>		- 1724.600 <sup>(b)</sup> ±3.718		
H <sub>2</sub> edta <sup>2-</sup>		- 1739.800 <sup>(b)</sup> ±3.696		
H <sub>3</sub> edta <sup>-</sup>		- 1732.700 <sup>(b)</sup> ±3.674		
H <sub>4</sub> edta(cr)		- 1759.800 ±1.500		
H <sub>4</sub> edta(aq)		- 1730.800 <sup>(b)</sup> ±3.354		
Ni(edta) <sup>2-</sup>		- 1785.912 <sup>(b)</sup> ±3.873		
Am(edta) <sup>-</sup>		- 2332.100 <sup>(b)</sup> ±4.508		
Pu(edta) <sup>-</sup>		- 2305.290 <sup>(b)</sup> ±4.401		
Mg(edta) <sup>2-</sup>		- 2152.000 <sup>(b)</sup> ±3.820		
Ca(edta) <sup>2-</sup>		- 2270.000 <sup>(b)</sup> ±3.903		
Na(edta) <sup>3-</sup>		- 1949.140 <sup>(b)</sup> ±4.803		

(b) Value calculated internally from reaction data (see Table III–6).

Table III–6: Selected thermodynamic data for reactions involving edta 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 computer media from the OECD Nuclear Energy Agency.

Species	Reaction	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$ (kJ · mol <sup>-1</sup> )	$\Delta_r H_m^{\circ}$ (kJ · mol <sup>-1</sup> )	$\Delta_r S_m^{\circ}$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
edta <sup>4-</sup>	Hedta <sup>3-</sup> $\rightleftharpoons$ H <sup>+</sup> + edta <sup>4-</sup>	- 11.240 ±0.030	64.158 ±0.171	19.800 ±0.500	- 148.779 <sup>(a)</sup> ±1.773
Hedta <sup>3-</sup>	H <sub>2</sub> edta <sup>2-</sup> $\rightleftharpoons$ H <sup>+</sup> + Hedta <sup>3-</sup>	- 6.800 ±0.020	38.815 ±0.114	15.200 ±0.400	- 79.204 <sup>(a)</sup> ±1.395
H <sub>2</sub> edta <sup>2-</sup>	H <sub>3</sub> edta <sup>-</sup> $\rightleftharpoons$ H <sup>+</sup> + H <sub>2</sub> edta <sup>2-</sup>	- 3.150 ±0.020	17.980 ±0.114	- 7.100 ±0.400	- 84.120 <sup>(a)</sup> ±1.395
H <sub>3</sub> edta <sup>-</sup>	H <sub>4</sub> edta(aq) $\rightleftharpoons$ H <sup>+</sup> + H <sub>3</sub> edta <sup>-</sup>	- 2.230 ±0.050	12.729 ±0.285	- 1.900 ±1.500	- 49.066 <sup>(a)</sup> ±5.121
H <sub>4</sub> edta(aq)	H <sub>4</sub> edta(cr) $\rightleftharpoons$ H <sub>4</sub> edta(aq)	- 3.800 ±0.190	21.691 ±1.085	29.000 ±3.000	24.516 <sup>(a)</sup> ±10.699
H <sub>5</sub> edta <sup>+</sup>	H <sup>+</sup> + H <sub>4</sub> edta(aq) $\rightleftharpoons$ H <sub>5</sub> edta <sup>+</sup>	1.300 ±0.100	- 7.420 ±0.571		
H <sub>6</sub> edta <sup>2+</sup>	H <sup>+</sup> + H <sub>5</sub> edta <sup>+</sup> $\rightleftharpoons$ H <sub>6</sub> edta <sup>2+</sup>	- 0.500 ±0.200	2.854 ±1.142		
Ni(edta) <sup>2-</sup>	Ni <sup>2+</sup> + edta <sup>4-</sup> $\rightleftharpoons$ Ni(edta) <sup>2-</sup>	20.540 ±0.130	- 117.243 ±0.742	- 26.100 ±0.400	305.696 <sup>(a)</sup> ±2.827

(Continued on next page)

Table III-6 (continued)

Species	Reaction			
	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$ (kJ · mol <sup>-1</sup> )	$\Delta_r H_m^{\circ}$ (kJ · mol <sup>-1</sup> )	$\Delta_r S_m^{\circ}$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
Ni(Hedta) <sup>-</sup>	Ni(edta) <sup>2-</sup> + H <sup>+</sup> ⇌ Ni(Hedta) <sup>-</sup>			
	3.660	- 20.891		
	±0.160	±0.913		
Am(edta) <sup>-</sup>	Am <sup>3+</sup> + edta <sup>4-</sup> ⇌ Am(edta) <sup>-</sup>			
	19.670	- 112.277	- 10.600	341.027 <sup>(a)</sup>
	±0.110	±0.628	±2.000	±7.031
Am(Hedta)(aq)	Am(edta) <sup>-</sup> + H <sup>+</sup> ⇌ Am(Hedta)(aq)			
	2.170	- 12.386		
	±0.250	±1.427		
Pu(edta) <sup>-</sup>	Pu <sup>3+</sup> + edta <sup>4-</sup> ⇌ Pu(edta) <sup>-</sup>			
	20.180	- 115.188	- 8.700	357.163 <sup>(a)</sup>
	±0.370	±2.112	±1.200	±8.147
Pu(Hedta)(aq)	Pu(edta) <sup>-</sup> + H <sup>+</sup> ⇌ Pu(Hedta)(aq)			
	1.840	- 10.503		
	±0.260	±1.484		
Np(edta)(aq)	Np <sup>4+</sup> + edta <sup>4-</sup> ⇌ Np(edta)(aq)			
	31.200	- 178.091		
	±0.600	±3.425		
NpO <sub>2</sub> edta <sup>3-</sup>	NpO <sub>2</sub> <sup>+</sup> + edta <sup>4-</sup> ⇌ NpO <sub>2</sub> edta <sup>3-</sup>			
	9.230	- 52.685		
	±0.130	±0.742		
NpO <sub>2</sub> (Hedta) <sup>2-</sup>	NpO <sub>2</sub> <sup>+</sup> + Hedta <sup>3-</sup> ⇌ NpO <sub>2</sub> (Hedta) <sup>2-</sup>			
	5.820	- 33.221		
	±0.110	±0.628		
NpO <sub>2</sub> (H <sub>2</sub> edta) <sup>-</sup>	NpO <sub>2</sub> <sup>+</sup> + H <sub>2</sub> edta <sup>2-</sup> ⇌ NpO <sub>2</sub> (H <sub>2</sub> edta) <sup>-</sup>			
	4.470	- 25.515		
	±0.140	±0.799		
Uedta(aq)	U <sup>4+</sup> + edta <sup>4-</sup> ⇌ Uedta(aq)			
	29.500	- 168.387		
	±0.200	±1.142		
UO <sub>2</sub> edta <sup>2-</sup>	UO <sub>2</sub> <sup>2+</sup> + edta <sup>4-</sup> ⇌ UO <sub>2</sub> edta <sup>2-</sup>			
	13.700	- 78.200		
	±0.200	±1.142		

(Continued on next page)

Table III-6 (continued)

Species	Reaction	$\log_{10} K^{\circ}$	$\Delta_r G_m^{\circ}$	$\Delta_r H_m^{\circ}$	$\Delta_r S_m^{\circ}$
			(kJ · mol <sup>-1</sup> )	(kJ · mol <sup>-1</sup> )	(J · K <sup>-1</sup> · mol <sup>-1</sup> )
(UO <sub>2</sub> ) <sub>2</sub> edta(aq)	$2\text{UO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons (\text{UO}_2)_2\text{edta}(\text{aq})$	20.600	-117.586		
		±0.400	±2.283		
UO <sub>2</sub> (Hedta) <sup>-</sup>	$\text{UO}_2^{2+} + \text{Hedta}^{3-} \rightleftharpoons \text{UO}_2(\text{Hedta})^{-}$	8.370	-47.776		
		±0.100	±0.571		
Mg(edta) <sup>2-</sup>	$\text{Mg}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Mg}(\text{edta})^{2-}$	10.900	-62.218	19.800	275.089 <sup>(a)</sup>
		±0.100	±0.571	±0.400	±2.338
Mg(Hedta) <sup>-</sup>	$\text{Mg}(\text{edta})^{2-} + \text{H}^{+} \rightleftharpoons \text{Mg}(\text{Hedta})^{-}$	4.500	-25.686		
		±0.200	±1.142		
Ca(edta) <sup>2-</sup>	$\text{Ca}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ca}(\text{edta})^{2-}$	12.690	-72.435	-22.200	168.489 <sup>(a)</sup>
		±0.060	±0.342	±0.400	±1.766
Ca(Hedta) <sup>-</sup>	$\text{Ca}(\text{edta})^{2-} + \text{H}^{+} \rightleftharpoons \text{Ca}(\text{Hedta})^{-}$	3.540	-20.206		
		±0.090	±0.514		
Na(edta) <sup>3-</sup>	$\text{Na}^{+} + \text{edta}^{4-} \rightleftharpoons \text{Na}(\text{edta})^{3-}$	2.800	-15.983	-4.000	40.190 <sup>(a)</sup>
		±0.200	±1.142	±3.000	±10.766
Kedta <sup>3-</sup>	$\text{K}^{+} + \text{edta}^{4-} \rightleftharpoons \text{Kedta}^{3-}$	1.800	-10.274		
		±0.300	±1.712		

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

Table III-7: Selected thermodynamic data for reactions involving isa 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. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
			(kJ · mol <sup>-1</sup> )	(kJ · mol <sup>-1</sup> )	(J · K <sup>-1</sup> · mol <sup>-1</sup> )
Hisa(aq)*	$H^+ + isa^- \rightleftharpoons Hisa(aq)^* \text{ (1)}$	4.000	- 22.832		
		±0.500	±2.854		
Ca(isa) <sup>+</sup>	$Ca^{2+} + isa^- \rightleftharpoons Ca(isa)^+$	1.700	- 9.704		
		±0.300	±1.712		
Ca(isa-H)(aq)	$Ca^{2+} + isa^- \rightleftharpoons Ca(isa-H)(aq) + H^+$	- 10.400	59.364		
		±0.500	±2.854		
Ca(isa) <sub>2</sub> (cr)	$Ca^{2+} + 2 isa^- \rightleftharpoons Ca(isa)_2(cr)$	6.400	- 36.531		
		±0.200	±1.142		

- (1) This reaction refers to a "composite" protonation equilibrium where  $[Hisa(aq)^*] = [Hisa(aq)] + [isa_t(aq)]$ , see discussion in Section IX.3.2.

## Chapter IV

# Selected auxiliary data

This chapter presents the chemical thermodynamic data for auxiliary compounds and complexes which are used within the NEA TDB Project. Most of these auxiliary species are used in the evaluation of the recommended data reported in Chapter III. Additionally, data for species of Ni, U, Np, Pu and Am, selected in the corresponding NEA TDB Reviews, have also been included in Table IV–1 for the convenience of the reader. It is therefore essential to always use these auxiliary data in conjunction with the selected data for the organic ligands reviewed in this volume. The use of other auxiliary data can lead to inconsistencies and erroneous results.

The values in the tables of this chapter for auxiliary compounds and complexes are either CODATA Key Values, taken from [\[89COX/WAG\]](#), or were evaluated within the NEA TDB project, as described in the corresponding chapters of the uranium review [\[92GRE/FUG\]](#), the technetium review [\[99RAR/RAN\]](#), the neptunium and plutonium review [\[2001LEM/FUG\]](#), the Update review [\[2003GUI/FAN\]](#), the nickel review [\[2005GAM/BUG\]](#) and the selenium review [\[2005OLI/NOL\]](#).

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

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

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

- for CODATA values from [\[89COX/WAG\]](#), 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 [\[92GRE/FUG\]](#), [\[99RAR/RAN\]](#), [\[2003GUI/FAN\]](#), [\[2005GAM/BUG\]](#) and [\[2005OLI/NOL\]](#), the  $\pm$  terms are derived from total uncertainties in the corresponding equilibrium constant of reaction (*cf.* Table IV–2), and from the  $\pm$  terms listed for the necessary CODATA key values.

CODATA [\[89COX/WAG\]](#) values are available for  $\text{CO}_2(\text{g})$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$ . From the values given for  $\Delta_f H_m^\circ$  and  $S_m^\circ$  the values of  $\Delta_f G_m^\circ$  and, consequently, all the relevant equilibrium constants and enthalpy changes can be calculated. The propagation of errors during this procedure, however, leads to uncertainties in the resulting equilibrium constants that are significantly higher than those obtained from experimental determination of the constants. Therefore, reaction data for  $\text{CO}_2(\text{g})$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ , which were absent from the corresponding Table IV–2 in [\[92GRE/FUG\]](#), are included in this volume to provide the user of selected data for the organic ligands (*cf.* Chapter III) with the data needed to obtain the lowest possible uncertainties on reaction properties.

Note that the values in Table IV–1 and Table IV–2 may contain more digits than those listed in either [\[89COX/WAG\]](#) or in the chapters devoted to data selection in [\[92GRE/FUG\]](#), [\[95SIL/BID\]](#), [\[2001LEM/FUG\]](#), [\[2003GUI/FAN\]](#), [\[2005GAM/BUG\]](#) and [\[2005OLI/NOL\]](#), because the data in the present chapter are retrieved directly from the computerised data base and rounded to three digits after the decimal point throughout.



Table IV–1: Selected thermodynamic data for auxiliary compounds and complexes adopted in the NEA TDB project, including the CODATA Key Values [89COX/WAG] and NEA TDB data for species of Ni, U, Np, Pu and Am needed for the calculation of the values in tables III-1, III-3 and III-5. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a standard state of infinite dilution ( $I = 0$ ). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values in bold typeface are CODATA Key Values and are taken directly from 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 the chapters devoted to data selection in [92GRE/FUG], [95SIL/BID], [2001LEM/FUG], [2003GUI/FAN], [2005GAM/BUG] and [2005OLI/NOL]. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The reference listed for each entry in this table indicates the NEA TDB Review where the corresponding data have been adopted as NEA TDB Auxiliary data. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
O(g) [92GRE/FUG]	<b>231.743</b> <sup>(a)</sup> <b>±0.100</b>	<b>249.180</b> <b>±0.100</b>	<b>161.059</b> <b>±0.003</b>	<b>21.912</b> <b>±0.001</b>
O <sub>2</sub> (g) [92GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>205.152</b> <b>±0.005</b>	<b>29.378</b> <b>±0.003</b>
H(g) [92GRE/FUG]	<b>203.276</b> <sup>(a)</sup> <b>±0.006</b>	<b>217.998</b> <b>±0.006</b>	<b>114.717</b> <b>±0.002</b>	<b>20.786</b> <b>±0.001</b>
H <sup>+</sup> [92GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>	<b>0.000</b>
H <sub>2</sub> (g) [92GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>130.680</b> <b>±0.003</b>	<b>28.836</b> <b>±0.002</b>
OH <sup>-</sup> [92GRE/FUG]	<b>-157.220</b> <sup>(a)</sup> <b>±0.072</b>	<b>-230.015</b> <b>±0.040</b>	<b>-10.900</b> <b>±0.200</b>	
H <sub>2</sub> O(g) [92GRE/FUG]	<b>-228.582</b> <sup>(a)</sup> <b>±0.040</b>	<b>-241.826</b> <b>±0.040</b>	<b>188.835</b> <b>±0.010</b>	<b>33.609</b> <b>±0.030</b>
H <sub>2</sub> O(l) [92GRE/FUG]	<b>-237.140</b> <sup>(a)</sup> <b>±0.041</b>	<b>-285.830</b> <b>±0.040</b>	<b>69.950</b> <b>±0.030</b>	<b>75.351</b> <b>±0.080</b>
H <sub>2</sub> O <sub>2</sub> (aq) [92GRE/FUG]		<b>-191.170</b> <b>±0.100</b>		
He(g) [92GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>126.153</b> <b>±0.002</b>	<b>20.786</b> <b>±0.001</b>
Ne(g) [92GRE/FUG]	<b>0.000</b>	<b>0.000</b>	<b>146.328</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
Ar(g) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>154.846</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
Kr(g) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>164.085</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
Xe(g) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>169.685</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
F(g) <a href="#">[92GRE/FUG]</a>	<b>62.280</b> <sup>(a)</sup> <b>±0.300</b>	<b>79.380</b> <b>±0.300</b>	<b>158.751</b> <b>±0.004</b>	<b>22.746</b> <b>±0.002</b>
F <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>- 281.523</b> <sup>(a)</sup> <b>±0.692</b>	<b>- 335.350</b> <b>±0.650</b>	<b>- 13.800</b> <b>±0.800</b>	
F <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>202.791</b> <b>±0.005</b>	<b>31.304</b> <b>±0.002</b>
HF(aq) <a href="#">[92GRE/FUG]</a>	<b>- 299.675</b> <b>±0.702</b>	<b>- 323.150</b> <b>±0.716</b>	<b>88.000</b> <sup>(a)</sup> <b>±3.362</b>	
HF(g) <a href="#">[92GRE/FUG]</a>	<b>- 275.400</b> <sup>(a)</sup> <b>±0.700</b>	<b>- 273.300</b> <b>±0.700</b>	<b>173.779</b> <b>±0.003</b>	<b>29.137</b> <b>±0.002</b>
HF <sub>2</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>- 583.709</b> <b>±1.200</b>	<b>- 655.500</b> <b>±2.221</b>	<b>92.683</b> <sup>(a)</sup> <b>±8.469</b>	
Cl(g) <a href="#">[92GRE/FUG]</a>	<b>105.305</b> <sup>(a)</sup> <b>±0.008</b>	<b>121.301</b> <b>±0.008</b>	<b>165.190</b> <b>±0.004</b>	<b>21.838</b> <b>±0.001</b>
Cl <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>- 131.217</b> <sup>(a)</sup> <b>±0.117</b>	<b>- 167.080</b> <b>±0.100</b>	<b>56.600</b> <b>±0.200</b>	
Cl <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>223.081</b> <b>±0.010</b>	<b>33.949</b> <b>±0.002</b>
ClO <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>- 37.669</b> <b>±0.962</b>			
ClO <sub>2</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>10.250</b> <b>±4.044</b>			
ClO <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>- 7.903</b> <sup>(a)</sup> <b>±1.342</b>	<b>- 104.000</b> <b>±1.000</b>	<b>162.300</b> <b>±3.000</b>	
ClO <sub>4</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>- 7.890</b> <sup>(a)</sup> <b>±0.600</b>	<b>- 128.100</b> <b>±0.400</b>	<b>184.000</b> <b>±1.500</b>	
HCl(g) <a href="#">[92GRE/FUG]</a>	<b>- 95.298</b> <sup>(a)</sup> <b>±0.100</b>	<b>- 92.310</b> <b>±0.100</b>	<b>186.902</b> <b>±0.005</b>	<b>29.136</b> <b>±0.002</b>
HClO(aq) <a href="#">[92GRE/FUG]</a>	<b>- 80.023</b> <b>±0.613</b>			
HClO <sub>2</sub> (aq) <a href="#">[92GRE/FUG]</a>	<b>- 0.938</b> <b>±4.043</b>			

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
Br(g) <a href="#">[92GRE/FUG]</a>	<b>82.379</b> <sup>(a)</sup> <b>±0.128</b>	<b>111.870</b> <b>±0.120</b>	<b>175.018</b> <b>±0.004</b>	<b>20.786</b> <b>±0.001</b>
Br <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>- 103.850</b> <sup>(a)</sup> <b>±0.167</b>	<b>- 121.410</b> <b>±0.150</b>	<b>82.550</b> <b>±0.200</b>	
Br <sub>2</sub> (aq) <a href="#">[92GRE/FUG]</a>	4.900 ±1.000			
Br <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	<b>3.105</b> <sup>(a)</sup> <b>±0.142</b>	<b>30.910</b> <b>±0.110</b>	<b>245.468</b> <b>±0.005</b>	<b>36.057</b> <b>±0.002</b>
Br <sub>2</sub> (l) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>152.210</b> <b>±0.300</b>	
BrO <sup>-</sup> <a href="#">[92GRE/FUG]</a>	- 32.095 ±1.537			
BrO <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	19.070 <sup>(a)</sup> ±0.634	- 66.700 ±0.500	161.500 ±1.300	
HBr(g) <a href="#">[92GRE/FUG]</a>	<b>- 53.361</b> <sup>(a)</sup> <b>±0.166</b>	<b>- 36.290</b> <b>±0.160</b>	<b>198.700</b> <b>±0.004</b>	<b>29.141</b> <b>±0.003</b>
HBrO(aq) <a href="#">[92GRE/FUG]</a>	- 81.356 <sup>(b)</sup> ±1.527			
I(g) <a href="#">[92GRE/FUG]</a>	<b>70.172</b> <sup>(a)</sup> <b>±0.060</b>	<b>106.760</b> <b>±0.040</b>	<b>180.787</b> <b>±0.004</b>	<b>20.786</b> <b>±0.001</b>
I <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>- 51.724</b> <sup>(a)</sup> <b>±0.112</b>	<b>- 56.780</b> <b>±0.050</b>	<b>106.450</b> <b>±0.300</b>	
I <sub>2</sub> (cr) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>116.140</b> <b>±0.300</b>	
I <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	<b>19.323</b> <sup>(a)</sup> <b>±0.120</b>	<b>62.420</b> <b>±0.080</b>	<b>260.687</b> <b>±0.005</b>	<b>36.888</b> <b>±0.002</b>
IO <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	- 126.338 <sup>(a)</sup> ±0.779	- 219.700 ±0.500	118.000 ±2.000	
HI(g) <a href="#">[92GRE/FUG]</a>	<b>1.700</b> <sup>(a)</sup> <b>±0.110</b>	<b>26.500</b> <b>±0.100</b>	<b>206.590</b> <b>±0.004</b>	<b>29.157</b> <b>±0.003</b>
HIO <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	- 130.836 ±0.797			
S(cr)(orthorhombic) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>32.054</b> <b>±0.050</b>	<b>22.750</b> <b>±0.050</b>
S(g) <a href="#">[92GRE/FUG]</a>	<b>236.689</b> <sup>(a)</sup> <b>±0.151</b>	<b>277.170</b> <b>±0.150</b>	<b>167.829</b> <b>±0.006</b>	<b>23.674</b> <b>±0.001</b>
S <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	120.695 ±11.610			

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
S <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	<b>79.686</b> <sup>(a)</sup> <b>±0.301</b>	<b>128.600</b> <b>±0.300</b>	<b>228.167</b> <b>±0.010</b>	<b>32.505</b> <b>±0.010</b>
SO <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	– <b>300.095</b> <sup>(a)</sup> <b>±0.201</b>	– <b>296.810</b> <b>±0.200</b>	<b>248.223</b> <b>±0.050</b>	<b>39.842</b> <b>±0.020</b>
SO <sub>3</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	– 487.472 ±4.020			
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	– 519.291 ±11.345			
SO <sub>4</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	– <b>744.004</b> <sup>(a)</sup> <b>±0.418</b>	– <b>909.340</b> <b>±0.400</b>	<b>18.500</b> <b>±0.400</b>	
HS <sup>-</sup> <a href="#">[92GRE/FUG]</a>	<b>12.243</b> <sup>(a)</sup> <b>±2.115</b>	– <b>16.300</b> <b>±1.500</b>	<b>67.000</b> <b>±5.000</b>	
H <sub>2</sub> S(aq) <a href="#">[92GRE/FUG]</a>	– <b>27.648</b> <sup>(a)</sup> <b>±2.115</b>	– <b>38.600</b> <b>±1.500</b>	<b>126.000</b> <b>±5.000</b>	
H <sub>2</sub> S(g) <a href="#">[92GRE/FUG]</a>	– <b>33.443</b> <sup>(a)</sup> <b>±0.500</b>	– <b>20.600</b> <b>±0.500</b>	<b>205.810</b> <b>±0.050</b>	<b>34.248</b> <b>±0.010</b>
HSO <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	– 528.684 ±4.046			
HS <sub>2</sub> O <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	– 528.366 ±11.377			
H <sub>2</sub> SO <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	– 539.187 ±4.072			
HSO <sub>4</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	– <b>755.315</b> <sup>(a)</sup> <b>±1.342</b>	– <b>886.900</b> <b>±1.000</b>	<b>131.700</b> <b>±3.000</b>	
Te(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	49.221 ±0.050	25.550 ±0.100
TeO <sub>2</sub> (cr) <a href="#">[2003GUI/FAN]</a>	– 265.996 <sup>(a)</sup> ±2.500	– 321.000 ±2.500	69.890 ±0.150	60.670 ±0.150
N(g) <a href="#">[92GRE/FUG]</a>	<b>455.537</b> <sup>(a)</sup> <b>±0.400</b>	<b>472.680</b> <b>±0.400</b>	<b>153.301</b> <b>±0.003</b>	<b>20.786</b> <b>±0.001</b>
N <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>191.609</b> <b>±0.004</b>	<b>29.124</b> <b>±0.001</b>
N <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	348.200 ±2.000	275.140 ±1.000	107.710 <sup>(a)</sup> ±7.500	
NO <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	– <b>110.794</b> <sup>(a)</sup> <b>±0.417</b>	– <b>206.850</b> <b>±0.400</b>	<b>146.700</b> <b>±0.400</b>	

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
HN <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	321.372 ±2.051	260.140 ±10.050	147.381 ±34.403	
NH <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	-26.673 ±0.305	-81.170 ±0.326	109.040 ±0.913	
NH <sub>3</sub> (g) <a href="#">[92GRE/FUG]</a>	-16.407 <sup>(a)</sup> ±0.350	-45.940 ±0.350	192.770 ±0.050	35.630 ±0.005
NH <sub>4</sub> <sup>+</sup> <a href="#">[92GRE/FUG]</a>	-79.398 <sup>(a)</sup> ±0.278	-133.260 ±0.250	111.170 ±0.400	
P(am)(red) <a href="#">[92GRE/FUG]</a>		-7.500 ±2.000		
P(cr)(white, cubic) <a href="#">[92GRE/FUG]</a>	0.000	0.000	41.090 ±0.250	23.824 ±0.200
P(g) <a href="#">[92GRE/FUG]</a>	280.093 <sup>(a)</sup> ±1.003	316.500 ±1.000	163.199 ±0.003	20.786 ±0.001
P <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	103.469 <sup>(a)</sup> ±2.006	144.000 ±2.000	218.123 ±0.004	32.032 ±0.002
P <sub>4</sub> (g) <a href="#">[92GRE/FUG]</a>	24.419 <sup>(a)</sup> ±0.448	58.900 ±0.300	280.010 ±0.500	67.081 ±1.500
PO <sub>4</sub> <sup>3-</sup> <a href="#">[92GRE/FUG]</a>	-1025.491 ±1.576	-1284.400 ±4.085	-220.970 ±12.846	
P <sub>2</sub> O <sub>7</sub> <sup>4-</sup> <a href="#">[92GRE/FUG]</a>	-1935.503 ±4.563			
HPO <sub>4</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	-1095.985 <sup>(a)</sup> ±1.567	-1299.000 ±1.500	-33.500 ±1.500	
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	-1137.152 <sup>(a)</sup> ±1.567	-1302.600 ±1.500	92.500 ±1.500	
H <sub>3</sub> PO <sub>4</sub> (aq) <a href="#">[92GRE/FUG]</a>	-1149.367 ±1.576	-1294.120 ±1.616	161.912 ±2.575	
HP <sub>2</sub> O <sub>7</sub> <sup>3-</sup> <a href="#">[92GRE/FUG]</a>	-1989.158 ±4.482			
H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	-2027.117 ±4.445			
H <sub>3</sub> P <sub>2</sub> O <sub>7</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	-2039.960 ±4.362			
H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (aq) <a href="#">[92GRE/FUG]</a>	-2045.668 ±3.299	-2280.210 ±3.383	274.919 ±6.954	
As(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	35.100 ±0.600	24.640 ±0.500

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
AsO <sub>2</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	- 350.022 <sup>(a)</sup> ±4.008	- 429.030 ±4.000	40.600 ±0.600	
AsO <sub>4</sub> <sup>3-</sup> <a href="#">[92GRE/FUG]</a>	- 648.360 <sup>(a)</sup> ±4.008	- 888.140 ±4.000	- 162.800 ±0.600	
As <sub>2</sub> O <sub>5</sub> (cr) <a href="#">[92GRE/FUG]</a>	- 782.449 <sup>(a)</sup> ±8.016	- 924.870 ±8.000	105.400 ±1.200	116.520 ±0.800
As <sub>4</sub> O <sub>6</sub> (cubic) <a href="#">[92GRE/FUG]</a>	- 1152.445 <sup>(a)</sup> ±16.032	- 1313.940 ±16.000	214.200 ±2.400	191.290 ±0.800
As <sub>4</sub> O <sub>6</sub> (monoclinic) <a href="#">[92GRE/FUG]</a>	- 1154.009 <sup>(a)</sup> ±16.041	- 1309.600 ±16.000	234.000 ±3.000	
As <sub>4</sub> O <sub>6</sub> (g) <a href="#">[2005GAM/BUG]</a>	- 1092.716 <sup>(a)</sup> ±16.116	- 1196.250 ±16.000	408.600 ±6.000	
HAsO <sub>2</sub> (aq) <a href="#">[92GRE/FUG]</a>	- 402.925 <sup>(a)</sup> ±4.008	- 456.500 ±4.000	125.900 ±0.600	
H <sub>2</sub> AsO <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	- 587.078 <sup>(a)</sup> ±4.008	- 714.790 ±4.000	110.500 ±0.600	
H <sub>3</sub> AsO <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	- 639.681 <sup>(a)</sup> ±4.015	- 742.200 ±4.000	195.000 ±1.000	
HAsO <sub>4</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	- 714.592 <sup>(a)</sup> ±4.008	- 906.340 ±4.000	- 1.700 ±0.600	
H <sub>2</sub> AsO <sub>4</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	- 753.203 <sup>(a)</sup> ±4.015	- 909.560 ±4.000	117.000 ±1.000	
H <sub>3</sub> AsO <sub>4</sub> (aq) <a href="#">[92GRE/FUG]</a>	- 766.119 <sup>(a)</sup> ±4.015	- 902.500 ±4.000	184.000 ±1.000	
(As <sub>2</sub> O <sub>5</sub> ) <sub>3</sub> · 5 H <sub>2</sub> O(cr) <a href="#">[92GRE/FUG]</a>		- 4248.400 ±24.000		
Sb(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	45.520 ±0.210	25.260 ±0.200
Bi(cr) <a href="#">[2001LEM/FUG]</a>	0.000	0.000	56.740 ±0.420	25.410 ±0.200
C(cr) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>5.740</b> <b>±0.100</b>	<b>8.517</b> <b>±0.080</b>
C(g) <a href="#">[92GRE/FUG]</a>	<b>671.254</b> <sup>(a)</sup> <b>±0.451</b>	<b>716.680</b> <b>±0.450</b>	<b>158.100</b> <b>±0.003</b>	<b>20.839</b> <b>±0.001</b>
CO(g) <a href="#">[92GRE/FUG]</a>	- <b>137.168</b> <sup>(a)</sup> <b>±0.173</b>	- <b>110.530</b> <b>±0.170</b>	<b>197.660</b> <b>±0.004</b>	<b>29.141</b> <b>±0.002</b>
CO <sub>2</sub> (aq) <a href="#">[92GRE/FUG]</a>	- <b>385.970</b> <sup>(a)</sup> <b>±0.270</b>	- <b>413.260</b> <b>±0.200</b>	<b>119.360</b> <b>±0.600</b>	

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
CO <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	– 394.373 <sup>(a)</sup> ±0.133	– 393.510 ±0.130	213.785 ±0.010	37.135 ±0.002
CO <sub>3</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	– 527.900 <sup>(a)</sup> ±0.390	– 675.230 ±0.250	– 50.000 ±1.000	
HCO <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	– 586.845 <sup>(a)</sup> ±0.251	– 689.930 ±0.200	98.400 ±0.500	
CN <sup>-</sup> <a href="#">[2005OLI/NOL]</a>	166.939 <sup>(b)</sup> ±2.519	147.350 <sup>(b)</sup> ±3.541	101.182 <sup>(b)</sup> ±8.475	
HCN(aq) <a href="#">[2005OLI/NOL]</a>	114.368 <sup>(b)</sup> ±2.517	103.750 <sup>(b)</sup> ±3.536	131.271 <sup>(b)</sup> ±8.440	
HCN(g) <a href="#">[2005OLI/NOL]</a>	119.517 <sup>(a)</sup> ±2.500	129.900 ±2.500	201.710 ±0.100	
SCN <sup>-</sup> <a href="#">[92GRE/FUG]</a>	92.700 ±4.000	76.400 ±4.000	144.268 <sup>(a)</sup> ±18.974	
Si(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	18.810 ±0.080	19.789 ±0.030
Si(g) <a href="#">[92GRE/FUG]</a>	405.525 <sup>(a)</sup> ±8.000	450.000 ±8.000	167.981 ±0.004	22.251 ±0.001
SiO <sub>2</sub> (α– quartz) <a href="#">[92GRE/FUG]</a>	– 856.287 <sup>(a)</sup> ±1.002	– 910.700 ±1.000	41.460 ±0.200	44.602 ±0.300
SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	– 1175.651 ±1.265	– 1381.960 ±15.330	– 1.488 ±51.592	
SiO(OH) <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	– 1251.740 ±1.162	– 1431.360 ±3.743	88.024 ±13.144	
Si(OH) <sub>4</sub> (aq) <a href="#">[92GRE/FUG]</a>	– 1307.735 <sup>(b)</sup> ±1.156	– 1456.960 <sup>(b)</sup> ±3.163	189.973 <sup>(b)</sup> ±11.296	
Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	– 2269.878 ±2.878			
Si <sub>2</sub> O <sub>5</sub> (OH) <sub>5</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	– 2332.096 ±2.878			
Si <sub>3</sub> O <sub>6</sub> (OH) <sub>3</sub> <sup>3-</sup> <a href="#">[92GRE/FUG]</a>	– 3048.536 ±3.870			
Si <sub>3</sub> O <sub>5</sub> (OH) <sub>5</sub> <sup>3-</sup> <a href="#">[92GRE/FUG]</a>	– 3291.955 ±3.869			
Si <sub>4</sub> O <sub>8</sub> (OH) <sub>4</sub> <sup>4-</sup> <a href="#">[92GRE/FUG]</a>	– 4075.179 ±5.437			
Si <sub>4</sub> O <sub>7</sub> (OH) <sub>5</sub> <sup>3-</sup> <a href="#">[92GRE/FUG]</a>	– 4136.826 ±4.934			

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
SiF <sub>4</sub> (g) <a href="#">[92GRE/FUG]</a>	– 1572.773 <sup>(a)</sup> ±0.814	– 1615.000 ±0.800	282.760 ±0.500	73.622 ±0.500
Ge(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	31.090 ±0.150	23.222 ±0.100
Ge(g) <a href="#">[92GRE/FUG]</a>	331.209 <sup>(a)</sup> ±3.000	372.000 ±3.000	167.904 ±0.005	30.733 ±0.001
GeO <sub>2</sub> (tetragonal) <a href="#">[92GRE/FUG]</a>	– 521.404 <sup>(a)</sup> ±1.002	– 580.000 ±1.000	39.710 ±0.150	50.166 ±0.300
GeF <sub>4</sub> (g) <a href="#">[92GRE/FUG]</a>	– 1150.018 <sup>(a)</sup> ±0.584	– 1190.200 ±0.500	301.900 ±1.000	81.602 ±1.000
Sn(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	51.180 ±0.080	27.112 ±0.030
Sn(g) <a href="#">[92GRE/FUG]</a>	266.223 <sup>(a)</sup> ±1.500	301.200 ±1.500	168.492 ±0.004	21.259 ±0.001
Sn <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	– 27.624 <sup>(a)</sup> ±1.557	– 8.900 ±1.000	– 16.700 ±4.000	
SnO(tetragonal) <a href="#">[92GRE/FUG]</a>	– 251.913 <sup>(a)</sup> ±0.220	– 280.710 ±0.200	57.170 ±0.300	47.783 ±0.300
SnO <sub>2</sub> (cassiterite, tetragonal) <a href="#">[92GRE/FUG]</a>	– 515.826 <sup>(a)</sup> ±0.204	– 577.630 ±0.200	49.040 ±0.100	53.219 ±0.200
Pb(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	64.800 ±0.300	26.650 ±0.100
Pb(g) <a href="#">[92GRE/FUG]</a>	162.232 <sup>(a)</sup> ±0.805	195.200 ±0.800	175.375 ±0.005	20.786 ±0.001
Pb <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	– 24.238 <sup>(a)</sup> ±0.399	0.920 ±0.250	18.500 ±1.000	
PbSO <sub>4</sub> (cr) <a href="#">[92GRE/FUG]</a>	– 813.036 <sup>(a)</sup> ±0.447	– 919.970 ±0.400	148.500 ±0.600	
B(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	5.900 ±0.080	11.087 ±0.100
B(g) <a href="#">[92GRE/FUG]</a>	521.012 <sup>(a)</sup> ±5.000	565.000 ±5.000	153.436 ±0.015	20.796 ±0.005
B <sub>2</sub> O <sub>3</sub> (cr) <a href="#">[92GRE/FUG]</a>	– 1194.324 <sup>(a)</sup> ±1.404	– 1273.500 ±1.400	53.970 ±0.300	62.761 ±0.300
B(OH) <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	– 969.268 <sup>(a)</sup> ±0.820	– 1072.800 ±0.800	162.400 ±0.600	
B(OH) <sub>3</sub> (cr) <a href="#">[92GRE/FUG]</a>	– 969.667 <sup>(a)</sup> ±0.820	– 1094.800 ±0.800	89.950 ±0.600	86.060 ±0.400

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
BF <sub>3</sub> (g) <a href="#">[92GRE/FUG]</a>	– 1119.403 <sup>(a)</sup> ±0.803	– 1136.000 ±0.800	254.420 ±0.200	50.463 ±0.100
Al(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	28.300 ±0.100	24.200 ±0.070
Al(g) <a href="#">[92GRE/FUG]</a>	289.376 <sup>(a)</sup> ±4.000	330.000 ±4.000	164.554 ±0.004	21.391 ±0.001
Al <sup>3+</sup> <a href="#">[92GRE/FUG]</a>	– 491.507 <sup>(a)</sup> ±3.338	– 538.400 ±1.500	– 325.000 ±10.000	
Al <sub>2</sub> O <sub>3</sub> (corundum) <a href="#">[92GRE/FUG]</a>	– 1582.257 <sup>(a)</sup> ±1.302	– 1675.700 ±1.300	50.920 ±0.100	79.033 ±0.200
AlF <sub>3</sub> (cr) <a href="#">[92GRE/FUG]</a>	– 1431.096 <sup>(a)</sup> ±1.309	– 1510.400 ±1.300	66.500 ±0.500	75.122 ±0.400
Tl <sup>+</sup> <a href="#">[99RAR/RAN]</a>	– 32.400 ±0.300			
Zn(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	41.630 ±0.150	25.390 ±0.040
Zn(g) <a href="#">[92GRE/FUG]</a>	94.813 <sup>(a)</sup> ±0.402	130.400 ±0.400	160.990 ±0.004	20.786 ±0.001
Zn <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	– 147.203 <sup>(a)</sup> ±0.254	– 153.390 ±0.200	– 109.800 ±0.500	
ZnO(cr) <a href="#">[92GRE/FUG]</a>	– 320.479 <sup>(a)</sup> ±0.299	– 350.460 ±0.270	43.650 ±0.400	
Cd(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	51.800 ±0.150	26.020 ±0.040
Cd(g) <a href="#">[92GRE/FUG]</a>	77.230 <sup>(a)</sup> ±0.205	111.800 ±0.200	167.749 ±0.004	20.786 ±0.001
Cd <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	– 77.733 <sup>(a)</sup> ±0.750	– 75.920 ±0.600	– 72.800 ±1.500	
CdO(cr) <a href="#">[92GRE/FUG]</a>	– 228.661 <sup>(a)</sup> ±0.602	– 258.350 ±0.400	54.800 ±1.500	
CdSO <sub>4</sub> · 2.667 H <sub>2</sub> O(cr) <a href="#">[92GRE/FUG]</a>	– 1464.959 <sup>(a)</sup> ±0.810	– 1729.300 ±0.800	229.650 ±0.400	
Hg(g) <a href="#">[92GRE/FUG]</a>	31.842 <sup>(a)</sup> ±0.054	61.380 ±0.040	174.971 ±0.005	20.786 ±0.001
Hg(l) <a href="#">[92GRE/FUG]</a>	0.000	0.000	75.900 ±0.120	
Hg <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	164.667 <sup>(a)</sup> ±0.313	170.210 ±0.200	– 36.190 ±0.800	

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
Hg <sub>2</sub> <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	<b>153.567</b> <sup>(a)</sup> <b>±0.559</b>	<b>166.870</b> <b>±0.500</b>	<b>65.740</b> <b>±0.800</b>	
HgO(montroydite, red) <a href="#">[92GRE/FUG]</a>	<b>- 58.523</b> <sup>(a)</sup> <b>±0.154</b>	<b>- 90.790</b> <b>±0.120</b>	<b>70.250</b> <b>±0.300</b>	
Hg <sub>2</sub> Cl <sub>2</sub> (cr) <a href="#">[92GRE/FUG]</a>	<b>- 210.725</b> <sup>(a)</sup> <b>±0.471</b>	<b>- 265.370</b> <b>±0.400</b>	<b>191.600</b> <b>±0.800</b>	
Hg <sub>2</sub> SO <sub>4</sub> (cr) <a href="#">[92GRE/FUG]</a>	<b>- 625.780</b> <sup>(a)</sup> <b>±0.411</b>	<b>- 743.090</b> <b>±0.400</b>	<b>200.700</b> <b>±0.200</b>	
Cu(cr) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>33.150</b> <b>±0.080</b>	<b>24.440</b> <b>±0.050</b>
Cu(g) <a href="#">[92GRE/FUG]</a>	<b>297.672</b> <sup>(a)</sup> <b>±1.200</b>	<b>337.400</b> <b>±1.200</b>	<b>166.398</b> <b>±0.004</b>	<b>20.786</b> <b>±0.001</b>
Cu <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	<b>65.040</b> <sup>(a)</sup> <b>±1.557</b>	<b>64.900</b> <b>±1.000</b>	<b>- 98.000</b> <b>±4.000</b>	
CuCl(g) <a href="#">[2003GUI/FAN]</a>		76.800 ±10.000		
CuSO <sub>4</sub> (cr) <a href="#">[92GRE/FUG]</a>	<b>- 662.185</b> <sup>(a)</sup> <b>±1.206</b>	<b>- 771.400</b> <b>±1.200</b>	<b>109.200</b> <b>±0.400</b>	
Ag(cr) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>42.550</b> <b>±0.200</b>	<b>25.350</b> <b>±0.100</b>
Ag(g) <a href="#">[92GRE/FUG]</a>	<b>246.007</b> <sup>(a)</sup> <b>±0.802</b>	<b>284.900</b> <b>±0.800</b>	<b>172.997</b> <b>±0.004</b>	<b>20.786</b> <b>±0.001</b>
Ag <sup>+</sup> <a href="#">[92GRE/FUG]</a>	<b>77.096</b> <sup>(a)</sup> <b>±0.156</b>	<b>105.790</b> <b>±0.080</b>	<b>73.450</b> <b>±0.400</b>	
AgCl(cr) <a href="#">[92GRE/FUG]</a>	<b>- 109.765</b> <sup>(a)</sup> <b>±0.098</b>	<b>- 127.010</b> <b>±0.050</b>	<b>96.250</b> <b>±0.200</b>	
Ni <sup>2+</sup> <a href="#">[2005GAM/BUG]</a>	<b>- 45.773</b> <b>±0.771</b>	<b>- 55.012</b> <sup>(a)</sup> <b>±0.878</b>	<b>- 131.800</b> <b>±1.400</b>	<b>- 46.100</b> <b>±7.500</b>
Ti(cr) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>30.720</b> <b>±0.100</b>	<b>25.060</b> <b>±0.080</b>
Ti(g) <a href="#">[92GRE/FUG]</a>	<b>428.403</b> <sup>(a)</sup> <b>±3.000</b>	<b>473.000</b> <b>±3.000</b>	<b>180.298</b> <b>±0.010</b>	<b>24.430</b> <b>±0.030</b>
TiO <sub>2</sub> (rutile) <a href="#">[92GRE/FUG]</a>	<b>- 888.767</b> <sup>(a)</sup> <b>±0.806</b>	<b>- 944.000</b> <b>±0.800</b>	<b>50.620</b> <b>±0.300</b>	<b>55.080</b> <b>±0.300</b>
TiCl <sub>4</sub> (g) <a href="#">[92GRE/FUG]</a>	<b>- 726.324</b> <sup>(a)</sup> <b>±3.229</b>	<b>- 763.200</b> <b>±3.000</b>	<b>353.200</b> <b>±4.000</b>	<b>95.408</b> <b>±1.000</b>

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Table IV–1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>–1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>–1</sup> )	$S_m^\circ$ (J · K <sup>–1</sup> · mol <sup>–1</sup> )	$C_{p,m}^\circ$ (J · K <sup>–1</sup> · mol <sup>–1</sup> )
Am <sup>3+</sup> <a href="#">[95SIL/BID]</a>	–598.698 <sup>(a)</sup> ±4.755	–616.700 ±1.500	–201.000 ±15.000	
Pu <sup>3+</sup> <a href="#">[2001LEM/FUG]</a>	–578.984 ±2.688	–591.790 ±1.964	–184.510 <sup>(b)</sup> ±6.154	
Np <sup>4+</sup> <a href="#">[2001LEM/FUG]</a>	–491.774 <sup>(a)</sup> ±5.586	–556.022 ±4.185	–426.390 <sup>(b)</sup> ±12.386	
NpO <sub>2</sub> <sup>+</sup> <a href="#">[2001LEM/FUG]</a>	–907.765 <sup>(a)</sup> ±5.628	–978.181 ±4.629	–45.904 ±10.706	–4.000 ±25.000
U(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	50.200 ±0.200	27.660 ±0.050
U <sup>4+</sup> <a href="#">[2003GUI/FAN]</a>	–529.860 <sup>(b)</sup> ±1.765	–591.200 ±3.300	–416.895 <sup>(a)</sup> ±12.553	–220.000 ±50.000
UO <sub>2</sub> <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	–952.551 <sup>(a)</sup> ±1.747	–1019.000 ±1.500	–98.200 ±3.000	42.400 ±3.000
Th(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	51.800 ±0.500	26.230 ±0.050
Th(g) <a href="#">[92GRE/FUG]</a>	560.745 <sup>(a)</sup> ±6.002	602.000 ±6.000	190.170 ±0.050	20.789 ±0.100
ThO <sub>2</sub> (cr) <a href="#">[92GRE/FUG]</a>	–1169.238 <sup>(a)</sup> ±3.504	–1226.400 ±3.500	65.230 ±0.200	
Be(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	9.500 ±0.080	16.443 ±0.060
Be(g) <a href="#">[92GRE/FUG]</a>	286.202 <sup>(a)</sup> ±5.000	324.000 ±5.000	136.275 ±0.003	20.786 ±0.001
BeO(bromellite) <a href="#">[92GRE/FUG]</a>	–580.090 <sup>(a)</sup> ±2.500	–609.400 ±2.500	13.770 ±0.040	25.565 ±0.100
Mg(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	32.670 ±0.100	24.869 ±0.020
Mg(g) <a href="#">[92GRE/FUG]</a>	112.521 <sup>(a)</sup> ±0.801	147.100 ±0.800	148.648 ±0.003	20.786 ±0.001
Mg <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	–455.375 <sup>(a)</sup> ±1.335	–467.000 ±0.600	–137.000 ±4.000	
MgO(cr) <a href="#">[92GRE/FUG]</a>	–569.312 <sup>(a)</sup> ±0.305	–601.600 ±0.300	26.950 ±0.150	37.237 ±0.200
MgF <sub>2</sub> (cr) <a href="#">[92GRE/FUG]</a>	–1071.051 <sup>(a)</sup> ±1.210	–1124.200 ±1.200	57.200 ±0.500	61.512 ±0.300
Ca(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	41.590 ±0.400	25.929 ±0.300

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
Ca(g) <a href="#">[92GRE/FUG]</a>	<b>144.021</b> <sup>(a)</sup> <b>±0.809</b>	<b>177.800</b> <b>±0.800</b>	<b>154.887</b> <b>±0.004</b>	<b>20.786</b> <b>±0.001</b>
Ca <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	– 552.806 <sup>(a)</sup> <b>±1.050</b>	– 543.000 <b>±1.000</b>	– 56.200 <b>±1.000</b>	
CaO(cr) <a href="#">[92GRE/FUG]</a>	– 603.296 <sup>(a)</sup> <b>±0.916</b>	– 634.920 <b>±0.900</b>	<b>38.100</b> <b>±0.400</b>	<b>42.049</b> <b>±0.400</b>
CaF(g) <a href="#">[2003GUI/FAN]</a>	– 302.118 ±5.104	– 276.404 ±5.100	229.244 ±0.500	33.671 ±0.500
CaCl(g) <a href="#">[2003GUI/FAN]</a>	– 129.787 ±5.001	– 103.400 ±5.000	241.634 ±0.300	35.687 ±0.010
Sr(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	55.700 ±0.210	
Sr <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	– 563.864 <sup>(a)</sup> ±0.781	– 550.900 ±0.500	– 31.500 ±2.000	
SrO(cr) <a href="#">[92GRE/FUG]</a>	– 559.939 <sup>(a)</sup> ±0.914	– 590.600 ±0.900	55.440 ±0.500	
SrCl <sub>2</sub> (cr) <a href="#">[92GRE/FUG]</a>	– 784.974 <sup>(a)</sup> ±0.714	– 833.850 ±0.700	114.850 ±0.420	
Sr(NO <sub>3</sub> ) <sub>2</sub> (cr) <a href="#">[92GRE/FUG]</a>	– 783.146 <sup>(a)</sup> ±1.018	– 982.360 ±0.800	194.600 ±2.100	
Ba(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	62.420 ±0.840	
Ba(g) <a href="#">[2003GUI/FAN]</a>	152.852 ±5.006	185.000 ±5.000	170.245 ±0.010	20.786 ±0.001
Ba <sup>2+</sup> <a href="#">[92GRE/FUG]</a>	– 557.656 <sup>(a)</sup> ±2.582	– 534.800 ±2.500	8.400 ±2.000	
BaO(cr) <a href="#">[92GRE/FUG]</a>	– 520.394 <sup>(a)</sup> ±2.515	– 548.100 ±2.500	72.070 ±0.380	
BaF(g) <a href="#">[2003GUI/FAN]</a>	– 349.569 ±6.705	– 324.992 ±6.700	246.219 ±0.210	34.747 ±0.300
BaCl <sub>2</sub> (cr) <a href="#">[92GRE/FUG]</a>	– 806.953 <sup>(a)</sup> ±2.514	– 855.200 ±2.500	123.680 ±0.250	
Li(cr) <a href="#">[92GRE/FUG]</a>	<b>0.000</b>	<b>0.000</b>	<b>29.120</b> <b>±0.200</b>	<b>24.860</b> <b>±0.200</b>
Li(g) <a href="#">[92GRE/FUG]</a>	<b>126.604</b> <sup>(a)</sup> <b>±1.002</b>	<b>159.300</b> <b>±1.000</b>	<b>138.782</b> <b>±0.010</b>	<b>20.786</b> <b>±0.001</b>

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
Li <sup>+</sup> <a href="#">[92GRE/FUG]</a>	– 292.918 <sup>(a)</sup> ±0.109	– 278.470 ±0.080	12.240 ±0.150	
Na(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	51.300 ±0.200	28.230 ±0.200
Na(g) <a href="#">[92GRE/FUG]</a>	76.964 <sup>(a)</sup> ±0.703	107.500 ±0.700	153.718 ±0.003	20.786 ±0.001
Na <sup>+</sup> <a href="#">[92GRE/FUG]</a>	– 261.953 <sup>(a)</sup> ±0.096	– 240.340 ±0.060	58.450 ±0.150	
NaF(cr) <a href="#">[2001LEM/FUG]</a>	– 546.327 <sup>(a)</sup> ±0.704	– 576.600 ±0.700	51.160 ±0.150	
NaCl(cr) <a href="#">[2001LEM/FUG]</a>	– 384.221 ±0.147	– 411.260 ±0.120	72.150 ±0.200	50.500
NaNO <sub>3</sub> (cr) <a href="#">[2003GUI/FAN]</a>		– 467.580 ±0.410		
K(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	64.680 ±0.200	29.600 ±0.100
K(g) <a href="#">[92GRE/FUG]</a>	60.479 <sup>(a)</sup> ±0.802	89.000 ±0.800	160.341 ±0.003	20.786 ±0.001
K <sup>+</sup> <a href="#">[92GRE/FUG]</a>	– 282.510 <sup>(a)</sup> ±0.116	– 252.140 ±0.080	101.200 ±0.200	
KCl(cr) <a href="#">[2005GAM/BUG]</a>		– 436.461 ±0.129		
KBr(cr) <a href="#">[2005GAM/BUG]</a>		– 393.330 ±0.188		
KI(cr) <a href="#">[2005GAM/BUG]</a>		– 329.150 ±0.137		
Rb(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	76.780 ±0.300	31.060 ±0.100
Rb(g) <a href="#">[92GRE/FUG]</a>	53.078 <sup>(a)</sup> ±0.805	80.900 ±0.800	170.094 ±0.003	20.786 ±0.001
Rb <sup>+</sup> <a href="#">[92GRE/FUG]</a>	– 284.009 <sup>(a)</sup> ±0.153	– 251.120 ±0.100	121.750 ±0.250	
Cs(cr) <a href="#">[92GRE/FUG]</a>	0.000	0.000	85.230 ±0.400	32.210 ±0.200
Cs(g) <a href="#">[92GRE/FUG]</a>	49.556 <sup>(a)</sup> ±1.007	76.500 ±1.000	175.601 ±0.003	20.786 ±0.001

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Table IV-1: (continued)

Compound and review where adopted	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )	$C_{p,m}^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
Cs <sup>+</sup> <a href="#">[92GRE/FUG]</a>	– <b>291.456</b> <sup>(a)</sup> <b>±0.535</b>	– <b>258.000</b> <b>±0.500</b>	<b>132.100</b> <b>±0.500</b>	
CsCl(cr) <a href="#">[2001LEM/FUG]</a>	– 413.807 <sup>(a)</sup> ±0.208	– 442.310 ±0.160	101.170 ±0.200	52.470
CsBr(cr) <a href="#">[2001LEM/FUG]</a>	– 391.171 ±0.305	– 405.600 ±0.250	112.940 ±0.400	52.930

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

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

Table IV–2: Selected thermodynamic data for reactions involving auxiliary compounds and complexes used in the evaluation of thermodynamic data for the NEA TDB Project data. All ionic species listed in this table are aqueous species. The selection of these data is described in Chapter VI of [\[92GRE/FUG\]](#) and [\[2005OLI/NOL\]](#). Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a standard state of infinite dilution ( $I = 0$ ). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The reference listed for each entry in this table indicates the NEA TDB Review where the corresponding data have been adopted as NEA TDB Auxiliary data. The data presented in this table are available on computer media from the OECD Nuclear Energy Agency.

Species and review where adopted	Reaction	$\log_{10} K^\circ$	$\Delta_r G_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_r S_m^\circ$
			(kJ · mol <sup>-1</sup> )	(kJ · mol <sup>-1</sup> )	(J · K <sup>-1</sup> · mol <sup>-1</sup> )
HF(aq) <a href="#">[92GRE/FUG]</a>	$F^- + H^+ \rightleftharpoons HF(aq)$	3.180 ±0.020	-18.152 ±0.114	12.200 ±0.300	101.800 <sup>(a)</sup> ±1.077
HF <sub>2</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	$F^- + HF(aq) \rightleftharpoons HF_2^-$	0.440 ±0.120	-2.511 ±0.685	3.000 ±2.000	18.486 <sup>(a)</sup> ±7.090
ClO <sup>-</sup> <a href="#">[92GRE/FUG]</a>	$HClO(aq) \rightleftharpoons ClO^- + H^+$	-7.420 ±0.130	42.354 ±0.742	19.000 ±9.000	-78.329 <sup>(a)</sup> ±30.289
ClO <sub>2</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	$HClO_2(aq) \rightleftharpoons ClO_2^- + H^+$	-1.960 ±0.020	11.188 ±0.114		
HClO(aq) <a href="#">[92GRE/FUG]</a>	$Cl_2(g) + H_2O(l) \rightleftharpoons Cl^- + H^+ + HClO(aq)$	-4.537 ±0.105	25.900 ±0.600		
HClO <sub>2</sub> (aq) <a href="#">[92GRE/FUG]</a>	$H_2O(l) + HClO(aq) \rightleftharpoons 2H^+ + HClO_2(aq) + 2e^-$	-55.400 <sup>(b)</sup> ±0.700	316.230 ±3.996		
BrO <sup>-</sup> <a href="#">[92GRE/FUG]</a>	$HBrO(aq) \rightleftharpoons BrO^- + H^+$	-8.630 ±0.030	49.260 ±0.171	30.000 ±3.000	-64.600 <sup>(a)</sup> ±10.078
HBrO(aq) <a href="#">[92GRE/FUG]</a>	$Br_2(aq) + H_2O(l) \rightleftharpoons Br^- + H^+ + HBrO(aq)$	-8.240 ±0.200	47.034 ±1.142		

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Table IV-2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^\circ$	$\Delta_f G_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>-1</sup> )	$\Delta_f S_m^\circ$ (J · K <sup>-1</sup> · mol <sup>-1</sup> )
HIO <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	$H^+ + IO_3^- \rightleftharpoons HIO_3(aq)$	0.788 ±0.029	-4.498 ±0.166	
S <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	$HS^- \rightleftharpoons H^+ + S^{2-}$	-19.000 ±2.000	108.450 ±11.416	
SO <sub>3</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	$H_2O(l) + SO_4^{2-} + 2 e^- \rightleftharpoons 2OH^- + SO_3^{2-}$	-31.400 <sup>(b)</sup> ±0.700	179.230 ±3.996	
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	$3H_2O(l) + 2SO_3^{2-} + 4 e^- \rightleftharpoons 6OH^- + S_2O_3^{2-}$	-39.200 <sup>(b)</sup> ±1.400	223.760 ±7.991	
H <sub>2</sub> S(aq) <a href="#">[92GRE/FUG]</a>	$H_2S(aq) \rightleftharpoons H^+ + HS^-$	-6.990 ±0.170	39.899 ±0.970	
HSO <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	$H^+ + SO_3^{2-} \rightleftharpoons HSO_3^-$	7.220 ±0.080	-41.212 ±0.457	66.000 ±30.000
HS <sub>2</sub> O <sub>3</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	$H^+ + S_2O_3^{2-} \rightleftharpoons HS_2O_3^-$	1.590 ±0.150	-9.076 ±0.856	359.590 <sup>(a)</sup> ±100.630
H <sub>2</sub> SO <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	$H^+ + HSO_3^- \rightleftharpoons H_2SO_3(aq)$	1.840 ±0.080	-10.503 ±0.457	16.000 ±5.000
HSO <sub>4</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$	1.980 ±0.050	-11.302 ±0.285	88.891 <sup>(a)</sup> ±16.840
HN <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	$H^+ + N_3^- \rightleftharpoons HN_3(aq)$	4.700 ±0.080	-26.828 ±0.457	-15.000 ±10.000
NH <sub>3</sub> (aq) <a href="#">[92GRE/FUG]</a>	$NH_4^+ \rightleftharpoons H^+ + NH_3(aq)$	-9.237 ±0.022	52.725 ±0.126	52.090 ±0.210
				-2.130 <sup>(a)</sup> ±0.821

(Continued on next page)



Table IV-2 (continued)

Species and review where adopted	Reaction	$\log_{10} K^{\circ}$	$\Delta_f G_m^{\circ}$	$\Delta_f H_m^{\circ}$	$\Delta_f S_m^{\circ}$
			(kJ · mol <sup>-1</sup> )	(kJ · mol <sup>-1</sup> )	(J · K <sup>-1</sup> · mol <sup>-1</sup> )
HNO <sub>2</sub> (aq) <a href="#">[92GRE/FUG]</a>	H <sup>+</sup> + NO <sub>2</sub> <sup>-</sup> ⇌ HNO <sub>2</sub> (aq)	3.210 ±0.160	-18.323 ±0.913	-11.400 ±3.000	23.219 <sup>(a)</sup> ±10.518
PO <sub>4</sub> <sup>3-</sup> <a href="#">[92GRE/FUG]</a>	HPO <sub>4</sub> <sup>2-</sup> ⇌ H <sup>+</sup> + PO <sub>4</sub> <sup>3-</sup>	-12.350 ±0.030	70.494 ±0.171	14.600 ±3.800	-187.470 <sup>(a)</sup> ±12.758
P <sub>2</sub> O <sub>7</sub> <sup>4-</sup> <a href="#">[92GRE/FUG]</a>	HP <sub>2</sub> O <sub>7</sub> <sup>3-</sup> ⇌ H <sup>+</sup> + P <sub>2</sub> O <sub>7</sub> <sup>4-</sup>	-9.400 ±0.150	53.656 ±0.856		
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	H <sup>+</sup> + HPO <sub>4</sub> <sup>2-</sup> ⇌ H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	7.212 ±0.013	-41.166 ±0.074	-3.600 ±1.000	126.000 <sup>(a)</sup> ±3.363
H <sub>3</sub> PO <sub>4</sub> (aq) <a href="#">[92GRE/FUG]</a>	H <sup>+</sup> + H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ⇌ H <sub>3</sub> PO <sub>4</sub> (aq)	2.140 ±0.030	-12.215 ±0.171	8.480 ±0.600	69.412 <sup>(a)</sup> ±2.093
HP <sub>2</sub> O <sub>7</sub> <sup>3-</sup> <a href="#">[92GRE/FUG]</a>	H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>2-</sup> ⇌ H <sup>+</sup> + HP <sub>2</sub> O <sub>7</sub> <sup>3-</sup>	-6.650 ±0.100	37.958 ±0.571		
H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>2-</sup> <a href="#">[92GRE/FUG]</a>	H <sub>3</sub> P <sub>2</sub> O <sub>7</sub> <sup>-</sup> ⇌ H <sup>+</sup> + H <sub>2</sub> P <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	-2.250 ±0.150	12.843 ±0.856		
H <sub>3</sub> P <sub>2</sub> O <sub>7</sub> <sup>-</sup> <a href="#">[92GRE/FUG]</a>	H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (aq) ⇌ H <sup>+</sup> + H <sub>3</sub> P <sub>2</sub> O <sub>7</sub> <sup>-</sup>	-1.000 ±0.500	5.708 ±2.854		
H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (aq) <a href="#">[92GRE/FUG]</a>	2H <sub>3</sub> PO <sub>4</sub> (aq) ⇌ H <sub>2</sub> O(l) + H <sub>4</sub> P <sub>2</sub> O <sub>7</sub> (aq)	-2.790 ±0.170	15.925 ±0.970	22.200 ±1.000	21.045 <sup>(a)</sup> ±4.673
CO <sub>2</sub> (aq) <a href="#">[92GRE/FUG]</a>	H <sup>+</sup> + HCO <sub>3</sub> <sup>-</sup> ⇌ CO <sub>2</sub> (aq) + H <sub>2</sub> O(l)	6.354 ±0.020	-36.269 ±0.114		
CO <sub>2</sub> (g) <a href="#">[92GRE/FUG]</a>	CO <sub>2</sub> (aq) ⇌ CO <sub>2</sub> (g)	1.472 ±0.020	-8.402 ±0.114		

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Table IV–2 (continued)

Species and review where adopted	Reaction			
	$\log_{10} K^\circ$	$\Delta_f G_m^\circ$ (kJ · mol <sup>–1</sup> )	$\Delta_f H_m^\circ$ (kJ · mol <sup>–1</sup> )	$\Delta_f S_m^\circ$ (J · K <sup>–1</sup> · mol <sup>–1</sup> )
HCO <sub>3</sub> <sup>–</sup> <a href="#">[92GRE/FUG]</a>	CO <sub>3</sub> <sup>2–</sup> + H <sup>+</sup> ⇌ HCO <sub>3</sub> <sup>–</sup> 10.329 ±0.020	– 58.958 ±0.114		
CN <sup>–</sup> <a href="#">[2005OLI/NOL]</a>	HCN(aq) ⇌ CN <sup>–</sup> + H <sup>+</sup> – 9.210 ±0.020	52.571 ±0.114	43.600 ±0.200	– 30.089 <sup>(a)</sup> ±0.772
HCN(aq) <a href="#">[2005OLI/NOL]</a>	HCN(g) ⇌ HCN(aq) 0.902 ±0.050	– 5.149 ±0.285	– 26.150 ±2.500	– 70.439 <sup>(a)</sup> ±8.440
SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2–</sup> <a href="#">[92GRE/FUG]</a>	Si(OH) <sub>4</sub> (aq) ⇌ 2H <sup>+</sup> + SiO <sub>2</sub> (OH) <sub>2</sub> <sup>2–</sup> – 23.140 ±0.090	132.080 ±0.514	75.000 ±15.000	– 191.460 <sup>(a)</sup> ±50.340
SiO(OH) <sub>3</sub> <sup>–</sup> <a href="#">[92GRE/FUG]</a>	Si(OH) <sub>4</sub> (aq) ⇌ H <sup>+</sup> + SiO(OH) <sub>3</sub> <sup>–</sup> – 9.810 ±0.020	55.996 ±0.114	25.600 ±2.000	– 101.950 <sup>(a)</sup> ±6.719
Si(OH) <sub>4</sub> (aq) <a href="#">[92GRE/FUG]</a>	2H <sub>2</sub> O(l) + SiO <sub>2</sub> (quar) ⇌ Si(OH) <sub>4</sub> (aq) – 4.000 ±0.100	22.832 ±0.571	25.400 ±3.000	8.613 <sup>(a)</sup> ±10.243
Si <sub>2</sub> O <sub>3</sub> (OH) <sub>4</sub> <sup>2–</sup> <a href="#">[92GRE/FUG]</a>	2Si(OH) <sub>4</sub> (aq) ⇌ 2H <sup>+</sup> + H <sub>2</sub> O(l) + Si <sub>2</sub> O <sub>3</sub> (OH) <sub>4</sub> <sup>2–</sup> – 19.000 ±0.300	108.450 ±1.712		
Si <sub>2</sub> O <sub>2</sub> (OH) <sub>5</sub> <sup>–</sup> <a href="#">[92GRE/FUG]</a>	2Si(OH) <sub>4</sub> (aq) ⇌ H <sup>+</sup> + H <sub>2</sub> O(l) + Si <sub>2</sub> O <sub>2</sub> (OH) <sub>5</sub> <sup>–</sup> – 8.100 ±0.300	46.235 ±1.712		
Si <sub>3</sub> O <sub>6</sub> (OH) <sub>3</sub> <sup>3–</sup> <a href="#">[92GRE/FUG]</a>	3Si(OH) <sub>4</sub> (aq) ⇌ 3H <sup>+</sup> + 3H <sub>2</sub> O(l) + Si <sub>3</sub> O <sub>6</sub> (OH) <sub>3</sub> <sup>3–</sup> – 28.600 ±0.300	163.250 ±1.712		
Si <sub>3</sub> O <sub>5</sub> (OH) <sub>5</sub> <sup>3–</sup> <a href="#">[92GRE/FUG]</a>	3Si(OH) <sub>4</sub> (aq) ⇌ 3H <sup>+</sup> + 2H <sub>2</sub> O(l) + Si <sub>3</sub> O <sub>5</sub> (OH) <sub>5</sub> <sup>3–</sup> – 27.500 ±0.300	156.970 ±1.712		

(Continued on next page)

Table IV–2 (continued)

Species and review where adopted	Reaction	$\log_{10} K^{\circ}$	$\Delta_f G_m^{\circ}$	$\Delta_f H_m^{\circ}$	$\Delta_f S_m^{\circ}$
			(kJ · mol <sup>–1</sup> )	(kJ · mol <sup>–1</sup> )	(J · K <sup>–1</sup> · mol <sup>–1</sup> )
Si <sub>4</sub> O <sub>8</sub> (OH) <sub>4</sub> <sup>4–</sup> <a href="#">[92GRE/FUG]</a>	4Si(OH) <sub>4</sub> (aq) $\rightleftharpoons$ 4H <sup>+</sup> + 4H <sub>2</sub> O(l) + Si <sub>4</sub> O <sub>8</sub> (OH) <sub>4</sub> <sup>4–</sup>				
		– 36.300	207.200		
		±0.500	±2.854		
Si <sub>4</sub> O <sub>7</sub> (OH) <sub>5</sub> <sup>3–</sup> <a href="#">[92GRE/FUG]</a>	4Si(OH) <sub>4</sub> (aq) $\rightleftharpoons$ 3H <sup>+</sup> + 4H <sub>2</sub> O(l) + Si <sub>4</sub> O <sub>7</sub> (OH) <sub>5</sub> <sup>3–</sup>				
		– 25.500	145.560		
		±0.300	±1.712		

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

(b) Value calculated from a selected standard potential.



## **Part III**

### **Discussion of data selection**



## Chapter V

# Criteria for data evaluation and particular problems encountered in the review procedure

### V.1. Criteria for data evaluation

In this review the NEA guidelines for the review procedure and data selection were applied. However, the review team felt it necessary to summarise in addition the criteria for data evaluation with special emphasis on organic ligands. As these criteria were applied implicitly in all the review work, and as they are mentioned explicitly in the discussion of publications in the following chapters and in Appendix A, they are presented and discussed here.

The following check list for data evaluation was proposed jointly on the occasion of the second plenary meeting:

- Check the pH scale used.

Is the calibration method for the pH-electrodes indicated in the publication? The pH-electrodes should have been calibrated preferably in the concentration scale, and not with standard buffers to the activity scale. That is, “pH” should refer to  $-\log_{10}[\text{H}^+]$ . The latter quantity is sometimes reported as pcH or  $\text{pH}_c$ . In some cases it is reported that the glass electrodes were calibrated with standard buffers, and  $[\text{H}^+]$  calculated from pH, for example with the Davies equation. In general, this procedure is not accepted in this review. In the case of ligand protonation constants references were discarded when they reported mixed equilibrium constants, *i.e.*, involving both, proton activities and ligand concentration.

- Check that a reliable reference electrode has been used.

An unfortunate choice of an experimental set-up is using a calomel reference electrode and NaClO<sub>4</sub> as background electrolyte. The calomel reference electrode contains a saturated KCl or 1 M KCl solution. Under such conditions the measurements are very difficult because of the potential precipitation of KClO<sub>4</sub> occurring at the contact between the two solutions (KCl and NaClO<sub>4</sub>).

- Check whether suitable metal salts have been used in the experiments.

Sometimes, an experiment was mainly set-up from the viewpoint of convenience or analytical accuracy, and little attention was paid to the ambiguities of results caused by this choice. For example, sulphate metal salts have occasionally been used because these salts allow the preparation of solutions with exact compositions by weighing. However, the drawback of this choice is the ambiguity of data interpretation due to the additional effects caused by metal sulphate complexation.

- Check that the temperature at which the measurements have been done is given.

This obviously important information for deriving reliable thermodynamic data is often missing, or given only in ambiguous terms. For example, the term “room temperature” varies with the year and the geographic situation of the investigation between 15 and 30°C.

- Check whether the ionic strength was reasonably constant under the experimental conditions.

A background electrolyte providing a constant ionic medium must be used. The nature of the background electrolyte, the ionic strength, and the total ligand concentrations must be given. For studies where  $I \leq 0.1$  M the condition of constant ionic medium is quite difficult to achieve. For example, pH values below 2 cannot be reached at  $I < 0.1$  M without disturbing substantially the composition of the ionic medium. In the case of citrate, and even more so in the case of edta, the use of large concentrations of the reacting species with respect to the concentration of the background electrolyte, *e.g.*, 0.1 M KNO<sub>3</sub>, can result in total ionic strengths much higher than 0.1 M. Sometimes this effect has been remedied in experimental studies by considering the contribution of the reacting species to the total ionic strength and reducing the concentration of the added inert salt in order to reach  $I = 0.1$  M (KNO<sub>3</sub>). In such cases the ionic medium is shown in parenthesis in this review indicating that the concentration of KNO<sub>3</sub> can be lower than 0.1 M.

- Check that the speciation model used for analysing the results is compatible with the one chosen by the TDB review.

As an example, speciation models of metal – edta systems at low pH sometimes ignore the presence of the species H<sub>5</sub>edta<sup>+</sup> and H<sub>6</sub>edta<sup>2+</sup> under these con-



ditions. In such cases the data have been re-interpreted in this review if the experimental data have been reported in a suitable form.

- Check that the protonation constants used are compatible with the values selected in the TDB review.

If necessary and possible, *i.e.*, if the experimental data have been reported in a suitable form, the data have been recalculated using protonation constants selected in this review.

- Check the method used, if any, for extrapolation to zero ionic strength.

If necessary and possible, *i.e.*, if the experimental data have been reported in a suitable form, the data have been recalculated in this review using SIT. The SIT approach has been found acceptable for ionic strengths up to about 5 molal.

- Check that all the complexes whose stability constants are extracted from the measurement data are significant under the experimental conditions.

Sometimes chemical models are proposed where the complexes purportedly being studied represent a minor fraction of the total concentration of the investigated substance. If possible, *i.e.*, if the experimental data have been reported in a suitable form, in this review alternative chemical models have been used to analyse the data.

In addition to this check list, special attention has been paid concerning the characterisation of solid compounds. A large number of metal – organic compounds have been reported in the literature, but their degree of characterisation varies considerably. In this review, oxalate, citrate, edta and isa compounds are mentioned only if their stoichiometry has been confirmed at least by elemental analysis, or it is indicated explicitly that the authors assumed a certain stoichiometry without further evidence. If solubility data or thermodynamic constants have been reported, an important criteria for the reliability of these values is the proper characterisation of the solid compound in equilibrium with the solution. In many cases the complete lack of any characterisation of the solid prevented the selection of thermodynamic data by this review.

## V.2. Particular problems of commonly used experimental methods

Most commonly, the following methods are used to determine stability constants.

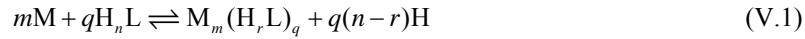
- (1) Potentiometry
- (2) Two-phase distribution (solvent extraction and ion exchange)
- (3) Spectrophotometry

However, since, for the polyprotic acid  $H_nL$ , any of the dissociated species  $H_rL^{r-n}$  ( $r = 0$  to  $n - 1$ ) may form complexes with metal ions, the following problems are commonly encountered in the papers examined by this review:

- (a) Assignment of complex species.
- (b) Error propagation in the method of data processing (errors from the data and from the mathematical transformation).
- (c) Error propagation from the dissociation constants used in the calculation.
- (d) Side reactions (hydrolysis).

### V.2.1. Potentiometry

In this method, titration curves, pH vs.  $C_{OH^-}$  (total concentration of  $OH^-$ ), are obtained for the solution containing known concentrations of  $H_nL$  ( $C_L$ ) and the metal ion ( $C_M$ ). The complex formation of the metal ion  $M$  with  $H_nL$  (in the following discussions, charges will be omitted for brevity) liberates several protons according to the reaction,



and the resulting proton concentration is measured potentiometrically. If the ratio of the number of protons to the number of ligands in the complex is more freely defined, the reaction may be considered as,



In this case, the complex  $M_mH_rL_q$  is considered as a mixed ligand complex with  $H_rL$  and  $H_sL$  ( $r \neq s$ ) or with  $H_rL$  and  $OH$ . Note that it is not possible to discriminate by potentiometry between these two kinds of mixed ligand complexes.

The stability constant for the Reaction (V.3), which is to be determined, is defined as:



$$\beta_{q(H_rL),m} = \frac{[M_m(H_rL)_q]}{[M]^m \cdot [H_rL]^q} \quad (V.4)$$

When organic acid is added as  $H_nL$  and metal ions as a salt of a non-complexing anion, mass balance equations for ligand (L), metal ion (M) and proton (H) are:

$$C_L = \sum_{i=0}^n [H_iL] + \sum_m \sum_r \sum_q q [M_m(H_rL)_q], \quad (V.5)$$

$$C_M = [M] + \sum_m \sum_r \sum_q m [M_m(H_rL)_q], \quad (V.6)$$

$$nC_L - C_{OH^-} - [H] + [OH] = \sum_{i=1}^n i [H_iL] + \sum_m \sum_r \sum_q qr [M_m(H_rL)_q], \quad (V.7)$$

where

$$[H_r L] = \beta_r^H [H]^r [L] = \left( \prod_{i=1}^r K_i \right) [H]^r [L] = C'_L \alpha_r, \quad (V.8)$$

$$C'_L = \sum_{i=0}^n [H_i L] \quad (V.9)$$

$$\alpha_r = \frac{[H_r L]}{\sum_{i=0}^n [H_i L]} = \frac{\beta_r^H [H]^r}{1 + \sum_{i=1}^n \beta_i^H [H]^i} \quad (V.10)$$

$$\text{and} \quad [OH] = K_w / [H]. \quad (V.11)$$

If  $[H]$ ,  $[L]$ , and  $[M]$  and all formation constants ( $q$ ,  $r$ ,  $m$  and  $\log_{10} \beta_{q(H_r L)_m}$ ,  $\log_{10} \beta_i^H$ ) are known, equilibrium concentrations of all species can be calculated straightforwardly. Alternatively, when  $C_M$ ,  $C_L$ ,  $C_{OH}$  and all formation constants ( $q$ ,  $r$ ,  $m$  and  $\log_{10} \beta_{q(H_r L)_m}$ ,  $\log_{10} \beta_i^H$ ) are known, these equations can be solved to give  $[H]$ ,  $[L]$ , and  $[M]$ , which in turn enable to calculate equilibrium concentrations of all species. When some of  $q$ ,  $r$  and  $m$  are larger than 1, Eqs. (V.4) - (V.11) can be solved only implicitly.

Potentiometric determination of stability constants is the estimation of the best set of  $\log_{10} \beta_{q(H_r L)_m}$  and  $q$ ,  $r$ ,  $m$  from the various data sets of ( $C_M$ ,  $C_L$ ,  $C_{OH}$  and  $[H]$ , where  $[H]$  is measured for various  $C_M$ ,  $C_L$ ,  $C_{OH}$ ) with known  $\log_{10} \beta_i^H$ . In principle, one can carry out this by adopting the following procedure.

- (i) Prepare the data sets of  $[H]$  (observed) for various  $C_M$ ,  $C_L$ ,  $C_{OH}$ .
- (ii) Make estimates of the set of  $q$ ,  $r$ ,  $m$  and  $\log_{10} \beta_{q(H_r L)_m}$ .
- (iii) For each data set, solve Eqs. (V.4) - (V.11) to obtain  $[H]$ ,  $[L]$ , and  $[M]$  for a given set of  $C_M$ ,  $C_L$  and  $C_{OH}$  using the above estimates and  $\log_{10} \beta_i^H$ .
- (iv) Compare  $[H]$ (estimated) and  $[H]$ (observed).
- (v) Change estimates of the set of  $q$ ,  $r$ ,  $m$  and  $\log_{10} \beta_{q(H_r L)_m}$ .
- (vi) Repeat (iii)-(v) until  $[H]$ (estimated) sufficiently agrees with  $[H]$ (observed).

Although this is numerically possible, it is somewhat difficult since the procedure is doubly implicit. To simplify Eqs. (V.5) - (V.7), among the terms,  $\sum \sum \sum q [M_m (H_r L)_q]$ ,  $\sum \sum \sum m [M_m (H_r L)_q]$  and  $\sum \sum \sum q r [M_m (H_r L)_q]$  appearing in Eqs. (V.5) - (V.7), at least two of them must be directly related to allow substitution of each other. Therefore, in many papers, certain assumptions on the complex species are made to simplify the problem.

When only one ligand species ( $H_r L$ ) forms complexes containing one metal ion ( $m = 1$ ), the second term in the right hand side of Eq.(V.7) can be transformed as follows:

$$\sum_r \sum_q q r [M (H_r L)_q] = r \sum_q q [M (H_r L)_q]. \quad (V.12)$$

Substituting Eqs. (V.5), (V.8) and (V.11) into Eq.(V.7) gives:

$$nC_L - C_{OH} - [H] + [H]/K_w = C'_L \sum_{i=1}^n i\alpha_i + r(C_L - C'_L). \quad (V.13)$$

Only one unknown,  $C'_L$  in this equation can be explicitly estimated from measured  $[H]$  with  $C_L$ ,  $C_{OH}$ ,  $\log_{10} K_w$  and  $\log_{10} \beta_i^H$ . Thus,  $\bar{n}_L$  (the average number of ligand bound per metal ion) can be directly calculated as:

$$\bar{n}_L = \frac{\sum q[M(H_r L)_q]}{C_M} = \frac{C_L - C'_L}{C_M}. \quad (V.14)$$

Since  $[H_r L]$  can be calculated by Eq.(V.8),  $\bar{n}_L$  can be expressed as a function of  $[H_r L]$ .

$$\bar{n}_L = \frac{\sum q[M(H_r L)_q]}{C_M} = \frac{\sum q \beta_{q(H_r L)} [H_r L]^q}{1 + \sum_q \beta_{q(H_r L)} [H_r L]^q} \quad (V.15)$$

Therefore, a plot of  $(C_L - C'_L)/C_M$  vs.  $\log_{10}[H_r L]$  can be analysed (graphically or by nonlinear curve-fitting) to give values of  $\log_{10} \beta_{q(H_r L)}$ .

In some papers, the above titration curve is compared with that of the metal-ion blank solution. In the absence of a metal ion, the proton balance is expressed by,

$$nC_L - C_{OH}^* - [H] + [OH] = C_L \sum_{i=1}^n i\alpha_i. \quad (V.16)$$

By comparing Eq.(V.16) with Eq.(V.13) at the same pH,

$$\Delta C_{OH} = C_{OH} - C_{OH}^* = (C_L - C'_L) \left( \sum_{i=1}^n i\alpha_i - r \right). \quad (V.17)$$

Then  $\bar{n}_L$  is calculated as,

$$\bar{n}_L = \frac{\Delta C_{OH}}{C_M (\sum i\alpha_i - r)} \quad (V.18)$$

Although this seems to make it easier to obtain  $\bar{n}_L$  (without calculating  $C'_L$ ), this is only apparently easier since the blank titration can be calculated from a given set of  $C_L$ ,  $C_{OH}$ ,  $\log_{10} K_w$  and  $\log_{10} \beta_i^H$ . Also, this makes the error estimation difficult, since the errors in the blank titration and those in  $\log_{10} K_w$  and  $\log_{10} \beta_i^H$  will be introduced in a complicated manner.

When only one complex species is formed, Eqs. (V.5) - (V.7) can be expressed as:

$$C_L = \sum_{i=0}^n [H_i L] + q[M_m(H_r L)_q] = C'_L + q[M_m(H_r L)_q], \quad (V.19)$$

$$C_M = [M] + m[M_m(H_r L)_q] \quad (V.20)$$

$$nC_L - C_{OH} - [H] + [OH] = \sum_{i=1}^n i[H_i L] + qr[M_m(H_r L)_q]. \quad (V.21)$$

Substituting Eq.(V.19) into Eq.(V.21) gives

$$nC_L - C_{OH} - [H] + K_w/[H] = C'_L \sum_{i=1}^n i \alpha_i + r(C_L - C'_L), \quad (V.22)$$

which enables us to calculate  $C'_L$ . Then

$$[M_m(H_rL)_q] = (C_L - C'_L)/q \quad (V.23)$$

$$[M] = C_M - m(C_L - C'_L)/q \quad (V.24)$$

$$[H_rL] = C'_L \alpha_r \quad (V.25)$$

are used to directly calculate  $\log_{10} \beta_{q(H_rL)}$  by Eq.(V.3).

Except for the simplest cases discussed above, titration curves cannot be resolved to explicitly give  $\log_{10} \beta_{q(H_rL)}$  without a complex nonlinear least-squares method. Error propagation in the data processing (errors from the data and from the mathematical transformation) is quite complicated in this potentiometric determination of  $\log_{10} \beta_{q(H_rL)}$ . Thus, reproduction of the titration curve with a set of assumed species and their  $\log_{10} \beta_{q(H_rL)}$  and the comparison of those parameters with results obtained using different sets of assumed species and their  $\log_{10} \beta_{q(H_rL)}$  are recommended to judge the reliability of the work.

Potentiometry is effective only when the concentrations of the different species *change* along the titration curve. Therefore the number of species that may be investigated using potentiometry depends strongly on the concentration ranges studied, both of ligand, metal and pH. Because of that a large and constant ionic medium is essential to avoid changes of activity coefficients, while allowing a wide range of concentrations to be covered. When interpreting the data it is therefore useful to calculate the amounts of the different species along a titration. If the percentage of the species is very small, perhaps < 5%, then it is very difficult to determine its equilibrium constant. Also if there are only one or two titrations covering a small range of ligand concentrations, then the uncertainty is increased.

### V.2.2. Two-phase distribution (solvent extraction and ion exchange)

The distribution ratio,  $D$ , of a metal ion between two phases in the presence of a complex-forming reagent is expressed by:

$$D = \frac{C_{M,o}}{[M] + \sum_r \sum_q [M(H_rL)_q]} = \frac{D_0}{1 + \sum_r \sum_q \beta_{q(H_rL)} [H_rL]^q}, \quad (V.26)$$

where  $C_{M,o}$  is the concentration of M in the organic or ion exchanger phase and  $D_0$  is the distribution ratio in the absence of the ligand. Only monomeric complexes are consid-

ered for simplicity. In ion exchange studies, the term “distribution coefficient” and the symbol  $K_d$  are used in place of “distribution ratio” and  $D$ .

When only one ligand species forms complexes, Eq.(V.26) can be simplified to:

$$D = \frac{D_0}{1 + \beta_{1(H_r, L)}[H_r L] + \beta_{2(H_r, L)}[H_r L]^2 + \dots} \quad (V.27)$$

In the past, when complicated mathematical treatment was unavailable, this equation was transformed into:

$$\frac{D_0/D - 1}{[H_r L]} = \beta_{1(H_r, L)} + \beta_{2(H_r, L)}[H_r L] + \dots \quad (V.28)$$

$\beta_{1(H_r, L)}$  and  $\beta_{2(H_r, L)}$  were obtained as an intercept and a slope of the plot of this equation.

When different ligand species (such as L, HL and  $H_2L$  ...) may form complexes, Eq.(V.27) is transformed into,

$$D = \frac{D_0}{1 + \sum_r \sum_q \beta_{q(H_r, L)}[H_r L]^q} = \frac{D_0}{1 + \sum_r \sum_q \beta_{q(H_r, L)}(\beta_r^H[H]^r)^q [L]^q}, \quad (V.29)$$

and apparent constants

$$\beta_q^{\text{app}} = \beta_{q(H_r, L)} \sum_r (\beta_r^H[H]^r)^q \quad (V.30)$$

are obtained at a certain pH. From the dependence of  $\log_{10} \beta_q^{\text{app}}$  on pH,  $\log_{10} \beta_{q(H_r, L)}$  can be estimated.

Check points that should be considered are:

(a)  $\log_{10} D_0$  or  $\log_{10} K_d^\circ$ :

Dependence of  $\log_{10} D_0$  on pH, concentrations of extractants and ionic strength (in solvent extraction), or dependence of  $\log_{10} K_d^\circ$  on pH, concentrations of competing ions and ionic strength must be carefully examined.

(b) Side reactions:

In connection with (a), the effect of possible side reactions must be checked. Hydrolysis and complex formation by the extractant are especially important. When some side reaction is serious, Eq.(V.26) should be expressed as:

$$D = \frac{C_{M,0}}{[M] + \sum_x [MX_x] + \sum_r \sum_q [M(H_rL)_q]}, \quad (V.31)$$

Although the condition  $[M] + \sum [MX_x] \ll \sum \sum [M(H_rL)_q]$  seems to indicate that the effect of complex formation by X is well masked by the main complex formation with H<sub>r</sub>L, this does not guarantee that  $[M] \gg \sum [MX_x]$ . This means that  $\sum [MX_x]$  cannot be neglected in the analysis since Eq.(V.31) is transformed into:

$$D = \frac{D_0}{\frac{\sum_r \sum_q \beta_{q(H_rL)} [H_rL]^q}{1 + \sum_x \beta_x [X]^x}}. \quad (V.32)$$

(c) Distribution of metal-containing species.

Complexes should not be carried into the organic or exchanger phase. Especially, in ion exchange, complex species may be also transferred into the exchanger phase.

(d) Error propagation:

Usually in solvent extraction, the concentrations of the metal ion in both, organic and aqueous phases, are measured to obtain  $D$  values. If absolute errors in the determination of metal-ion concentration are nearly equal, the relative errors in  $D$  ( $|\Delta D / D| = |\Delta \ln D|$ ) will be nearly constant. In this case, the best set of parameters will be obtained by minimising the residual sum of squares,

$$S = \sum (\log_{10} D_{\text{observed}} - \log_{10} D_{\text{calculated}})^2 \quad (V.33)$$

where  $\log_{10} D_{\text{calculated}}$  is the value calculated by Eq.(V.26) with the variable  $\log_{10}[H_rL]$  and assumed parameters  $\log_{10} \beta_{q(H_rL)}$ . Since the variable(s) and parameters should be selected in a way that their uncertainties will equally contribute to the residual sum, the variable and parameters should be taken as  $\log_{10}[H_rL]$  (not  $[H_rL]$ ),  $\log_{10} \beta_{q(H_rL)}$  (not  $\beta_{q(H_rL)}$ ) and  $\log_{10} D_0$  (not  $D_0$ ). Thus, the best form that should be taken for a least-squares method is:

$$\log_{10} D = \log_{10} D_0 - \log \left( 1 + \sum_r \sum_q 10^{\log_{10} \beta_{q(H_rL)} + q \log_{10} [H_rL]} \right) \quad (V.34)$$

Curve fitting of the plots of  $\log_{10} D$  vs.  $\log_{10}[H_rL]$  to this equation can be performed since the right-hand side of Eq.(V.34) can be calculated straightforwardly using the variable ( $\log_{10}[H_rL]$ ) and fitting parameters ( $\log_{10} \beta_{q(H_rL)}$  and  $\log_{10} D_0$ ). On the contrary, any transformation such as Eq.(V.28) will complicate the error consideration. The absolute error in  $D_0/D$  changes with the magnitude of  $D$ . If  $D_0/D$  or  $(D_0/D - 1)$  is taken as a fitting value for the non-weighted least-squares curve-fitting, the data with small  $D$  are heavily weighted since the absolute errors in  $D_0/D$  are larger with smaller  $D$ . This unjustified weighting is lessened since  $D_0/D - 1$  is divided by  $[H_rL]$  in the

left hand side of Eq.(V.28). However, data plots with small  $[H,L]$  will all be distributed close to the y-axis because the right hand side of Eq.(V.28) is linear in  $[H,L]$ . The useful parameter range of such  $[H,L]$  plots is where the predominant species is gradually changing from  $M(H,L)$  to  $M(H,L)_2$ . Moreover, the error in  $D_0$  will give a systematic error to the plots. As a result, it is difficult to estimate the reliability of the values of  $\log_{10} \beta_{q(H,L)}$  which are converted from  $\beta_{q(H,L)}$  obtained by this type of plot. Linearity of the plot in the region where  $[H,L] \rightarrow 0$  should be carefully examined to check the validity of Eq.(V.28) in the selected  $[H,L]$  range.

On the other hand, usually in the ion exchange method, the concentration of metal ion in the aqueous phase  $C_{M,aq}$  is measured and compared with the total concentration  $C_{M,t}$

$$D = \frac{C_{M,t} - C_{M,aq}}{C_{M,aq}} \quad (V.35)$$

where  $D$  is equivalent to  $K_d$ . In this case, the absolute errors in  $C_{M,aq}$  or the fraction remained in the aqueous phase ( $f_{aq} = C_{M,a} / C_{M,t}$ ) are nearly equal. Therefore, the residual sum of squares to be minimised is,

$$S = \sum (f_{aq,observed} - f_{aq,calculated})^2 \quad (V.36)$$

where  $f_{aq}$  can be calculated as:

$$f_{aq} = \frac{C_{M,a}}{C_{M,t}} = \frac{1}{D+1} = \frac{1}{10^{\log_{10} D} + 1} \quad (V.37)$$

where  $\log_{10} D$  is calculated by Eq.(V.34) straightforwardly using the variable ( $\log_{10}[H,L]$ ) and fitting parameters ( $\log_{10} \beta_{q(H,L)}$  and  $\log_{10} D_0$ ). When the transformation given by Eq.(V.28) is used, relative errors in  $D_0 / D - 1$  are similar since it is expressed as:

$$\frac{D_0}{D} - 1 = \frac{(1/f_{aq}^0) - (1/f_{aq})}{(1/f_{aq}) - 1} \quad (V.38)$$

where the absolute errors in  $(1/f_{aq}^0)$  and  $(1/f_{aq})$  are similar ( $f_{aq}^0$  is the fraction remained in the aqueous phase in the absence of complexant). A similar discussion as for solvent extraction applies here, and it can be concluded that also in this case, it is difficult to estimate the reliability of the values of  $\log_{10} \beta_{q(H,L)}$ .

Generally speaking, in the case of solvent extraction there is a new liquid phase, with uncertainties in activity coefficients in the organic phase, unknown parallel reactions, unknown species extracted, etc. This increases the uncertainty of the method as compared with potentiometry and spectrophotometry where only one liquid phase is present.



### V.2.3. Spectrophotometry

When the number of complexes is one or two, spectrophotometry with the analytical method such as mole ratio method or continuous variation method usually gives reliable information about the composition of the complex(es) and their molar absorptivity. The problem in this method is the error from the mass balance relationship. For example, in the simplest case,  $\beta_{q(\text{H}_r\text{L})}$  is obtained as,

$$\beta_{q(\text{H}_r\text{L})} = \frac{[\text{M}(\text{H}_r\text{L})_q]}{[\text{M}][\text{H}_r\text{L}]^q} = \frac{[\text{M}(\text{H}_r\text{L})_q]}{(C_M - [\text{M}(\text{H}_r\text{L})_q])(C_L - q[\text{M}(\text{H}_r\text{L})_q])\alpha_r} \quad (\text{V.39})$$

where  $\alpha_r$  is

$$\alpha_r = \frac{[\text{H}_r\text{L}]}{\sum_{i=0}^n [\text{H}_i\text{L}]} = \frac{\beta_r^{\text{H}}[\text{H}]^r}{1 + \sum_{i=1}^n \beta_i^{\text{H}}[\text{H}]^i} \quad (\text{V.40})$$

$[\text{M}(\text{H}_r\text{L})_q]$  is obtained from the absorbance at a certain wavelength ( $\lambda$ ) and the molar absorptivity ( $\epsilon_{\text{M}(\text{H}_r\text{L})_q}^\lambda$ ) of the complex at  $\lambda$ .

$$[\text{M}(\text{H}_r\text{L})_q] = A_\lambda / \epsilon_{\text{M}(\text{H}_r\text{L})_q}^\lambda \quad (\text{V.41})$$

Since molar absorptivity ( $\epsilon_{\text{M}(\text{H}_r\text{L})_q}^\lambda$ ) is obtained from the absorbance of a 'known' concentration of the complex (usually under the condition where nearly all metal ions are in the form of the complex), it includes the same uncertainty as the determination of the concentration. Therefore  $(C_M - [\text{M}(\text{H}_r\text{L})_q])$  and  $(C_L - q[\text{M}(\text{H}_r\text{L})_q])$  in Eq.(V.39) are reliable only when they are larger than the error limit of  $C_M$  and  $C_L$ . That is, when the stability of the complex is very high,  $[\text{M}]$  or  $[\text{H}_r\text{L}]$  cannot be estimated reliably. Usually, such conditions are avoided since the experiment is done where the absorbance (or the concentration of the complex) is gradually changing. However, when the number of complexes is large, the situation may be more complex. When the number of complexes is large, the best set of  $\beta_{q(\text{H}_r\text{L})}$ 's and molar absorptivities ( $\epsilon_{\text{M}(\text{H}_r\text{L})_q}^\lambda$ 's) are estimated by minimising the following residual sum of squares:

$$S = \sum_{\lambda} \sum_n (A_{\lambda,n,\text{observed}} - A_{\lambda,n,\text{calculated}})^2 \quad (\text{V.42})$$

where the summation is carried out over several wavelengths ( $\lambda$ ) and all  $n$  spectra. Total metal and total ligand concentrations give strict conditions for mass balances. In other words, they are considered not to contain any error. Since  $(C_M - [\text{M}(\text{H}_r\text{L})_q])$  and  $(C_L - q[\text{M}(\text{H}_r\text{L})_q])$  cannot become negative, the errors in  $C_M$  and  $C_L$  may give serious systematic errors. If the same stock solution is used to prepare sample solutions, the problem is more serious. Although many wavelengths can be selected to improve the fitting, systematic errors may be introduced because each spectrum contains the error in the preparation of that solution. To minimise  $S$  by Eq.(V.42), spectrophotometry seems to have a tendency to assume larger number of complexes since larger number of pa-

rameters ( $\beta_{q(H,L)}$ 's and  $\varepsilon_{M(H,L)_q}^\lambda$ 's) easily give smaller  $S$ .  $S$  must be checked whether its size is reasonable as compared with the precisions of  $C_M$  and  $C_L$ . Also, the deviations of residuals must be examined whether they have some inclined tendency. Usually, these kind of examinations are not carried out in the papers, and the second best way may be to reproduce species distributions and absorption spectra from the reported parameters.

In summary, in the case of spectrophotometry, additional parameters must be estimated (molar absorptivities). This is a disadvantage against potentiometry, where less fitting parameters need to be obtained. Also, in general, the precision of the measurements is lower for a spectrophotometer than for a voltmeter. In case where species do not differ very much in absorption coefficients a distinction between species might be impossible (for example protonation of many ligands). And furthermore, spectrophotometry (similar to solvent extraction) requires in many cases that potentiometric measurements (of lower precision) are made in any case to determine  $[H^+]$ . So in general spectrophotometry requires double measurements: potentiometric and optical absorbance. However, clearly the advantage of this method is that there is positive confirmation that a complex is formed when it has absorption in a characteristic wavelength.

### V.3. Ionic medium effects on protonation constants for organic ligands

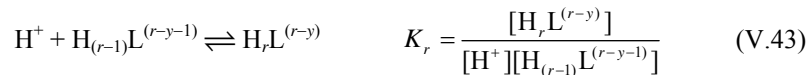
#### V.3.1. Introduction

The activity coefficients of aqueous ions and molecules at "low" ionic strengths,  $I < 0.1$  M, are dominated by the Debye-Hückel term. Owing to this, the activity coefficients are not highly dependent on the nature of the background electrolyte. However, at higher ionic strengths,  $I > 0.1$  M, the nature of the ionic components of the background electrolyte will affect the value of the protonation constants.

For polycarboxylic acids, equilibrium constants for the formation of  $Na^+$  and  $K^+$  complexes have often been reported. These experimental studies are based on potentiometric data, from both pH and ion-selective glass electrodes. Such complexes would affect the protonation constants determined in sodium or potassium electrolyte media. However, it is in general not possible to differentiate between weak complex formation ( $K < 10$ ) and the variation of activity coefficients, based solely on potentiometric data.

#### V.3.2. Evaluation of protonation data excluding complexes with medium cations

The following nomenclature is used for the protonation of a ligand,  $L^{y-}$ , cf. Section II.1.6.1:



The standard SIT equations may be used to describe changes in activity coefficients. For 1:1 background electrolytes of composition MX these equations are:

$$\log_{10} K_r = \log_{10} K_r^o + \log_{10} \gamma_{\text{H}^+} + \log_{10} \gamma_{\text{H}_{(r-1)}\text{L}^{(r-y-1)}} - \log_{10} \gamma_{\text{H}_r\text{L}^{(r-y)}} \quad (\text{V.44})$$

The activity coefficients are according to the SIT methodology given by (Section B.1):

$$\log_{10} \gamma_i = -z_i^2 D + \sum_k \varepsilon(i, k) m_k \quad (\text{V.45})$$

resulting in:

$$\log_{10} K_r - \Delta z^2 D = \log_{10} K_r^o - \Delta \varepsilon I_m \quad (\text{V.46})$$

where (cf. Eqs. (B.6) to (B.8) in Appendix B):

$$D = \frac{A\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \quad (\text{V.47})$$

$$\Delta z^2 = (r-y)^2 - (r-y-1)^2 - 1 = 2r - 2y - 2$$

$$\Delta \varepsilon = \varepsilon(\text{H}_r\text{L}^{(r-y)}, \text{M}^+) - \varepsilon(\text{H}_{(r-1)}\text{L}^{(r-y-1)}, \text{M}^+) - \varepsilon(\text{H}^+, \text{X}^-)$$

and  $I_m$  is the ionic strength in molal units of the background electrolyte (for a 1:1 electrolyte with formula MX,  $I_m$  is equal to  $[\text{M}^+]$ ), and  $A = 0.509$  at 25°C (Table B.2).

As discussed in Appendix B the  $\varepsilon$ -values are in general not dependent on ionic strength at moderate concentrations of background salt. This (lack of) dependence is illustrated in Figure V-1 for a few electrolytes. There are however exceptions, such as the tetraalkylammonium halides, as indicated in the same figure. For these exceptions the following relationship has been proposed (cf. Appendix B):  $\varepsilon(i, k, I_m) = \varepsilon_1(i, k) + \varepsilon_2(i, k) \log_{10}(I_m)$ . If the  $\varepsilon$ -values are not dependent on the ionic strength, as is the general case, then the experimental values for the protonation constants, corrected for the Debye-Hückel term as indicated in the left hand side of Eq.(V.46), when plotted against  $I_m$  should produce a straight line from which the values of  $\log_{10} K_r^o$  and  $\Delta \varepsilon$  are obtained.

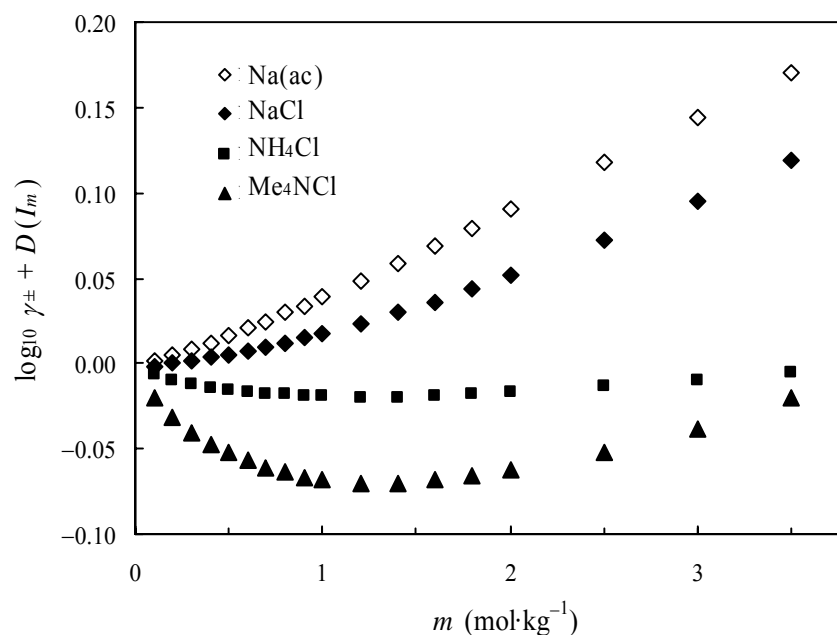
For protonation constants it is possible to separate  $\Delta \varepsilon$  in two parts, so that all data for a given background cation may be treated simultaneously:

$$\log_{10} K_r - \Delta z^2 D - \varepsilon(\text{H}^+, \text{X}^-) \cdot I_m = \log_{10} K_r^o - \Delta \varepsilon^* \cdot I_m \quad (\text{V.48})$$

where  $\Delta \varepsilon^* = \varepsilon(\text{H}_r\text{L}^{(r-y)}, \text{M}^+) - \varepsilon(\text{H}_{(r-1)}\text{L}^{(r-y-1)}, \text{M}^+)$  depends only on the cationic composition of the background electrolyte ( $\text{Na}^+$ ,  $\text{K}^+$ , etc.). In this case the left hand side of Eq.(V.48), with the experimental values of  $\log_{10} K_r$ , corrected both for the Debye-

Hückel term and the specific interaction term for  $H^+$ , when plotted against  $I_m$  should produce a straight line from which the values of  $\log_{10} K_r^\circ$  and  $\Delta\epsilon^*$  may be obtained. Eq.(V.48) has been used in Sections VI.3.2 and VI.3.3 (Figures VI-2 and VI-3), Sections VII.3.2 to VII.3.4 (Figures VII-5 to VII-7), and Sections VIII.3.2 to VIII.3.6 (Figures VIII-7 to VIII-12).

Figure V-1: Mean ionic activity coefficients adjusted with a Debye-Hückel term for some 1:1 electrolytes (sodium acetate and chloride, ammonium chloride and tetramethylammonium chloride). The values of  $\epsilon(i,k,I_m)$  in Eq.(V.45) correspond to the slope of lines passing through the origin, and they are only slightly dependent on the ionic strength for most salts. The figure shows however that in the case of tetraalkylammonium halides the ionic interactions can be better described by assuming ion interaction coefficients that are functions of the ionic strength rather than constants. Ciavatta [80CIA] proposed the relationship  $\epsilon(i,k,I_m) = \epsilon_1(i,k) + \epsilon_2(i,k) \log_{10} I_m$  and this function has been adopted by this review, see also Section B.3 and Table B-6.



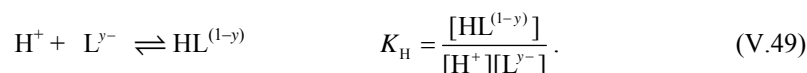
### V.3.3. Complex formation with medium cations

It is often claimed that polycarboxylic acids form complexes with alkali metal ions. This could concern  $\text{edta}^{4-}$ ,  $\text{cit}^{3-}$ , and to a lesser extent species with lower electric charge, such as  $\text{Hedta}^{3-}$ ,  $\text{Hcit}^{2-}$ , and  $\text{ox}^{2-}$ . In several studies the difference in protonation con-

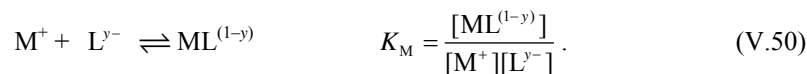
stants obtained in tetraalkylammonium and alkali metal electrolytes has been used to derive formation constants, *e.g.*, for  $\text{Na}^+$  and  $\text{K}^+$ . It is assumed in these studies that no complexes are formed between the ligands and tetraalkylammonium ions, and that the observed medium effects can be ascribed to complex formation. However, as indicated in Figure V-1 the activity coefficients in tetraalkylammonium salts are quite different from those in alkali metal salts, although the differences do not necessarily implicate alkali metal ion complex formation, *e.g.*, between  $\text{Na}^+$  and chloride. Therefore, different ionic medium effects on protonation constants when comparing Na/K electrolytes with tetraalkylammonium salts are not necessarily an indication of complex formation between the ligand and  $\text{Na}^+$  or  $\text{K}^+$ .

This section illustrates how the SIT model of activity coefficients may be applied to estimate medium effects on protonation constants if complex formation indeed occurs between the ligand and the medium cation.

The first protonation of a ligand,  $\text{L}^{y-}$ , is described as:



If the possibility of complex formation with the medium cation,  $\text{M}^+$ , is considered, the equilibrium and its constant are expressed as:



Note that a special nomenclature is used in this section for the equilibrium constants. If the concentration of  $\text{ML}^{(1-y)}$  is not negligible, the protonation constant that is measured experimentally is in fact:

$$K_{\text{H}}^{\dagger} = \frac{[\text{HL}^{(1-y)}]}{[\text{H}^+][\text{L}^{y-}] + [\text{ML}^{(1-y)}]} \quad (\text{V.51})$$

From Eq.(V.50),  $[\text{ML}^{(1-y)}] = K_{\text{M}} [\text{M}^+][\text{L}^{y-}]$ , and it follows that:

$$\log_{10} K_{\text{H}}^{\dagger} = \log_{10} K_{\text{H}} - \log_{10} (1 + K_{\text{M}} [\text{M}^+]) \quad (\text{V.52})$$

The ionic media dependence of  $\log_{10} K_{\text{H}}$  may be calculated with the SIT model, *cf.* Eq.(V.46):

$$\log_{10} K_{\text{H}} = \log_{10} K_{\text{H}}^{\circ} + (\Delta z^2)_{\text{H}} D - \Delta \epsilon_{\text{H}} I_m \quad (\text{V.53})$$

where  $\Delta \epsilon_{\text{H}} = \epsilon(\text{HL}^{(1-y)}, \text{M}^+) - \epsilon(\text{L}^{y-}, \text{M}^+) - \epsilon(\text{H}^+, \text{X}^-)$ , and  $(\Delta z^2)_{\text{H}} = (1-y)^2 - y^2 - 1$ . Inserting Eq.(V.53) in Eq.(V.52):

$$\log_{10} K_{\text{H}}^{\dagger} - (\Delta z^2)_{\text{H}} \cdot D = \log_{10} K_{\text{H}}^{\circ} - \Delta \epsilon_{\text{H}} \cdot I_m - \log_{10} (1 + K_{\text{M}} [\text{M}^+]) \quad (\text{V.54})$$

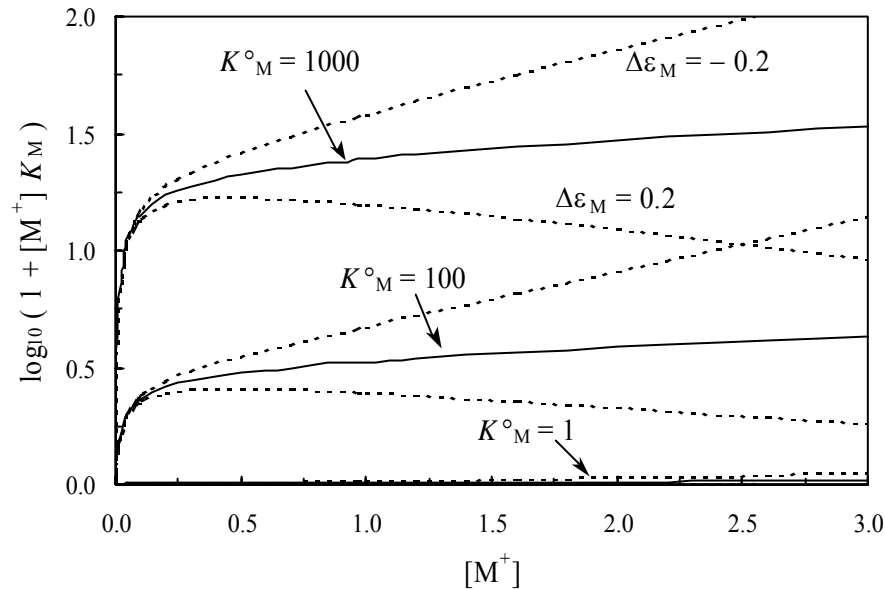
A comparison of Eq.(V.54) with Eq.(V.46) reveals that the term  $-\log_{10}(1 + K_M[M^+])$  accounts for the effect of  $ML^{(1-y)}$  in SIT plots. Eq.(V.54) may be considered from two extreme situations: either unimportant or considerable complex formation with  $M^+$ . For negligible complex formation with the background cation,  $K_M[M^+] \ll 1$ , and Eq.(V.54) is essentially equal to Eq.(V.46). In that case the SIT plot is unaffected. When the formation of  $ML^{(1-y)}$  is significant,  $K_M[M^+] \gtrsim 1$ , and the term  $\log_{10}(1 + K_M[M^+])$  will have an effect on the SIT plot, as indicated in Eq.(V.54). For consistency, the ionic strength dependence of  $K_M$  should also be evaluated with the SIT methodology (cf. Eq.(V.46)):

$$\log_{10} K_M = \log_{10} K_M^\circ + (\Delta z^2)_M D - \Delta \varepsilon_M I_m \quad (V.55)$$

where  $\Delta \varepsilon_M = \varepsilon(ML^{(1-y)}, M^+) - \varepsilon(L^{y-}, M^+) - \varepsilon(M^+, X^-)$ . It should be noted that  $(\Delta z^2)_H = (\Delta z^2)_M$ .

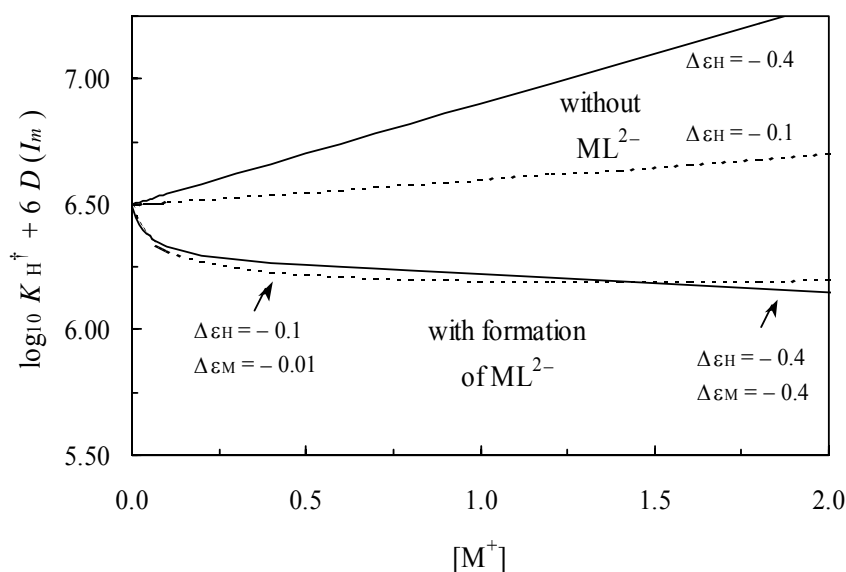
Figure V-2 shows values of  $\log_{10}(1 + K_M[M^+])$  versus  $[M^+]$ , for some values of  $K_M^\circ$ , when the charge of the ligand is  $-4$  (e.g., for  $\text{edta}^{4-}$ ). In general, the value of  $\Delta \varepsilon_M$  in Eq.(V.55) is unknown, and this uncertainty is indicated in the figure.

Figure V-2: Expected deviations in SIT plots for reaction:  $H^+ + L^{4-} \rightleftharpoons HL^{3-}$ , caused by the simultaneous reaction:  $M^+ + L^{4-} \rightleftharpoons ML^{3-}$ , where  $M^+$  is the alkali metal cation of the background electrolyte. The continuous curves show the deviations caused by three different values of  $K_M^\circ$  and  $\Delta \varepsilon_M = 0$  in Eq.(V.55). The dotted lines show the effect of setting  $\Delta \varepsilon_M = \pm 0.2$ .



The effect of complex formation with the background cation on an SIT plot is shown in Figure V-3. It may be shown that the parameters  $\Delta\epsilon_H$  and  $\Delta\epsilon_M$  have opposite effects on the slope of the plot, and they have a large degree of correlation, as illustrated in Figure V-3.

Figure V-3: The effect of alkali metal complex formation on SIT plots. In this artificial example the following reactions are used:  $H^+ + L^{3-} \rightleftharpoons HL^{2-}$  ( $\log_{10} K_H^o = 6.5$ ) and  $M^+ + L^{3-} \rightleftharpoons ML^{2-}$  ( $\log_{10} K_M^o = 1.4$ ), for both reactions  $(\Delta z^2)_H = (\Delta z^2)_M = -6$ , and  $M^+$  is the alkali metal cation of the background electrolyte. The upper two lines show SIT plots in the absence of complex formation, calculated using Eq.(V.46) with  $\Delta\epsilon_H = -0.4$  (continuous line) and  $\Delta\epsilon_H = -0.1$  (dotted line). The lower curves show the effects of  $ML^{2-}$  formation, calculated with Eqs.(V.54) and (V.55) using  $\Delta\epsilon_H = \Delta\epsilon_M = -0.4$  (continuous curve) and  $\Delta\epsilon_H = -0.1$ ,  $\Delta\epsilon_M = -0.01$  (dotted curve), illustrating that similar results are obtained with widely different values of  $\Delta\epsilon_H$  and  $\Delta\epsilon_M$ .



Several effects may be inferred from Figure V-2 and Figure V-3 for non-negligible alkali cation complexation in SIT plots:

- The slope of the SIT plot is affected, *i.e.*, the value of  $\Delta\epsilon$  obtained is not necessarily equal to  $\Delta\epsilon_H$ .
- At  $I_m \lesssim 0.2$  molal, the SIT plot is not linear.

- The value of  $\log_{10} K_H^o$  obtained from data at  $I_m \gtrsim 0.2$  molal may have a substantial error, proportional to the value  $\log_{10} K_M^o$ . Data obtained in  $\text{Na}^+$  and  $\text{K}^+$  media will result in values of  $\log_{10} K_H^o$  more negative than those from data in tetraalkylammonium media.
- $\Delta\epsilon_H$  and  $\Delta\epsilon_M$  can *not* be obtained from the ionic strength dependence of  $\log_{10} K_H^\dagger$ . This is due to their large covariance, *cf.* Figure V-3. Additional information is needed in order to obtain the different  $\epsilon$ -values.

When analysing data from several electrolytes, for example  $\text{NaCl}$ ,  $\text{NaClO}_4$ ,  $\text{NaNO}_3$ , *etc.*, it may be convenient to separate  $\Delta\epsilon_M$  in two parts, so that all data for a given background cation may be treated simultaneously, in a similar way as  $\Delta\epsilon_H$  (compare Eqs.(V.46) and (V.48)). In that case Eq.(V.54) becomes,

$$\log_{10} K_H^\dagger - (\Delta z^2)_H \cdot D - \epsilon(\text{H}^+, \text{X}^-) \cdot I_m = \log_{10} K_H^o - \Delta\epsilon_H^* I_m - \log_{10} (1 + K_M[\text{M}^+]) \quad (\text{V.56})$$

where  $\Delta\epsilon_H^* = \epsilon(\text{HL}^{(1-y)}, \text{M}^+) - \epsilon(\text{L}^{y-}, \text{M}^+)$ . Similarly Eq.(V.55) may be rewritten as:

$$\log_{10} K_M = \log_{10} K_M^o + (\Delta z^2)_M \cdot D - \Delta\epsilon_M^* I_m + \epsilon(\text{M}^+, \text{X}^-) \cdot I_m \quad (\text{V.57})$$

where  $\Delta\epsilon_M^* = \epsilon(\text{ML}^{(1-y)}, \text{M}^+) - \epsilon(\text{L}^{y-}, \text{M}^+)$ . Again,  $(\Delta z^2)_H = (\Delta z^2)_M = (1-y)^2 - y^2 - 1$ . Furthermore, the difference  $\Delta\epsilon_M^* - \Delta\epsilon_H^* = \epsilon(\text{ML}^{(1-y)}, \text{M}^+) - \epsilon(\text{HL}^{(1-y)}, \text{M}^+)$  is expected to be a small value.

### V.3.4. Complex formation with medium cations versus the SIT formalism

Figure V-3 shows that in the case where complex formation occurs between the ligand and the background cation a curved SIT plot is obtained. Similar curves may be obtained assuming an ionic strength dependence of the SIT parameters:  $\Delta\epsilon_H(I_m) = \Delta\epsilon_{H,1} + \Delta\epsilon_{H,2} \log_{10}(I_m)$ . This corroborates the assertion that it is practically not possible to distinguish between weak complex formation and ionic activity effects. Each chemical system must be examined separately and a decision taken on the existence of alkali metal ion complexes. During this review it has been seen that for  $\text{edta}^{4-}$  the formation of a complex such as  $\text{Na(edta)}^{3-}$  may be justified, and that for oxalate there is no evidence for the formation of sodium complexes. In the case of citrate, both formalisms might be applied with equal success to explain the ionic strength dependence of protonation constants. However, as there is no additional evidence (such as spectroscopic) for the formation of  $\text{Na(cit)}^{2-}$ , it has been estimated in this review that the simplest approach is to use the SIT model for activity coefficients taking into account, when needed, an ionic strength variation of the  $\Delta\epsilon_H$  parameter. The SIT approach has been found acceptable for ionic strengths up to about 5 molal.



### V.3.5. Accessory data

The use of Eq.(V.48) has two requirements: conversion of equilibrium constants to molal units, and values of  $\varepsilon(\text{H}^+, \text{X}^-)$ . To convert equilibrium constants to molal units, the density of the background electrolyte is needed as described in Section II.2. Molar to molal conversion factors for  $\text{KNO}_3$ ,  $\text{NaBr}$ , and  $\text{KBr}$ , and for tetraalkylammonium salts that are not tabulated in Table II.5 (Chapter II), are given in Table V-1.

Table V-1: The ratio between molarity,  $c$ , and molality,  $m$ , for selected electrolytes. Values calculated from densities [77ANS/SUR], [85SOH/NOV] and apparent molar volumes [66CON/VER].

$\varrho = m / c$									
$c$ (M)	NaBr	KBr	$\text{KNO}_3$	$\text{Me}_4\text{NCl}$	$\text{Me}_4\text{NBr}$	$\text{Et}_4\text{NCl}$	$\text{Et}_4\text{NBr}$	$\text{Et}_4\text{NI}$	$\text{Pr}_4\text{NBr}$
0.1	1.005	1.006	1.007	1.012	1.013	1.019	1.019	1.021	1.026
0.25	1.009	1.012	1.013	1.030	1.032	1.046	1.047	1.052	1.065
0.5	1.015	1.021	1.024	1.060	1.064	1.090	1.097	1.107	1.136
1	1.029	1.040	1.045	1.121	1.138	1.188	1.210	1.23	1.31
2	1.058	1.081	1.093						
3	1.089	1.129							
4	1.124								

$\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ , and  $\text{Pr}_4\text{N}^+$  represent tetramethyl-, tetraethyl-, and tetrapropylammonium ions respectively.

Specific ion interaction parameters for  $\text{H}^+$  with  $\text{Br}^-$  and  $\text{I}^-$  were calculated from the activity coefficients tabulated in [59ROB/STO]:

$$\varepsilon(\text{H}^+, \text{Br}^-) = (0.15 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(\text{H}^+, \text{I}^-) = (0.19 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}.$$

### V.3.6. Ionic medium effects on reaction enthalpies

For small temperature intervals (between 0 and 50°C) changes of equilibrium constants may be calculated with the constant heat-capacity method [97PUI/RAR]:

$$\log_{10} K_r(T) = \log_{10} K_r(T_0) + \frac{\Delta_r H(T_0)}{R \ln(10)} \left( \frac{1}{T_0} - \frac{1}{T} \right) + \frac{\Delta_r C_p}{R \ln(10)} \left( \frac{T_0}{T} - 1 + \ln \left( \frac{T}{T_0} \right) \right).$$

The ionic medium dependence of the reaction enthalpies may be estimated with the SIT model [97GRE/PLY2]:

$$\Delta_r H_m = \Delta_r H_m^0 + \Delta z^2 D_L - RT^2 m \Delta \varepsilon_L \quad (\text{V.58})$$

where:

$$D_L = \frac{3}{4} \times \frac{A_L \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}},$$

$A_L$  is the Debye-Hückel constant (at 25°C and 1 atm  $A_L = 1.986 \text{ kJ} \cdot \text{kg}^{1/2} \cdot \text{mol}^{-3/2}$ ), and

$$\Delta \varepsilon_L = \sum_i \nu_i \varepsilon_L(i, j),$$

where the stoichiometric coefficients  $\nu_i$  are positive for products and negative for reactants, and  $\varepsilon_L(i, j)$  are the relative partial molar enthalpy specific ion interaction coefficients:

$$\varepsilon_L(i, j) = \left( \frac{\partial \varepsilon(i, j)}{\partial T} \right)_p$$

where  $i$  refers to a reactant and  $j$  to the counter-ion of the background electrolyte.

According to the SIT model, a diagram of  $\Delta_r H_m - \Delta z^2 D_L$  against the molality of the background electrolyte,  $m$ , will produce a linear plot from which  $\Delta_r H_m^\circ$  and  $RT^2 \cdot \Delta \varepsilon_L$  may be obtained. These equations apply to  $\Delta_r H_m$  obtained either from calorimetric measurements or from the temperature variation of protonation constants in *molal* units. For moderate ionic strengths ( $\leq 1 \text{ M}$ ) and temperature intervals (0 to 50°C) if the equilibrium constants are instead given in *molar* concentration units, equivalent equations might be used but different  $\Delta \varepsilon_L$  values will be found.

#### V.4. Weak complexes *versus* strong specific ion interaction

Common background electrolytes used in experiments to determine stability constants are  $\text{NaClO}_4$ ,  $\text{KNO}_3$  and  $\text{NaCl}$ . The interaction of  $\text{Na}^+$  and  $\text{K}^+$  with organic ligands has been discussed in Section V.3. In this section, the interaction of  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$  with metal ions, especially actinides is discussed.

Within the framework of SIT, metal ion – perchlorate interactions are treated in all cases as specific ion interactions, using the corresponding SIT interaction coefficients  $\varepsilon(\text{M}^{x+}, \text{ClO}_4^-)$  as reported in Appendix B.

In the cases of  $\text{NO}_3^-$  and  $\text{Cl}^-$  the situation is less obvious, as there are two alternative methods to treat metal ion interactions with nitrate and chloride:

- (A) Simple treatment as specific ion interaction, as in the case of perchlorate, with corresponding SIT coefficients  $\varepsilon(\text{M}^{x+}, \text{NO}_3^-)$  and  $\varepsilon(\text{M}^{x+}, \text{Cl}^-)$ . In this procedure any possible effects of nitrate or chloride complexation are included in the respective ion interaction coefficients, and consequently nitrate or chloride complexes are not included in the speciation model.

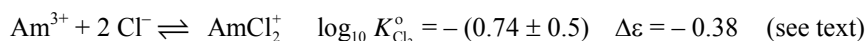
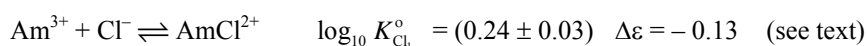
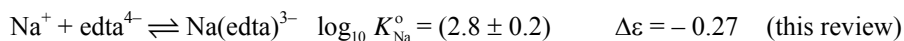
- (B) Complex treatment using nitrate or chloride complexation constants together with SIT interaction coefficients valid for perchlorate solutions, and consequently correcting experimental equilibrium constants measured in nitrate or chloride solutions for nitrate or chloride complexation effects. Note, that this treatment requires SIT interaction coefficients for all charged metal – nitrate or metal – chloride complexes included in the speciation model.

In general, procedure (A) is used in NEA TDB reviews for metal ions and complexes of low charge, and procedure (B) is used in the case of highly charged metal ions. However, the procedures applied in different NEA TDB reviews are not consistent and hence somewhat confusing. This topic is not yet settled, and it should be addressed in future NEA TDB reviews more thoroughly.

For the time being, in this review it was decided to follow procedure (B) if nitrate or chloride complexation constants have been selected by previous NEA TDB reviews, and to follow procedure (A) if no such selected values are available. As a consequence, Np(V) and Pu(III) – chloride interactions were treated according to procedure (A), whereas for U(VI) and Am(III) – chloride interactions procedure (B) was applied by explicitly considering chloride complexes.

The procedures applied and decisions made in this review are illustrated by the following two examples.

As a first example we discuss how Am – edta data measured in NaCl solution have been corrected in this review for complexation effects of  $\text{Na(edta)}^{3-}$ ,  $\text{AmCl}^{2+}$  and  $\text{AmCl}_2^+$ . The following equilibria have been considered:



The  $\log_{10} K^{\circ}$ , valid at  $I = 0$ , together with their  $\Delta\epsilon$  values have been used to calculate  $K$  at the appropriate ionic strength, given by the NaCl concentration, and subsequently to correct the experimental  $\log_{10} K$  values for complexation effects according to the following formula:

$$\log_{10} K_{\text{corr}} = \log_{10} K + \log_{10} (1 + K_{\text{Na}} \cdot [\text{Na}^+]) + \log_{10} (1 + K_{\text{Cl}_1} \cdot [\text{Cl}^-] + K_{\text{Cl}_2} \cdot [\text{Cl}^-]^2)$$

The stability constants  $\log_{10} K_{\text{Cl}_1}^{\circ}$  and  $\log_{10} K_{\text{Cl}_2}^{\circ}$  for the Am chloride complexes have been taken from [2003GUI/FAN]. The  $\Delta\epsilon$  values were calculated from  $\epsilon(\text{Am}^{3+}, \text{Cl}^-) \approx \epsilon(\text{Am}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.03)$ ,  $\epsilon(\text{AmCl}^{2+}, \text{Cl}^-) \approx \epsilon(\text{AmCl}^{2+}, \text{ClO}_4^-) = (0.39 \pm 0.04)$ ,  $\epsilon(\text{AmCl}_2^+, \text{Cl}^-) \approx \epsilon(\text{AmF}_2^+, \text{ClO}_4^-) = (0.17 \pm 0.04)$ , and  $\epsilon(\text{Na}^+, \text{Cl}^-) = (0.03 \pm 0.01)$ , all values taken from [95SIL/BID].

Note that [2003GUI/FAN] report a value  $\epsilon(\text{Am}^{3+}, \text{Cl}^-) = (0.23 \pm 0.02)$  with the remark (footnote G on page 729) that this value “is assumed to be equal to  $\epsilon(\text{Nd}^{3+}, \text{Cl}^-)$ ”

which is calculated from trace activity coefficients of  $\text{Nd}^{3+}$  ion in 0 – 4 m NaCl. These trace activity coefficients are based on the Pitzer ion interaction parameters evaluated in [97KON/FAN] from osmotic coefficients in aqueous  $\text{NdCl}_3 - \text{NaCl}$  and  $\text{NdCl}_3 - \text{CaCl}_2$ .” Alternatively, inspection by this review of the osmotic coefficients for  $\text{NdCl}_3$  solutions given by [59ROB/STO] also result in  $\varepsilon(\text{Nd}^{3+}, \text{Cl}^-) = (0.23 \pm 0.02)$ . The latter value is derived ignoring Nd – chloride complexation.

Very similar values  $\varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) = (0.21 \pm 0.02)$  and  $\varepsilon(\text{UO}_2^{2+}, \text{NO}_3^-) = (0.24 \pm 0.03)$  were obtained from osmotic coefficients reported by [59ROB/STO] for  $\text{UO}_2\text{Cl}_2$  and  $\text{UO}_2(\text{NO}_3)_2$  solutions, respectively. For the latter case [92GRE/FUG] remark (footnote (i) on page 695) “it is recalled that these coefficients are not used in the present review because they were calculated by Ciavatta [80CIA] without taking chloride and nitrate complexation into account”. Instead,  $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03)$  should be used in chloride solutions together with the equilibrium constants for  $\text{UO}_2\text{Cl}^+$  and  $\text{UO}_2\text{Cl}_2(\text{aq})$  as evaluated in [92GRE/FUG]. Hence, in analogy to the U(VI) chloride system, this review used  $\varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.03)$  together with the equilibrium constants for  $\text{AmCl}^{2+}$  and  $\text{AmCl}_2^+$  given in [2003GUI/FAN].

As a second example, some subtleties are discussed in the following concerning U(VI) – chloride complexation effects.

In the case of  $\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$  this review used the following SIT interaction coefficients (taken from [92GRE/FUG]) to calculate  $\Delta\varepsilon$  for the U(VI) – chloride complexation:

$$\varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) = \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03)$$

$$\varepsilon(\text{Cl}^-, \text{Na}^+) = (0.03 \pm 0.01)$$

$$\varepsilon(\text{UO}_2\text{Cl}^+, \text{Cl}^-) = (0.33 \pm 0.03).$$

This gives  $\Delta\varepsilon = -0.16$  for  $\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$ , in contrast to  $\Delta\varepsilon = -0.25$ , as reported in [92GRE/FUG], p. 195. Where does this discrepancy come from?

The solution of this puzzle is found in [92GRE/FUG], p.192, line 21: For deriving  $\varepsilon(\text{UO}_2\text{Cl}^+, \text{Cl}^-) = 0.33$  from their fitted  $\Delta\varepsilon = -0.25$  Grenthe *et al.* used  $\varepsilon(\text{Cl}^-, \text{H}^+) = 0.12$ . There is no further comment on this choice in [92GRE/FUG], but inspection of Table V.22 and Figure V.10 reveals that the data they used for the SIT plot (especially the ones at high ionic strength) were measured in  $\text{H}(\text{Cl}, \text{ClO}_4)$  media, and hence, the SIT interaction coefficient for  $\text{H}^+ - \text{Cl}^-$  interaction was used.

But in the case of NaCl solutions one cannot just use the  $\Delta\varepsilon$  derived for  $\text{H}(\text{Cl}, \text{ClO}_4)$  media, and this review calculated an appropriate  $\Delta\varepsilon$  using  $\varepsilon(\text{Cl}^-, \text{Na}^+) = 0.03$  instead of  $\varepsilon(\text{Cl}^-, \text{H}^+) = 0.12$ . This results in a difference in  $\Delta\varepsilon$  of 0.09.

In the case of  $\text{UO}_2^{2+} + 2 \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}_2(\text{aq})$  this review used the following SIT interaction coefficients to calculate  $\Delta\epsilon$  for the second U(VI) – chloride complexation:

$$\epsilon(\text{UO}_2^{2+}, \text{Cl}^-) = \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03)$$

$$\epsilon(\text{Cl}^-, \text{Na}^+) = (0.03 \pm 0.01)$$

$$\epsilon(\text{UO}_2\text{Cl}_2(\text{aq}), \text{NaCl}) = 0.$$

This gives  $\Delta\epsilon = -0.52$  for  $\text{UO}_2^{2+} + 2 \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}_2(\text{aq})$ , in contrast to  $\Delta\epsilon = -0.62$ , as reported in [\[92GRE/FUG\]](#), p. 196. This puzzle is more complicated than the first one.

Again, we have the difference in media:  $\text{H}(\text{Cl}, \text{ClO}_4)$  in [\[92GRE/FUG\]](#) and  $\text{NaCl}$  in this example. But applying  $\epsilon(\text{Cl}^-, \text{H}^+) = 0.12$  gives  $\Delta\epsilon = -0.70$ , and not  $\Delta\epsilon = -0.62$  as derived in Figure V.11 of [\[92GRE/FUG\]](#). The solution to this puzzle is again found in [\[92GRE/FUG\]](#), p. 192, last 4 lines: The authors realised this discrepancy but simply stated "which is compatible with the value obtained from linear regression". This is true considering the uncertainties assigned to the  $\Delta\epsilon$  values. However, the real question is not addressed by this statement: Following the SIT procedure, [\[92GRE/FUG\]](#) should have calculated  $\epsilon(\text{UO}_2\text{Cl}_2(\text{aq}), \text{H}(\text{Cl}, \text{ClO}_4)) = (0.08 \pm 0.17)$  from their fitted  $\Delta\epsilon$ . Now, there is an ambiguity: We can either argue that this value is not significantly different from zero (as assumed a priori for neutral species in the NEA TDB review), or we can decide that this value has to be put in the table of selected SIT interaction coefficients in Appendix B. Obviously, without explicitly saying so, Grenthe *et al.* decided to follow the first line of argument; and this review decided to follow the (not explicitly stated) decisions in [\[92GRE/FUG\]](#).



## Chapter VI

# Discussion of data selection for oxalate compounds and complexes

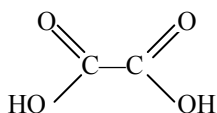
### VI.1 Introduction

Oxalic acid (ethane-1,2-dioic acid) has the chemical formula  $\text{HOOC-COOH}$  ( $\text{C}_2\text{H}_2\text{O}_4$ ; molecular weight =  $90.0355 \text{ g}\cdot\text{mol}^{-1}$ ; CAS Registry Number: 144-62-7).

The anhydrous acid is not found in nature and must be prepared from the dihydrate ( $\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ; molecular weight:  $126.066 \text{ g}\cdot\text{mol}^{-1}$ ; CAS Registry Number: 6153-56-6) even when produced industrially. Oxalic acid is widely distributed in the vegetal and animal kingdoms, nearly always in the form of its salts. The potassium salt is found in common sorrel (*oxalis acetosella*) and the name oxalic acid is derived from that plant.

Oxalic acid appears to have been discovered by Scheele, but the first account of its properties has been published by Bergman in 1776 [\[1808THO\]](#). In his seminal paper “On Oxalic Acid” Thomson [\[1808THO\]](#) reported detailed chemical analyses of oxalic acid, alkali and alkali earth oxalates concerning formation, water of crystallisation and decomposition of these compounds. He interpreted his careful analytical work in terms of the law of multiple proportions of elements and stated “from the knowledge of this curious law, it is difficult to avoid concluding that each of these elements consist of atoms of determinate weight, which combine according to certain fixed proportions”, *i.e.*, this classic paper on oxalic acid contains the first systematic application of Dalton’s atomic hypothesis.

Figure VI-1: Structural formula of oxalic acid



The two carboxylic groups of oxalic acid may dissociate in acidic aqueous solutions. In reactions and formulae in this review oxalic acid is denoted as  $\text{H}_2\text{ox}$ , and the oxalate ligand in aqueous solutions is denoted as  $\text{ox}^{2-}$ . In formulae where the abbreviation is preceded by a lower case it is enclosed in parenthesis, as in  $\text{Ca}(\text{ox})\cdot\text{H}_2\text{O}(\text{cr})$  or  $\text{Na}(\text{ox})^-$ , but no parentheses are needed in formulae as  $\text{Kox}^-$ . Also the protonated form of the oxalate ligand is enclosed in parenthesis, as in  $\text{Ca}(\text{Hox})^+$ .

Oxalate may coordinate metal ions with its two carboxylic groups. Because of its ability to form 5-membered chelate rings, oxalate is quite a strong complexing agent. Complexes with stoichiometry  $1:x$  ( $x > 1$ ) are common. However, the limiting complex actually formed in aqueous solution depends on the charge and size of the metal ion.

Most thermodynamic constants selected in this review are stability constants. In order to convert these stability constants into values of standard Gibbs energy of formation the value of  $\Delta_f G_m^\circ(\text{ox}^{2-}, 298.15 \text{ K})$  is needed. The derivation of this constant is not a straightforward procedure. The enthalpy of formation of oxalic acid  $\Delta_f H_m^\circ(\text{H}_2\text{ox}, \text{aq}, 298.15 \text{ K})$ , derived from heat of combustion and heat of dissolution of  $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}(\text{cr})$  (*cf.* Section VI.2), and the standard enthalpy changes of oxalate protonation ( $\Delta_f H_m^\circ(1)$  and  $\Delta_f H_m^\circ(2)$ , *cf.* Section VI.3) are used to calculate  $\Delta_f H_m^\circ(\text{ox}^{2-}, 298.15 \text{ K})$ . Solubility and calorimetric data of  $\text{Ca}(\text{ox})\cdot\text{H}_2\text{O}(\text{cr})$  are then used to derive  $S_m^\circ(\text{ox}^{2-}, 298.15 \text{ K})$  (*cf.* Section VI.5). The latter two quantities allow calculating  $\Delta_f G_m^\circ(\text{ox}^{2-}, 298.15 \text{ K})$ . There is no redundant information to confirm the results of this procedure.

## VI.2 Oxalic acid

The solid formed at equilibrium in the system oxalic acid – water is the dihydrate,  $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}(\text{cr})$ . It forms colourless and odourless crystals and it is stable in air at room temperature. Anhydrous oxalic acid,  $\text{H}_2\text{ox}(\text{cr})$ , is prepared by dehydration of  $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}(\text{cr})$ . Vacuum sublimation at  $80 - 100^\circ\text{C}$  results in needle-shaped crystals of  $\beta\text{-H}_2\text{ox}$ , whereas slow evaporation of acetone or ether solutions under  $\text{N}_2$  atmosphere deposits crystals of  $\alpha\text{-H}_2\text{ox}$  [53BRA/COT], [74DER/SMI].

### VI.2.1 $\text{H}_2\text{ox}(\text{cr})$

Anhydrous oxalic acid exists in two crystalline forms, the orthorhombic  $\alpha\text{-H}_2\text{ox}$  (space group  $Pcab$ ) and the monoclinic  $\beta\text{-H}_2\text{ox}$  (space group  $P2_1/c$ ). The dimorphism of  $\text{H}_2\text{ox}(\text{cr})$  has been elucidated already in the early days of crystallographic X-ray studies by Hoffmann and Mark [24HOF/MAR] and Hendricks [35HEN] who determined the unit-cell dimensions, space groups, and the main structural features. The first detailed crystal structure analysis of  $\alpha\text{-H}_2\text{ox}$  has been reported by Cox *et al.* [52COX/DOU]. Very precise structures of  $\alpha\text{-H}_2\text{ox}$  and  $\beta\text{-H}_2\text{ox}$  have been determined by Derissen and Smit [74DER/SMI].

The vapour pressure measurements in the system  $\text{H}_2\text{ox}(\text{cr}) - \text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}(\text{cr}) - \text{water vapour}$  by Bradley and Cotson [53BRA/COT] showed that  $\alpha\text{-H}_2\text{ox}$  is the stable

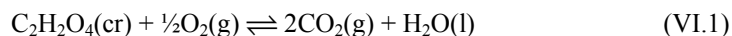


modification at room temperature. Their experiments indicate that  $\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}(\text{cr})$  gives the  $\beta$ -form on dehydration, and that a mixture of the  $\alpha$ - and the  $\beta$ -form slowly reverts to the pure  $\alpha$ -form at temperatures below  $100^\circ\text{C}$ . The thermodynamic  $\alpha \rightarrow \beta$  transition temperature is in the range  $120 - 123^\circ\text{C}$ , as determined by differential scanning calorimetry [78DER/SMI].

The heat of combustion,  $\Delta_c H_m^\circ$ , of anhydrous oxalic acid,  $\text{H}_2\text{ox}(\text{cr})$ , has been studied extensively since the advent of combustion calorimetry in the 19<sup>th</sup> century [1875BER3], [1880REC], [1882THO], [1884STO/REC], [1885STO], [1886LOU], [1889JAH], [1889STO/KLE], [26VER/HAR], [34BEC/ROT], [64WIL/SHI].

Although the early studies in combustion calorimetry reveal rather consistent results (in Table VI-1, note that the discrepant results of [1884STO/REC] and [1885STO] have later been rejected by the same group on the basis of improved new measurements [1889STO/KLE]), studies published before the 1930's are in general rejected in this review. As discussed by Domalski [72DOM], international agreement on a chemical standard to be used in calibrating bomb calorimeters came during the 1920's, and substantial improvements in calorimetric procedures, measuring instruments, and calculative methods were achieved in the 1930's. Hence, from the above list only the results of Becker and Roth [34BEC/ROT] and Wilhoit and Shiao [64WIL/SHI] are further considered by this review.

In order to calculate the enthalpy of formation  $\Delta_f H_m^\circ(\text{H}_2\text{ox}, \text{cr}, 298.15 \text{ K})$  from the corresponding heat of combustion  $\Delta_c H_m^\circ(\text{H}_2\text{ox}, \text{cr}, 298.15 \text{ K})$  according to the reaction:



only the enthalpies of formation of  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  are needed. Both constants are taken from CODATA [89COX/WAG]:  $\Delta_f H_m^\circ(\text{CO}_2, \text{g}, 298.15 \text{ K}) = -(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}) = -(285.83 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$ . The enthalpy of formation of  $\text{O}_2(\text{g})$  is zero by definition.

In many papers the heats of combustion and the enthalpies of formation are expressed in  $\text{kcal}\cdot\text{mol}^{-1}$ . In this review, values for the heats of combustion in  $\text{kJ}\cdot\text{mol}^{-1}$  were obtained by multiplying the values reported in  $\text{kcal}\cdot\text{mol}^{-1}$  by 4.184. Calculations of the enthalpies of formation in  $\text{kJ}\cdot\text{mol}^{-1}$  were obtained from the difference between the heats of combustion and the corresponding sum of the enthalpies of formation of the combustion products, both in  $\text{kJ}\cdot\text{mol}^{-1}$ . Following this path, rather than the multiplication of the reported enthalpies of formation by 4.184, avoided rounding variations in the last place, which otherwise would occur.

The enthalpy of formation of  $\alpha\text{-H}_2\text{ox}$  has been calculated as a weighted mean of the values reported by [34BEC/ROT] (who, according to their preparation procedures, most probably examined a rather pure  $\alpha$ -phase) and [64WIL/SHI] (who explicitly

checked their samples by X-ray diffraction to avoid the presence of the  $\beta$ -phase), and the following value has been selected:

$$\Delta_f H_m^\circ (\text{H}_2\text{ox}, \alpha, 298.15 \text{ K}) = - (828.8 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

There are no heat of combustion data for  $\beta$ -H<sub>2</sub>ox. However, the heat of the  $\alpha \rightarrow \beta$  transition,  $\Delta_{\text{tr}} H_m^\circ$ , has been derived from vapour pressure measurements [53BRA/COT] and heats of solution data [72DOM], and it was directly determined by a differential scanning calorimeter (DSC) study [78DER/SMI]. Note that the value  $\Delta_{\text{tr}} H_m (120^\circ\text{C}) = 1.3 \text{ kJ}\cdot\text{mol}^{-1}$  given in Table I of [88PET/TSY] and quoted by [96DOM/HEA] as new measurements actually were taken from [78DER/SMI].

As discussed in [78DER/SMI], the value for  $\Delta_{\text{tr}} H_m$ , derived from heats of sublimation of  $\alpha$ - and  $\beta$ -oxalic acid by [53BRA/COT] seems too large. This is corroborated by an unpublished re-determination of the vapour pressure of  $\alpha$ -H<sub>2</sub>ox cited in [78DER/SMI], and by an also unpublished study of heats of solution data of  $\alpha$  and  $\beta$ -oxalic acids cited in [72DOM]. Hence, this review prefers the direct measurement by DSC [78DER/SMI], and assumes that  $\Delta_{\text{tr}} H_m (120\text{--}123^\circ\text{C}) = (1.30 \pm 0.25) \text{ kJ}\cdot\text{mol}^{-1}$  does not significantly vary with temperature. Combining this value with the selected value for  $\Delta_f H_m^\circ (\text{H}_2\text{ox}, \alpha, 298.15 \text{ K})$  the following value is selected:

$$\Delta_f H_m^\circ (\text{H}_2\text{ox}, \beta, 298.15 \text{ K}) = - (827.5 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

Heat capacity and entropy data of anhydrous oxalic acid has been reported in several papers [39SAT/SOG], [64DAV], [82LUF/REE], [85DAL/GUS].

Sato and Sogabe [39SAT/SOG] used an ice calorimeter to measure the specific heat of anhydrous oxalic acid in the temperature range 0 – 100°C. However, they only report a mean value  $[C_{p,m}]_0^{100^\circ\text{C}} (\text{H}_2\text{ox}, \text{cr}) = 118.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , and according to their preparation procedure, *i.e.*, “oxalic acid was dehydrated at 90°C until its weight became constant and was used in the measurement”, they might have measured a mixture of  $\alpha$ - and  $\beta$ -H<sub>2</sub>ox. Hence, the results of [39SAT/SOG] are not credited in this review.

David [64DAV] applied differential thermal analysis (DTA) and gives a mean value  $C_{p,m} (\text{H}_2\text{ox}, \text{cr}) = 146 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . Neither the preparation of the anhydrous oxalic acid nor the temperature range of the DTA measurements are reported and thus, the results of [64DAV] are not considered in this review.

Dalidovich *et al.* [85DAL/GUS] used a dynamic calorimeter to measure the heat capacities of H<sub>2</sub>ox(cr) and H<sub>2</sub>ox·2H<sub>2</sub>O(cr) and give coefficients for a four-parameter heat capacity equation in the range 150 – 360 K and 170 – 300 K for H<sub>2</sub>ox(cr) and H<sub>2</sub>ox·2H<sub>2</sub>O(cr), respectively. However, no experimental data are reported in [85DAL/GUS]. Furthermore, they state that “anhydrous samples were prepared by drying the crystallohydrates in a thin layer at the dehydration temperature” but no attempts were reported to check the  $\alpha$ - and  $\beta$ -phase problem. Hence, their value  $C_{p,m} (\text{H}_2\text{ox}, \text{cr}, 298.15 \text{ K}) = 104.8 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  is not credited in this review.

Luff and Reed [82LUF/REE] report a careful low-temperature heat capacity study of  $\alpha$ -H<sub>2</sub>ox. They state that “petrographic examination of the material showed the material to be essentially homogeneous  $\alpha$ -form anhydrous oxalic acid” and report the experimental heat capacity data in the temperature range 10 – 320 K. The standard molar heat capacity and entropies determined by Luff and Reed [82LUF/REE] are selected in this review, with the following assigned uncertainties derived from deviations of observed heat capacities from smoothed values, Fig. 1 in [82LUF/REE].

$$C_{p,m}^{\circ}(\text{H}_2\text{ox}, \alpha, 298.15 \text{ K}) = (105.9 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_m^{\circ}(\text{H}_2\text{ox}, \alpha, 298.15 \text{ K}) = (115.6 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The standard Gibbs energy of formation of  $\alpha$ -H<sub>2</sub>ox is calculated from the values of the standard entropy and of the enthalpy of formation selected above:

$$\Delta_f G_m^{\circ}(\text{H}_2\text{ox}, \alpha, 298.15 \text{ K}) = - (698.5 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

The enthalpy of solution of H<sub>2</sub>ox(cr) has been evaluated calorimetrically  $\Delta_{\text{sol}} H_m^{\circ} = (8.85 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1}$  by Apelblat [86APE]. For a lower temperature and a finite amount of water, Becker and Roth [34BEC/ROT] obtained  $\Delta_{\text{sol}} H_m = (8.49 \pm 0.24) \text{ kJ}\cdot\text{mol}^{-1}$  in good agreement with the more accurate value of [86APE].

Table VI-1: Literature values for  $\Delta_f H_m^{\circ}$ . Uncertainties estimated in this review.

Method	Enthalpy changes (kJ·mol <sup>-1</sup> )	Reference
H <sub>2</sub> ox(cr)		
cal	$\Delta_c H_m (17^{\circ}\text{C}) = - (252 \pm 20)$	[1875BER3]
cal	$\Delta_c H_m (18^{\circ}\text{C}) = - (248 \pm 21)$	[1880REC]
cal	$\Delta_c H_m = -250$	[1882THO]
cal	$\Delta_c H_m (18^{\circ}\text{C}) = - (214 \pm 13)$	[1884STO/REC]
cal	$\Delta_c H_m (18^{\circ}\text{C}) = - (215 \pm 13)$	[1885STO]
cal	$\Delta_c H_m (17^{\circ}\text{C}) = - (265 \pm 25)$	[1886LOU]
cal	$\Delta_c H_m (0\text{-}30^{\circ}\text{C}) = - (253 \pm 5)$	[1889JAH]
cal	$\Delta_c H_m (20^{\circ}\text{C}) = - (252 \pm 5)$	[1889STO/KLE]
vapour pressure	$\Delta_{\text{hyd}} H_m (18\text{-}50^{\circ}\text{C}) = - (25.8 \pm 2.2)$	[10JOR]
cal	$\Delta_c H_m (21^{\circ}\text{C}) = - (251.5 \pm 1.4)$	[26VER/HAR]
cal	$\Delta_{\text{sol}} H_m (20.5^{\circ}\text{C}, \text{H}_2\text{ox}\cdot 2100\text{H}_2\text{O(l)}) = (8.49 \pm 0.24)$	[34BEC/ROT]
cal	$\Delta_c H_m^{\circ} (25^{\circ}\text{C}) = - (245.6 \pm 2.3)$	[34BEC/ROT] <sup>b, c</sup>
cal	$\Delta_f H_m^{\circ} (25^{\circ}\text{C}) = - (827.3 \pm 2.3)$	[34BEC/ROT]

(Continued on next page)

Table VI-1 (continued)

Method	Enthalpy changes (kJ·mol <sup>-1</sup> )	Reference
<b>H<sub>2</sub>ox(cr)</b>		
vapour pressure	$\Delta_{\text{trs}}H_{\text{m}} = 4.9$	[53BRA/COT]
cal	$\Delta_{\text{c}}H_{\text{m}}^{\circ} (25^{\circ}\text{C}) = -(242.9 \pm 2.0)$	[64WIL/SHI] <sup>a</sup>
cal	$\Delta_{\text{f}}H_{\text{m}}^{\circ} (25^{\circ}\text{C}) = -(830.0 \pm 2.0)$	[64WIL/SHI]
cal	$\Delta_{\text{trs}}H_{\text{m}} = 1.3 \text{ kJ}\cdot\text{mol}^{-1}$	[72DOM] <sup>c</sup>
DSC	$\Delta_{\text{trs}}H_{\text{m}} (120\text{--}123^{\circ}\text{C}) = (1.30 \pm 0.25)$	[78DER/SMI]
cal	$\Delta_{\text{sol}}H_{\text{m}}^{\circ} (25^{\circ}\text{C}, m \rightarrow 0) = (8.85 \pm 0.20)$	[86APE]
cal	$\Delta_{\text{hyd}}H_{\text{m}}^{\circ} (25^{\circ}\text{C}) = -(26.5 \pm 2.1)$	[86APE]
<b>H<sub>2</sub>ox·2H<sub>2</sub>O(cr)</b>		
cal	$\Delta_{\text{c}}H_{\text{m}} (?^{\circ}\text{C}) = -224.7$	[1895JOR/STA]
cal	$\Delta_{\text{sol}}H_{\text{m}} (19.7^{\circ}\text{C}, \text{H}_2\text{ox}\cdot 2100\text{H}_2\text{O(l)}) = (36.06 \pm 0.45)$	[34BEC/ROT]
cal	$\Delta_{\text{c}}H_{\text{m}}^{\circ} (25^{\circ}\text{C}) = -(217.5 \pm 1.5)$	[34BEC/ROT] <sup>c</sup>
cal	$\Delta_{\text{f}}H_{\text{m}}^{\circ} (25^{\circ}\text{C}) = -(1427.0 \pm 1.5)$	[34BEC/ROT]
cal	$\Delta_{\text{sol}}H_{\text{m}}^{\circ} (25^{\circ}\text{C}, m \rightarrow 0) = (35.65 \pm 0.38)$	[52SPE/MIL] <sup>d</sup>
cal	$\Delta_{\text{sol}}H_{\text{m}}^{\circ} (25^{\circ}\text{C}, m \rightarrow 0) = (35.23 \pm 0.14)$	[86APE]
$\partial m_{\text{sat}}/\partial T$	$\Delta_{\text{sol}}H_{\text{m}} (m_{\text{sat}}) = 26.5$	[87APE/MAN]

- a: The conversion of combustion data presented in Table IV of [64WIL/SHI] for the process at constant volume,  $\Delta_{\text{c}}U_{\text{m}}^{\circ}$ , to that at constant pressure is made by means of the equation  $\Delta_{\text{c}}H_{\text{m}}^{\circ} = \Delta_{\text{c}}U_{\text{m}}^{\circ} + \Delta nRT$ , where  $\Delta n = 1.5$  is the difference between the number of moles of gaseous products and gaseous reactants involved in combustion Reaction (VI.1), *i.e.*,  $\Delta nRT = 3.72 \text{ kJ}\cdot\text{mol}^{-1}$  at 298.15 K.
- b: The combustion data,  $\Delta_{\text{c}}H_{\text{m}}$ , of [34BEC/ROT] on H<sub>2</sub>ox·2H<sub>2</sub>O(cr) were combined with their data on the heats of solution,  $\Delta_{\text{sol}}H_{\text{m}}$ , of H<sub>2</sub>ox(cr) and H<sub>2</sub>ox·2H<sub>2</sub>O(cr) to obtain the value  $\Delta_{\text{c}}H_{\text{m}}$  of H<sub>2</sub>ox(cr).
- c:  $\Delta_{\text{c}}H_{\text{m}}$  corrected to the reference temperature 298.15 K by [72DOM].
- d: Recalculated and extrapolated to infinite dilution by [86APE].
- e: Derived from the unpublished data of Taylor on the heats of solution of  $\alpha$ - and  $\beta$ -oxalic acids as cited in [72DOM].

## VI.2.2 H<sub>2</sub>ox·2H<sub>2</sub>O(cr)

Oxalic acid dihydrate exists in two crystalline forms; both modifications are monoclinic and are distinguished only in their space group settings:  $P2_1/n$  for  $\alpha$ -H<sub>2</sub>ox·2H<sub>2</sub>O and  $P2_1/a$  for  $\beta$ -H<sub>2</sub>ox·2H<sub>2</sub>O. The dimorphism of H<sub>2</sub>ox·2H<sub>2</sub>O(cr) was not realised in the early days of X-ray crystallography [24HOF/MAR]. Decades later, Dunitz and Robertson [47DUN/ROB] and Ahmed and Cruickshank [53AHM/CRU] discuss and try to re-interpret older inconsistent data, actually describing the structure of  $\alpha$ -H<sub>2</sub>ox·2H<sub>2</sub>O, but they still are not aware of the existence of  $\beta$ -H<sub>2</sub>ox·2H<sub>2</sub>O as a possible explanation for the unsatisfactory agreement of reported crystal structures. Only the advent of neutron

diffraction resolved the puzzle [69COP/SAB], [69COP/SAB2]. Meanwhile, very accurate structure data are available and  $\alpha$ -H<sub>2</sub>ox·2H<sub>2</sub>O(cr) is now used as a standard to calibrate X-ray diffractometers [94LEH/LUG], [2000HER].

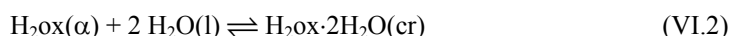
Concerning the differences between  $\alpha$ -H<sub>2</sub>ox·2H<sub>2</sub>O and  $\beta$ -H<sub>2</sub>ox·2H<sub>2</sub>O, Coppens and Sabine [69COP/SAB] found that “intramolecular distances and angles in the oxalic acid molecule are remarkably similar in the two polymorphs”. Moreover, a curious experience reported in [69COP/SAB] is important for this review: “The  $\alpha$  and  $\beta$  form appear to grow at random. Initially Dr B.M. Craven at the Crystallographic Laboratory of the University of Pittsburgh attempted to grow the  $\alpha$  form. The first crystal from the solution was  $\alpha$  and the second  $\beta$ . The  $\alpha$  crystal was lost and subsequently only the  $\beta$  form would grow at Pittsburgh. We repeated Craven’s experiments at Brookhaven and obtained only the  $\alpha$  form. No attempt was made to examine this effect further.”

No study of the thermodynamic properties of H<sub>2</sub>ox·2H<sub>2</sub>O(cr) could be identified in this review which would distinguish between  $\alpha$  and  $\beta$  form. However, considering the results and experiences quoted above [69COP/SAB], the differences in thermodynamic properties of the  $\alpha$  and  $\beta$  form are perhaps so small that they are already included in the uncertainties assigned to the values selected in this review.

The heat of combustion of oxalic acid dihydrate has been determined by Jorissen and van de Stadt [1895JOR/STA] and by Becker and Roth [34BEC/ROT]. Only the latter study is considered in this review, and the selected enthalpy of formation value of [34BEC/ROT] as re-evaluated by Domalski [72DOM] is:

$$\Delta_f H_m^\circ (\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = - (1427.0 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}.$$

As a consistency check, the enthalpy change for the hydration reaction:



is calculated to be  $\Delta_{\text{hydr}} H_m^\circ = - (26.5 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$ , in agreement with the experimental values  $\Delta_{\text{hydr}} H_m^\circ = - (25.8 \pm 2.2) \text{ kJ} \cdot \text{mol}^{-1}$  [10JOR] and  $- (26.34 \pm 0.17) \text{ kJ} \cdot \text{mol}^{-1}$  [86APE].

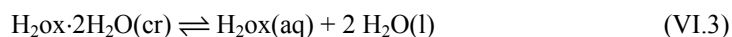
Dalidovich *et al.* [85DAL/GUS] report coefficients for a four-parameter heat capacity equation in the range 170 – 300 K for H<sub>2</sub>ox·2H<sub>2</sub>O(cr). However, no experimental data are reported in [85DAL/GUS], and their value  $C_{p,m}(\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = 185.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  is not credited in this review.

No low-temperature heat capacity study could be identified by this review and hence, the standard Gibbs energy of formation of H<sub>2</sub>ox·2H<sub>2</sub>O(cr) cannot be calculated because of the missing value for the standard entropy of H<sub>2</sub>ox·2H<sub>2</sub>O(cr).

### VI.2.3 H<sub>2</sub>ox(aq)

The solubility of H<sub>2</sub>ox·2H<sub>2</sub>O(cr) in pure water and in various acids has been studied extensively [12MAS], [23HER/NEU], [28FLO], [31CHA/BEL], [36TRA], [49REA], [51NOR], [72KUK/KOB], [82WIL/SUL] and [87APE/MAN]. In pure water the solubility of the dihydrate is quite high. The following values have been reported: 1.48 mol·dm<sup>-3</sup> (30°C) [12MAS], 1.18 mol·dm<sup>-3</sup> (25°C) [23HER/NEU], 1.21 mol·kg<sup>-1</sup> (25°C) [28FLO], 1.57 mol·kg<sup>-1</sup> (30°C) [51NOR], and 1.31 mol·kg<sup>-1</sup> (25°C) [87APE/MAN]. The value determined by [87APE/MAN] is considered to be the most reliable one by this review.

The solubility of oxalic acid dihydrate is of interest because it could be used to calculate the value of  $\Delta_f G_m^\circ(\text{H}_2\text{ox, aq, 298.15 K})$  from the following reaction,



$$\Delta_r G_m^\circ(\text{VI.3}) = \Delta_f G_m^\circ(\text{H}_2\text{ox, aq}) + 2 \Delta_f G_m^\circ(\text{H}_2\text{O, l}) - \Delta_f G_m^\circ(\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O, cr})$$

$$\log_{10} K^\circ(\text{VI.3}) = - \Delta_r G_m^\circ(\text{VI.3}) / (R T \ln(10)) = \log_{10} a_{\text{H}_2\text{ox}} + 2 \log_{10} a_{\text{H}_2\text{O}}$$

Water activities,  $a_{\text{H}_2\text{O}}$ , for binary oxalic acid – water mixtures have been measured in the range 0.4 – 1.1 molal [96KIR/MAU] and 0.25 – 1.23 molal [2001MAF/MEI] which, in combination with the reported oxalic acid solubility [87APE/MAN], allow estimation of  $\Delta_r G_m^\circ(\text{VI.3})$ . However,  $\Delta_f G_m^\circ(\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O, cr})$  could not be calculated in this review because of the lack of a low-temperature heat capacity study for the determination of the standard entropy of H<sub>2</sub>ox·2H<sub>2</sub>O(cr).

The enthalpy change for Reaction (VI.3) may be determined either calorimetrically or from the temperature dependence of the solubility of the saturated solutions. The values found in the literature are given in Table VI-1.

The calorimetric values in dilute solutions [34BEC/ROT], [52SPE/MIL], [86APE] should be more accurate than the value derived from the temperature dependence of concentration of saturated solutions [87APE/MAN]. Selecting the weighted average of the two values determined from solution calorimetry at 25°C and extrapolated to infinite dilution [52SPE/MIL], [86APE] leads to:

$$\Delta_{\text{sol}} H_m^\circ = \Delta_r H_m^\circ(\text{VI.3}) = (35.28 \pm 0.13) \text{ kJ} \cdot \text{mol}^{-1}.$$

Using the value of  $\Delta_r H_m^\circ(\text{VI.3})$  determined calorimetrically and  $\Delta_f H_m^\circ(\text{H}_2\text{ox} \cdot 2\text{H}_2\text{O, cr, 298.15 K})$  selected above leads to:

$$\Delta_f H_m^\circ(\text{H}_2\text{ox, aq, 298.15 K}) = - (820.1 \pm 1.5) \text{ kJ} \cdot \text{mol}^{-1}.$$

As a consistency check, the enthalpy change for the reaction:



is calculated to be  $\Delta_{\text{sol}} H_m^\circ(\text{VI.4}) = (8.7 \pm 2.1) \text{ kJ} \cdot \text{mol}^{-1}$ , in agreement with the values  $\Delta_{\text{sol}} H_m^\circ = (8.85 \pm 0.20) \text{ kJ} \cdot \text{mol}^{-1}$  [86APE], and  $\Delta_{\text{sol}} H_m^\circ(20.5^\circ\text{C}) = (8.49 \pm 0.24) \text{ kJ} \cdot \text{mol}^{-1}$

[34BEC/ROT] obtained calorimetrically.

The selected value of  $\Delta_f H_m^\circ(\text{H}_2\text{ox}, \text{aq}, 298.15 \text{ K})$  and the selected values of  $\Delta_r H_m^\circ$  for oxalate protonation (*cf.* Section VI.3.5) were used to calculate:

$$\Delta_f H_m^\circ(\text{ox}^{2-}, 298.15 \text{ K}) = -(830.7 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}.$$

From this value and the selected values  $S_m^\circ(\text{ox}^{2-}, 298.15 \text{ K}) = (47.6 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $\Delta_f G_m^\circ(\text{ox}^{2-}, 298.15 \text{ K}) = -(680.1 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$  (*cf.* Section VI.5.1) together with the selected protonation constants of oxalate (*cf.* Section VI.3.5) it is possible to calculate:

$$\Delta_f G_m^\circ(\text{H}_2\text{ox}, \text{aq}, 298.15 \text{ K}) = -(712.4 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

which may be combined with the entropy for  $\text{ox}^{2-}$  selected in Section VI.5.1 and the selected reaction entropy changes for the protonation of oxalate listed in Table III-2 yielding:

$$S_m^\circ(\text{H}_2\text{ox}, \text{aq}, 298.15 \text{ K}) = (191.3 \pm 3.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

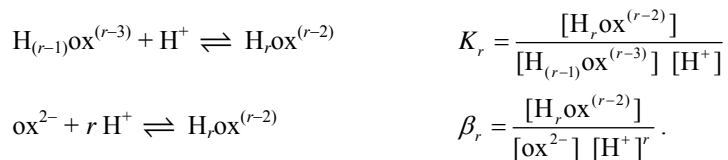
The partial molar heat capacity at infinite dilution for undissociated oxalic acid has been reported to be  $C_{p,m}^\circ(\text{H}_2\text{ox}, \text{aq}, 298.15 \text{ K}) = (95.1 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [89SIJ/ROS].

The partial molar volume of the undissociated acid in water has been reported in several papers:  $V_m^\circ(\text{H}_2\text{ox}, 298.15 \text{ K}) = (49.1 \pm 1.0) \text{ cm}^3\cdot\text{mol}^{-1}$  [75HOI],  $(49.4 \pm 0.6) \text{ cm}^3\cdot\text{mol}^{-1}$  [89SIJ/ROS], and  $46.33 \text{ cm}^3\cdot\text{mol}^{-1}$  [90APE/MAN]. The average of this somewhat discrepant data set is  $V_m^\circ(\text{H}_2\text{ox}, 298.15 \text{ K}) = (48 \pm 2) \text{ cm}^3\cdot\text{mol}^{-1}$ . For the oxalate ions Apelblat and Manzurola [90APE/MAN] determined  $V_m^\circ(\text{Hox}^-, 298.15 \text{ K}) = (34 \pm 2) \text{ cm}^3\cdot\text{mol}^{-1}$  and  $V_m^\circ(\text{ox}^{2-}, 298.15 \text{ K}) = (25 \pm 2) \text{ cm}^3\cdot\text{mol}^{-1}$  (uncertainties assigned by this review).

## VI.3 Protonation constants of oxalate

### VI.3.1 Introduction

Oxalic acid is a diprotic acid. In this review oxalic acid is denoted as  $\text{H}_2\text{ox}$ , and the standard TDB nomenclature is used for the protonation of the ligand with  $r = 1$  and 2:



In one study [70LUK] the formation of  $\text{H}_3\text{ox}^+$  in strong acids has been postulated based on electromigration experiments in concentrated perchloric acid solutions. However, the existence of the species  $\text{H}_3\text{ox}^+$  has not been confirmed by any other method, and this review does not consider this cationic species.

A large number of references ( $\approx 150$ ) were found from a literature search for the acid-base equilibria of oxalate. The majority of these references contain studies on metal complexation, where the authors needed values for the dissociation constants of oxalic acid under the same experimental conditions as the metal-complexation study.

Because of the large number of references, it was advantageous to judge the quality of the experimental details quite rigorously. The following criteria were considered when discarding references within the screening process:

- The dissociation constants of oxalic acid reported in the following references were discarded from the Clear indication must be given that the acid-base constants were determined experimentally in the actual study, and not taken from another publication.
- The calibration method for the pH-electrode must be indicated. They must have been calibrated in the concentration scale, and not with standard pH-buffers. That is, “pH” must refer to  $-\log_{10}[\text{H}^+]$ . References were discarded when they reported mixed equilibrium constants, *i.e.*, involving both proton activities and ligand concentrations. In some cases it is reported that the glass electrodes were calibrated with standard buffers, and  $[\text{H}^+]$  calculated from pH, for example with the Davies equation. This procedure is not accepted in this review.
- A background electrolyte providing a constant ionic strength must be used.
- The temperature, ionic strength, and the nature of the background electrolyte must be given.

The dissociation constants of oxalic acid reported in the following references were discarded from the review procedure because they did not fulfil one or more of the criteria indicated above: [\[24LAR\]](#), [\[28SIM\]](#), [\[28SIM2\]](#), [\[31GAN/ING\]](#), [\[36BRI/JAR\]](#), [\[37CLA/VOS\]](#), [\[38CAN/KIB\]](#), [\[40VOS/BEC\]](#), [\[54SCH/LAI\]](#), [\[57BAB/DUB\]](#), [\[57DUT/SUR\]](#), [\[58GEL/MAT\]](#), [\[58MOS/GEL\]](#), [\[60YAM/DAV\]](#), [\[61GRI/AST\]](#), [\[61ZOL/MAR2\]](#), [\[62BRU/KAI\]](#), [\[62MCD/LON\]](#), [\[63PAR/BAR\]](#), [\[63STA\]](#), [\[64SEK\]](#), [\[65SEK4\]](#), [\[66LYL/NAO\]](#), [\[66MAK/YUS\]](#), [\[68HAR\]](#), [\[69HAV\]](#), [\[70COU/FAU\]](#), [\[70GRE/BRY2\]](#), [\[71GEL\]](#), [\[71GOR/MIK\]](#), [\[72MEN\]](#), [\[73CHU/SKO2\]](#), [\[74MOR/SEK\]](#), [\[74NAZ/FLY2\]](#), [\[74SIN/GHO\]](#), [\[74SIN/TAN\]](#), [\[75BOT\]](#), [\[75FRI/PIZ\]](#), [\[75SIN/TAN\]](#), [\[75VOT/BAR\]](#), [\[76BRI/ELD\]](#), [\[76YAD/GHO\]](#), [\[77DEL2\]](#), [\[77DUC/BER\]](#), [\[77JAI/KUM\]](#), [\[77REB/BAR\]](#), [\[78JAI/SHA\]](#), [\[78SIN\]](#), [\[79ELE/ELD\]](#), [\[79FRI/SYC\]](#), [\[80MIS/MIT\]](#), [\[82INO/TOC\]](#), [\[82SAC/CHA\]](#), [\[83BAR/SUS\]](#), [\[83GUP/CHA\]](#), [\[83OLI/WIK\]](#), [\[84VEN/SWA\]](#), [\[84ZHO/XU\]](#), [\[86CHO/DAD\]](#), [\[87GAM\]](#), [\[88CAS/FAU\]](#), [\[88DAS/KAL\]](#), [\[88GHA/MAN\]](#), [\[89DAS/DAS\]](#), [\[89PRA/RAO\]](#), [\[89RED/RAM\]](#), [\[90ULL/BHA\]](#), [\[92DAN/ROB\]](#), [\[92TRI/TRI\]](#), [\[96DAS/MOH\]](#), [\[98ALD/BIA\]](#), [\[99CIA/IUL\]](#), [\[2001MAF/MEI\]](#). These references are *not* discussed in Appendix A.

A few references found in the databases of Smith & Martell [\[2003SMI/MAR\]](#) and IUPAC [\[2002PET/POW\]](#) obviously are typo errors. They do not contain dissociation constants of oxalic acid or do not even refer to oxalate at all: [\[50MEI\]](#), [\[50MEI2\]](#),



[\[57GEL/MAT2\]](#), [\[60SCH/FIS\]](#), [\[70BRA/LEP\]](#), [\[70SCH/HOW\]](#), [\[79MAY/CHA\]](#), [\[89FUE/REB\]](#).

Data from a few other references could not be accepted for other reasons. These references [\[39PAR/GIB\]](#), [\[39PAR/NIC\]](#), [\[49REA\]](#), [\[70DAV/WAT\]](#), [\[70STE/PAZ\]](#), [\[72NIK/ANT\]](#), [\[81SIN/GHO\]](#), [\[85RED/RAO\]](#), [\[86RED/RAO\]](#), [\[90RED/SAT\]](#), [\[94ERT/MOH\]](#), [\[94RED/SHI\]](#), [\[96ARA/ARC\]](#), [\[96BOR/LIS\]](#), [\[98KHA/RAD\]](#) are discussed in Appendix A.

The data reported in the remaining references are listed in Table VI-2.

If data were reported over a range of temperatures these values have been used in this review for the determination of enthalpy changes from the  $T$ -variation of  $\log_{10} K$ , see Section VI.3.4. In these cases [\[39HAR/FAL\]](#), [\[48PIN/BAT\]](#), [\[61MCA/NAN\]](#), [\[69KUR/FAR\]](#), [\[70DAV/WAT\]](#), [\[76KAL\]](#), [\[90ROB/STE\]](#), [\[92ROB/STE\]](#), [\[98KET/WES\]](#) (*cf.* Appendix A) only  $\log_{10} K$  data at 25°C and  $I > 0$  were included in the weighted least-squares procedure for determining  $\log_{10} K_r^\circ$ .

If data were reported solely at temperatures not too different from 25°C the  $\log_{10} K$  data have been extrapolated to 25°C using the temperature parameters evaluated in this review. These are: [\[69GRE/GAR\]](#), [\[72MAG/BIS\]](#) (20°C) and [\[76MAK/TOU\]](#), [\[81DAN/RIG\]](#), [\[82JAC/COS\]](#), [\[83DAN/RIG\]](#), [\[83DAN/RIG2\]](#) (37°C). The corrections were obtained from reaction enthalpies selected in Section VI.3.4. Ionic media corrections to the reaction enthalpies consist of two parts (*cf.* Section V.3.6): a Debye-Hückel expression, and a specific ion interaction ( $\Delta\epsilon_L$ ) term. The resulting reaction enthalpies are all relatively small, and because of the limited temperature interval involved (−5°C and +12°C), the calculated corrections for  $\log_{10} K_r$  were always  $\leq 0.05 \log_{10}$ -units.

A single measurement in  $\text{Bu}_4\text{NClO}_4$  at 40°C [\[69POS/VED\]](#), the value reported in  $\text{LiClO}_4$  at 70°C [\[88KIT\]](#), and the value reported in  $\text{NaClO}_4$  at 60°C [\[2000CIA/IUL\]](#) were not included in the weighted least-squares procedure.

Uncertainties reported in the original publications have been multiplied by a factor 1.96 to obtain error limits closer to a 95% total uncertainty level, *i.e.*, including random and possible systematic deviations. In cases where no uncertainty limits were reported, a value of  $\pm 0.1 \log_{10}$ -units has been used in the weighted least-squares procedure. Reported uncertainties below  $\pm 0.01$  in  $\log_{10} K_1$  in the original papers were increased to  $\pm 0.02$  ( $\approx \pm 0.01 \times 1.96$ ), and reported uncertainties below  $\pm 0.05$  in  $\log_{10} K_2$  in the original papers were increased to  $\pm 0.1$  in the least-squares regression analysis.

The data finally selected for multi-linear least-squares regressions for determining  $\log_{10} K_n^\circ$  are listed in Table VI-3 and Table VI-4. The protonation constants were corrected to molal units and extrapolated to 25°C where necessary.

Table VI-2: Literature data on the protonation constants for oxalate considered in this review. Data in *italics* were reported in molal units. Uncertainties are included as reported in the references.

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	$\rightarrow 0$	NaCl	0	4.228		<a href="#">[39HAR/FAL]</a>
			5	4.235		
			10	4.244		
			15	4.255		
			20	4.268		
			25	4.286		
			30	4.308		
			35	4.331		
			40	4.356		
			45	4.388		
con	$\rightarrow 0$		50	4.417		
con	$\rightarrow 0$		25	4.276	1.27	<a href="#">[41DAR]</a>
pot	$\rightarrow 0$	NaCl	0	4.201		<a href="#">[48PIN/BAT]</a>
			5	4.207		
			10	4.218		
			15	4.231		
			20	4.247		
			25	4.266		
			30	4.287		
			35	4.312		
			40	4.338		
			45	4.369		
			50	4.399		
pot	0.1	NaClO <sub>4</sub>	25	(3.81 ± 0.02)	(1.37 ± 0.02)	<a href="#">[60MCA/NAN]</a>
pot	$\rightarrow 0$	HCl	0		1.24	<a href="#">[61MCA/NAN]</a>
			15		1.25	
			25		1.25	
			35		1.29	
			45		1.29	
pot	0.5	NaClO <sub>4</sub>	5	(3.63 ± 0.01)	(1.32 ± 0.01)	<a href="#">[65BAU/SMI]</a>
			15	(3.65 ± 0.01)	(1.23 ± 0.01)	
			25	(3.67 ± 0.01)	(1.20 ± 0.01)	
pot	1	NaClO <sub>4</sub>	25	(3.57 ± 0.02)	(1.07 ± 0.05)	<a href="#">[65BOT/CIA]</a>
pot	0.1	NaClO <sub>4</sub>	25	3.85	1.13	<a href="#">[65NAG/UMA]</a>
pot	0.1	KNO <sub>3</sub>	25	(3.81 ± 0.01)		<a href="#">[66LHE/MAR]</a>
pot	0.1	NaClO <sub>4</sub>	25		(1.32 ± 0.02)	<a href="#">[66MOO/SUT]</a>

(Continued on next page)

Table VI-2: (continued)

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	1	NaClO <sub>4</sub>	25	(3.55 ± 0.01)	(1.08 ± 0.01)	<a href="#">[66MOO/SUT]</a>
	3			(3.80 ± 0.01)	(1.26 ± 0.03)	
pot	1	KNO <sub>3</sub>	25	(3.62 ± 0.01)	1.1	<a href="#">[67RAJ/MAR]</a>
pot	0.52	LiClO <sub>4</sub>	25	(3.50 ± 0.03)	(1.00 ± 0.05)	<a href="#">[68DEN/MEI]</a>
pot	0.1	KNO <sub>3</sub>	25	(3.82 ± 0.01)	(1.26 ± 0.05)	<a href="#">[69CON/MAR]</a>
pot	1	NaClO <sub>4</sub>	20	(3.55 ± 0.01)	(1.01 ± 0.02)	<a href="#">[69GRE/GAR]</a>
pot	→ 0	HCl	25		(1.30 ± 0.01)	<a href="#">[69KUR/FAR]</a>
			30		(1.31 ± 0.01)	
			35		(1.32 ± 0.01)	
			40		(1.33 ± 0.01)	
			45		(1.34 ± 0.01)	
			50		(1.36 ± 0.01)	
			55		(1.36 ± 0.01)	
pot	0.1	Bu <sub>4</sub> NClO <sub>4</sub>	40	4.27	1.27	<a href="#">[69POS/VED]</a>
pot	0.1	NaClO <sub>4</sub>	20	3.90	1.28	<a href="#">[69VOR/IVA]</a>
pot	0.5	NaCl	25	(3.60 ± 0.02)		<a href="#">[70ASC/BRI]</a>
pot	1	LiClO <sub>4</sub>	25	(3.35 ± 0.01)	(0.84 ± 0.05)	<a href="#">[70CIA/GRI]</a>
pot	1	NaClO <sub>4</sub>	20	(3.60 ± 0.01)	(1.13 ± 0.01)	<a href="#">[72MAG/BIS]</a>
pot	0.1	NaClO <sub>4</sub>	25	3.81	1.31	<a href="#">[73ARM/DUN]</a>
pot	1	NaClO <sub>4</sub>	40		(1.03 ± 0.01)	<a href="#">[76KAL]</a>
			45		(1.04 ± 0.02)	
			50		(1.03 ± 0.01)	
			55		(1.06 ± 0.04)	
		KNO <sub>3</sub>	35		(1.04 ± 0.02)	
			40		(0.96 ± 0.00)	
			45		(1.05 ± 0.01)	
			50		(1.00 ± 0.01)	
			55		(1.05 ± 0.03)	
pot	0.15	NaClO <sub>4</sub>	37	(3.68 ± 0.01)	(1.09 ± 0.03)	<a href="#">[76MAK/TOU]</a>
pot	0.1	KNO <sub>3</sub>	25	(3.88 ± 0.01)		<a href="#">[77BRO/PET]</a>
pot	1	NaClO <sub>4</sub>	25	(3.56 ± 0.01)	(1.01 ± 0.01)	<a href="#">[77HED/OLI]</a>
pot	0.1	KNO <sub>3</sub>	25	(3.85 ± 0.02)	(1.25 ± 0.05)	<a href="#">[80GRA/MUS]</a>
pot	0.1	Et <sub>4</sub> NI	37	(3.98 ± 0.02)		<a href="#">[81DAN/RIG]</a>
				(3.98 ± 0.02)		
	0.1	NaNO <sub>3</sub>		(3.86 ± 0.03)		
	0.3			(3.71 ± 0.01)		
	0.1	KNO <sub>3</sub>		(3.89 ± 0.01)		
	0.3			(3.73 ± 0.02)		

(Continued on next page)

Table VI-2: (continued)

Method	$I$ (M)	Electrolyte	$t$ (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	0.15	NaCl	37	$(3.76 \pm 0.01)$	$(1.40 \pm 0.01)$	<a href="#">[82JAC/COS]</a>
pot	3	NaClO <sub>4</sub>	25	$(3.82 \pm 0.01)$	$(1.27 \pm 0.01)$	<a href="#">[83CRU/HEY]</a>
sp				$(3.84 \pm 0.01)$	$(1.26 \pm 0.01)$	
pot	0.15	LiNO <sub>3</sub>	37	$(3.70 \pm 0.01)$		<a href="#">[83DAN/RIG2]</a>
		NaNO <sub>3</sub>		$(3.82 \pm 0.01)$		
		KNO <sub>3</sub>		$(3.84 \pm 0.01)$		
pot	0.10	Et <sub>4</sub> NI	37	$(3.99 \pm 0.01)$		<a href="#">[83DAN/RIG]</a>
	0.30			$(3.98 \pm 0.01)$		
	0.56			$(4.08 \pm 0.01)$		
	0.96			$(4.18 \pm 0.01)$		
pot	0.15	KNO <sub>3</sub>	25	$(3.75 \pm 0.01)$	$(0.99 \pm 0.01)$	<a href="#">[84JOH/JON]</a>
pot	0.04	Et <sub>4</sub> NI	25	$(4.00 \pm 0.02)$		<a href="#">[85ROB/STE]</a>
	0.25			$(3.93 \pm 0.02)$		
	0.81			$(4.09 \pm 0.02)$		
pot	0.6	NaCl	25	$(3.57 \pm 0.01)$	$(0.97 \pm 0.01)$	<a href="#">[85SJO/OEH2]</a>
pot	1	NaCl	25	$(3.52 \pm 0.02)$	$(0.89 \pm 0.02)$	<a href="#">[86CRU/HEY]</a>
pot	1	LiClO <sub>4</sub>	70	$(3.46 \pm 0.03)$	$(1.09 \pm 0.03)$	<a href="#">[88KIT]</a>
pot	0.5	NaCl	25	$(3.60 \pm 0.010)$	$(1.16 \pm 0.03)$	<a href="#">[89FUE/REB2]</a>
pot	0.04	Et <sub>4</sub> NI	5	$(3.987 \pm 0.006)$		<a href="#">[90ROB/STE]</a>
	0.16			$(3.903 \pm 0.006)$		
	0.36			$(3.926 \pm 0.006)$		
	0.64			$(4.014 \pm 0.006)$		
	1			$(4.135 \pm 0.006)$		
	0.04		15	$(4.005 \pm 0.006)$		
	0.16			$(3.918 \pm 0.006)$		
	0.36			$(3.940 \pm 0.006)$		
	0.64			$(4.027 \pm 0.006)$		
	1			$(4.147 \pm 0.006)$		
	0.04		25	$(4.039 \pm 0.006)$		
	0.16			$(3.949 \pm 0.006)$		
	0.36			$(3.970 \pm 0.006)$		
	0.64			$(4.056 \pm 0.006)$		
	1			$(4.174 \pm 0.006)$		
	0.04		35	$(4.086 \pm 0.006)$		
	0.16			$(3.993 \pm 0.006)$		
	0.36			$(4.012 \pm 0.006)$		
	0.64			$(4.097 \pm 0.006)$		
	1			$(4.215 \pm 0.006)$		

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Table VI-2: (continued)

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	0.04	Et <sub>4</sub> NI	45	(4.144 ± 0.006)		<a href="#">[90ROB/STE]</a>
	0.16			(4.049 ± 0.006)		
	0.36			(4.065 ± 0.006)		
	0.64			(4.149 ± 0.006)		
	1			(4.266 ± 0.006)		
	0.04		55	(4.213 ± 0.006)		
	0.16			(4.114 ± 0.006)		
	0.36		55	(4.128 ± 0.006)		
	0.64			(4.210 ± 0.006)		
	1			(4.326 ± 0.006)		
pot	0.1	KNO <sub>3</sub>	25	(3.87 ± 0.04)		<a href="#">[92AZA/ELN]</a>
pot	0.04	NaCl	10	(3.91 ± 0.01)	(1.14 ± 0.10)	<a href="#">[92ROB/STE]</a>
	0.17			(3.73 ± 0.01)	(1.08 ± 0.10)	
	0.40			(3.62 ± 0.01)	(1.05 ± 0.10)	
	0.76			(3.55 ± 0.01)	(1.04 ± 0.10)	
	1.25			(3.50 ± 0.01)	(1.02 ± 0.10)	
	0.04		25	(3.95 ± 0.01)	(1.17 ± 0.10)	
	0.17			(3.76 ± 0.01)	(1.11 ± 0.10)	
	0.39			(3.65 ± 0.01)	(1.08 ± 0.10)	
	0.74			(3.58 ± 0.01)	(1.06 ± 0.10)	
	1.23			(3.54 ± 0.01)	(1.04 ± 0.10)	
	0.04		37	(4.00 ± 0.01)	(1.19 ± 0.10)	
	0.17			(3.80 ± 0.01)	(1.13 ± 0.10)	
	0.40			(3.69 ± 0.01)	(1.09 ± 0.10)	
	0.74			(3.61 ± 0.01)	(1.07 ± 0.10)	
	1.22			(3.57 ± 0.01)	(1.05 ± 0.10)	
	0.04		45	(4.04 ± 0.01)	(1.21 ± 0.10)	
	0.16			(3.84 ± 0.01)	(1.14 ± 0.10)	
	0.40			(3.72 ± 0.01)	(1.11 ± 0.10)	
	0.75			(3.63 ± 0.01)	(1.11 ± 0.10)	
	1.21			(3.59 ± 0.01)	(1.09 ± 0.10)	
	0.04	KCl	10	(3.93 ± 0.01)	(1.15 ± 0.10)	
	0.17			(3.78 ± 0.01)	(1.10 ± 0.10)	
	0.40			(3.71 ± 0.01)	(1.08 ± 0.10)	
	0.77			(3.67 ± 0.01)	(1.07 ± 0.10)	
	1.32			(3.63 ± 0.01)	(1.07 ± 0.10)	
	0.04		25	(3.96 ± 0.01)	(1.18 ± 0.10)	
	0.17			(3.80 ± 0.01)	(1.12 ± 0.10)	

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Table VI-2: (continued)

Method	$I$ (M)	Electrolyte	$t$ (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	0.41	KCl	25	$(3.71 \pm 0.01)$	$(1.10 \pm 0.10)$	<a href="#">[92ROB/STE]</a>
	0.77			$(3.65 \pm 0.010)$	$(1.10 \pm 0.10)$	
	1.30			$(3.61 \pm 0.01)$	$(1.09 \pm 0.10)$	
	0.04		37	$(4.01 \pm 0.01)$	$(1.19 \pm 0.10)$	
	0.17			$(3.83 \pm 0.01)$	$(1.13 \pm 0.10)$	
	0.41			$(3.72 \pm 0.010)$	$(1.11 \pm 0.10)$	
	0.77			$(3.64 \pm 0.01)$	$(1.11 \pm 0.10)$	
	1.30			$(3.59 \pm 0.01)$	$(1.10 \pm 0.10)$	
	0.04		45	$(4.05 \pm 0.01)$	$(1.21 \pm 0.10)$	
	0.17			$(3.85 \pm 0.01)$	$(1.15 \pm 0.10)$	
	0.40			$(3.73 \pm 0.01)$	$(1.13 \pm 0.10)$	
	0.76			$(3.64 \pm 0.01)$	$(1.14 \pm 0.10)$	
	1.29			$(3.59 \pm 0.01)$	$(1.13 \pm 0.10)$	
	0.04	Et <sub>4</sub> NI	10	$(3.96 \pm 0.01)$	$(1.09 \pm 0.08)$	
	0.17			$(3.87 \pm 0.01)$	$(1.02 \pm 0.08)$	
	0.39			$(3.87 \pm 0.01)$	$(1.05 \pm 0.08)$	
	0.73			$(3.92 \pm 0.01)$	$(1.19 \pm 0.08)$	
	1.22			$(3.98 \pm 0.01)$	$(1.26 \pm 0.08)$	
	0.04		25	$(4.00 \pm 0.01)$	$(1.13 \pm 0.08)$	
	0.17			$(3.90 \pm 0.01)$	$(1.05 \pm 0.08)$	
	0.39			$(3.91 \pm 0.01)$	$(1.16 \pm 0.08)$	
	0.73			$(3.96 \pm 0.01)$	$(1.22 \pm 0.08)$	
	1.23			$(4.04 \pm 0.01)$	$(1.29 \pm 0.08)$	
	0.04		37	$(4.06 \pm 0.010)$	$(1.14 \pm 0.08)$	
	0.17			$(3.96 \pm 0.01)$	$(1.07 \pm 0.08)$	
	0.39			$(3.96 \pm 0.01)$	$(1.18 \pm 0.08)$	
	0.73			$(4.03 \pm 0.01)$	$(1.23 \pm 0.08)$	
	1.24			$(4.12 \pm 0.01)$	$(1.29 \pm 0.08)$	
	0.04		45	$(4.11 \pm 0.01)$	$(1.13 \pm 0.08)$	
	0.17			$(4.01 \pm 0.01)$	$(1.18 \pm 0.08)$	
	0.39			$(4.01 \pm 0.01)$	$(1.19 \pm 0.08)$	
	0.73			$(4.07 \pm 0.01)$	$(1.25 \pm 0.08)$	
	1.24			$(4.16 \pm 0.01)$	$(1.32 \pm 0.08)$	
pot	0.15	NaCl	25	3.76		<a href="#">[93GLA/MAJ]</a>
			37	3.95		
pot	0.2	KCl	25	$(3.73 \pm 0.01)$	$(1.08 \pm 0.09)$	<a href="#">[94KIS/SOV]</a>
pot	0.1	KCl	25	$(3.86 \pm 0.02)$		<a href="#">[95LU/MOT]</a>
pot	0.1	NaCl	25	3.822		<a href="#">[95MIR/SAD]</a>

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Table VI-2: (continued)

Method	$I$ (M)	Electrolyte	$t$ (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	0.3	NaCl	25	3.645		<a href="#">[95MIR/SAD]</a>
	0.5			3.572		
	1			3.504		
	2			3.509		
	3			3.621		
	4			3.756		
	0.1	NaClO <sub>4</sub>		3.809		
	0.3			3.633		
	0.5			3.565		
	1			3.542		
	2			3.622		
	3			3.811		
	4			4.012		
	pot			0.3	NaClO <sub>4</sub>	
0.5		(3.65 ± 0.01)	(1.28 ± 0.03)			
1		(3.60 ± 0.01)	(1.33 ± 0.04)			
3		(3.84 ± 0.01)	(1.49 ± 0.02)			
5		(4.23 ± 0.01)	(1.42 ± 0.04)			
7		(4.71 ± 0.01)	(1.75 ± 0.01)			
9		(5.11 ± 0.04)	(2.13 ± 0.05)			
pot		0.1	Me <sub>4</sub> NI	25		3.87
pot	0.5	NaClO <sub>4</sub>	25	(3.64 ± 0.01)	(1.0 ± 0.1)	<a href="#">[97BAR/CEC]</a>
pot	3	NaClO <sub>4</sub>	25	(3.83 ± 0.01)		<a href="#">[98FER/MAN]</a>
pot	0.185	NaCl	0	(3.655 ± 0.01)		<a href="#">[98KET/WES]</a>
	0.334			(3.577 ± 0.016)		
	2.002			(3.506 ± 0.014)		
	3.149			(3.553 ± 0.014)		
	5.000			(3.834 ± 0.014)		
	0.100		25	(3.803 ± 0.010)		
	0.185			(3.706 ± 0.009)		
	0.334			(3.613 ± 0.015)		
	0.334			(3.618 ± 0.015)		
	1.001			(3.541 ± 0.015)		
	1.001			(3.553 ± 0.015)		
	1.001			(3.556 ± 0.015)		
	2.002			(3.467 ± 0.014)		
	2.002			(3.496 ± 0.014)		
	3.149			(3.517 ± 0.014)		

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Table VI-2: (continued)

Method	$I$ (M)	Electrolyte	$t$ (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	5.000	NaCl	25	$(3.733 \pm 0.014)$		<a href="#">[98KET/WES]</a>
	0.100		50	$(3.910 \pm 0.009)$		
	0.185			$(3.801 \pm 0.008)$		
	0.334			$(3.706 \pm 0.015)$		
	0.100			$(3.561 \pm 0.014)$		
	0.185					
	0.334			$(3.457 \pm 0.014)$		
	2.002			$(3.535 \pm 0.014)$		
	3.149			$(3.526 \pm 0.014)$		
	3.149			$(3.529 \pm 0.014)$		
	5.001			$(3.677 \pm 0.014)$		
	5.001			$(3.684 \pm 0.014)$		
	0.100		75	$(4.052 \pm 0.008)$		
	0.185			$(3.940 \pm 0.008)$		
	0.334			$(3.832 \pm 0.015)$		
	1.001			$(3.649 \pm 0.014)$		
	2.002			$(3.568 \pm 0.014)$		
	3.150			$(3.562 \pm 0.014)$		
	3.150			$(3.573 \pm 0.014)$		
	5.002			$(3.665 \pm 0.014)$		
	0.100		100	$(4.219 \pm 0.008)$		
	0.185			$(4.112 \pm 0.008)$		
	0.334			$(3.980 \pm 0.014)$		
	1.002			$(3.767 \pm 0.014)$		
	2.003			$(3.678 \pm 0.014)$		
	2.003			$(3.675 \pm 0.014)$		
	3.151			$(3.617 \pm 0.014)$		
	5.004			$(3.666 \pm 0.014)$		
	0.100		125	$(4.406 \pm 0.008)$		
	0.185			$(4.291 \pm 0.007)$		
	0.334			$(4.145 \pm 0.014)$		
	1.002			$(3.898 \pm 0.014)$		
	2.004			$(3.777 \pm 0.014)$		
	3.153			$(3.683 \pm 0.014)$		
	5.006			$(3.690 \pm 0.014)$		
	0.100		150	$(4.605 \pm 0.007)$		
	0.185			$(4.494 \pm 0.007)$		
	0.334			$(4.322 \pm 0.014)$		
	2.006			$(3.880 \pm 0.014)$		

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Table VI-2: (continued)

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	1.003	NaCl	150	$(4.036 \pm 0.014)$		<a href="#">[98KET/WES]</a>
	2.006			$(3.880 \pm 0.014)$		
	3.156			$(3.762 \pm 0.014)$		
	5.012			$(3.713 \pm 0.014)$		
	0.100		175	$(4.836 \pm 0.007)$		
	0.185			$(4.741 \pm 0.007)$		
	0.335			$(4.495 \pm 0.014)$		
	1.005			$(4.216 \pm 0.014)$		
	2.009			$(3.977 \pm 0.014)$		
	3.161			$(3.850 \pm 0.014)$		
	5.020			$(3.749 \pm 0.014)$		
	3.172		0		$(1.001 \pm 0.086)$	
	4.998				$(1.351 \pm 0.012)$	
	0.100		5		$(1.271 \pm 0.296)$	
	0.100				$(1.183 \pm 0.369)$	
	0.316				$(1.051 \pm 0.098)$	
	0.316				$(1.050 \pm 0.098)$	
	0.601				$(0.989 \pm 0.086)$	
	0.602				$(0.974 \pm 0.089)$	
	1.002				$(0.961 \pm 0.066)$	
	0.100		25		$(1.282 \pm 0.235)$	
	0.100				$(1.184 \pm 0.294)$	
	0.316				$(1.068 \pm 0.0800)$	
	0.316				$(1.064 \pm 0.081)$	
	0.601				$(0.953 \pm 0.079)$	
	0.602				$(0.966 \pm 0.078)$	
	1.002				$(0.941 \pm 0.059)$	
	2.001				$(0.957 \pm 0.089)$	
	3.002				$(0.981 \pm 0.013)$	
	3.172				$(1.104 \pm 0.065)$	
	4.002				$(1.033 \pm 0.014)$	
	4.999				$(1.203 \pm 0.012)$	
	0.100		50		$(1.310 \pm 0.183)$	
	0.100				$(1.216 \pm 0.222)$	
	0.101				$(1.174 \pm 0.178)$	
	0.316				$(1.089 \pm 0.066)$	
	0.316				$(1.090 \pm 0.066)$	

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Table VI-2: (continued)

Method	$I$ (M)	Electrolyte	$t$ (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	0.332	NaCl	50		$(1.009 \pm 0.013)$	<a href="#">[98KET/WES]</a>
	0.601				$(1.033 \pm 0.061)$	
	0.602				$(1.033 \pm 0.061)$	
	1.002				$(1.000 \pm 0.047)$	
	1.030				$(0.901 \pm 0.043)$	
	1.982				$(0.826 \pm 0.086)$	
	2.002				$(0.808 \pm 0.092)$	
	3.002				$(0.978 \pm 0.013)$	
	3.172				$(1.010 \pm 0.060)$	
	3.172				$(1.024 \pm 0.060)$	
	4.002				$(1.034 \pm 0.012)$	
	5.000				$(1.135 \pm 0.011)$	
	0.099		75		$(1.351 \pm 0.142)$	
	0.100				$(1.284 \pm 0.162)$	
	0.101				$(1.248 \pm 0.125)$	
	0.316				$(1.159 \pm 0.051)$	
	0.316				$(1.156 \pm 0.051)$	
	0.332				$(1.080 \pm 0.012)$	
	0.601				$(1.122 \pm 0.047)$	
	0.601				$(1.121 \pm 0.047)$	
	1.002				$(1.059 \pm 0.039)$	
	1.030				$(0.953 \pm 0.039)$	
	1.982				$(0.864 \pm 0.072)$	
	2.002				$(0.851 \pm 0.075)$	
	3.003				$(1.017 \pm 0.011)$	
	3.172				$(1.121 \pm 0.048)$	
	3.173				$(1.075 \pm 0.050)$	
	4.003				$(1.051 \pm 0.010)$	
	5.001				$(1.127 \pm 0.010)$	
	0.099		100		$(1.385 \pm 0.112)$	
	0.100				$(1.369 \pm 0.116)$	
	0.100				$(1.339 \pm 0.087)$	
	0.315				$(1.238 \pm 0.039)$	
	0.315				$(1.240 \pm 0.039)$	
	0.331				$(1.169 \pm 0.013)$	
	0.601				$(1.178 \pm 0.039)$	
	0.601				$(1.177 \pm 0.039)$	
	1.001				$(1.124 \pm 0.033)$	

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Table VI-2: (continued)

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	1.030	NaCl	100		(1.036 ± 0.035)	<a href="#">[98KET/WES]</a>
	1.982				(0.925 ± 0.060)	
	2.002				(0.909 ± 0.061)	
	3.004				(1.064 ± 0.009)	
	3.173				(1.123 ± 0.042)	
	3.173				(1.154 ± 0.041)	
	4.004				(1.100 ± 0.009)	
	5.003				(1.143 ± 0.009)	
	0.099		125		(1.489 ± 0.083)	
	0.099				(1.438 ± 0.063)	
	0.100				(1.472 ± 0.086)	
	0.315				(1.338 ± 0.031)	
	0.315				(1.340 ± 0.031)	
	0.331				(1.270 ± 0.014)	
	0.601				(1.272 ± 0.033)	
	0.601				(1.273 ± 0.033)	
	1.002				(1.214 ± 0.029)	
	1.030				(1.146 ± 0.033)	
	1.982				(1.028 ± 0.051)	
	2.003				(1.002 ± 0.050)	
	3.006				(1.114 ± 0.008)	
	3.175				(1.188 ± 0.037)	
	3.175				(1.192 ± 0.037)	
	4.007				(1.185 ± 0.008)	
	0.101	NaCF <sub>3</sub> SO <sub>3</sub>	5		(1.318 ± 0.142)	
	0.101				(1.290 ± 0.150)	
	0.101				(1.289 ± 0.151)	
	0.316				(1.084 ± 0.065)	
	0.316				(1.085 ± 0.065)	
	0.600				(1.082 ± 0.039)	
	0.600				(1.002 ± 0.046)	
	1.001				(1.040 ± 0.061)	
	1.001				(1.040 ± 0.061)	
	0.101		25		(1.236 ± 0.150)	
	0.101				(1.244 ± 0.147)	
	0.101				(1.231 ± 0.152)	
	0.102				(1.206 ± 0.160)	

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Table VI-2: (continued)

Method	$I$ (M)	Electrolyte	$t$ (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	0.316	NaCF <sub>3</sub> SO <sub>3</sub>	25		$(1.060 \pm 0.062)$	<a href="#">[98KET/WES]</a>
	0.316				$(1.048 \pm 0.063)$	
	0.600				$(1.044 \pm 0.039)$	
	0.600				$(0.995 \pm 0.043)$	
	1.001				$(0.995 \pm 0.058)$	
	1.001				$(1.010 \pm 0.058)$	
	0.101		50		$(1.248 \pm 0.122)$	
	0.101				$(1.242 \pm 0.123)$	
	0.101				$(1.238 \pm 0.124)$	
	0.102				$(1.203 \pm 0.134)$	
	0.316				$(1.082 \pm 0.051)$	
	0.316				$(1.084 \pm 0.051)$	
	0.600		75		$(1.060 \pm 0.033)$	
	0.600				$(1.019 \pm 0.036)$	
	1.001				$(1.066 \pm 0.049)$	
	1.001				$(1.070 \pm 0.049)$	
	0.101				$(1.311 \pm 0.088)$	
	0.101				$(1.305 \pm 0.089)$	
	0.101				$(1.282 \pm 0.093)$	
	0.101				$(1.319 \pm 0.087)$	
	0.316				$(1.150 \pm 0.037)$	
	0.600				$(1.105 \pm 0.026)$	
	0.600				$(1.092 \pm 0.027)$	
	1.000				$(1.142 \pm 0.042)$	
	1.001				$(1.127 \pm 0.043)$	
	0.101		100		$(1.405 \pm 0.060)$	
	0.101				$(1.390 \pm 0.062)$	
	0.101				$(1.400 \pm 0.061)$	
	0.315				$(1.253 \pm 0.026)$	
	0.600				$(1.184 \pm 0.020)$	
	1.000				$(1.197 \pm 0.038)$	
	1.000		125		$(1.197 \pm 0.038)$	
	0.101				$(1.503 \pm 0.045)$	
	0.101				$(1.498 \pm 0.045)$	
	0.600				$(1.293 \pm 0.015)$	
	1.001				$(1.313 \pm 0.034)$	
	1.001				$(1.303 \pm 0.034)$	

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Table VI-2: (continued)

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	0.100	NaCF <sub>3</sub> SO <sub>3</sub>	5	(3.760 ± 0.011)		<a href="#">[98KET/WES]</a>
	0.100			(3.769 ± 0.011)		
	0.100			(3.764 ± 0.011)		
	0.100			(3.769 ± 0.011)		
	0.273			(3.633 ± 0.011)		
	0.316			(3.599 ± 0.011)		
	0.600			(3.539 ± 0.011)		
	0.600			(3.540 ± 0.011)		
	1.000			(3.520 ± 0.011)		
	0.100		25	(3.821 ± 0.011)		
	0.100			(3.826 ± 0.011)		
	0.100			(3.819 ± 0.011)		
	0.100			(3.819 ± 0.011)		
	0.273			(3.675 ± 0.011)		
	0.316			(3.641 ± 0.011)		
	0.600			(3.571 ± 0.011)		
	0.600			(3.573 ± 0.011)		
	1.000			(3.541 ± 0.011)		
	0.100		50	(3.936 ± 0.011)		
	0.100			(3.937 ± 0.011)		
	0.100			(3.931 ± 0.011)		
	0.100			(3.930 ± 0.011)		
	0.273			(3.772 ± 0.011)		
	0.316			(3.739 ± 0.011)		
	0.600			(3.656 ± 0.011)		
	0.600			(3.658 ± 0.011)		
	1.000			(3.615 ± 0.011)		
	0.100		75	(4.086 ± 0.011)		
	0.100			(4.074 ± 0.011)		
	0.100			(4.074 ± 0.011)		
	0.273			(3.905 ± 0.011)		
	0.316			(3.871 ± 0.011)		
	0.600			(3.775 ± 0.011)		
	0.600			(3.778 ± 0.011)		
	1.000			(3.721 ± 0.011)		
	0.100		100	(4.256 ± 0.011)		
	0.100			(4.257 ± 0.011)		
	0.100			(4.243 ± 0.011)		

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Table VI-2: (continued)

Method	$I$ (M)	Electrolyte	$t$ (°C)	$\log_{10} K_1$	$\log_{10} K_2$	Reference
pot	0.100	NaCF <sub>3</sub> SO <sub>3</sub>	100	$(4.246 \pm 0.011)$		<a href="#">[98KET/WES]</a>
	0.273			$(4.060 \pm 0.011)$		
	0.316			$(4.027 \pm 0.011)$		
	0.600			$(3.919 \pm 0.011)$		
	0.600			$(3.918 \pm 0.011)$		
	1.000			$(3.849 \pm 0.011)$		
	0.100		125	$(4.450 \pm 0.011)$		
	0.100			$(4.438 \pm 0.011)$		
	0.100			$(4.440 \pm 0.011)$		
	0.273			$(4.234 \pm 0.011)$		
	0.316			$(4.200 \pm 0.011)$		
	0.601			$(4.076 \pm 0.011)$		
	0.601			$(4.076 \pm 0.011)$		
	1.001			$(3.992 \pm 0.011)$		
pot	0.3	NaCl	25	$(3.67 \pm 0.02)$	$(1.06 \pm 0.05)$	<a href="#">[99MIZ/BON]</a>
	1			$(3.52 \pm 0.02)$	$(0.9 \pm 0.2)$	
	2			$(3.54 \pm 0.02)$	$(0.9 \pm 0.1)$	
	3			$(3.55 \pm 0.02)$	$(0.86 \pm 0.07)$	
	4			$(3.74 \pm 0.02)$	$(1.04 \pm 0.05)$	
	5			$(3.85 \pm 0.02)$	$(1.2 \pm 0.2)$	
pot	0.2	KCl	25	$(3.75 \pm 0.02)$	$(1.3 \pm 0.2)$	<a href="#">[2000BUG/KIS]</a>
pot	1.0	NaClO <sub>4</sub>	60	$(3.68 \pm 0.01)$	$(0.99 \pm 0.05)$	<a href="#">[2000CIA/IUL]</a>
ise-ox	2.0	NaClO <sub>4</sub>	25	$(3.57 \pm 0.02)$	$(1.14 \pm 0.03)$	<a href="#">[2000FER/IUL]</a>
	3.0			$(3.81 \pm 0.02)$	$(1.14 \pm 0.02)$	
ise-ox	1.0	NaClO <sub>4</sub>	25	$(3.57 \pm 0.02)$	$(1.00 \pm 0.03)$	<a href="#">[2000VAS/CAR]</a>
pot	1.0	NaClO <sub>4</sub>	25	$(3.583 \pm 0.003)$	$(1.27 \pm 0.05)$	<a href="#">[2001CIA/TOM2]</a>
sp	3.0	NaClO <sub>4</sub>	25	$(3.83 \pm 0.01)$	$(1.09 \pm 0.01)$	<a href="#">[2002HAV/SOT]</a>
pot	0.10	NaCl	25	$(3.841 \pm 0.005)$	$(1.097 \pm 0.025)$	<a href="#">[2004CRE/ROB]</a>
	0.25			$(3.705 \pm 0.011)$	$(1.028 \pm 0.028)$	
	0.50			$(3.605 \pm 0.010)$	$(0.977 \pm 0.027)$	
	1.00			$(3.530 \pm 0.009)$	$(0.938 \pm 0.035)$	
	2.00			$(3.532 \pm 0.015)$	$(0.942 \pm 0.042)$	
	3.00			$(3.620 \pm 0.015)$	$(0.998 \pm 0.045)$	
	4.50			$(3.854 \pm 0.012)$	$(1.149 \pm 0.050)$	
	0.10			$(3.929 \pm 0.009)$	$(1.131 \pm 0.020)$	
	0.25			$(3.908 \pm 0.014)$	$(1.112 \pm 0.020)$	
	0.50			$(3.973 \pm 0.009)$	$(1.127 \pm 0.030)$	
	1.00			$(4.154 \pm 0.015)$	$(1.176 \pm 0.020)$	

Table VI-3: Accepted data on the protonation constants for oxalate. The protonation constants were corrected to molal units and extrapolated to 25°C where necessary. Uncertainties are estimated in this review.

Electrolyte	$I$ (molal)	$\Delta \log_{10} K$ (molal)	$\Delta \log_{10} K_I$ (25°C)	$\log_{10} K_1$	$\Delta \log_{10} K_2$ (25°C)	$\log_{10} K_2$	Reference
LiClO <sub>4</sub>	0.53	– 0.011		(3.49 ± 0.06)		(0.99 ± 0.10)	[68DEN/MEI]
	1.05	– 0.021		(3.33 ± 0.02)		(0.82 ± 0.10)	[70CIA/GRI]
LiNO <sub>3</sub>	0.15	– 0.003	– 0.038	(3.66 ± 0.05)			[83DAN/RIG2]
NaClO <sub>4</sub>	0.10	– 0.003		(3.81 ± 0.04)		(1.37 ± 0.10)	[60MCA/NAN]
	0.51	– 0.011		(3.66 ± 0.02)		(1.19 ± 0.10)	[65BAU/SMI]
	1.05	– 0.022		(3.55 ± 0.04)		(1.05 ± 0.10)	[65BOT/CIA]
	0.10	– 0.003		(3.85 ± 0.10)		(1.13 ± 0.10)	[65NAG/UMA]
	0.10	– 0.003				(1.32 ± 0.10)	[66MOO/SUT]
	1.05	– 0.022		(3.53 ± 0.02)		(1.06 ± 0.10)	
	3.50	– 0.067		(3.73 ± 0.02)		(1.19 ± 0.10)	
	1.05	– 0.022	0.007	(3.54 ± 0.02)	0.001	(0.99 ± 0.10)	[69GRE/GAR]
	0.10	– 0.003	0.017	(3.91 ± 0.10)	0.007	(1.28 ± 0.10)	[69VOR/IVA]
	1.05	– 0.022	0.007	(3.59 ± 0.02)	0.001	(1.11 ± 0.10)	[72MAG/BIS]
	0.10	– 0.003		(3.81 ± 0.10)		(1.31 ± 0.10)	[73ARM/DUN]
	0.15	– 0.004	– 0.037	(3.64 ± 0.10)	– 0.016	(1.07 ± 0.10)	[76MAK/TOU]
	1.05	– 0.022		(3.54 ± 0.02)		(0.99 ± 0.10)	[77HED/OLI]
	3.50	– 0.067		(3.75 ± 0.02)		(1.20 ± 0.10)	[83CRU/HEY]
	3.50	– 0.067		(3.77 ± 0.02)		(1.19 ± 0.10)	
	0.10	– 0.003		(3.81 ± 0.06)			[95MIR/SAD]
	0.31	– 0.007		(3.63 ± 0.06)			
	0.51	– 0.011		(3.55 ± 0.06)			
	1.05	– 0.022		(3.52 ± 0.06)			
	2.21	– 0.044		(3.58 ± 0.06)			
	3.50	– 0.067		(3.74 ± 0.06)			
	4.95	– 0.093		(3.92 ± 0.06)			
	0.31	– 0.007		(3.72 ± 0.02)			[96CHO/CHE]
	0.51	– 0.011		(3.64 ± 0.02)		(1.27 ± 0.10)	
	1.05	– 0.022		(3.58 ± 0.02)		(1.31 ± 0.10)	
	3.50	– 0.067		(3.77 ± 0.02)		(1.42 ± 0.10)	
	6.58	– 0.119		(4.11 ± 0.02)		(1.30 ± 0.10)	
	0.51	– 0.011		(3.63 ± 0.02)		(0.99 ± 0.20)	[97BAR/CEC]
	3.50	– 0.067		(3.76 ± 0.02)			[98FER/MAN]
	2.21	– 0.044		(3.53 ± 0.04)		(1.10 ± 0.10)	[2000FER/IUL]

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Table VI-3: (continued)

Electrolyte	$I$ (molal)	$\Delta \log_{10} K$ (molal)	$\Delta \log_{10} K$ (25°C)	$\log_{10} K_1$	$\Delta \log_{10} K_2$ (25°C)	$\log_{10} K_2$	Reference
NaClO <sub>4</sub>	3.50	− 0.067		(3.74 ± 0.04)		(1.07 ± 0.10)	<a href="#">[2000FER/IUL]</a>
	1.05	− 0.022		(3.55 ± 0.04)		(0.98 ± 0.10)	<a href="#">[2000VAS/CAR]</a>
	1.05	− 0.022		(3.56 ± 0.02)		(1.25 ± 0.10)	<a href="#">[2001CIA/TOM2]</a>
	3.50	− 0.067		(3.76 ± 0.02)		(1.02 ± 0.10)	<a href="#">[2002HAV/SOT]</a>
NaCl	0.51	− 0.005		(3.59 ± 0.04)			<a href="#">[70ASC/BRJ]</a>
	0.61	− 0.006		(3.56 ± 0.02)		(0.96 ± 0.10)	<a href="#">[85SJO/OEH2]</a>
	1.02	− 0.009		(3.51 ± 0.04)		(0.88 ± 0.10)	<a href="#">[86CRU/HEY]</a>
	0.51	− 0.005		(3.59 ± 0.02)		(1.15 ± 0.10)	<a href="#">[89FUE/REB2]</a>
	0.04			(3.95 ± 0.02)		(1.17 ± 0.20)	<a href="#">[92ROB/STE]</a>
	0.17			(3.76 ± 0.02)		(1.11 ± 0.20)	
	0.39			(3.65 ± 0.02)		(1.08 ± 0.20)	
	0.74			(3.58 ± 0.02)		(1.06 ± 0.20)	
	1.23			(3.54 ± 0.02)		(1.04 ± 0.20)	
	0.15	− 0.002		(3.76 ± 0.10)			<a href="#">[93GLA/MAJ]</a>
	0.10	− 0.002		(3.82 ± 0.06)			<a href="#">[95MIR/SAD]</a>
	0.30	− 0.003		(3.64 ± 0.06)			
	0.51	− 0.005		(3.57 ± 0.06)			
	1.02	− 0.009		(3.49 ± 0.06)			
	2.09	− 0.018		(3.49 ± 0.06)			
	3.20	− 0.028		(3.59 ± 0.06)			
	4.37	− 0.039		(3.72 ± 0.06)			
	0.100			(3.803 ± 0.020)			<a href="#">[98KET/WES]</a>
	0.185			(3.706 ± 0.020)			
	0.334			(3.613 ± 0.029)			
	0.334			(3.618 ± 0.029)			
	1.001			(3.541 ± 0.029)			
	1.001			(3.553 ± 0.029)			
	1.001			(3.556 ± 0.029)			
	2.002			(3.467 ± 0.027)			
	2.002			(3.496 ± 0.027)			
	3.149			(3.517 ± 0.027)			
	5.000			(3.733 ± 0.027)			
	0.100					(1.28 ± 0.46)	
	0.100					(1.18 ± 0.58)	
	0.316					(1.07 ± 0.16)	
	0.316					(1.06 ± 0.16)	

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Table VI-3: (continued)

Electrolyte	$I$ (molal)	$\Delta \log_{10} K$ (molal)	$\Delta \log_{10} K_I$ (25°C)	$\log_{10} K_1$	$\Delta \log_{10} K_2$ (25°C)	$\log_{10} K_2$	Reference
NaCl	0.601					(0.95 ± 0.15)	<a href="#">[98KET/WES]</a>
	0.602					(0.97 ± 0.15)	
	1.002					(0.94 ± 0.12)	
	2.001					(0.96 ± 0.17)	
	3.002					(0.98 ± 0.10)	
	3.172					(1.10 ± 0.13)	
	4.002					(1.03 ± 0.10)	
	4.999					(1.20 ± 0.10)	<a href="#">[99MIZ/BON]</a>
	0.3	− 0.003		(3.67 ± 0.04)		(1.06 ± 0.10)	
	1	− 0.009		(3.51 ± 0.04)		(0.89 ± 0.39)	
	2	− 0.018		(3.52 ± 0.04)		(0.88 ± 0.20)	
	3	− 0.028		(3.52 ± 0.04)		(0.83 ± 0.14)	
	4	− 0.039		(3.70 ± 0.04)		(1.00 ± 0.10)	
	5	− 0.050		(3.80 ± 0.04)		(1.15 ± 0.39)	
	0.10	− 0.002		(3.84 ± 0.02)		(1.10 ± 0.20)	<a href="#">[2004CRE/ROB]</a>
	0.25	− 0.003		(3.70 ± 0.02)		(1.02 ± 0.20)	
	0.51	− 0.005		(3.60 ± 0.02)		(0.97 ± 0.20)	
	1.02	− 0.009		(3.52 ± 0.02)		(0.93 ± 0.20)	
	2.09	− 0.018		(3.51 ± 0.03)		(0.92 ± 0.20)	
	3.20	− 0.028		(3.59 ± 0.03)		(0.97 ± 0.20)	
	4.98	− 0.044		(3.81 ± 0.04)		(1.11 ± 0.20)	
NaNO <sub>3</sub>	0.10	− 0.003	− 0.040	(3.82 ± 0.06)			<a href="#">[81DAN/RIG]</a>
	0.30	− 0.005	− 0.034	(3.67 ± 0.05)			
	0.15	− 0.003	− 0.038	(3.78 ± 0.05)			<a href="#">[83DAN/RIG2]</a>
NaCF <sub>3</sub> SO <sub>3</sub>	0.101					(1.24 ± 0.29)	<a href="#">[98KET/WES]</a>
	0.101					(1.24 ± 0.29)	
	0.101					(1.23 ± 0.30)	
	0.102					(1.21 ± 0.31)	
	0.316					(1.06 ± 0.12)	
	0.316					(1.05 ± 0.12)	
	0.600					(1.04 ± 0.10)	
	0.600					(1.00 ± 0.10)	
	1.001					(1.00 ± 0.11)	
	1.001					(1.01 ± 0.11)	
	0.100			(3.821 ± 0.022)			
	0.100			(3.826 ± 0.022)			
	0.100			(3.819 ± 0.022)			
	0.100			(3.819 ± 0.022)			
	0.273			(3.675 ± 0.022)			
	0.316			(3.641 ± 0.022)			
	0.600			(3.571 ± 0.022)			
	0.600			(3.573 ± 0.022)			

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Table VI-3: (continued)

Electrolyte	$I$ (molal)	$\Delta \log_{10} K$ (molal)	$\Delta \log_{10} K_I$ (25°C)	$\log_{10} K_1$	$\Delta \log_{10} K_2$ (25°C)	$\log_{10} K_2$	Reference
NaCF <sub>3</sub> SO <sub>3</sub>	1.000			(3.541 ± 0.022)			[98KET/WES]
KCl	0.04			(3.96 ± 0.04)		(1.18 ± 0.20)	[92ROB/STE]
	0.17			(3.80 ± 0.04)		(1.12 ± 0.20)	
	0.41			(3.71 ± 0.04)		(1.10 ± 0.20)	
	0.77			(3.65 ± 0.04)		(1.10 ± 0.20)	
	1.30			(3.61 ± 0.04)		(1.09 ± 0.20)	
	0.20	− 0.004		(3.73 ± 0.04)		(1.08 ± 0.18)	[94KIS/SOV]
	0.10	− 0.002		(3.86 ± 0.04)			[95LU/MOT]
	0.20	− 0.004		(3.75 ± 0.04)		(1.30 ± 0.39)	[2000BUG/KIS]
KNO <sub>3</sub>	0.10	− 0.003		(3.81 ± 0.04)			[66LHE/MAR]
	1.05	− 0.019		(3.60 ± 0.04)		(1.08 ± 0.10)	[67RAJ/MAR]
	0.10	− 0.003		(3.82 ± 0.04)		(1.26 ± 0.10)	[69CON/MAR]
	0.10	− 0.003		(3.88 ± 0.04)			[77BRO/PET]
	0.10	− 0.003		(3.85 ± 0.04)		(1.25 ± 0.10)	[80GRA/MUS]
	0.10	− 0.003	− 0.040	(3.85 ± 0.05)			[81DAN/RIG]
	0.30	− 0.006	− 0.034	(3.69 ± 0.05)			
	0.15	− 0.003	− 0.038	(3.80 ± 0.05)			[83DAN/RIG2]
	0.15	− 0.003		(3.75 ± 0.04)		(0.99 ± 0.10)	[84JOH/JON]
	0.10	− 0.003		(3.87 ± 0.08)			[92AZA/ELN]
Et <sub>4</sub> NI	0.10	− 0.009	− 0.042	(3.93 ± 0.05)			[81DAN/RIG]
	0.32	− 0.027	− 0.040	(3.91 ± 0.05)			
	0.10	− 0.009	− 0.042	(3.94 ± 0.05)			[83DAN/RIG]
	0.32	− 0.027	− 0.040	(3.91 ± 0.05)			
	0.63	− 0.050	− 0.040	(3.99 ± 0.05)			
	1.17	− 0.086	− 0.042	(4.05 ± 0.05)			
	0.04	− 0.004		(4.00 ± 0.04)			[85ROB/STE]
	0.26	− 0.022		(3.91 ± 0.04)			
	0.96	− 0.072		(4.02 ± 0.04)			
	0.04	− 0.004		(4.04 ± 0.05)			[90ROB/STE]
	0.17	− 0.014		(3.93 ± 0.05)			
	0.39	− 0.032		(3.94 ± 0.05)			
	0.73	− 0.057		(4.00 ± 0.05)			
	1.23	− 0.090		(4.08 ± 0.05)			
	0.04			(4.00 ± 0.02)		(1.13 ± 0.16)	[92ROB/STE]
	0.17			(3.90 ± 0.02)		(1.05 ± 0.16)	
	0.39			(3.91 ± 0.02)		(1.16 ± 0.16)	
	0.73			(3.96 ± 0.020)		(1.22 ± 0.16)	
	1.23			(4.04 ± 0.02)		(1.29 ± 0.16)	
	0.10	− 0.009		(3.92 ± 0.02)		(1.12 ± 0.20)	[2004CRE/ROB]
	0.26	− 0.022		(3.89 ± 0.03)		(1.09 ± 0.20)	
	0.55	− 0.044		(3.93 ± 0.02)		(1.08 ± 0.20)	
	1.23	− 0.090		(4.06 ± 0.03)		(1.09 ± 0.20)	
Me <sub>4</sub> NI	0.10	− 0.009		(3.86 ± 0.10)		(1.14 ± 0.10)	[96XUE/TRA]

Table VI-4: Accepted data on the protonation constants for oxalate. The experimental emf data reported in [\[39HAR/FAL\]](#) and [\[48PIN/BAT\]](#) have been later re-evaluated together with new measurements by Kettler *et al.* [\[98KET/WES\]](#). The concentrations and  $\log_{10} K$  values at 25°C included here have kindly been provided by R.M. Kettler (private communication) for this review. Uncertainties are estimated in this review.

$I_m$	[Na <sup>+</sup> ]	[K <sup>+</sup> ]	[Cl <sup>-</sup> ]	[Hox <sup>-</sup> ]	[ox <sup>2-</sup> ]	$\log_{10} K_1$	Reference
0.029	0.0242		0.0066	0.0086	0.0045	(3.967 ± 0.020)	<a href="#">[39HAR/FAL]</a>
0.053	0.0447		0.0121	0.0159	0.0083	(3.881 ± 0.020)	
0.067	0.0564		0.0153	0.0200	0.0105	(3.845 ± 0.020)	
0.077	0.0647		0.0176	0.0230	0.0121	(3.822 ± 0.020)	
0.093	0.0782		0.0212	0.0278	0.0146	(3.789 ± 0.020)	
0.120	0.1012		0.0275	0.0359	0.0189	(3.741 ± 0.020)	
0.141	0.1190		0.0323	0.0423	0.0222	(3.706 ± 0.020)	
0.165	0.1393		0.0378	0.0495	0.0260	(3.674 ± 0.020)	<a href="#">[48PIN/BAT]</a>
0.052	0.0312	0.0104	0.0104	0.0104	0.0104	(3.889 ± 0.020)	
0.058	0.0393	0.0031	0.0079	0.0031	0.0157	(3.880 ± 0.020)	
0.064	0.0431	0.0034	0.0086	0.0034	0.0172	(3.864 ± 0.020)	
0.069	0.0440	0.0042	0.0021	0.0042	0.0209	(3.852 ± 0.020)	
0.073	0.0492	0.0039	0.0098	0.0039	0.0197	(3.840 ± 0.020)	
0.077	0.0520	0.0042	0.0104	0.0042	0.0208	(3.833 ± 0.020)	
0.084	0.0570	0.0046	0.0114	0.0046	0.0228	(3.813 ± 0.020)	
0.085	0.0543	0.0052	0.0026	0.0052	0.0258	(3.812 ± 0.020)	
0.100	0.0635	0.0060	0.0030	0.0060	0.0302	(3.786 ± 0.020)	
0.103	0.0620	0.0207	0.0207	0.0207	0.0207	(3.770 ± 0.020)	
0.105	0.0706	0.0057	0.0141	0.0057	0.0283	(3.780 ± 0.020)	
0.107	0.0723	0.0058	0.0145	0.0058	0.0289	(3.777 ± 0.020)	
0.112	0.0755	0.0060	0.0151	0.0060	0.0302	(3.771 ± 0.020)	
0.114	0.0724	0.0069	0.0034	0.0069	0.0345	(3.769 ± 0.020)	
0.119	0.0755	0.0072	0.0036	0.0072	0.0360	(3.756 ± 0.020)	
0.128	0.0867	0.0069	0.0173	0.0069	0.0347	(3.741 ± 0.020)	
0.140	0.0949	0.0076	0.0190	0.0076	0.0380	(3.727 ± 0.020)	
0.145	0.0921	0.0088	0.0044	0.0088	0.0439	(3.723 ± 0.020)	
0.145	0.0982	0.0079	0.0196	0.0079	0.0393	(3.717 ± 0.020)	
0.146	0.0986	0.0079	0.0197	0.0079	0.0394	(3.715 ± 0.020)	
0.147	0.0884	0.0295	0.0295	0.0295	0.0295	(3.708 ± 0.020)	
0.155	0.1049	0.0084	0.0210	0.0084	0.0420	(3.706 ± 0.020)	
0.160	0.1082	0.0087	0.0216	0.0087	0.0433	(3.697 ± 0.020)	
0.167	0.1061	0.0101	0.0051	0.0101	0.0505	(3.694 ± 0.020)	
0.177	0.1193	0.0095	0.0239	0.0095	0.0477	(3.675 ± 0.020)	

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Table VI-4: (continued)

$I_m$	[Na <sup>+</sup> ]	[K <sup>+</sup> ]	[Cl <sup>-</sup> ]	[Hox <sup>-</sup> ]	[ox <sup>2-</sup> ]	$\log_{10} K_1$	Reference
0.183	0.1238	0.0099	0.0248	0.0099	0.0495	(3.670 ± 0.020)	<a href="#">[48PIN/BAT]</a>
0.191	0.1290	0.0103	0.0258	0.0103	0.0516	(3.661 ± 0.020)	
0.206	0.1391	0.0111	0.0278	0.0111	0.0557	(3.644 ± 0.020)	
0.207	0.1315	0.0125	0.0063	0.0125	0.0626	(3.648 ± 0.020)	
0.209	0.1256	0.0419	0.0419	0.0419	0.0419	(3.638 ± 0.020)	
0.212	0.1434	0.0115	0.0287	0.0115	0.0574	(3.641 ± 0.020)	
0.226	0.1463	0.0133	0.0133	0.0133	0.0665	(3.627 ± 0.020)	
0.228	0.1540	0.0123	0.0308	0.0123	0.0616	(3.623 ± 0.020)	
0.262	0.1770	0.0142	0.0354	0.0142	0.0708	(3.594 ± 0.020)	
0.274	0.1646	0.0549	0.0549	0.0549	0.0549	(3.572 ± 0.020)	
0.276	0.1866	0.0149	0.0373	0.0149	0.0747	(3.583 ± 0.020)	
0.295	0.1771	0.0590	0.0590	0.0590	0.0590	(3.556 ± 0.020)	
0.317	0.2144	0.0172	0.0429	0.0172	0.0858	(3.550 ± 0.020)	
0.321	0.2166	0.0173	0.0433	0.0173	0.0867	(3.546 ± 0.020)	
0.324	0.2189	0.0175	0.0438	0.0175	0.0876	(3.543 ± 0.020)	
0.327	0.2078	0.0198	0.0099	0.0198	0.0990	(3.547 ± 0.020)	
0.362	0.2444	0.0196	0.0489	0.0196	0.0978	(3.518 ± 0.020)	
0.367	0.2202	0.0734	0.0734	0.0734	0.0734	(3.505 ± 0.020)	
0.374	0.2524	0.0202	0.0505	0.0202	0.1010	(3.510 ± 0.020)	
0.375	0.2534	0.0203	0.0507	0.0203	0.1014	(3.508 ± 0.020)	
0.406	0.2740	0.0219	0.0548	0.0219	0.1096	(3.490 ± 0.020)	
0.442	0.2988	0.0239	0.0598	0.0239	0.1195	(3.471 ± 0.020)	
0.450	0.2908	0.0264	0.0264	0.0264	0.1322	(3.470 ± 0.020)	
0.468	0.3159	0.0253	0.0632	0.0253	0.1264	(3.455 ± 0.020)	
0.478	0.3233	0.0259	0.0647	0.0259	0.1293	(3.448 ± 0.020)	
0.480	0.3053	0.0291	0.0145	0.0291	0.1454	(3.456 ± 0.020)	
0.487	0.2919	0.0973	0.0973	0.0973	0.0973	(3.432 ± 0.020)	
0.538	0.3636	0.0291	0.0727	0.0291	0.1455	(3.418 ± 0.020)	
0.557	0.3763	0.0301	0.0753	0.0301	0.1505	(3.406 ± 0.020)	
0.561	0.3789	0.0303	0.0758	0.0303	0.1516	(3.408 ± 0.020)	
0.641	0.4076	0.0388	0.0194	0.0388	0.1941	(3.379 ± 0.020)	
0.689	0.4459	0.0405	0.0405	0.0405	0.2027	(3.357 ± 0.020)	
0.724	0.4893	0.0391	0.0979	0.0391	0.1957	(3.333 ± 0.020)	
0.734	0.4958	0.0397	0.0992	0.0397	0.1983	(3.334 ± 0.020)	
0.747	0.4831	0.0439	0.0439	0.0439	0.2196	(3.335 ± 0.020)	
0.747	0.5046	0.0404	0.1009	0.0404	0.2019	(3.329 ± 0.020)	

### VI.3.2 Analysis of $K_1$

The 131 data in Table VI-3 for the first protonation of oxalate:



were treated with the SIT methodology described in Appendix B and in Section V.3.1, using a weighted multi-linear least-squares regression procedure. This procedure assumes that a common value of  $\log_{10} K_1^0$  should fit all the data measured in  $\text{LiClO}_4$ ,  $\text{LiNO}_3$ ,  $\text{NaClO}_4$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{NaCF}_3\text{SO}_3$ ,  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{Et}_4\text{NI}$  and  $\text{Me}_4\text{NI}$  media.

$$\begin{aligned} \log_{10} K_1 + 4D - \varepsilon(\text{H}^+, \text{ClO}_4^-) \cdot m_{\text{ClO}_4^-} - \varepsilon(\text{H}^+, \text{Cl}^-) \cdot m_{\text{Cl}^-} - \varepsilon(\text{H}^+, \text{NO}_3^-) \cdot m_{\text{NO}_3^-} - \varepsilon(\text{H}^+, \text{I}^-) \cdot m_{\text{I}^-} \\ = \log_{10} K_1^0 - \Delta\varepsilon_1^*(\text{Li}^+) \cdot m_{\text{Li}^+} - \Delta\varepsilon_1^*(\text{Na}^+) \cdot m_{\text{Na}^+} - \Delta\varepsilon_1^*(\text{K}^+) \cdot m_{\text{K}^+} - \Delta\varepsilon_1^*(\text{R}_4\text{N}^+) \cdot m_{\text{R}_4\text{N}^+} \\ + \varepsilon(\text{H}^+, \text{CF}_3\text{SO}_3^-) \cdot m_{\text{CF}_3\text{SO}_3^-} \end{aligned} \quad (\text{VI.6})$$

In Eq.(VI.6) the SIT interaction parameters  $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02)$ ,  $\varepsilon(\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.01)$ ,  $\varepsilon(\text{H}^+, \text{NO}_3^-) = (0.07 \pm 0.01)$  (*cf.* Appendix B) and  $\varepsilon(\text{H}^+, \text{I}^-) = (0.19 \pm 0.01)$  (*cf.* Section V.3.5) have been used, and  $\Delta\varepsilon_1^*(\text{M}^+) = \varepsilon(\text{Hox}^-, \text{M}^+) - \varepsilon(\text{ox}^{2-}, \text{M}^+)$  are fit parameters, where  $\text{M}^+$  is the cation of the background electrolyte, *i.e.*,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{R}_4\text{N}^+$  (tetraethylammonium and tetramethylammonium data have been fitted by a common tetraalkylammonium parameter). In the case of  $\text{NaCF}_3\text{SO}_3$  media,  $\varepsilon(\text{H}^+, \text{CF}_3\text{SO}_3^-)$  is an additional fit parameter.

When applying the SIT model to the activity coefficients of tetraalkyl ammonium halides, it may be shown that the specific ion-interaction coefficient,  $\varepsilon(\text{R}_4\text{N}^+, \text{X}^-)$ , depends on the ionic strength (*cf.* Section V.3.2). A proper representation of the data is achieved by setting:

$$\varepsilon(\text{R}_4\text{N}^+, \text{X}^-) = \varepsilon_1(\text{R}_4\text{N}^+, \text{X}^-) + \varepsilon_2(\text{R}_4\text{N}^+, \text{X}^-) \cdot \log_{10}[\text{R}_4\text{N}^+].$$

A pronounced ionic strength dependence is found in  $\log_{10} K_1$  data (Figure VI-2f) but not in  $\log_{10} K_2$  data (Figure VI-3e). Because of this, the protonation constant of oxalate in tetraalkylammonium salts was fitted to the SIT equations by setting:

$$\Delta\varepsilon_1^*(\text{R}_4\text{N}^+) = ( \varepsilon(\text{R}_4\text{N}^+, \text{Hox}^-) - \varepsilon_1(\text{R}_4\text{N}^+, \text{ox}^{2-}) ) - \varepsilon_2(\text{R}_4\text{N}^+, \text{ox}^{2-}) \cdot \log_{10}[\text{R}_4\text{N}^+]$$

The regression plots are shown in Figure VI-2, and the results, with the values selected in this review, are reported in Table VI-5.

Table VI-5: Selected values of  $\log_{10} K_1^\circ$  (VI.5) and  $\Delta\epsilon_1^*$  at 25°C.

$\log_{10} K_1^\circ$ (VI.5) = $(4.25 \pm 0.01)$	
Medium <sup>a</sup>	$\Delta\epsilon_1^*$ (kg·mol <sup>-1</sup> )
Li <sup>+</sup>	$(0.23 \pm 0.03)$
Na <sup>+</sup>	$(0.01 \pm 0.01)$
K <sup>+</sup>	$-(0.08 \pm 0.02)$
R <sub>4</sub> N <sup>+</sup>	$-(0.39 \pm 0.01) + (0.58 \pm 0.06) \log_{10} [\text{R}_4\text{N}^+]$
$\epsilon(\text{H}^+, \text{CF}_3\text{SO}_3^-) = (0.11 \pm 0.02)$	

a: R<sub>4</sub>N<sup>+</sup> represents tetraalkylammonium

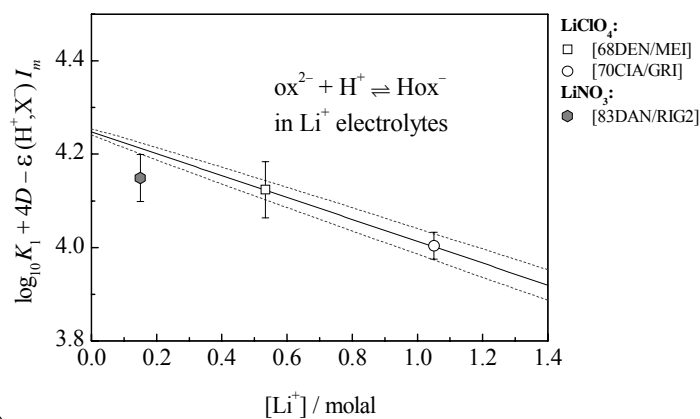
The 70 data in mixed media, *i.e.*, data measured in NaCl – Na<sub>2</sub>ox – NaHox media [39HAR/FAL] and in NaCl – Na<sub>2</sub>ox – KHox media [48PIN/BAT] presented in Table VI-4 have been re-evaluated together with new measurements by Kettler *et al.* [98KET/WES] using their results for  $\log_{10} K_2$  in an iterative procedure. Hence, the data in Table VI-4 might be biased by the [98KET/WES] results.

If all the 201 data in Table VI-3 and Table VI-4 are used for a weighted multi-linear least-squares regression procedure, additional fit parameters for  $\epsilon(\text{H}^+, \text{ox}^{2-})$  and  $\epsilon(\text{H}^+, \text{Hox}^-)$  are obtained, because Hox<sup>-</sup> and ox<sup>2-</sup> represent a non-negligible fraction of species contributing to the ionic medium. All other fit parameters differ from the values in Table VI-5 by less than their assigned uncertainties, *i.e.*, for  $\log_{10} K_1^\circ$  the difference is 0.003, and in the case of  $\Delta\epsilon_1^*$  it is 0.005, 0.002, 0.006 and 0.004 for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and R<sub>4</sub>N<sup>+</sup>, respectively. Hence, the data sets measured in “self-media” presented in Table VI-4 are compatible with the other data in Table VI-3.

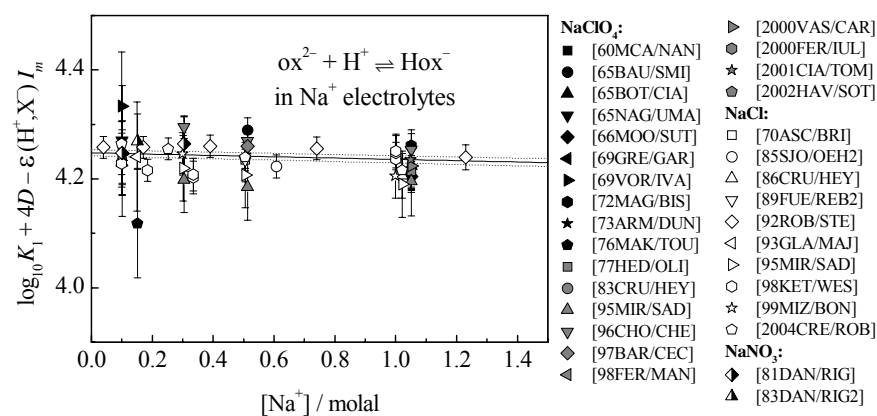
However, the free concentrations [Hox<sup>-</sup>] and [ox<sup>2-</sup>] shown in Table VI-4 can only be calculated together with the values of the protonation constants in an iterative procedure. Due to this procedure, there is a risk for significant co-variance between the protonation constants calculated at each ionic medium and the calculated [Hox<sup>-</sup>] and [ox<sup>2-</sup>] values, and this co-variance might be a source of systematic errors in the fitted  $\epsilon(\text{H}^+, \text{ox}^{2-})$  and  $\epsilon(\text{H}^+, \text{Hox}^-)$  values. Hence, these fit parameters are not credited in this review.

Figure VI-2: Multi-linear least-squares SIT regression plots for the reaction:  
 $\text{ox}^{2-} + \text{H}^+ \rightleftharpoons \text{Hox}^-$ .

a)

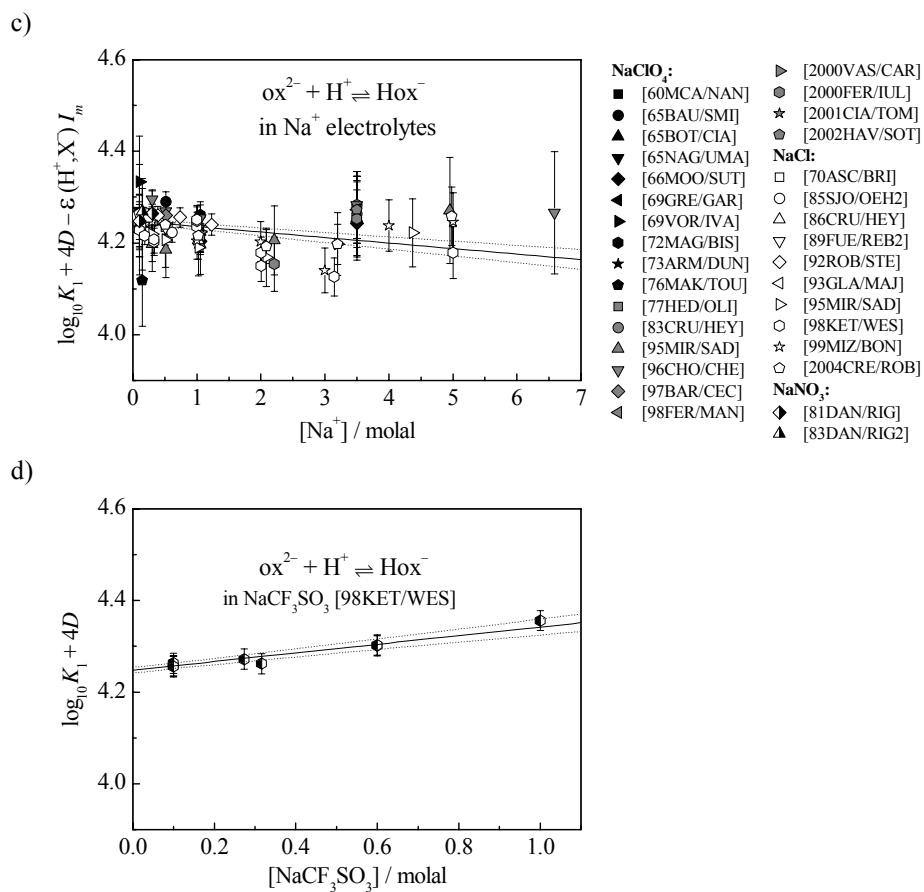


b)



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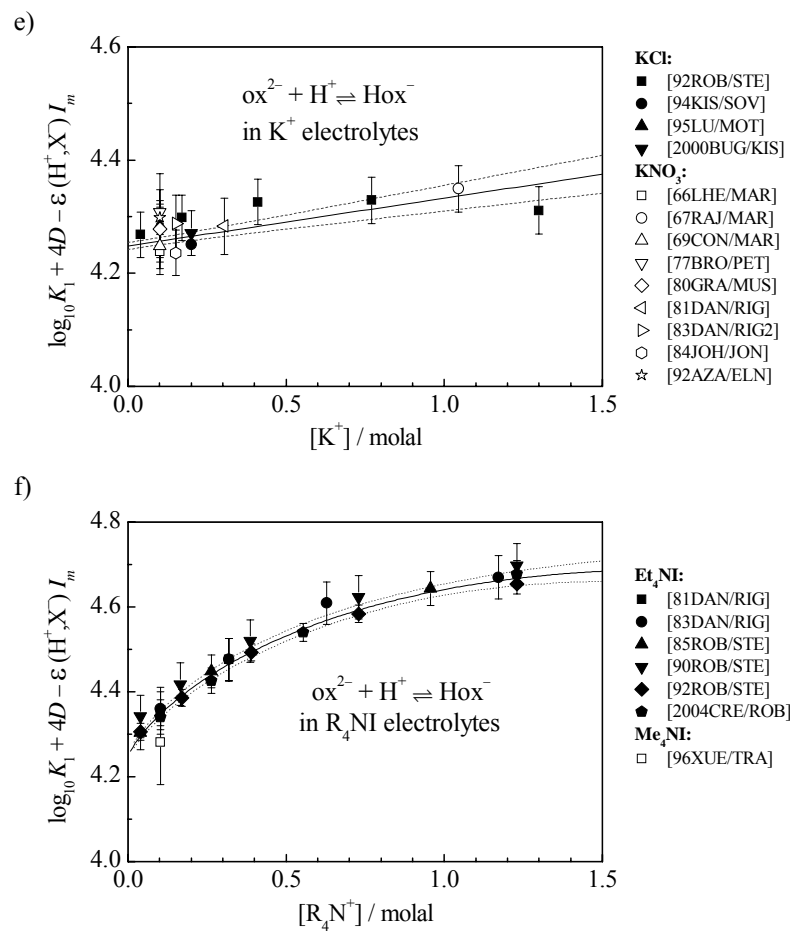
Figure VI-2 (continued)



(Continued on next page)

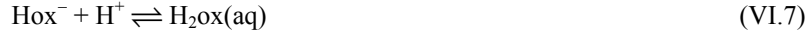


Figure VI-2 (continued)



### VI.3.3 Analysis of $K_2$

The 91 data in Table VI-3 for the second protonation of oxalate:



were treated with the SIT methodology described in Appendix B and in Section V.3.1, using a weighted multi-linear least-squares regression procedure. This procedure assumes that a common value of  $\log_{10} K_2^\circ$  (VI.7) should fit all the data measured in  $\text{LiClO}_4$ ,  $\text{NaClO}_4$ ,  $\text{NaCl}$ ,  $\text{NaCF}_3\text{SO}_3$ ,  $\text{KCl}$ ,  $\text{KNO}_3$ ,  $\text{Et}_4\text{NI}$  and  $\text{Me}_4\text{NI}$  media.

$$\begin{aligned} \log_{10} K_2 + 2D - \varepsilon(\text{H}^+, \text{ClO}_4^-) \cdot m_{\text{ClO}_4^-} - \varepsilon(\text{H}^+, \text{Cl}^-) \cdot m_{\text{Cl}^-} - \varepsilon(\text{H}^+, \text{NO}_3^-) \cdot m_{\text{NO}_3^-} - \varepsilon(\text{H}^+, \text{I}^-) \cdot m_{\text{I}^-} \\ - \varepsilon(\text{H}^+, \text{CF}_3\text{SO}_3^-) \cdot m_{\text{CF}_3\text{SO}_3^-} = \log_{10} K_2^\circ - \Delta\varepsilon_2^*(\text{Li}^+) \cdot m_{\text{Li}^+} - \Delta\varepsilon_2^*(\text{Na}^+) \cdot m_{\text{Na}^+} - \Delta\varepsilon_2^*(\text{K}^+) \cdot m_{\text{K}^+} \\ - \Delta\varepsilon_2^*(\text{R}_4\text{N}^+) \cdot m_{\text{R}_4\text{N}^+} \end{aligned} \quad (\text{VI.8})$$

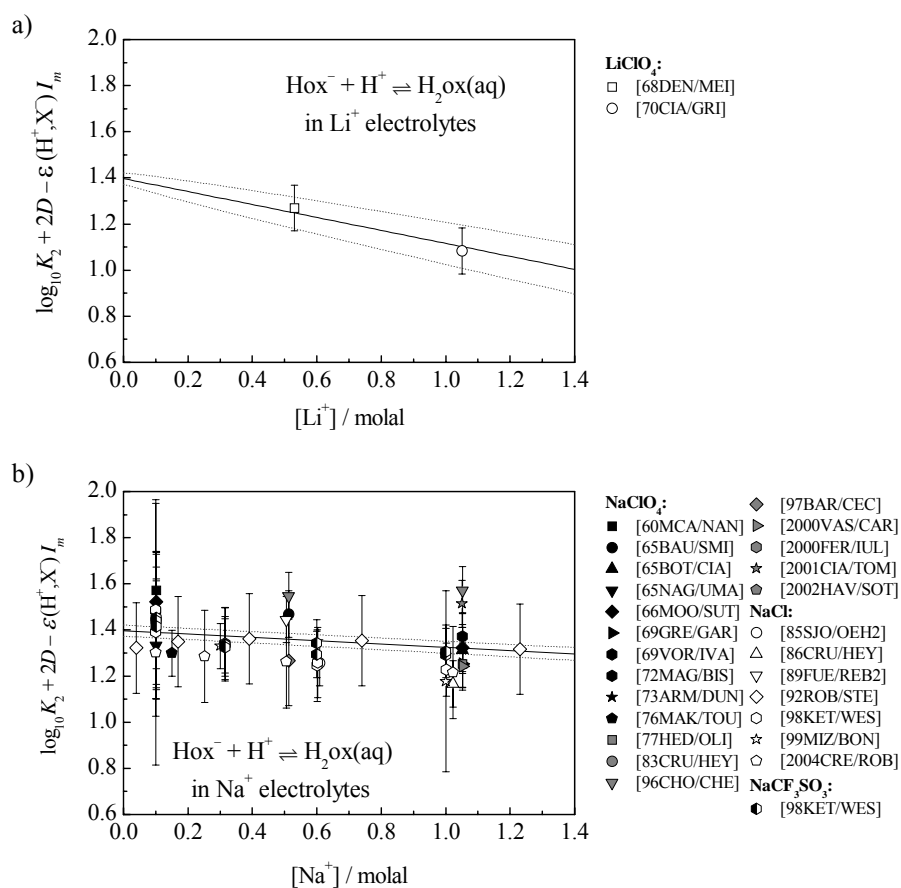
In Eq.(VI.8) the SIT interaction parameters  $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02)$ ,  $\varepsilon(\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.01)$ ,  $\varepsilon(\text{H}^+, \text{NO}_3^-) = (0.07 \pm 0.01)$  (*cf.* Appendix B),  $\varepsilon(\text{H}^+, \text{I}^-) = (0.19 \pm 0.01)$  (*cf.* Section V.3.5) and  $\varepsilon(\text{H}^+, \text{CF}_3\text{SO}_3^-) = (0.11 \pm 0.02)$  (selected in Section VI.3.2) have been used, and  $\Delta\varepsilon_2^*(\text{M}^+) = \varepsilon(\text{H}_2\text{ox}, \text{MX}) - \varepsilon(\text{Hox}^-, \text{M}^+)$  are fit parameters, where  $\text{M}^+$  is the cation of the background electrolyte, *i.e.*,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{R}_4\text{N}^+$  (tetraethylammonium and tetramethylammonium data have been fitted by a common tetraalkylammonium parameter). The regression plots are shown in Figure VI-3, and the results, with the values selected in this review, are reported in Table VI-6.

Table VI-6: Selected values of  $\log_{10} K_2^\circ$  (VI.7) and  $\Delta\varepsilon_2^*$  at 25°C.

$\log_{10} K_2^\circ$ (VI.7) = $(1.40 \pm 0.03)$	
Medium <sup>a</sup>	$\Delta\varepsilon_2^*$ (kg·mol <sup>-1</sup> )
$\text{Li}^+$	$(0.28 \pm 0.09)$
$\text{Na}^+$	$(0.07 \pm 0.01)$
$\text{K}^+$	$(0.01 \pm 0.08)$
$\text{R}_4\text{N}^+$	$(0.01 \pm 0.09)$

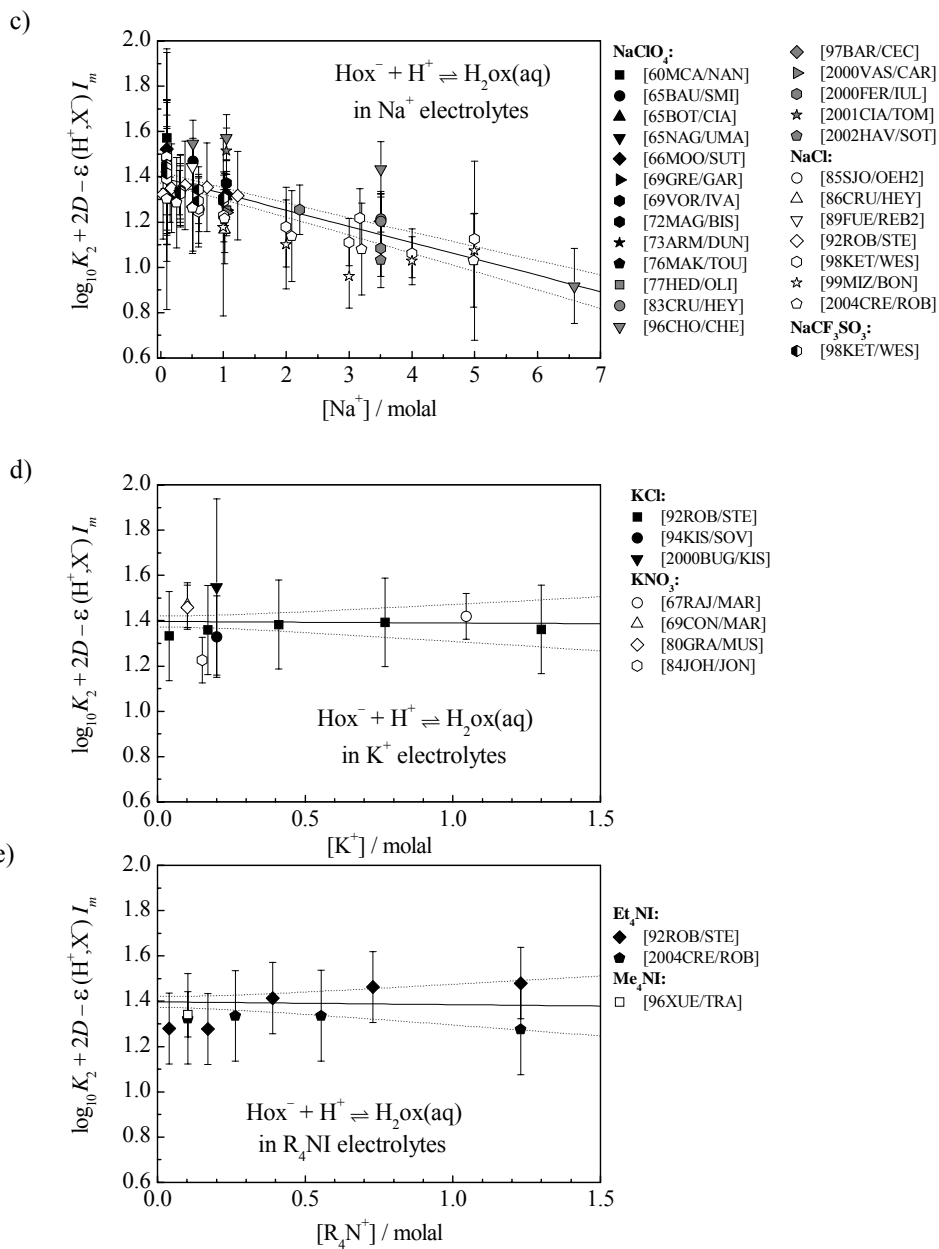
a:  $\text{R}_4\text{N}^+$  represents tetraalkylammonium.

Figure VI-3: Multi-linear least-squares SIT regression plots for the reaction:  
 $\text{Hox}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{ox}(\text{aq})$ .



(Continued on next page)

Figure VI-3(continued)



### VI.3.4 Temperature effects

Temperature effects on the equilibrium constants for the protonation of oxalate have been determined both calorimetrically and by the determination of the protonation constants at different temperatures. As expected for the dissociation of carboxylic groups, the reported enthalpy changes for the individual protonation steps:



are small:  $\Delta_r H_m$  values range between  $-7$  and  $+7 \text{ kJ}\cdot\text{mol}^{-1}$ , depending on the ionic media. The corresponding heat capacity changes,  $\Delta_r C_{p,m}$ , are reported to be in the range  $15$  to  $380 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . For temperatures between  $0$  and  $50^\circ\text{C}$  these values correspond to quite small changes of the equilibrium constants.

A number of calorimetric investigations on the protonation of oxalate have been reported [\[67CHR/IZA\]](#), [\[71VAS/KOC2\]](#), [\[73BAR/RED\]](#), [\[73VAS/SHE2\]](#), [\[75BAR/DUB\]](#), [\[76VAS/SHE\]](#), [\[87LIN/GU\]](#), [\[91BEI/GRA\]](#), [\[98ALD/BIA\]](#). All these papers have been scrutinised in detail in order to extract reliable information and the uncertainties of the reported values have been estimated in this review (*cf.* Appendix A).

A few papers had to be rejected [\[67MAK2\]](#), [\[70DAV/WAT\]](#), [\[81CER/CAS\]](#) for various reasons. For details see Appendix A.

Large uncertainties are expected in the determination of enthalpy changes from the  $T$ -variation of  $\log_{10} K$ . For the studies considered in this review where this methodology has been applied [\[39HAR/FAL\]](#), [\[48PIN/BAT\]](#), [\[61MCA/NAN\]](#), [\[69KUR/FAR\]](#), [\[76KAL\]](#), [\[90ROB/STE\]](#), [\[92ROB/STE\]](#), [\[98KET/WES\]](#) the uncertainty was estimated from the rules of error propagation and the relationship:

$$\Delta_r H_m = RT^2 \ln(10) \left( \frac{\partial \log_{10} K(T)}{\partial T} \right)_p.$$

For example, for an uncertainty of  $\pm 0.02$  in the values,  $\log_{10} K$  determined over the temperature range  $5$  to  $50^\circ\text{C}$ , the total uncertainty in  $\Delta_r H_m$  was estimated to be  $\pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$ . This method was used to increase, when necessary, the uncertainties in  $\Delta_r H_m$  obtained from regression analyses of the  $T$ -variation of  $\log_{10} K$  (*cf.* Appendix A). For this procedure the total uncertainty in the individual measurements of  $\log_{10} K$  was set to at least  $\pm 0.02$   $\log_{10}$ -units. For studies where both  $\Delta_r H_m$  and  $\Delta_r C_{p,m}$  were obtained from the  $T$ -variation of  $\log_{10} K_r$  the uncertainty assigned with the method outlined above was decreased by one third. In addition, the uncertainty of  $\Delta_r C_{p,m}$  obtained from regression analyses was increased, when necessary, by using the relationship:

$$\Delta_r C_{p,m} = \left( \frac{\partial \Delta_r H(T)}{\partial T} \right)_p.$$

The selected  $\Delta_r H_m$  data and the corresponding uncertainties assigned by this review are listed in Table VI-7. These data were treated according to the SIT model, described in Appendix B and in Section V.3.6, and a multi-linear least-squares regression was performed (*cf.* Figure VI-4 and Figure VI-5).

In the case of  $\Delta_r H_m$  ((VI.9),  $r = 1$ ) an initial 8 dimensional regression analysis revealed that the results obtained for chloride, nitrate and trifluoromethanesulfonate media cannot be distinguished from a statistical point of view. Hence, all these data have been fitted subsequently with a common  $\Delta \varepsilon_{L,1}$  parameter. In addition,  $\Delta \varepsilon_{L,1}$  parameters for  $\text{NaClO}_4$  and  $\text{Et}_4\text{NI}$  media have been fitted in the final 3 dimensional regression analysis. Note that the KCl data of [92ROB/STE], obtained from the  $T$ -variation of  $\log_{10} K$  data, are in marked disagreement with the calorimetric results of [75BAR/DUB]. The latter KCl data perfectly agree with the overall behaviour of NaCl and  $\text{KNO}_3$  data (Figure VI-4), and there is no obvious reason why KCl data should behave different than all other chloride and nitrate data. The KCl data of [92ROB/STE] need confirmation; they have been excluded from the final multi-linear least-squares regression. There is also a large discrepancy between  $\text{Et}_4\text{NI}$  values derived at  $I > 0.5$  from the  $T$ -variation of  $\log_{10} K$  data in [90ROB/STE] and [92ROB/STE]. This discrepancy indicates the order of magnitude of the uncertainty of deriving  $\Delta_r H_m$  ((VI.9),  $r = 1$ ) from a few  $\log_{10} K$  data over a narrow temperature range.

In the case of  $\Delta_r H_m$  ((VI.9),  $r = 2$ ) an initial multi-dimensional regression analysis revealed that the results obtained for all media cannot be distinguished from a statistical point of view. Hence, all these data have been fitted subsequently with a common parameter (Figure VI-5).

The standard enthalpy changes were found to be:

$$\Delta_r H_m^\circ ((\text{VI.9}), r = 1) = (7.3 \pm 0.1) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^\circ ((\text{VI.9}), r = 2) = (3.3 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}.$$

From the slopes of the regressions it is possible to obtain values for  $\Delta \varepsilon_{L,r}$ . The multi-linear least-squares regression of the protonation enthalpies  $\Delta_r H_m$  ((VI.9),  $r = 1$ ) for oxalate in (Li,Na,K) $\text{NO}_3$ , (Na,K)Cl and  $\text{NaCF}_3\text{SO}_3$  media gave:  $\Delta \varepsilon_{L,1} = (2.26 \pm 0.08) \cdot 10^{-3}$ , in  $\text{NaClO}_4$  media:  $\Delta \varepsilon_{L,1} = (3.3 \pm 0.2) \cdot 10^{-3}$  and in  $\text{Et}_4\text{NI}$  media:  $\Delta \varepsilon_{L,1} = -(1.5 \pm 0.6) \cdot 10^{-3}$ . The least-squares regression of the protonation enthalpies  $\Delta_r H_m$  ((VI.9),  $r = 2$ ) for oxalate gave  $\Delta \varepsilon_{L,2} = (2.3 \pm 0.3) \cdot 10^{-3}$  in all Li, Na, K media (all in units of  $\text{kg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ ).

Table VI-7: Literature data on the enthalpy and heat capacity changes for oxalate protonation, with the uncertainties assigned in this review. Data in italics were reported in molal units.

Method	<i>I</i>	Medium	<i>t</i>	$\Delta_r H_m$ ( <i>r</i> = 1)	$\Delta_r H_m$ ( <i>r</i> = 2)	$\Delta_r C_{p,m}$ ( <i>r</i> = 1)	$\Delta_r C_{p,m}$ ( <i>r</i> = 2)	Reference
	(M)		(°C)	kJ·mol <sup>-1</sup>	kJ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	
$\partial pK_a / \partial T$	<i>I</i> → 0	NaCl	0 - 50	(6.7 ± 0.7)		(241 ± 13)		<a href="#">[39HAR/FAL]</a>
$\partial pK_a / \partial T$	<i>I</i> → 0	NaCl	0 - 50	(7.0 ± 0.7)		(231 ± 13)		<a href="#">[48PIN/BAT]</a>
$\partial pK_a / \partial T$	<i>I</i> → 0	HCl	0 - 45		(2.0 ± 1.1)			<a href="#">[61MCA/NAN]</a>
cal	<i>I</i> → 0	(H <sub>2</sub> Na)ClO	25	(6.3 ± 0.8)	(4.3 ± 0.8)			<a href="#">[67CHR/IZA]</a>
		4						
$\partial pK_a / \partial T$	<i>I</i> → 0	HCl	25 - 55		(4.0 ± 1.8)			<a href="#">[69KUR/FAR]</a>
cal	<i>I</i> → 0		25		(3.1 ± 0.8)			<a href="#">[71VAS/KOC2]</a>
cal	2	KCl	25	(1.2 ± 0.4)	– (2.9 ± 0.8)			<a href="#">[73BAR/RED]</a> , <a href="#">[75BAR/DUB]</a>
cal	0.5	NaClO <sub>4</sub>	25	(3.9 ± 0.4)				<a href="#">[73VAS/SHE2]</a>
	1.0			(2.2 ± 0.4)				
	2.0			– (1.1 ± 0.4)				
	0.5	NaCl		(4.3 ± 0.4)				
	1.0			(2.9 ± 0.4)				
	2.0			(0.8 ± 0.4)				
	0.5	NaNO <sub>3</sub>		(4.7 ± 0.4)				
	1.0			(3.5 ± 0.4)				
	2.0			(1.4 ± 0.4)				
	0.5			(4.6 ± 0.4)				
	1.0			(3.6 ± 0.4)				
	2.0			(1.6 ± 0.4)				
	0.5	KNO <sub>3</sub>		(4.9 ± 0.4)				
	1.0			(2.9 ± 0.4)				
	0.5	LiNO <sub>3</sub>		(4.8 ± 0.4)				
	1.0			(3.4 ± 0.4)				
	2.0			(0.3 ± 0.4)				
$\partial pK_a / \partial T$	1	NaClO <sub>4</sub>	40 – 55		(3.5 ± 2.9)			<a href="#">[76KAL]</a>
	1	KNO <sub>3</sub>	35 - 55		(2.3 ± 5.0)			

(Continued on next page)

Table VI-7: (continued)

Method	<i>I</i>	Medium	<i>t</i>	$\Delta_r H_m$ ( <i>r</i> = 1)	$\Delta_r H_m$ ( <i>r</i> = 2)	$\Delta_r C_{p,m}$ ( <i>r</i> = 1)	$\Delta_r C_{p,m}$ ( <i>r</i> = 2)	Reference
	(M)		(°C)	kJ·mol <sup>-1</sup>	kJ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	
cal	0.5	NaNO <sub>3</sub>	5 - 35	(4.4 ± 0.3)		(180 ± 17)		<a href="#">[76VAS/SHE]</a>
	1.0			(3.3 ± 0.3)		(183 ± 15)		
	2.0			(1.1 ± 0.3)		(220 ± 14)		
	0.15	NaNO <sub>3</sub>	8 - 30		(2.8 ± 0.6)		(148 ± 18)	
cal	1	KNO <sub>3</sub>	25	(2.7 ± 0.8)				<a href="#">[87LIN/GU]</a>
∂pK <sub>a</sub> / ∂T	0.04	Et <sub>4</sub> NI		(6.9 ± 0.7)		(272 ± 14)		<a href="#">[90ROB/STE]</a>
	0.16			(6.4 ± 0.7)		(269 ± 14)		
	0.36			(6.1 ± 0.7)		(258 ± 14)		
	0.64			(5.9 ± 0.7)		(254 ± 14)		
	1			(5.8 ± 0.7)		(255 ± 14)		
cal	1	(H,N <sub>a</sub> )ClO <sub>4</sub>	25	(4.7 ± 0.8)				<a href="#">[91BEI/GRA]</a>
∂pK <sub>a</sub> / ∂T	0.04	NaCl	10 - 45	(6.0 ± 0.9)		(220 ± 27)		<a href="#">[92ROB/STE]</a>
	0.17			(4.9 ± 0.9)		(243 ± 62)		
	0.40			(4.6 ± 0.9)		(173 ± 32)		
	0.75			(3.8 ± 0.9)		(71 ± 27)		
	1.23			(4.4 ± 0.9)		(15 ± 27)		
	0.04	KCl		(5.4 ± 0.9)		(76 ± 40)		
	0.41			(0.8 ± 0.9)		(103 ± 27)		
	0.77			− (1.7 ± 0.9)		(79 ± 39)		
	1.30			− (2.2 ± 0.9)		(46 ± 141)		
	0.04	Et <sub>4</sub> NI		(6.8 ± 0.9)		(323 ± 27)		
	0.17			(6.3 ± 0.9)		(379 ± 48)		
	0.39			(6.3 ± 0.9)		(290 ± 86)		
	0.73			(7.1 ± 1.1)		(286 ± 213)		
	1.23			(8.7 ± 1.3)		(208 ± 251)		
cal	0.5	NaClO <sub>4</sub>	25	(4.7 ± 0.8)				<a href="#">[98ALD/BIA]</a>
∂pK <sub>a</sub> / ∂T	0.10	NaCl	0 - 175	(5.1 ± 0.8)		(190 ± 12)		<a href="#">[98KET/WES]</a>
	0.19			(4.9 ± 0.7)		(195 ± 13)		
	0.33			(4.8 ± 0.3)		(159 ± 5)		
	1.00			(1.3 ± 1.0)		(161 ± 120)		
	2.00			(0.8 ± 0.8)		(122 ± 14)		
	3.15			− (0.6 ± 0.3)		(95 ± 5)		
	5.00			− (4.8 ± 0.4)		(78 ± 6)		

(Continued on next page)



Table VI-7: (continued)

Method	<i>I</i>	Medium	<i>t</i>	$\Delta_r H_m$ ( <i>r</i> = 1)	$\Delta_r H_m$ ( <i>r</i> = 2)	$\Delta_r C_{p,m}$ ( <i>r</i> = 1)	$\Delta_r C_{p,m}$ ( <i>r</i> = 2)	Reference
	(M)		(°C)	kJ·mol <sup>-1</sup>	kJ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>	
$\partial pK_a / \partial T$	0.10	NaCl	0 - 125		(0.0 ± 2.6)		(122 ± 68)	<a href="#">[98KET/WES]</a>
	0.32				(0.3 ± 2.0)		(128 ± 52)	
	0.60				(2.3 ± 1.9)		(95 ± 31)	
	1.00				(1.4 ± 1.9)		(98 ± 30)	
	2.0				− (2.5 ± 2.1)		(148 ± 35)	
	3.1				(0.4 ± 2.9)		(68 ± 70)	
	5.0				− (7.0 ± 1.9)		(152 ± 18)	
	0.10	NaCF <sub>3</sub> SO <sub>3</sub>	0 - 125		− (2.2 ± 1.9)		(187 ± 25)	
	0.32				− (0.3 ± 1.9)		(171 ± 14)	
	0.60				− (0.3 ± 1.9)		(144 ± 53)	
	1.00				(1.0 ± 1.90)		(120 ± 27)	
	0.10		0 - 125	(6.1 ± 0.4)		(177 ± 7)		
	0.27			(5.1 ± 0.4)		(168 ± 3)		
	0.32			(5.1 ± 0.4)		(167 ± 3)		
	0.60			(4.3 ± 0.4)		(158 ± 3)		
	1.00			(3.5 ± 0.4)		(149 ± 5)		

Figure VI-4: Enthalpy changes at 25°C and multi-linear least-squares SIT regression plots for the reaction:  $\text{ox}^{2-} + \text{H}^+ \rightleftharpoons \text{Hox}^-$ .

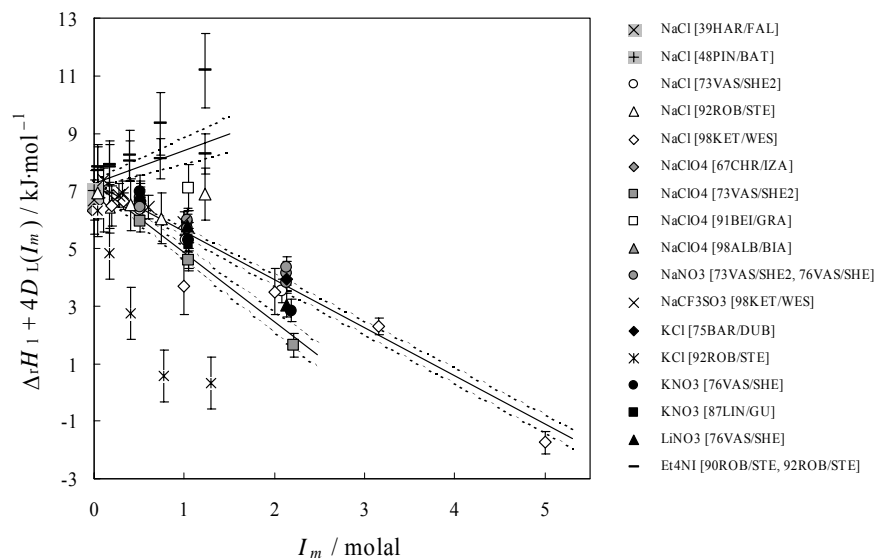
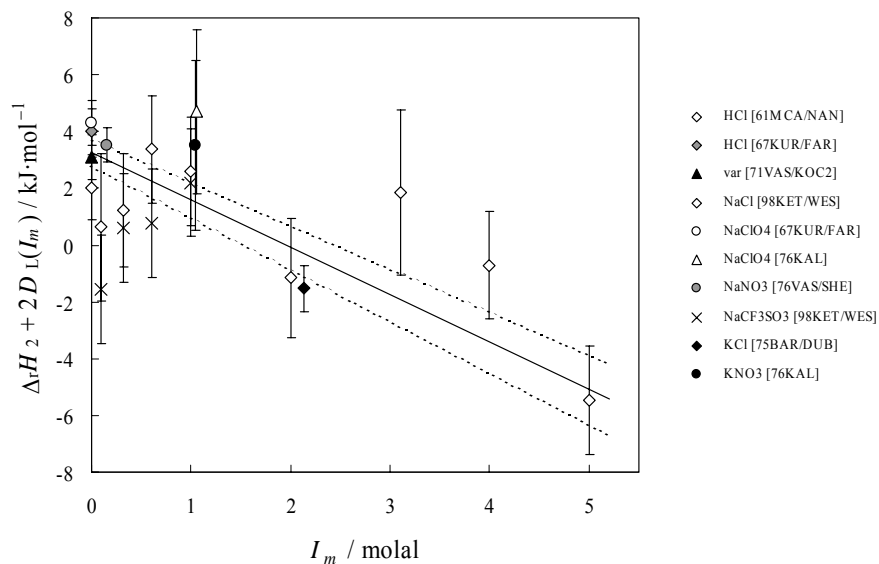


Figure VI-5: Enthalpy changes at 25°C and least-squares SIT regression plot for the reaction:  $\text{Hox}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{ox}(\text{aq})$ .



### VI.3.5 Selected protonation constants for oxalate

Summarising the results from the previous sections, the recommended standard values for the protonation constants of oxalate are:

$$\log_{10} K_1^\circ ((\text{VI.9}), r = 1, 298.15 \text{ K}) = (4.25 \pm 0.01)$$

$$\Delta_f H_m^\circ ((\text{VI.9}), r = 1) = (7.3 \pm 0.1) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\log_{10} K_2^\circ ((\text{VI.9}), r = 2, 298.15 \text{ K}) = (1.40 \pm 0.03)$$

$$\Delta_f H_m^\circ ((\text{VI.9}), r = 2) = (3.3 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

These values corresponds to the following overall standard protonation constants:

$$\text{ox}^{2-} + \text{H}^+ \rightleftharpoons \text{Hox}^- \quad \log_{10} \beta_1^\circ (298.15 \text{ K}) = (4.25 \pm 0.01)$$

$$\text{ox}^{2-} + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{ox}(\text{aq}) \quad \log_{10} \beta_2^\circ (298.15 \text{ K}) = (5.65 \pm 0.03).$$

Note that [\[98KET/WES\]](#) in their detailed evaluation of temperature and ionic strength effects, using an empirical multi-parameter fitting function and including the data of [\[39HAR/FAL\]](#), [\[48PIN/BAT\]](#) to their own extensive measurements, derived constants consistent with the present review:  $\log_{10} K_1^\circ (298.15 \text{ K}) = (4.264 \pm 0.014)$ ,  $\log_{10} K_2^\circ (298.15 \text{ K}) = (1.401 \pm 0.052)$ ,  $\Delta_f H_1^\circ = (7.3 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H_2^\circ = (0.7 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$ .

Using the selected values of  $\Delta_f H_m^\circ$  for oxalate protonation and  $\Delta_f H_m^\circ (\text{H}_2\text{ox}, \text{aq}, 298.15 \text{ K}) = -(820.1 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}$  selected in Section VI.2.3 leads to:

$$\Delta_f H_m^\circ (\text{Hox}^-, 298.15 \text{ K}) = -(823.4 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ (\text{ox}^{2-}, 298.15 \text{ K}) = -(830.7 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}.$$

Protonation constants for oxalate for different ionic media may be calculated using the SIT model described in Appendix B, and selected standard protonation constants and specific ion interaction coefficients. In Table VI-8 the results from such calculations are reported for some ionic media commonly used in chemical equilibrium studies.

Table VI-8: Calculated equilibrium constants in Molar units for some  $\text{ox}^{2-} / \text{H}^+ / \text{Na}^+ / \text{K}^+$  systems at 25°C. The SIT model for activity coefficients has been used with the  $\Delta\epsilon_n$  obtained in this review. Other parameters from Appendix B were used as appropriate. Care should be exercised when using values at the highest ionic strengths, because they are confirmed by few experimental data only, as indicated in the figures of Sections VI.3.2 and VI.3.3.

$I$ (M)	$I_m$ (molal)	$\log_{10}K_1$	$\log_{10}K_2$
NaClO <sub>4</sub>			
0	0.000	(4.25 ± 0.01)	(1.40 ± 0.03)
0.1	0.101	(3.83 ± 0.01)	(1.19 ± 0.03)
0.25	0.254	(3.71 ± 0.01)	(1.13 ± 0.03)
0.5	0.513	(3.62 ± 0.02)	(1.10 ± 0.03)
0.75	0.779	(3.59 ± 0.02)	(1.08 ± 0.03)
1	1.05	(3.59 ± 0.03)	(1.08 ± 0.04)
2	2.21	(3.64 ± 0.05)	(1.13 ± 0.06)
3	3.50	(3.77 ± 0.08)	(1.21 ± 0.08)
4	4.95	(3.94 ± 0.11)	(1.32 ± 0.11)
5	6.58	(4.15 ± 0.165)	(1.44 ± 0.15)
NaNO <sub>3</sub>			
0	0.000	(4.25 ± 0.01)	(1.40 ± 0.03)
0.1	0.101	(3.82 ± 0.01)	(1.18 ± 0.03)
0.25	0.253	(3.69 ± 0.01)	(1.11 ± 0.03)
0.5	0.509	(3.59 ± 0.01)	(1.06 ± 0.03)
0.75	0.769	(3.54 ± 0.01)	(1.03 ± 0.03)
1	1.03	(3.51 ± 0.02)	(1.00 ± 0.03)
2	2.14	(3.47 ± 0.03)	(0.96 ± 0.04)
3	3.33	(3.50 ± 0.05)	(0.95 ± 0.06)
4	4.61	(3.55 ± 0.07)	(0.94 ± 0.07)
5	6.02	(3.62 ± 0.09)	(0.95 ± 0.09)
NaCl			
0	0.000	(4.25 ± 0.01)	(1.40 ± 0.03)
0.1	0.100	(3.83 ± 0.01)	(1.20 ± 0.03)
0.25	0.252	(3.70 ± 0.01)	(1.14 ± 0.03)
0.5	0.506	(3.61 ± 0.01)	(1.12 ± 0.03)
0.75	0.762	(3.57 ± 0.01)	(1.11 ± 0.03)
1	1.02	(3.55 ± 0.02)	(1.12 ± 0.03)
2	2.09	(3.57 ± 0.03)	(1.20 ± 0.04)
3	3.20	(3.64 ± 0.05)	(1.32 ± 0.05)
4	4.37	(3.74 ± 0.06)	(1.45 ± 0.07)
5	5.61	(3.86 ± 0.08)	(1.59 ± 0.08)

(Continued on next page)

Table VI-8: (continued)

$I$ (M)	$I_m$ (molal)	$\log_{10}K_1$	$\log_{10}K_2$
KCl			
0	0.000	$(4.25 \pm 0.01)$	$(1.40 \pm 0.03)$
0.1	0.101	$(3.83 \pm 0.01)$	$(1.19 \pm 0.03)$
0.25	0.252	$(3.72 \pm 0.01)$	$(1.14 \pm 0.04)$
0.5	0.509	$(3.66 \pm 0.02)$	$(1.11 \pm 0.05)$
0.75	0.769	$(3.64 \pm 0.02)$	$(1.11 \pm 0.07)$
1	1.03	$(3.65 \pm 0.03)$	$(1.12 \pm 0.09)$
2	2.13	$(3.77 \pm 0.05)$	$(1.20 \pm 0.17)$
3	3.31	$(3.96 \pm 0.07)$	$(1.31 \pm 0.27)$
4	4.58	$(4.19 \pm 0.10)$	$(1.45 \pm 0.37)$
KNO <sub>3</sub>			
0	0.000	$(4.25 \pm 0.01)$	$(1.40 \pm 0.03)$
0.1	0.101	$(3.83 \pm 0.01)$	$(1.19 \pm 0.03)$
0.25	0.253	$(3.71 \pm 0.01)$	$(1.13 \pm 0.04)$
0.5	0.512	$(3.63 \pm 0.02)$	$(1.09 \pm 0.05)$
0.75	0.776	$(3.61 \pm 0.02)$	$(1.08 \pm 0.07)$
1	1.05	$(3.60 \pm 0.03)$	$(1.07 \pm 0.09)$
2	2.19	$(3.68 \pm 0.05)$	$(1.10 \pm 0.18)$
3	3.44	$(3.83 \pm 0.08)$	$(1.17 \pm 0.28)$

It is expected that the value of  $\varepsilon(\text{H}_2\text{ox}, \text{MX})$  will be small. In this review the approximation is made that  $\varepsilon(\text{H}_2\text{ox}, \text{MX}) = (0.00 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ . This approximation is corroborated by emf measurements [41LAR/TOM] from which the authors concluded that the activity coefficient of the undissociated oxalic acid does not change in value over an ionic strength range of 0.02 to 0.33 M. Table VI-9 contains selected specific ion interaction coefficients based on this approximation and on the  $\Delta\varepsilon_n$  selected in Sections VI.3.2 (Table VI-5) and VI.3.3 (Table VI-6).

Table VI-9: Selected specific ion interaction coefficients ( $\text{kg}\cdot\text{mol}^{-1}$ ) for oxalate and its protonated forms in  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and tetraethylammonium electrolytes.

	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{R}_4\text{N}^+$
$\varepsilon(\text{M}^+, \text{ox}^{2-})$	$-(0.51 \pm 0.09)$	$-(0.08 \pm 0.01)$	$(0.07 \pm 0.08)$	$(0.38 \pm 0.09) - (0.58 \pm 0.06) \log_{10}I_m$
$\varepsilon(\text{M}^+, \text{Hox}^-)$	$-(0.28 \pm 0.09)$	$-(0.07 \pm 0.01)$	$-(0.01 \pm 0.08)$	$-(0.01 \pm 0.09)$
$\varepsilon(\text{H}_2\text{ox}, \text{MX})$	$(0.00 \pm 0.01)$	$(0.00 \pm 0.01)$	$(0.00 \pm 0.01)$	$(0.00 \pm 0.01)$

## VI.4 Alkali metal oxalate compounds and complexes

### VI.4.1 Sodium and potassium oxalate compounds

The solids formed at equilibrium in the system sodium oxalate – oxalic acid – water are, besides  $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}(\text{cr})$  (*cf.* Section VI.2.2),  $\text{NaHox}\cdot \text{H}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{ox}(\text{cr})$ . The crystal structure of  $\text{NaHox}\cdot \text{H}_2\text{O}$  has been determined by Follner *et al.* [70FOL/KAN], whereas the crystal structure of  $\text{Na}_2\text{ox}(\text{cr})$  has first been reported by Jeffrey and Parry [54JEF/PAR] and was later refined by Reed and Olmstead [81REE/OLM]. Crystal structure – crystal morphology relations of  $\text{Na}_2\text{ox}(\text{cr})$  are discussed in [95STR/GRI], and for details on crystal growth effects of  $\text{Na}_2\text{ox}(\text{cr})$  from aqueous solutions see [2002LOW/OGD].

The solubility of  $\text{Na}_2\text{ox}(\text{cr})$  in pure water has been studied extensively (Table VI-10). The following values have been reported: 0.279 mol·kg<sup>-1</sup> (25°C) [05FOO/AND], 0.238 mol·kg<sup>-1</sup> (15°C) and 0.334 mol·kg<sup>-1</sup> (50°C) [16COL2] [17COL], 0.289 mol·kg<sup>-1</sup> (25°C) and 0.355 mol·kg<sup>-1</sup> (50°C) [19RIV/OCO], 0.241 mol·kg<sup>-1</sup> (15°C), 0.255 mol·kg<sup>-1</sup> (20°C) 0.269 mol·kg<sup>-1</sup> (25°C) [28FLO], 0.201 mol·kg<sup>-1</sup> (0°C), 0.275 mol·kg<sup>-1</sup> (25°C), 0.318 mol·kg<sup>-1</sup> (40°C), 0.341 mol·kg<sup>-1</sup> (50°C) [33FOO/VAN], 0.31 mol·kg<sup>-1</sup> (39°C) and 0.34 mol·kg<sup>-1</sup> (52°C) [36BOU2], 0.24 mol·dm<sup>-3</sup> (18°C) [36BRI/JAR], 0.21 mol·kg<sup>-1</sup> (0°C), 0.28 mol·kg<sup>-1</sup> (25°C), 0.36 mol·kg<sup>-1</sup> (60°C) 0.42 mol·kg<sup>-1</sup> (80°C) [46HIL/GOU], 0.205 mol·kg<sup>-1</sup> (0°C), 0.261 mol·kg<sup>-1</sup> (20°C), 0.292 mol·kg<sup>-1</sup> (30°C), 0.314 mol·kg<sup>-1</sup> (40°C), 0.339 mol·kg<sup>-1</sup> (50°C), 0.360 mol·kg<sup>-1</sup> (60°C), 0.385 mol·kg<sup>-1</sup> (70°C), 0.413 mol·kg<sup>-1</sup> (80°C), 0.439 mol·kg<sup>-1</sup> (90°C), 0.464 mol·kg<sup>-1</sup> (99.6°C) [51NOR], 0.278 mol·dm<sup>-3</sup> (25°C) [68MAT/KRO], 0.252 mol·kg<sup>-1</sup> (20°C) [79ZHI/KOL], 0.339 mol·kg<sup>-1</sup> (50°C) and 0.411 mol·kg<sup>-1</sup> (75°C) [80KOL/ZHI], 0.270 mol·kg<sup>-1</sup> (25°C), 0.270 mol·kg<sup>-1</sup> (25°C), 0.270 mol·kg<sup>-1</sup> (25°C), 0.210 mol·kg<sup>-1</sup> (0°C), 0.219 mol·kg<sup>-1</sup> (5°C), 0.243 mol·kg<sup>-1</sup> (15°C), 0.263 mol·kg<sup>-1</sup> (20°C), 0.270 mol·kg<sup>-1</sup> (25°C), 0.284 mol·kg<sup>-1</sup> (30°C), 0.301 mol·kg<sup>-1</sup> (35°C), 0.316 mol·kg<sup>-1</sup> (40°C), 0.326 mol·kg<sup>-1</sup> (45°C), 0.345 mol·kg<sup>-1</sup> (50°C), 0.355 mol·kg<sup>-1</sup> (55°C), 0.367 mol·kg<sup>-1</sup> (60°C) [2004MEN/APE].

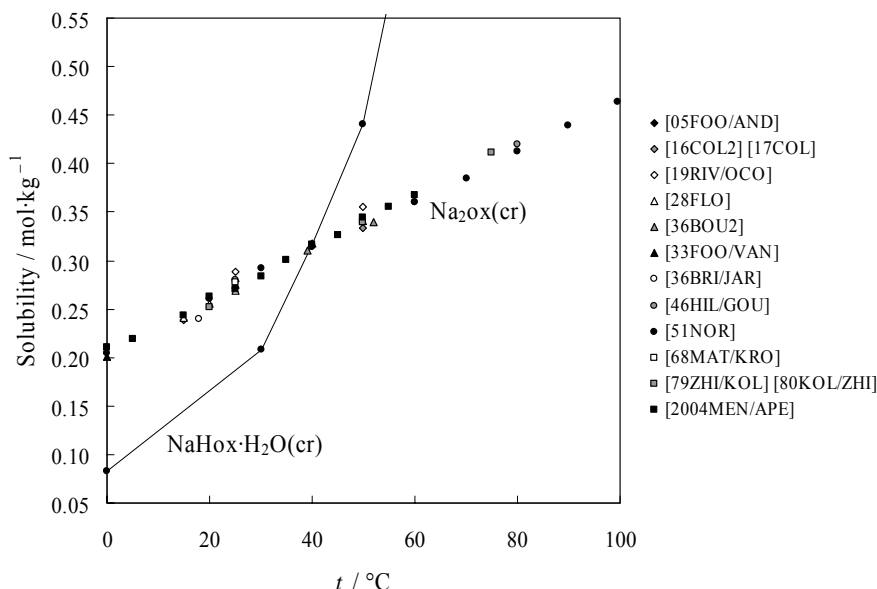
For the solubility of  $\text{NaHox}\cdot \text{H}_2\text{O}(\text{cr})$  in pure water the following values have been reported: 0.083 mol·kg<sup>-1</sup> (0°C), 0.208 mol·kg<sup>-1</sup> (30°C), 0.317 mol·kg<sup>-1</sup> (40°C), 0.440 mol·kg<sup>-1</sup> (50°C) and 1.73 mol·kg<sup>-1</sup> (101.0°C) [51NOR].

In addition, solubilities in a variety of systems have been reported:  $\text{Na}_2\text{ox}$  –  $\text{H}_2\text{ox}$  [05FOO/AND] [46HIL/GOU],  $\text{NaOH}$  –  $\text{H}_2\text{ox}$  –  $\text{H}_2\text{O}$  [51NOR] [91BOU/PHI],  $\text{Na}_2\text{ox}$  –  $(\text{NH}_4)_2\text{ox}$  [19RIV/OCO],  $\text{Na}_2\text{ox}$  –  $\text{Mg}(\text{ox})$  [36BRI/JAR],  $\text{Na}_2\text{ox}$  –  $\text{UO}_2\text{ox}$  [17COL],  $\text{Na}_2\text{ox}$  –  $\text{ZrO}(\text{ox})$  [36BOU2],  $\text{Na}_2\text{ox}$  –  $\text{NaCl}$  [16COL2],  $\text{Na}_2\text{ox}$  –  $\text{NaNO}_3$  [16COL2] [79ZHI/KOL] [80KOL/ZHI],  $\text{Na}_2\text{ox}$  –  $\text{Na}_2\text{SO}_4$  [16COL2] [46HIL/GOU],  $\text{Na}_2\text{ox}$  –  $\text{NaIO}_3$  [33FOO/VAN].

Table VI-10: Sodium and potassium oxalate compounds. References reporting solubility data are marked with (sol.). References reporting X-ray or neutron crystal structure data are marked with (str.).

Compound	Solubility in H <sub>2</sub> O at 25°C	Reference
Na <sub>2</sub> ox	$(0.28 \pm 0.01) \text{ mol} \cdot \text{kg}^{-1}$	<a href="#">[05FOO/AND]</a> (sol.), <a href="#">[16COL2]</a> (sol.) <a href="#">[17COL]</a> (sol.) <a href="#">[19RIV/OCO]</a> (sol.), <a href="#">[28FLO]</a> (sol.), <a href="#">[33FOO/VAN]</a> (sol.), <a href="#">[36BOU2]</a> (sol.), <a href="#">[36BRI/JAR]</a> (sol.), <a href="#">[46HIL/GOU]</a> (sol.), <a href="#">[51NOR]</a> (sol.), <a href="#">[54JEF/PAR]</a> (str.), <a href="#">[68MAT/KRO]</a> (sol.), <a href="#">[79ZHI/KOL]</a> (sol.), <a href="#">[80KOL/ZHI]</a> (sol.), <a href="#">[81REE/OLM]</a> (str.), <a href="#">[95STR/GRI]</a> , <a href="#">[2002LOW/OGD]</a> , <a href="#">[2004MEN/APE]</a> (sol.)
NaHox·H <sub>2</sub> O	$\approx 0.16 \text{ mol} \cdot \text{kg}^{-1}$	<a href="#">[51NOR]</a> (sol.), <a href="#">[70FOL/KAN]</a> (str.)
K <sub>2</sub> ox·H <sub>2</sub> O	$(2.2 \pm 0.2) \text{ mol} \cdot \text{kg}^{-1}$	<a href="#">[05FOO/AND]</a> (sol.), <a href="#">[08KOP/CAH]</a> (sol.), <a href="#">[13HAR/DRU]</a> (sol.), <a href="#">[16COL]</a> (sol.), <a href="#">[16COL2]</a> (sol.), <a href="#">[19RIV/OCO]</a> (sol.), <a href="#">[26WOS]</a> (sol.), <a href="#">[35HEN]</a> (str.), <a href="#">[36BOU]</a> (sol.), <a href="#">[42BEN]</a> (sol.), <a href="#">[69HOD/IBE]</a> (str.), <a href="#">[72KUP]</a> , <a href="#">[2004MEN/APE]</a> (sol.)
K <sub>4</sub> H <sub>2</sub> (ox) <sub>3</sub> ·2H <sub>2</sub> O		<a href="#">[72KUP]</a>
KHox	$0.5 \text{ mol} \cdot \text{kg}^{-1}$	<a href="#">[1864ALL]</a> (sol.), <a href="#">[35HEN]</a> (str.), <a href="#">[42BEN]</a> (sol.), <a href="#">[68PED]</a> (str.), <a href="#">[71MOO/POW]</a> (str.), <a href="#">[72KUP]</a>
KH <sub>3</sub> (ox) <sub>2</sub> ·2H <sub>2</sub> O	$0.11 \text{ mol} \cdot \text{kg}^{-1}$	<a href="#">[08KOP/CAH]</a> (sol.), <a href="#">[64HAA]</a> (str.), <a href="#">[72KUP]</a> , <a href="#">[79BAU]</a> (sol.), <a href="#">[81EMS/JON]</a> (str.)

Figure VI-6: Solubility of  $\text{Na}_2\text{ox}(\text{cr})$  and  $\text{NaHox}\cdot\text{H}_2\text{O}(\text{cr})$  in water as a function of temperature. The line is given as visual guideline only.



The solubility data of  $\text{Na}_2\text{ox}(\text{cr})$  in water as function of temperature, published over a century, reveal a very consistent picture (Figure VI-6), and a mean value of all data at  $25^\circ\text{C}$  is  $(0.28 \pm 0.01) \text{ mol}\cdot\text{kg}^{-1}$ . However, it is outside the scope of this review to develop a thermodynamic model of such highly soluble salts like  $\text{Na}_2\text{ox}(\text{cr})$ .

The solids formed at equilibrium in the system potassium oxalate – oxalic acid – water are, in the order of decreasing concentration of oxalic acid,  $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}(\text{cr})$  (*cf.* Section VI.2.2),  $\text{KH}_3(\text{ox})_2\cdot 2\text{H}_2\text{O}(\text{cr})$ ,  $\text{KHox}(\text{cr})$ ,  $\text{K}_4\text{H}_2(\text{ox})_3\cdot 2\text{H}_2\text{O}(\text{cr})$ , and finally  $\text{K}_2\text{ox}\cdot\text{H}_2\text{O}(\text{cr})$  [08KOP/CAH]. Large crystals in the centimeter scale can be grown from aqueous solutions of all these compounds [72KUP].

The crystal structure of  $\text{KH}_3(\text{ox})_2\cdot 2\text{H}_2\text{O}(\text{cr})$  was first determined by Haas [64HAA], although not exactly in positioning the protons, and later re-determined by Emsley *et al.* [81EMS/JON]. The crystal structure of  $\text{KHox}(\text{cr})$  has already been investigated in the early days of X-ray crystallography by Hendricks [35HEN], was later determined more precisely by single crystal X-ray diffraction [68PED], and by neutron diffraction in order to locate the hydrogen atoms unambiguously [71MOO/POW]. The crystal structure of  $\text{K}_2\text{ox}\cdot\text{H}_2\text{O}(\text{cr})$  has been investigated many times, from the advent of



X-ray crystallography [35HEN] until the precise refinement of its crystal and molecular structure [69HOD/IBE].

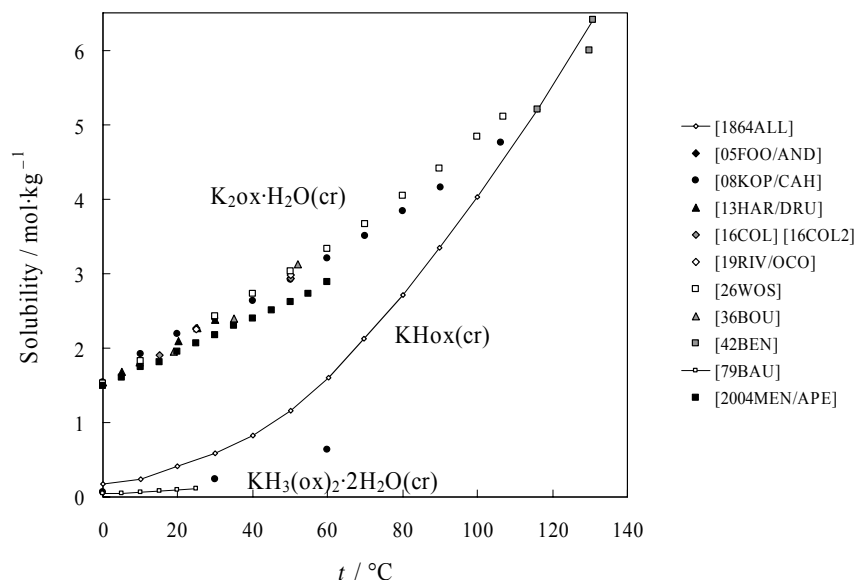
The solubility of  $K_2Ox \cdot H_2O(cr)$  in pure water has been studied extensively (Table VI-10). The following values have been reported: 2.27 mol·kg<sup>-1</sup> (25°C) [05FOO/AND], 1.54 mol·kg<sup>-1</sup> (0°C), 1.92 mol·kg<sup>-1</sup> (10°C), 2.19 mol·kg<sup>-1</sup> (20°C), 2.40 mol·kg<sup>-1</sup> (30°C), 2.63 mol·kg<sup>-1</sup> (40°C), 2.91 mol·kg<sup>-1</sup> (50°C), 3.20 mol·kg<sup>-1</sup> (60°C), 3.50 mol·kg<sup>-1</sup> (70°C), 3.83 mol·kg<sup>-1</sup> (80°C), 4.16 mol·kg<sup>-1</sup> (90.2°C), 4.76 mol·kg<sup>-1</sup> (106.2°C) [08KOP/CAH], 1.53 mol·kg<sup>-1</sup> (0.0°C), 1.68 mol·kg<sup>-1</sup> (5.1°C), 1.81 mol·kg<sup>-1</sup> (9.8°C), 2.10 mol·kg<sup>-1</sup> (20.1°C), 2.27 mol·kg<sup>-1</sup> (25.2°C), 2.38 mol·kg<sup>-1</sup> (30.0°C) [13HAR/DRU], 1.91 mol·kg<sup>-1</sup> (15°C) and 2.93 mol·kg<sup>-1</sup> (50°C) [16COL] [16COL2], 2.25 mol·kg<sup>-1</sup> (25°C) and 2.98 mol·kg<sup>-1</sup> (50°C) [19RIV/OCO], 1.52 mol·kg<sup>-1</sup> (0°C), 1.82 mol·kg<sup>-1</sup> (10°C), 2.42 mol·kg<sup>-1</sup> (30°C), 2.72 mol·kg<sup>-1</sup> (40°C), 3.03 mol·kg<sup>-1</sup> (50°C), 3.33 mol·kg<sup>-1</sup> (60°C), 3.66 mol·kg<sup>-1</sup> (70°C), 4.04 mol·kg<sup>-1</sup> (80°C), 4.40 mol·kg<sup>-1</sup> (90°C), 4.83 mol·kg<sup>-1</sup> (100°C), 5.10 mol·kg<sup>-1</sup> (107°C) [26WOS], 1.95 mol·kg<sup>-1</sup> (19°C), 2.39 mol·kg<sup>-1</sup> (35°C) and 3.13 mol·kg<sup>-1</sup> (52°C) [36BOU], 6.0 mol·kg<sup>-1</sup> (130°C) [42BEN], 1.483 mol·kg<sup>-1</sup> (0°C), 1.598 mol·kg<sup>-1</sup> (5°C), 1.739 mol·kg<sup>-1</sup> (10°C), 1.811 mol·kg<sup>-1</sup> (15°C), 1.957 mol·kg<sup>-1</sup> (20°C), 2.06 mol·kg<sup>-1</sup> (25°C), 2.17 mol·kg<sup>-1</sup> (30°C), 2.30 mol·kg<sup>-1</sup> (35°C), 2.39 mol·kg<sup>-1</sup> (40°C), 2.51 mol·kg<sup>-1</sup> (45°C), 2.62 mol·kg<sup>-1</sup> (50°C), 2.73 mol·kg<sup>-1</sup> (55°C), 2.89 mol·kg<sup>-1</sup> (60°C) [2004MEN/APE].

For the solubility of  $KHox(cr)$  in water the following values have been reported: 0.17 mol·kg<sup>-1</sup> (0°C), 0.24 mol·kg<sup>-1</sup> (10°C), 0.41 mol·kg<sup>-1</sup> (20°C), 0.59 mol·kg<sup>-1</sup> (30°C), 0.82 mol·kg<sup>-1</sup> (40°C), 1.16 mol·kg<sup>-1</sup> (50°C), 1.60 mol·kg<sup>-1</sup> (60°C), 2.12 mol·kg<sup>-1</sup> (70°C), 2.71 mol·kg<sup>-1</sup> (80°C), 3.35 mol·kg<sup>-1</sup> (90°C), 4.02 mol·kg<sup>-1</sup> (100°C) [1864ALL], 5.2 mol·kg<sup>-1</sup> (116°C), 6.4 mol·kg<sup>-1</sup> (131°C) [42BEN].

Potassium tetraoxalate,  $KH_3(ox)_2 \cdot 2H_2O(cr)$ , is used for preparation of one of the “operational standard reference solutions” for pH calibration [83COV/BAT]. In this context, the solubility of  $KH_3(ox)_2 \cdot 2H_2O(cr)$  in pure water has been measured as a function of temperature [79BAU] (see Appendix A). Older data reported are: 0.07 mol·kg<sup>-1</sup> (0°C), 0.23 mol·kg<sup>-1</sup> (30°C), 0.64 mol·kg<sup>-1</sup> (60°C), [08KOP/CAH].

In addition, solubilities in a variety of systems have been reported:  $K_2Ox - H_2Ox$  [05FOO/AND] [08KOP/CAH] [13HAR/DRU],  $K_2Ox - (NH_4)_2Ox$  [19RIV/OCO],  $K_2Ox - Ni(ox)$  [36VOS/ISR],  $K_2Ox - ZrO(ox)$  [36BOU],  $K_2Ox - KCl$  [16COL2],  $K_2Ox - KNO_3$  [16COL2],  $K_2Ox - K_2SO_4$  [16COL2].

Figure VI-7: Solubility of  $\text{K}_2\text{ox}\cdot\text{H}_2\text{O}(\text{cr})$ ,  $\text{KHox}(\text{cr})$  and  $\text{KH}_3(\text{ox})_2\cdot 2\text{H}_2\text{O}(\text{cr})$  in water as a function of temperature. The lines are given as visual guidelines only.



The solubility data of  $\text{K}_2\text{ox}\cdot\text{H}_2\text{O}(\text{cr})$  in water as function of temperature, published over a century, are fairly consistent (Figure VI-7), and a mean value of all data at  $25^\circ\text{C}$  is  $(2.2 \pm 0.2) \text{ mol}\cdot\text{kg}^{-1}$ . The most recent data set [2004MEN/APE] deviates with increasing temperature from the older data sets. The reason for this deviation is not clear. Remarkably, the two data sets available for  $\text{KHox}(\text{cr})$  [1864ALL] and [42BEN] show perfect agreement. Also, the very precise measurements of Baucke [79BAU] for  $\text{KH}_3(\text{ox})_2\cdot 2\text{H}_2\text{O}(\text{cr})$  corroborate data published a century ago [08KOP/CAH]. However, it is outside the scope of this review to develop a thermodynamic model for these highly soluble salts.

#### VI.4.2 Complexes with $\text{Na}^+$ and $\text{K}^+$

In the literature a number of publications has been found reporting stability constants for sodium and potassium oxalate complexes (Table VI-11). The stability constants were mainly evaluated from two types of experiments. The first type of experiments comprises measurements of oxalate protonation constants in various ionic media. The differences found for oxalate protonation constants in different electrolyte solutions of the same ionic strength were interpreted in terms of complex formation [81DAN/RIG].

[83DAN/RIG2], [92ROB/STE], [2004CRE/ROB]. The second type of experiments deals with solubility measurements of oxalate solids. These measurements have been interpreted with thermodynamic models taking Na and K oxalate complex formation into account explicitly [73FIN/ROT], [79TOM/NAN], [81BUR/FIN], [91BOU/PHI].

Table VI-11: Experimental equilibrium data for Na and K oxalate systems. The uncertainties are given as reported in the references.

Method <sup>a</sup>	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Na}^+ + \text{ox}^{2-} \rightleftharpoons \text{Na(ox)}^-$				
sol	$\rightarrow 0$	38	(1.12 ± 0.01)	[73FIN/ROT], [81BUR/FIN]
gl, Δp <i>K</i> <sub>a</sub>	0.10 M Et <sub>4</sub> NI / NaNO <sub>3</sub>	37	(0.53 ± 0.03)	[81DAN/RIG]
gl, Δp <i>K</i> <sub>a</sub>	0.15 M Et <sub>4</sub> N <sup>+</sup> / Na <sup>+</sup>	37	(0.46 ± 0.03)	[83DAN/RIG2]
sol	(2 – 10 M NaOH) $\rightarrow 0$	25	1.10	[91BOU/PHI]
		40	0.44	
		60	– 0.3	
gl, Δp <i>K</i> <sub>a</sub>	Et <sub>4</sub> NI / NaCl $\rightarrow 0$	25	0.88	[92ROB/STE]
		37	0.92	
gl, Δp <i>K</i> <sub>a</sub>	Et <sub>4</sub> NI / NaCl $\rightarrow 0$	25	(0.92 ± 0.02)	[2004CRE/ROB]
$\text{Na}^+ + \text{Hox}^- \rightleftharpoons \text{NaHox(aq)}$				
gl, Δp <i>K</i> <sub>a</sub>	Et <sub>4</sub> NI / NaCl $\rightarrow 0$	25	(0.02 ± 0.02)	[2004CRE/ROB]
$\text{K}^+ + \text{ox}^{2-} \rightleftharpoons \text{Kox}^-$				
con	0.07 M K <sub>2</sub> ox	18 (?)	– 0.42	[31BAN/RIG]
	0.15 M K <sub>2</sub> ox		– 0.59	
	0.29 M K <sub>2</sub> ox		– 0.62	
sol	(0.1 – 0.3 M KCl) $\rightarrow 0$	37	1.0	[79TOM/NAN]
gl, Δp <i>K</i> <sub>a</sub>	0.10 M Et <sub>4</sub> NI / KNO <sub>3</sub>	37	(0.43 ± 0.05)	[81DAN/RIG]
gl, Δp <i>K</i> <sub>a</sub>	0.15 M Et <sub>4</sub> N <sup>+</sup> / K <sup>+</sup>	37	(0.41 ± 0.03)	[83DAN/RIG2]
gl, Δp <i>K</i> <sub>a</sub>	Et <sub>4</sub> NI / KCl $\rightarrow 0$	25	0.71	[92ROB/STE]
		37	0.83	

a: Methods: con = conductivity measurements; gl = pH–glass electrode; sol = the formation constants for alkali-metal complexation were obtained as fit parameters from evaluating solubility data; Δp*K*<sub>a</sub> = the formation constants for alkali–metal complexation were obtained from differences in protonation constants determined in different background electrolytes (alkali electrolytes *versus* tetra-alkylammonium salts).

The earliest attempt of deriving potassium oxalate stability constants [31BAN/RIG] does not fit in either category. Banks *et al.* interpreted tabulated conductivity data for several salts in water in terms of dissociation constants of these salts. Conductivity measurements of unsymmetrical electrolytes like K<sub>2</sub>ox are difficult to interpret, and as discussed in Appendix A, the results of Banks *et al.* are not credited by this review.

The method of deriving Na and K oxalate complexes from protonation data, proposed by Sammartano and co-workers [\[81DAN/RIG\]](#), [\[83DAN/RIG2\]](#), [\[92ROB/STE\]](#), [\[2004CRE/ROB\]](#), works as follows. The protonation constants of oxalate were determined potentiometrically in different media, *i.e.*, in NaCl, KCl and Et<sub>4</sub>NI, and the data obtained for the different ionic strengths were simultaneously analysed in two different ways: (1) Taking into account the changes in ionic strength but neglecting any complex formation of oxalate with alkali-metal ions. The protonation constants as a function of the ionic strength are expressed by three semi-empirical equations for the three ionic media. (2) Considering both, the changes in ionic strength and a possible complex formation of oxalate with alkali-metal ions. In this case it is assumed that oxalate does not form complexes with the Et<sub>4</sub>N<sup>+</sup> cation and thus, the measurements in Et<sub>4</sub>NI are regarded as the reference case (“baseline”) where no complexation occurs. This also results in three semi-empirical equations describing stability constants as a function of ionic strength: one common oxalate protonation function for NaCl, KCl and Et<sub>4</sub>NI, which is identical with the Et<sub>4</sub>NI function derived in (1); two equations for the stability of Kox<sup>−</sup> and Na(ox)<sup>−</sup> as a function of ionic strength calculated from the differences KCl – Et<sub>4</sub>NI and NaCl – Et<sub>4</sub>NI, based on the functions derived in (1).

However, as indicated in Figure V–1 (Section V.3.2) the activity coefficients in tetraalkylammonium salts are quite different from those in alkali metal salts, although the differences do not necessarily implicate alkali metal ion complex formation, *e.g.*, between Na<sup>+</sup> and chloride. Therefore, different ionic medium effects on protonation constants when comparing Na/K electrolytes with tetraalkylammonium salts are not necessarily an indication of complex formation between the ligand and Na<sup>+</sup> or K<sup>+</sup>. In this review oxalate protonation data were successfully modelled using SIT with the interaction parameters  $\varepsilon(\text{ox}^{2-}, \text{Na}^+)$  and  $\varepsilon(\text{ox}^{2-}, \text{K}^+)$  without considering a complex Na(ox)<sup>−</sup> or Kox<sup>−</sup> in the speciation model (*cf.* Section VI.3).

The solubility of sodium oxalate has been investigated with the aim of developing a thermodynamic model for sodium oxalate solubility in “Bayer liquor” [\[91BOU/PHI\]](#), [\[93BEC/GRO\]](#). Processing of bauxites (aluminium ores) containing organic matter by the so-called “Bayer process” generates soluble organic sodium salts of various molecular weights. These organics accumulate in Bayer liquors and degrade to low molecular weight products, the ultimate species being sodium oxalate and carbonate. The Bayer process is based on the amphoteric nature of aluminium, *i.e.*, on the dissolution of aluminium hydroxide in strong sodium hydroxide solution. Thus, Bayer liquor is essentially a rather concentrated sodium aluminate solution, and sodium oxalate is an impurity, which limits alumina production from most Bayer refineries. Oxalate removal represents a significant fraction of the operating costs of many alumina refineries. Sodium oxalate solubility in Bayer liquor depends on various factors [\[87THE/BUS\]](#). The and Bush [\[87THE/BUS\]](#) correlated laboratory data on the apparent solubility of sodium oxalate in Bayer plant liquors with the pertinent variables by multi-

ple regression analysis. Bouzat and Philipponneau [91BOU/PHI] reported an attempt to develop a thermodynamic model of sodium oxalate solubility in concentrated sodium aluminate solutions. The model comprises the sodium complexes  $\text{Na}(\text{ox})^-$ ,  $\text{NaOH}(\text{aq})$ ,  $\text{NaCl}(\text{aq})$ ,  $\text{NaSO}_4^-$  and  $\text{NaCO}_3^-$ . The results of this model fit are not credited by this review (*cf.* Appendix A). Beckham and Grocott [93BEC/GRO] investigated the same chemical system and criticise the approach of [91BOU/PHI]. Beckham and Grocott [93BEC/GRO] propose a solubility model based on the solubility product of sodium oxalate and a set of purely empirical parameters. It is outside the scope of the present review to develop a thermodynamic model valid for highly concentrated sodium aluminate solutions like the Bayer liquor.

Several investigations of calcium oxalate solubility have been published where, in addition to the complex  $\text{Ca}(\text{ox})(\text{aq})$ , the complex  $\text{Na}(\text{ox})^-$  [73FIN/ROT], [81BUR/FIN], [89SIN], the complex  $\text{Kox}^-$  [85DAN/SON], or both  $\text{Na}(\text{ox})^-$  and  $\text{Kox}^-$  [79TOM/NAN] have been included into the speciation models. The ionic strength dependence has been calculated using the Davies equation [73FIN/ROT], [79TOM/NAN], [81BUR/FIN], [89SIN] or the SIT [85DAN/SON]. As discussed in Section VI.5.1, calcium oxalate solubility data can be modelled successfully applying SIT with the interaction parameters  $\varepsilon(\text{ox}^{2-}, \text{Na}^+)$  and  $\varepsilon(\text{ox}^{2-}, \text{K}^+)$  derived from oxalate protonation reactions but without considering a complex  $\text{Na}(\text{ox})^-$  or  $\text{Kox}^-$  in the speciation model (*cf.* Section VI.3).

## VI.5 Magnesium and calcium oxalate compounds and complexes

### VI.5.1 Magnesium and calcium oxalate compounds

Magnesium oxalate dihydrate,  $\text{Mg}(\text{ox}) \cdot 2\text{H}_2\text{O}(\text{cr})$ , is the magnesium oxalate compound forming at ambient conditions. It is found in nature as the mineral glushinskite [80WIL/JON]. Glushinskite is formed by lichens, fungi and other plants, and it may be termed a biomineral since it is found as a waste product in litter decomposition (see references in [2004FRO/ADE]).

Thermal analysis, Raman and infrared spectroscopy [2004FRO/ADE] revealed that glushinskite is the dihydrate phase in the temperature range up to 148°C. The phase change at 148°C involves dehydration and results in the formation of anhydrous magnesium oxalate,  $\text{Mg}(\text{ox}) \cdot 2\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{Mg}(\text{ox})(\text{cr}) + 2 \text{H}_2\text{O}(\text{g})$ , which above 397°C converts to magnesium oxide,  $\text{MgC}_2\text{O}_4(\text{cr}) \rightleftharpoons \text{MgO}(\text{cr}) + \text{CO}(\text{g}) + \text{CO}_2(\text{g})$ . The dehydration enthalpy is reported as  $\Delta_{\text{dehyd}} H_m^\circ = 110.5$  and  $100.1 \text{ kJ} \cdot \text{mol}^{-1}$ , determined by a transpiration method and by differential scanning calorimetry (DSC), respectively [2001TAN/FUR].

A number of studies have been published reporting solubility data for  $\text{Mg}(\text{ox}) \cdot 2\text{H}_2\text{O}(\text{cr})$  in pure water [03KOH], [08KOH], [24CHA/DHA], [25WAL], [34FRE], [36BRI/JAR], [42KAR], [51BAR/ARG] and [77FED/KHO] (Table VI-12)

and in solutions containing  $\text{H}_2\text{ox}$  [27BOB/MAL], [36BRI/JAR],  $\text{Na}_2\text{ox}$  [36BRI/JAR],  $\text{K}_2\text{ox}$  [51BAR/ARG],  $(\text{NH}_4)_2\text{ox}$  [27BOB/MAL],  $\text{H}_2\text{SO}_4$  [36BRI/JAR],  $\text{MgSO}_4$  [25WAL],  $\text{NH}_4\text{Cl}$  [27BOB/MAL],  $\text{NH}_4\text{Cl} - \text{NH}_3$  [34FRE], and  $\text{NaClO}_4$  [77FED/KHO].

In general, the solid phase has not been characterised in detail in these studies, but in the case of magnesium oxalate this omission poses no problem, as  $\text{Mg}(\text{ox}) \cdot 2\text{H}_2\text{O}(\text{cr})$  is the only phase forming in the temperature range of these investigations [2004FRO/ADE]. However, a general problem affecting all these solubility studies is the slow dissolution and even slower precipitation kinetics of  $\text{Mg}(\text{ox}) \cdot 2\text{H}_2\text{O}(\text{cr})$ . This peculiar property of magnesium oxalate has been described already one hundred years ago, “working with this compound needed a lot of time because the solution saturates slowly” [03KOH], and highly oversaturated solutions used in conductivity measurements approached equilibrium saturation only after two weeks [08KOH]. In a detailed analytical study Karaoglanov [42KAR] investigated this slow kinetics and came to the conclusion that the results of his  $\text{Mg}(\text{ox}) \cdot 2\text{H}_2\text{O}(\text{cr})$  precipitation experiments were not completely reproducible. Solubility studies showed a slightly decreasing concentration of dissolved magnesium oxalate, approaching constant values after 40 days [42KAR].

Table VI-12: Solubility data of magnesium and calcium oxalate compounds in pure water as reported in the literature.

$t$ (°C)	Equilibrium time	Concentration(M)	Reference	Remarks
$\text{Mg}(\text{ox}) \cdot 2\text{H}_2\text{O}(\text{cr})$				
18	2 – 4 hours	0.0027	[03KOH], [08KOH]	Conductivity measurements
18	24 hours	0.00264	[27SCH3]	Titration of oxalate with $\text{KMnO}_4$
36	?	0.00301	[24CHA/DHA]	Mg determined gravimetrically as $\text{MgSO}_4$
		0.00269		Salt precipitated in the cold
				Salt precipitated from boiling solutions
92	?	0.00362		Salt precipitated in the cold
		0.00350		Salt precipitated from boiling solutions
25	30 hours	0.00307	[25WAL]	Titration of oxalate with $\text{KMnO}_4$
18	“sufficiently long”	0.00331	[34FRE]	Mg determined with 8-oxy-chinolate
18	one month	0.00230	[36BRI/JAR]	
21	40 days	0.00327	[42KAR]	Titration of oxalate with $\text{KMnO}_4$ , Mg determined gravimetrically as $\text{Mg}_2\text{P}_2\text{O}_7$
25	4 days	0.00320	[51BAR/ARG]	Mg determined colorimetrically
25	?	0.00924	[77FED/KHO]	Mg determined complexometrically

(Continued on next page)

Table VI-12 (continued)

$t$ (°C)	Equilibrium time	Concentration(M)	Reference	Remarks
<b>“Ca(ox)”</b>				
25	15 minutes	$5.3 \times 10^{-5}$	[01RIC/MCC]	Titration of oxalate with $\text{KMnO}_4$
50		$7.5 \times 10^{-5}$		No characterisation of “Ca(ox)”
95		$1.1 \times 10^{-4}$		
18	30 minutes	$4.3 \times 10^{-5}$	[03KOH] [08KOH]	Conductivity measurements. $\text{H}_2\text{O}$
25		$4.8 \times 10^{-5}$		not determined, assumed to be $\text{Ca(ox)} \cdot \text{H}_2\text{O}$
25	“over night”	$7.1 \times 10^{-5}$	[16HEN/TAY]	No characterisation of “Ca(ox)”
20	1 – 2 hours	$5.2 \times 10^{-5}$	[27AUM2]	Prepared from $\text{H}_2\text{ox}$ and $\text{CaCl}_2$
		$5.7 \times 10^{-5}$		Prepared from $(\text{NH}_4)_2\text{ox}$ and $\text{CaCl}_2$
				“According to my experience $\text{Ca(ox)} \cdot \text{H}_2\text{O}$ ”
<b>Ca(ox)·H<sub>2</sub>O(cr)</b>				
26–27	“until saturation”	$2.3 \times 10^{-4}$	[03HER/MUH]	Ca in $\text{Ca(ox)} \cdot \text{H}_2\text{O}$ analysed. Solubility: Residue determined gravimetrically at 70°C
18	13 hours	$(4.7 \pm 0.2) \times 10^{-5}$	[27SCH3]	Oxalate in $\text{Ca(ox)} \cdot \text{H}_2\text{O}$ analysed. Solubility: Titration of oxalate with $\text{KMnO}_4$
25	“until equilibrium was obtained”	$6.7 \times 10^{-5}$	[33KOL/SAN]	“Saturated solutions were analyzed for oxalate or calcium by micro methods”
25	4 weeks	$6.2 \times 10^{-5}$	[34BAS]	Ca and oxalate in $\text{Ca(ox)} \cdot \text{H}_2\text{O}$ analysed
25	2 – 6 hours	$(4.84 \pm 0.06) \times 10^{-5}$	[39PED2]	Oxalate in $\text{Ca(ox)} \cdot \text{H}_2\text{O}$ analysed
30	10 minutes	$6.46 \times 10^{-5}$	[40SHE/PAL]	$\text{Ca(ox)} \cdot \text{H}_2\text{O}$ dried at 105°C
95		$1.13 \times 10^{-4}$		Titration of oxalate with $\text{KMnO}_4$
25	1 hour	$4.55 \times 10^{-5}$	[42MCC/RIE]	Titration of oxalate with $\text{Ce}^{\text{IV}}(\text{SO}_4)_2$
25	1 – 2 hours	$4.90 \times 10^{-5}$	[51NYD]	Ca determined by flame spectrography.
37		$6.2 \times 10^{-5}$	[71CHU/REE]	
38		$6.1 \times 10^{-5}$	[73FIN/ROT]	
37		$5.02 \times 10^{-5}$	[75PAK/OHA]	
37		$5.4 \times 10^{-5}$	[79TOM/NAN]	
37		$(4.7 \pm 0.5) \times 10^{-5}$	[80HOD]	
37	50 hours	$5.64 \times 10^{-5}$	[89SIN]	Ca and oxalate determined by ion chromatography

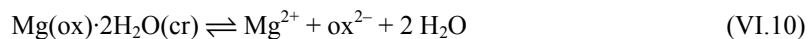
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Table VI-12 (continued)

$t$ (°C)	Equilibrium time	Concentration(M)	Reference	Remarks
Ca(ox)·2H <sub>2</sub> O(cr)				
37		$8.82 \times 10^{-5}$	[80TOM/NAN]	
Ca(ox)·3H <sub>2</sub> O(cr)				
37		$1.15 \times 10^{-4}$	[79TOM/NAN]	

The data reported in [24CHA/DHA] are not credited in this review because of the almost complete lack of details concerning the solubility experiments. The values of [77FED/KHO], obtained in NaClO<sub>4</sub> medium, are considered unreliable and are rejected by this review (see discussion in Appendix A). No other study in NaClO<sub>4</sub> medium could be identified by this review. Results obtained in solutions containing H<sub>2</sub>ox [27BOB/MAL], [36BRI/JAR], H<sub>2</sub>SO<sub>4</sub> [36BRI/JAR], MgSO<sub>4</sub> [25WAL], and NH<sub>4</sub>Cl – NH<sub>3</sub> [34FRE] are not further evaluated in this review because of the lack of appropriate SIT interaction parameters for NH<sub>3</sub>, and ambiguities concerning H<sup>+</sup> – oxalate interactions in concentrated H<sub>2</sub>ox and H<sub>2</sub>SO<sub>4</sub> solutions. In addition, potential Mg sulphate complexation in mixed sulphate – oxalate pose additional ambiguities.

In all other cases, *i.e.*, solubility of Mg(ox)·2H<sub>2</sub>O(cr) in pure water [03KOH], [08KOH], [25WAL], [27SCH3], [34FRE], [36BRI/JAR], [42KAR], [51BAR/ARG] and in solutions containing Na<sub>2</sub>ox [36BRI/JAR], K<sub>2</sub>ox [51BAR/ARG], (NH<sub>4</sub>)<sub>2</sub>ox [27BOB/MAL] and NH<sub>4</sub>Cl [27BOB/MAL], [34FRE], the analytical data reported were used to calculate the aqueous speciation using the Mg complexation constants for Mg(ox)(aq) and Mg(ox)<sub>2</sub><sup>2-</sup> selected in this review (*cf.* Section VI.5.2), and using the SIT interaction parameters  $\epsilon(\text{Mg}^{2+}, \text{Cl}^-) = (0.19 \pm 0.02)$  (*cf.* Appendix B),  $\epsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.08 \pm 0.01)$ ,  $\epsilon(\text{ox}^{2-}, \text{K}^+) = (0.07 \pm 0.08)$  and  $\epsilon(\text{Mg(ox)}_2^{2-}, \text{Na}^+) = -(0.15 \pm 0.03)$  selected in this review, and assuming  $\epsilon(\text{ox}^{2-}, \text{K}^+) \approx \epsilon(\text{ox}^{2-}, \text{NH}_4^+)$ ,  $\epsilon(\text{Mg(ox)}_2^{2-}, \text{Na}^+) \approx \epsilon(\text{Mg(ox)}_2^{2-}, \text{K}^+) = \epsilon(\text{Ca(ox)}_2^{2-}, \text{NH}_4^+)$ ,  $\epsilon(\text{Mg(ox)(aq)}, \text{NaCl}) \approx \epsilon(\text{Mg(ox)(aq)}, \text{NH}_4\text{Cl}) = \epsilon(\text{Mg(ox)(aq)}, (\text{NH}_4)_2\text{ox}) = \epsilon(\text{Mg(ox)(aq)}, \text{K}_2\text{ox}) = \epsilon(\text{Mg(ox)(aq)}, \text{Na}_2\text{ox}) = (0.0 \pm 0.1)$ , and  $\epsilon(\text{Mg}^{2+}, \text{ox}^{2-}) \approx 0.15$ . From each aqueous speciation the solubility product  $\log_{10} K_{s,0}$  for reaction:



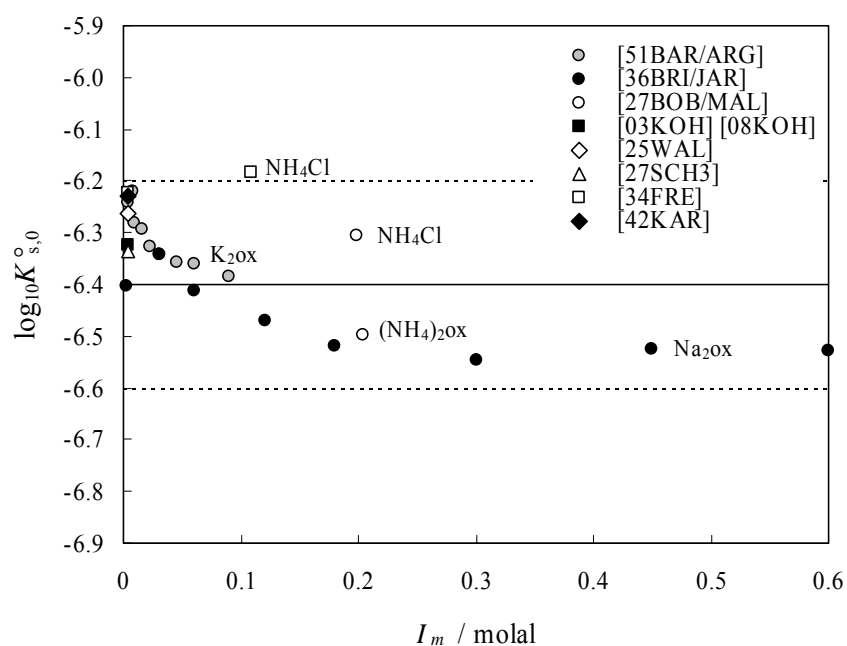
has been calculated and extrapolated to zero ionic strength using the same SIT interaction parameters (Figure VI-8).

The actual value of the SIT interaction parameters has no influence on the results in pure water, and also in the other cases at  $I \leq 0.6$  M the results do not depend in any significant way on the estimated SIT parameters. The complex Mg(ox)(aq) is the dominating species (> 60%) in pure water, whereas with increasing K<sub>2</sub>ox and Na<sub>2</sub>ox concentrations the complex Mg(ox)<sub>2</sub><sup>2-</sup> becomes the dominating species. The numerical



values of the calculated  $\log_{10} K_{s,0}^{\circ}$  depend on the selected complexation constants, but the scatter of the values revealed in Figure VI-8 is independent of the complexation constants and SIT interaction parameters used in the calculations. The above discussed slow kinetics of magnesium oxalate dissolution and precipitation could be the major cause of the observed scatter. For scoping calculations in modelling exercises related to radioactive waste disposal a value  $\log_{10} K_{s,0}^{\circ} \text{ (VI.10)} = -(6.4 \pm 0.2)$  could be used, encompassing the available literature data as shown in Figure VI-8, but none of the above discussed studies properly addresses the effect of slow kinetics on equilibrium solubility of  $\text{Mg(ox)} \cdot 2\text{H}_2\text{O(cr)}$  and therefore no value is recommended for its solubility product.

Figure VI-8: Solubility product of  $\text{Mg(ox)} \cdot 2\text{H}_2\text{O(cr)}$  according to Reaction (VI.10), calculated from analytical solubility data and extrapolated to zero ionic strength using parameters discussed in the text. Data close to zero ionic strength refer to solubility in pure water, in all other cases the added salt is indicated.



Calcium oxalate forms three different hydrates at ambient conditions,  $\text{Ca(ox)}\cdot\text{H}_2\text{O(cr)}$ ,  $\text{Ca(ox)}\cdot 2\text{H}_2\text{O(cr)}$ , and  $\text{Ca(ox)}\cdot 3\text{H}_2\text{O(cr)}$ . The monoclinic monohydrate,  $\text{Ca(ox)}\cdot\text{H}_2\text{O(cr)}$ , is found in nature as the mineral whewellite, its crystal structure data are reported in [80TAZ/DOM] [81DEG/PIR]. The tetragonal dihydrate,  $\text{Ca(ox)}\cdot 2\text{H}_2\text{O(cr)}$ , occurs in nature as the mineral weddellite. Single crystal X-ray diffraction [80TAZ/DOM] revealed that the structure contains a channel in which zeolitic water occurs and thus, the formula of weddellite actually is  $\text{Ca(ox)}\cdot(2+x)\text{H}_2\text{O(cr)}$  with  $x \leq 0.5$ . The trihydrate,  $\text{Ca(ox)}\cdot 3\text{H}_2\text{O(cr)}$ , is triclinic; its crystal structure data are given by [81BLO/KAN].

Whewellite and weddellite have been found in the litter layer of several different soils, indicating that oxalate is a major metabolic product of fungi in natural environments [77GRA/CRO]. Not only whewellite and weddellite but also the trihydrate is found in urinary stones [82HEI]. Urolithiasis, *i.e.*, the formation of kidney or bladder stones, constitutes a serious health problem, and about 70% of these stones have calcium oxalate as a major component [97KON/TRA].

$\text{Ca(ox)}\cdot\text{H}_2\text{O(cr)}$  exists in two phases, known as the low-temperature and high-temperatures phases [96KOC/GAL]. According to thermo-analytical, structural and spectroscopic measurements this order - disorder phase transition occurs between 0 and 100°C. The enthalpy of this transition is very small. It has been reported as  $\Delta_{\text{us}}H_{\text{m}}^{\circ} \approx 0.4 \text{ kJ}\cdot\text{mol}^{-1}$  [96KOC/GAL].

Latimer *et al.* [33LAT/SCH] report a careful low-temperature calorimetric study for determining the heat capacity and entropy of  $\text{Ca(ox)}\cdot\text{H}_2\text{O(cr)}$  in the range 19 to 300 K. The experimental data, reported in tabular form in [33LAT/SCH], have been re-evaluated in this review (*cf.* Appendix A), and the results of this numerical fit agree well with the results originally obtained by graphical integration [33LAT/SCH]. The heat capacity data show some scatter above  $-50^{\circ}\text{C}$  which might be an indication of the onset of the above discussed order - disorder phase transition of  $\text{Ca(ox)}\cdot\text{H}_2\text{O(cr)}$ . However, besides this “roughness” no systematic effect is revealed in the data (see Figures A-2 and A-4 in Appendix A) and this review selects:

$$C_{p,m}^{\circ}(\text{Ca(ox)}\cdot\text{H}_2\text{O, cr, 298.15 K}) = (153.34 \pm 2.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$S_{\text{m}}^{\circ}(\text{Ca(ox)}\cdot\text{H}_2\text{O, cr, 298.15 K}) = (156.37 \pm 2.00) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

In an early stage of this review it was intended to derive  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{ox}^{2-}, 298.15 \text{ K})$  via the enthalpy values of thermal decomposition of  $\text{Ca(ox)}\cdot\text{H}_2\text{O(cr)}$  and hence, an in-depth literature search and review concerning thermal decomposition of calcium oxalates was started. The result of this effort is summarised here.

Early thermogravimetric studies [47PEL/DUV], [59PET/WIE] revealed that whewellite  $\text{Ca(ox)}\cdot\text{H}_2\text{O(cr)}$  dehydrates in the temperature range 100 to  $240^{\circ}\text{C}$  forming anhydrous calcium oxalate,  $\text{Ca(ox)}\cdot\text{H}_2\text{O(cr)} \rightleftharpoons \text{Ca(ox)(cr)} + \text{H}_2\text{O(g)}$ , which converts to calcium carbonate above  $400^{\circ}\text{C}$ ,  $\text{CaC}_2\text{O}_4(\text{cr}) \rightleftharpoons \text{CaCO}_3(\text{cr}) + \text{CO(g)}$ , which finally

converts to calcium oxide in the temperature range 660 to 900°C,  $\text{CaCO}_3(\text{cr}) \rightleftharpoons \text{CaO}(\text{cr}) + \text{CO}_2(\text{g})$ . Whereas the dehydration of calcium oxalate monohydrate and the decarbonation of calcium carbonate are reversible reactions, the formation of calcium carbonate from anhydrous calcium oxalate is irreversible [59PET/WIE]. A recent study involving high resolution thermogravimetry combined with Raman spectroscopy [2004FRO/WEI] corroborates the early findings: Whewellite is stable up to around 161°C, above which temperature the anhydrous calcium oxalate is formed; at 479°C the oxalate transforms to calcium carbonate, and above 684°C calcium oxide is formed.

Weddellite,  $\text{Ca}(\text{ox}) \cdot 2\text{H}_2\text{O}(\text{cr})$ , dehydrates above 100°C first to the monohydrate  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}(\text{cr})$  and then to the anhydrous calcium oxalate [64WAL/LAN]. The results of this study have recently been corroborated by high resolution thermogravimetry combined with Raman and infrared emission spectroscopy [2003FRO/WEI]: Weddellite is the phase in the temperature range up to the pre-dehydration temperature of 97°C. At this temperature, the phase formed is whewellite,  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}(\text{cr})$ , and above 114°C the phase is the anhydrous calcium oxalate.

The dehydration of  $\text{Ca}(\text{ox}) \cdot 3\text{H}_2\text{O}(\text{cr})$  commences at 50°C at ambient pressure and the monohydrate is formed,  $\text{Ca}(\text{ox}) \cdot 3\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}(\text{cr}) + 2 \text{H}_2\text{O}(\text{g})$ . This reaction is irreversible even under elevated vapour pressure [64HOC/GER], [68GER/WAT].

The thermal and related structural effects of the above dehydration and decarbonation reactions, especially of  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}(\text{cr})$ , have been studied and discussed in detail in numerous studies [47PEL/DUV], [59PET/WIE], [64HOC/GER], [64SIM/NEW], [64WAL/LAN], [65GER/WAT], [65HOC/WAT], [68GER/WAT], [68PRI/FAZ], [84BRE/SKR], [87DOL], [95RAK/SKU], [2001MIA], [2003FRO/WEI] and [2004FRO/WEI].

Table VI-13: Enthalpies of dehydration of calcium oxalate monohydrate reported in the literature.

Method	$\Delta_{\text{dehyd}} H_{\text{m}}^{\circ}$ (kJ·mol <sup>-1</sup> )	Reference
$\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{Ca}(\text{ox})(\text{cr}) + \text{H}_2\text{O}(\text{g})$ (VI.11)		
TGA	65.7	[64HOC/GER]
TGA	(65.7 ± 3.8)	[68GER/WAT]
transpiration	69.5	[77SHI/TAN]
DTA (Pt pan)	74.8	[80TAN/MOR]
DTA (Ni block)	72.8	
DSC	(63.64 ± 0.17)	[80TAN/NEG]
TGA	(69 ± 3)	[88NER/VIT]
DSC	52.6	[90BIA/BUC]
TGA	(69.8 ± 3)	[91NER/PRO]
DSC	(52.8 ± 2)	[92BIA/BUC]

The dehydration enthalpy  $\Delta_{\text{dehyd}} H_{\text{m}}^{\circ}$  (VI.11) has been reported in several studies [64HOC/GER], [68GER/WAT], [80TAN/MOR], [80TAN/NEG], [88NER/VIT], [90BIA/BUC], [91NER/PRO], [92BIA/BUC] (Table VI-13). In a recent study [2001TAN/FUR] systematic differences between  $\Delta_{\text{dehyd}} H_{\text{m}}^{\circ}$  determined by a transpiration method and differential scanning calorimetry (DSC) for various salts have been reported and an empirical “correction” function is proposed. However, the large discrepancies in the reported results (Table VI-13) are not remedied by this empirical “correction” function, as for example DSC data reported by different authors vary considerably [80TAN/NEG], [90BIA/BUC], [92BIA/BUC]. None of the studies listed in Table VI-13 can be singled out as reliable, and an overall variation of more than 20  $\text{kJ}\cdot\text{mol}^{-1}$  in the reported  $\Delta_{\text{dehyd}} H_{\text{m}}^{\circ}$  values precludes any recommendation.

The value  $\Delta_{\text{f}} H_{\text{m}}^{\circ}(\text{ox}^{2-}, 298.15 \text{ K}) = -(830.7 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$  selected in this review has been derived on an alternative route *via* the heat of combustion of oxalic acid (*cf.* Section VI.2) and the heat of protonation of oxalate (*cf.* Section VI.3).

The field of urinary stone research triggered a series of detailed investigations on the kinetics of crystal growth of the monohydrate whewellite [74NAN/GAR], [92MIL/GRA], its dissolution kinetics [75GAR/NAN], on the growth and characterisation of dihydrate (weddelite) crystals [82LEP/TAW], and on the nucleation and crystal growth of the trihydrate [75GAR], [82HEI]. Although  $\text{Ca}(\text{ox})\cdot\text{H}_2\text{O}(\text{cr})$  is the thermodynamically stable form at ambient conditions, and the dihydrate and trihydrate are metastable [97KON/TRA], calcium oxalate crystallises from aqueous solutions in one or more of its hydrated forms depending upon pH, temperature, supersaturation, calcium to oxalate ratio and stirring dynamics of the system during nucleation and growth. Furthermore, soluble impurities can be the predominating factor in controlling the nucleation and growth rates of these hydrates and thus the eventual form of the solid phase [75GAR].

A large number of studies has been published within the last 100 years reporting solubility data for calcium oxalate hydrates in pure water [01RIC/MCC], [03HER/MUH], [03KOH], [08KOH], [16HEN/TAY], [27AUM2], [27SCH3], [29HAM], [33KOL/SAN], [34BAS], [39PED2], [40SHE/PAL], [49PED], [51NYD], [71CHU/REE], [73FIN/ROT], [79TOM/NAN], [80HOD], [80TOM/NAN], [89SIN], (Table VI-12), and in solutions containing NaCl [01GER], [29HAM], [33MAL/GLU], [42MCC/RIE], [73FIN/ROT], [73KNA/MAT], [79TOM/NAN], [79TOM/NAN2], [80TOM/NAN], [89SIN], [98STR/TRA], KCl [29HAM], [42MCC/RIE], [79TOM/NAN], [85DAN/SON], LiCl [29HAM], HCl, HCl – KCl and HCl –  $\text{KNO}_3$  [16HEN/TAY],  $\text{NH}_4\text{Cl}$  [29HAM], [33MAL/GLU], [40SHE/PAL],  $\text{CaCl}_2$  and  $\text{CaCl}_2$  – NaCl [73FIN/ROT],  $\text{MgCl}_2$  [29HAM], [33MAL/GLU], [71CHU/REE], [73KNA/MAT], [89SIN],  $\text{MgCl}_2$  – NaCl [29HAM], [73KNA/MAT], [89SIN],  $\text{NH}_4\text{NO}_3$  [33MAL/GLU], [40SHE/PAL],  $\text{Na}_2\text{SO}_4$  [29HAM], [33MAL/GLU], [40SHE/PAL], [42MCC/RIE],  $\text{K}_2\text{SO}_4$  [29HAM],  $(\text{NH}_4)_2\text{SO}_4$  [33KOL/SAN], [33MAL/GLU], [40SHE/PAL],  $\text{MgSO}_4$  [33MAL/GLU],  $\text{H}_3\text{PO}_4$  – NaOH [45HOO/WIJ],  $\text{Na}_2\text{HPO}_4$  [01GER], [29HAM],  $\text{Na}_3\text{PO}_4$

[71CHU/REE],  $(\text{NH}_4)_2\text{ox}$  [51NYD],  $\text{Na}_3\text{cit}$  [71CHU/REE], [73KNA/MAT], acetic acid [03HER/MUH],  $\text{NH}_3$  [34BAS], urea [39PED2], synthetic urine [71CHU/REE], [82LEP/TAW].

The solid, especially the number of hydration waters, has not been characterised in a number of older studies [01GER], [01RIC/MCC], [03KOH], [08KOH], [16HEN/TAY], [27AUM2], [30RUF], [33MAL/GLU], [45HOO/WIJ]. The results of these investigations have not been accepted in this review.

Inspection of the solubility values reported for  $\text{Ca}(\text{ox})\cdot\text{H}_2\text{O}$  in pure water (Table VI-12) reveals some scatter, part of which might be caused by significant amounts of other hydrates present in the experiments despite the claims of the authors to have used pure monohydrate, and some of which might be caused by inappropriate experimental procedures, *e.g.*, [03HER/MUH] and [33KOL/SAN]. Solubility data obtained in pure water as listed in Table VI-12 are not considered in the final data analysis of this review.

Also a number of solubility products have been reported in the literature as summarised in Table VI-14.

Table VI-14: Solubility products of magnesium and calcium oxalate compounds reported in the literature and re-evaluated in this review. If not stated otherwise in the remarks, the solubility products are given for zero ionic strength.

$t$ (°C)	$\log_{10} K_{s,0}$ <sup>a</sup>	$\log_{10} K_{s,0}$ <sup>b</sup>	Reference	Remarks
$\text{“Mg(ox)”} \rightleftharpoons \text{Mg}^{2+} + \text{ox}^{2-}$				
?	– 4.07		[30RUF]	Number given without any details
$\text{Mg(ox)}\cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Mg}^{2+} + \text{ox}^{2-} + 2\text{H}_2\text{O}$				
18	– 5.5		[36BRI/JAR]	Recalculated by this review, see Figure VI-8.
25	– 5.68		[77FED/KHO]	Rejected, see Appendix A
$\text{“Ca(ox)”} \rightleftharpoons \text{Ca}^{2+} + \text{ox}^{2-}$				
?	– 8.75		[30RUF]	Number given without any details
$\text{Ca(ox)}\cdot\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{ox}^{2-} + \text{H}_2\text{O}$				
37	– 8.51	– (8.53 ± 0.05)	[29HAM]	Data in NaCl and KCl re-evaluated
25	– 8.68	– (8.72 ± 0.06)	[42MCC/RIE]	Data in NaCl re-evaluated
25	– 8.67		[51NYD]	Calculated from solubility in water ignoring $\text{Ca(ox)(aq)}$ complexation
20	– 7.9		[63STA]	Valid for 0.1 M $\text{KClO}_4$ . Rejected, see Appendix A.

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Table VI-14 (continued)

$t$ (°C)	$\log_{10} K_{s,0}^a$	$\log_{10} K_{s,0}^b$	Reference	Remarks
$\text{Ca(ox)} \cdot \text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{ox}^{2-} + \text{H}_2\text{O}$				
20	-8.87		[71PAZ/STE]	Rejected, see Appendix A
38		$-(8.54 \pm 0.08)$	[73FIN/ROT]	Data in NaCl re-evaluated
37		$-(8.58 \pm 0.06)$	[73KNA/MAT]	Data in $I > 0.1$ M NaCl re-evaluated
15	-8.81		[74NAN/GAR]	No experimental raw data reported
25	$-(8.70 \pm 0.02)$			
35	-8.61			
45	-8.55			
37	$-(8.60 \pm 0.03)$		[75PAK/OHA]	No experimental raw data reported
37		$-(8.53 \pm 0.09)$	[79TOM/NAN]	Data in NaCl and KCl re-evaluated
15	-8.92	-8.79	[79TOM/NAN2]	Data in 0.15 M NaCl re-evaluated
25	-8.78	-8.63		
37	-8.66	-8.49		
50	-8.57	-8.38		
37	$-(8.65 \pm 0.10)$		[80HOD]	Calculated from solubility in water ignoring $\text{Ca(ox)(aq)}$ complexation
37	-8.55		[85DAN/SON]	
37	-8.66	$-(8.49 \pm 0.08)$	[89SIN]	Data in NaCl re-evaluated
20	$-(8.84 \pm 0.02)$	$-(8.82 \pm 0.11)$	[98STR/TRA]	Data in NaCl re-evaluated, results from ISE and AAS data averaged
25	$-(8.77 \pm 0.01)$	$-(8.74 \pm 0.07)$		
30	$-(8.71 \pm 0.01)$	$-(8.66 \pm 0.04)$		
37	$-(8.65 \pm 0.03)$	$-(8.58 \pm 0.08)$		
40	$-(8.62 \pm 0.02)$	$-(8.56 \pm 0.08)$		
$\text{Ca(ox)} \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{ox}^{2-} + 2\text{H}_2\text{O}$				
37	-8.3		[75GAR]	Number given without any details
15	-8.49	-8.37	[80TOM/NAN]	Data in 0.15 M NaCl re-evaluated
25	-8.38	-8.24		Data in 0.15 M NaCl re-evaluated
37		$-(8.18 \pm 0.12)$		Data re-evaluated, 0.03–0.3 M NaCl
50	-8.20	-8.01		Data in 0.15 M NaCl re-evaluated
20	$-(8.42 \pm 0.02)$	$-(8.39 \pm 0.09)$	[98STR/TRA]	Data in NaCl re-evaluated, results from ISE and AAS data averaged
25	$-(8.34 \pm 0.02)$	$-(8.30 \pm 0.06)$		
30	$-(8.26 \pm 0.03)$	$-(8.21 \pm 0.08)$		
37	$-(8.17 \pm 0.03)$	$-(8.12 \pm 0.07)$		
40	$-(8.13 \pm 0.04)$	$-(8.08 \pm 0.09)$		

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Table VI-14 (continued)

$t$ (°C)	$\log_{10} K_{s,0}$ <sup>a</sup>	$\log_{10} K_{s,0}$ <sup>b</sup>	Reference	Remarks
$\text{Ca(ox)} \cdot 3\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{ox}^{2-} + 3\text{H}_2\text{O}$				
37	– 8.08		[75GAR]	Number given without any details
37		– (8.00 ± 0.07)	[79TOM/NAN]	Data in NaCl and KCl re-evaluated
15	– 8.48	– 8.36	[79TOM/NAN2]	Data in 0.15 M NaCl re-evaluated
25	– 8.32	– 8.17		
37	– 8.14	– 7.98		
50	– 7.99	– 7.81		
20	– (8.33 ± 0.01)	– (8.29 ± 0.03)	[98STR/TRA]	Data in NaCl re-evaluated, results
25	– (8.24 ± 0.01)	– (8.20 ± 0.04)		from ISE and AAS data averaged
30	– (8.12 ± 0.02)	– (8.07 ± 0.06)		
37	– (8.02 ± 0.02)	– (7.96 ± 0.07)		
40	– (7.97 ± 0.02)	– (7.92 ± 0.11)		

a: Values and uncertainties given as reported in the literature.

b: Values and uncertainties re-evaluated and accepted by this review (see text for details).

The solubility product reported by Pak *et al.* [75PAK/OHA] fits well to the other data reported at 37°C (Table VI-14). The solid has been characterised in detail, and series of experiments varying pH, ionic strength and total concentrations of calcium and oxalate all resulted in consistent solubility products [75PAK/OHA]. However, the  $\text{Ca(ox)(aq)}$  stability constant  $\log_{10} K_{s,0} = 3.19$ , valid for 25°C, has been used in all calculations, and no experimental data are reported in [75PAK/OHA], preventing any recalculation. Hence, the result of this study has not been included in the final data analysis.

Further results listed Table VI-14 but rejected by this review are [30RUF], [51NYD], [75GAR], [80HOD] (see remarks in Table VI-14) and [63STA], [71PAZ/STE] (see discussion in Appendix A).

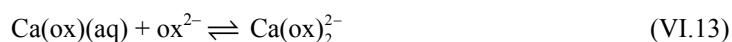
For the final data analysis this review considered only studies carried out in NaCl and KCl media with proper characterisation of the solids in equilibrium with the solutions: [29HAM], [42MCC/RIE], [73FIN/ROT], [73KNA/MAT], [79TOM/NAN], [79TOM/NAN2], [80TOM/NAN], [85DAN/SON], [89SIN], [98STR/TRA].

In all the above cases, when analytical equilibrium concentration data of dissolved calcium, oxalate, NaCl or KCl have been reported, the aqueous speciation was recalculated in this review as follows:

The complexes  $\text{Ca(ox)(aq)}$  and  $\text{Ca(ox)}_2^{2-}$  are included in the speciation calculations. For  $\text{Ca(ox)(aq)}$ ,



the values  $\log_{10} K_1^\circ$  (VI.12) =  $(3.19 \pm 0.06)$  valid at 25°C and selected in this review (*cf.* Section VI.5.2), and  $\log_{10} K_1^\circ$  (VI.12) =  $(3.27 \pm 0.07)$  valid at 37°C were used. For interpolation and extrapolation to other temperatures (15 to 50°C) a constant enthalpy of reaction has been calculated from these two values. For  $\text{Ca(ox)}_2^{2-}$ ,

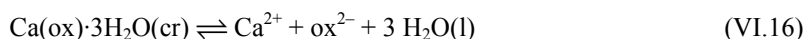
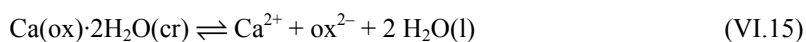
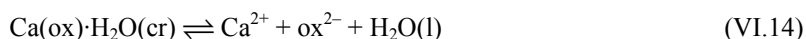


the value  $\log_{10} K_2^\circ$  (VI.13) =  $(0.83 \pm 0.19)$  valid at 25°C and selected in this review (*cf.* Section VI.5.2) was used. It has been assumed that the iso-coulombic Reaction (VI.13) is temperature independent.

In order to adjust the above constants to the actual ionic strength of a particular equilibrium experiment the SIT has been used (see Appendix B) with the following interaction coefficients:  $\varepsilon(\text{Ca}^{2+}, \text{Cl}^-) = (0.14 \pm 0.01)$  (*cf.* Appendix B),  $\varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.08 \pm 0.01)$  and  $\varepsilon(\text{ox}^{2-}, \text{K}^+) = (0.07 \pm 0.08)$  selected in this review (*cf.* Section VI.3.5), and it has been assumed that  $\varepsilon(\text{Mg(ox)(aq)}, \text{NaCl}) \approx \varepsilon(\text{Ca(ox)(aq)}, \text{NaCl}) = \varepsilon(\text{Ca(ox)(aq)}, \text{KCl}) = (0.0 \pm 0.1)$ , and  $\varepsilon(\text{Mg(ox)}_2^{2-}, \text{Na}^+) \approx \varepsilon(\text{Ca(ox)}_2^{2-}, \text{Na}^+) = \varepsilon(\text{Ca(ox)}_2^{2-}, \text{K}^+) = -(0.15 \pm 0.10)$  (*cf.* Section VI.5.2).

As the speciation calculations showed, the complex  $\text{Ca(ox)}_2^{2-}$  is unimportant ( $< 0.04\%$  of total oxalate in all cases) in the calcium oxalate equilibrium experiments considered in this review, and hence the uncertainties of its stability constant and related SIT interaction coefficient have no influence on the results. However, the complex stability of  $\text{Ca(ox)(aq)}$  turned out to be a critical parameter in a consistent re-evaluation of calcium oxalate solubility experiments (1 to 10 % of total oxalate, depending on ionic strength and temperature).

Using the results of the speciation calculations, *i.e.*, the calculated concentrations of  $[\text{Ca}^{2+}]$  and  $[\text{ox}^{2-}]$ , the solubility products of the reactions:



were calculated and extrapolated to zero ionic strength with the same SIT interaction parameters as used in the speciation calculations.

The very detailed and careful early study of precipitation and solubility of calcium oxalate hydrates by Hammarsten [29HAM] contains solubility data for  $\text{Ca(ox)} \cdot \text{H}_2\text{O}$  in various electrolytes. The solubility data in NaCl and KCl have been used to recalculate solubility products in this review.

McComas and Rieman [42MCC/RIE] prepared  $\text{Ca(ox)} \cdot \text{H}_2\text{O}$  by two different methods and measured its solubility at  $(25.0 \pm 0.2)^\circ\text{C}$  in NaCl (0.1 – 1.0 M). The measured equilibrium concentrations are reported in tabular form and solubility products have been recalculated there from in this review.



Finlayson *et al.* [73FIN/ROT] report that X-ray diffraction was used to verify that the powder they used was whewellite,  $\text{Ca(ox)}\cdot\text{H}_2\text{O}$ , before and after the solubility studies. The solubility data at 38°C in NaCl are reported in graphical form only [73FIN/ROT]. They have been digitised and solubility products have been recalculated in this review.

The  $\text{Ca(ox)}\cdot\text{H}_2\text{O}$  solubility data of Knappwost and Matouschek [73KNA/MAT] at 37°C in NaCl were reported in graphical form only. They have been digitised and solubility products have been recalculated in this review from measurements at  $I > 0.1$  M NaCl.

Solubility data for  $\text{Ca(ox)}\cdot\text{H}_2\text{O}$  and  $\text{Ca(ox)}\cdot 3\text{H}_2\text{O}$  in 0.15 M NaCl at various temperatures were reported by Tomažič and Nancollas [79TOM/NAN2]. Both hydrates were characterised by X-ray diffraction, scanning electron microscopy, chemical analysis and by determining the water content of the solids. The transformation of the trihydrate to the monohydrate during measurements has been followed by X-ray diffraction. The reported solubility data have been used to recalculate solubility products in this review.

Solubility data for  $\text{Ca(ox)}\cdot\text{H}_2\text{O}$  and  $\text{Ca(ox)}\cdot 3\text{H}_2\text{O}$  at 37°C in NaCl (0.03 – 0.3 M) and KCl (0.1 – 0.3 M) were reported by Tomažič and Nancollas [79TOM/NAN] including results already published in [79TOM/NAN2]. The same procedures have been applied as described in [79TOM/NAN2], and the reported solubility data in NaCl and KCl have been used to recalculate solubility products in this review.

Solubility data for  $\text{Ca(ox)}\cdot 2\text{H}_2\text{O}$  in 0.03 – 0.3 M NaCl at 37°C and 0.15 M NaCl at 15, 25 and 50°C were reported by Tomažič and Nancollas [80TOM/NAN]. The same procedures have been applied as described in [79TOM/NAN2], and the reported solubility data have been used to recalculate solubility products in this review.

The  $\text{Ca(ox)}\cdot\text{H}_2\text{O}$  solubility data of Singh [89SIN] at 37°C in NaCl have been used to recalculate solubility products in this review.

$\text{Ca(ox)}\cdot\text{H}_2\text{O}$ ,  $\text{Ca(ox)}\cdot 2\text{H}_2\text{O}$  and  $\text{Ca(ox)}\cdot 3\text{H}_2\text{O}$  solubilities were studied at 20, 25, 30, 37, and 40°C in 0.02, 0.05, 0.10 and 0.20 M NaCl by Streit *et al.* [98STR/TRA]. All calcium oxalate hydrates were characterised by a combination of X-ray diffraction, scanning electron microscopy and thermogravimetric analysis. After the solubility measurements, the  $\text{Ca(ox)}\cdot 2\text{H}_2\text{O}$  and  $\text{Ca(ox)}\cdot 3\text{H}_2\text{O}$  crystals were analysed again to confirm that no transformation to the thermodynamically stable  $\text{Ca(ox)}\cdot\text{H}_2\text{O}$  had occurred. During the solubility experiments the concentration of  $\text{Ca}^{2+}$  was continuously measured by a calcium ion selective electrode (ISE in Figure VI-9 and Figure VI-10). In addition, the total dissolved Ca concentrations were also measured by atomic adsorption spectroscopy (AAS in Figure VI-9 and Figure VI-10). The latter data have been used to recalculate a full speciation in this review, whereas the ISE data are assumed to represent free  $\text{Ca}^{2+}$  concentrations.

The results of these recalculations are summarised in Table VI-14 and shown in Figure VI-9 and Figure VI-10.

No attempt has been made in this review to assess individual uncertainties of the calculated solubility products. In the case of series of data derived for a certain temperature but varying ionic strength unweighted averages were calculated with 95% confidence intervals (Table VI-14).

Figure VI-9 and Figure VI-10 reveal that the re-evaluated solubility products, extrapolated to zero ionic strength with parameters selected and estimated in this review, do not show any systematic ionic strength dependence, which is an indication of the internal consistency of the speciation model derived in this review. Especially the applicability of SIT using the interaction parameter  $\varepsilon(\text{ox}^{2-}, \text{Na}^+)$  derived from oxalate protonation reactions but without considering a complex  $\text{Na}(\text{ox})^-$  in the speciation model (*cf.* Section VI.3) is corroborated by the consistent results obtained at  $I_m > 0.1$  M NaCl.

Figure VI-9: Solubility products of calcium oxalate hydrates at 25°C, calculated from analytical solubility data and extrapolated to zero ionic strength using parameters discussed in the text.

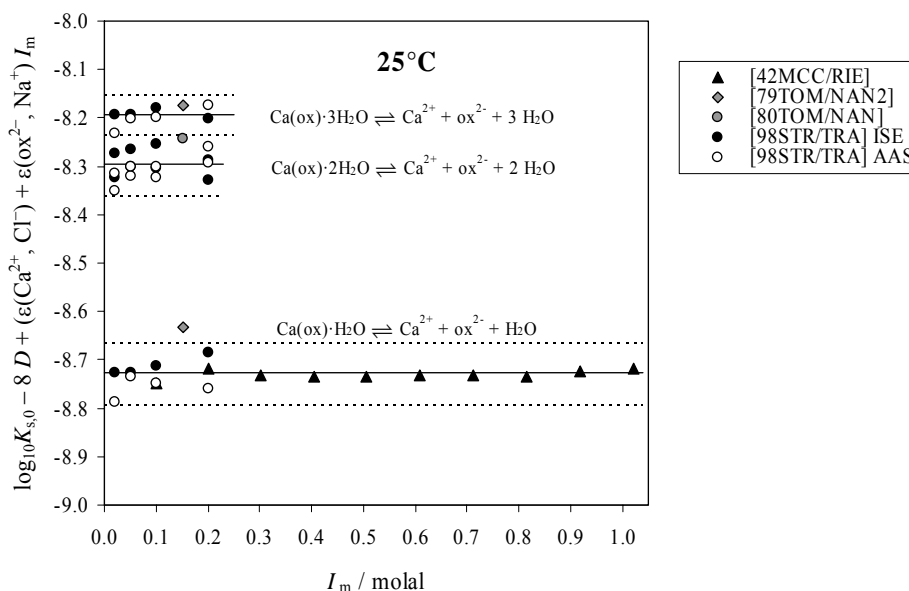
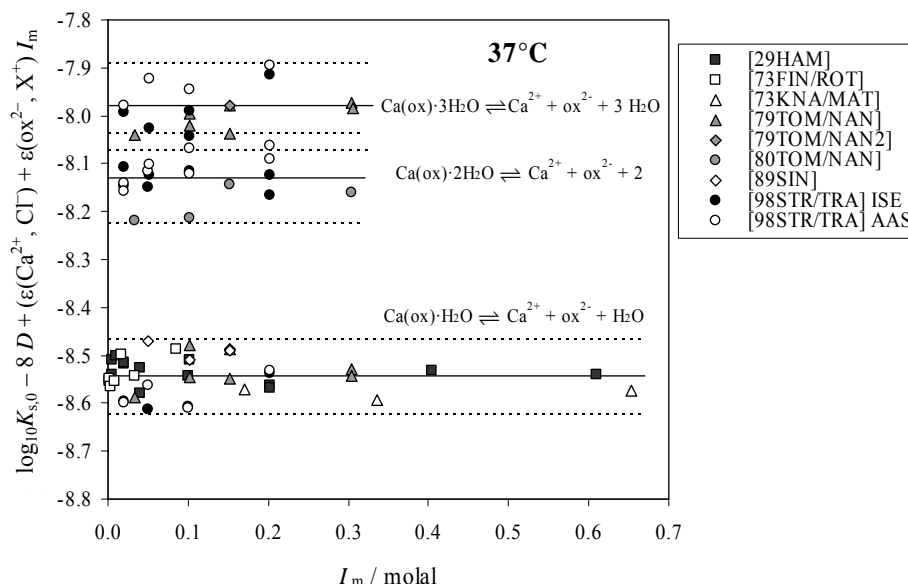


Figure VI-10: Solubility products of calcium oxalate hydrates at 37°C, calculated from analytical solubility data and extrapolated to zero ionic strength using parameters discussed in the text.



The data shown in Figure VI-9 and Figure VI-10 have been used to calculate global unweighted averages of solubility products at 25 and 37°C. The results obtained for 25°C have been selected:

$$\log_{10} K_{s,0}^o \text{ (VI.14)} = -(8.73 \pm 0.06)$$

$$\log_{10} K_{s,0}^o \text{ (VI.15)} = -(8.30 \pm 0.06)$$

$$\log_{10} K_{s,0}^o \text{ (VI.16)} = -(8.19 \pm 0.04)$$

whereas the results obtained for 37°C,  $\log_{10} K_{s,0} \text{ (VI.14)} = -(8.54 \pm 0.08)$ ,  $\log_{10} K_{s,0} \text{ (VI.15)} = -(8.13 \pm 0.09)$ , and  $\log_{10} K_{s,0} \text{ (VI.16)} = -(7.98 \pm 0.09)$  are used for consistency checks of the selected reaction enthalpies (Figure VI-11).

The solubility of  $\text{Ca(ox)} \cdot \text{H}_2\text{O}$  in 0.03 to 0.50 M KCl at 37°C has been measured by Daniele *et al.* [85DAN/SON]. The analytical solubility data are not reported, only calculated solubility products are given. However, the speciation model applied and the constants used by Daniele *et al.* are very similar to the ones selected by this review, and the solubility products were extrapolated to zero ionic strength using SIT in [85DAN/SON]. The reported result,  $\log_{10} K_{s,0} \text{ (VI.14)} = -8.55$ , is in good agreement with the value obtained from data mainly in NaCl at 37°C,  $\log_{10} K_{s,0} \text{ (VI.14)} = -(8.54 \pm 0.08)$ , in this review.

Enthalpies of dissolution or precipitation of calcium oxalate hydrates reported in the literature (Table VI-15) have either been derived from the temperature dependence of solubility products [74NAN/GAR], [79TOM/NAN2], [80TOM/NAN], [98STR/TRA] (method “ $\partial pK_a/\partial T$ ” in Table VI-15), or have been measured calorimetrically [74NAN/GAR], [92VEL/SOH], [93SOH/COS], [97SOH/KRO], [98STR/TRA].

Table VI-15: Enthalpies of dissolution of calcium oxalate hydrates reported in the literature and re-evaluated in this review. If not stated otherwise, the enthalpy values refer to 25°C.

Method	$\Delta_{\text{sol}} H_m^{\circ \text{ a}}$ (kJ·mol <sup>-1</sup> )	$\Delta_{\text{sol}} H_m^{\circ \text{ b}}$ (kJ·mol <sup>-1</sup> )	Reference
<b>Ca(ox)·H<sub>2</sub>O(cr) <math>\rightleftharpoons</math> Ca<sup>2+</sup> + ox<sup>2-</sup> + H<sub>2</sub>O(l)</b>			
cal	(22.3 ± 0.4) <sup>c</sup>	(22.3 ± 0.8)	[74NAN/GAR]
$\partial pK_a / \partial T$	(23.0 ± 0.4)		
$\partial pK_a / \partial T$	(17.3 ± 1.3)	(20.8 ± 3.0)	[79TOM/NAN2]
cal	(18.1 ± 0.4) <sup>c</sup>		[92VEL/SOH]
cal	17.5 <sup>c</sup>		[93SOH/COS]
cal	(19.83 ± 1.24) <sup>c</sup>	(19.8 ± 2.9)	[97SOH/KRO]
	(16.69 ± 0.58) <sup>c, d</sup>		
$\partial pK_a / \partial T$	(18.9 ± 0.9)	(23.0 ± 2.7)	[98STR/TRA]
cal	(20.8 ± 0.8)	(20.8 ± 0.8)	
<b>Ca(ox)·2H<sub>2</sub>O(cr) <math>\rightleftharpoons</math> Ca<sup>2+</sup> + ox<sup>2-</sup> + 2 H<sub>2</sub>O(l)</b>			
$\partial pK_a / \partial T$	(14.1 ± 1.3)		[80TOM/NAN]
$\partial pK_a / \partial T$	(25.6 ± 0.5)	(27.1 ± 2.0)	[98STR/TRA]
cal	(24.3 ± 1.4) <sup>c</sup>	(24.3 ± 1.4)	
<b>Ca(ox)·3H<sub>2</sub>O(cr) <math>\rightleftharpoons</math> Ca<sup>2+</sup> + ox<sup>2-</sup> + 3 H<sub>2</sub>O(l)</b>			
$\partial pK_a / \partial T$	(25.1 ± 0.7)	(28.0 ± 1.9)	[79TOM/NAN2]
$\partial pK_a / \partial T$	(32.1 ± 1.2)	(33.2 ± 3.3)	[98STR/TRA]
cal	(30.5 ± 2.3)	(30.5 ± 2.3)	

a: Values and uncertainties given as reported in the literature.

b: Values and uncertainties re-evaluated and accepted by this review (see text for details).

c: Value obtained from precipitation, multiplied by (−1).

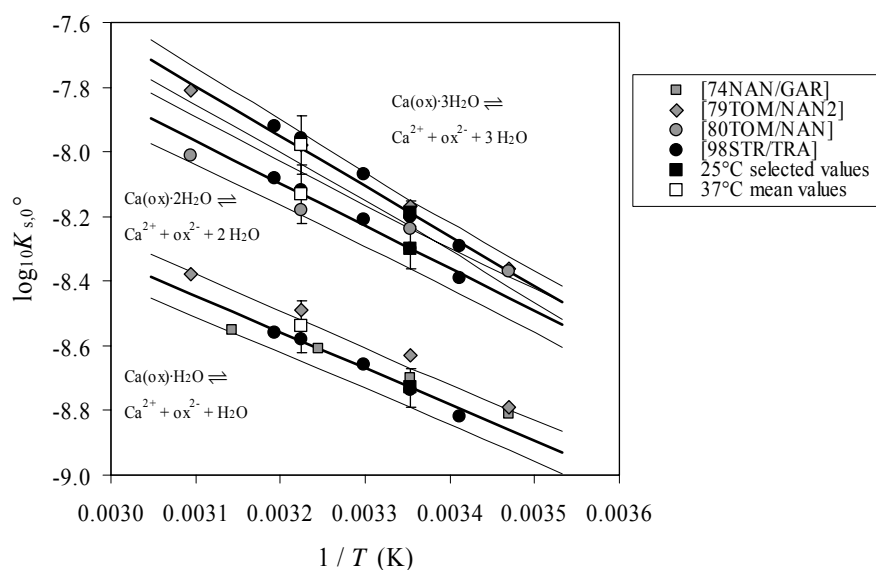
d: Enthalpy value refers to 37°C.

The temperature dependence of solubility products  $\log_{10} K_{s,0}$ , recalculated in this review from analytical solubility data reported in [79TOM/NAN2] and [98STR/TRA] (Table VI-14) has been described by a constant enthalpy model, *i.e.*, assuming  $\Delta_{\text{sol}} C_{p,m}^{\circ} = 0$ . The results of least-squares fits of unweighted  $\log_{10} K_{s,0}$  values,  $\Delta_{\text{sol}} H_m^{\circ}$  with 95% confidence intervals are summarised in Table VI-15.

Solubility products reported by Nancollas and Gardner [74NAN/GAR] are given as numbers only without any further details. No analytical equilibrium solubility data are provided which would allow consistency checks and recalculations. Attempts by this review to reproduce the reported enthalpy  $\Delta_{\text{sol}} H_m^{\circ} = (23.0 \pm 0.4)$  kJ·mol<sup>-1</sup>,

claimed to be derived from the reported solubility products [74NAN/GAR], failed and hence, this value has not been included in the final data analysis.

Figure VI-11: Temperature dependence of solubility products of calcium oxalate hydrates. The lines are calculated using  $\log_{10} K_{s,0}^{\circ}$  and  $\Delta_{\text{sol}} H_{\text{m}}^{\circ}$  values selected in this review with their assigned uncertainties.



The solubility products recalculated in this review from analytical solubility data reported in [80TOM/NAN] seem to belong to two discrepant data sets (Figure VI-11). Enthalpy values derived from data at 15 and 25°C, as well as from 37 and 50°C agree well with results obtained from [98STR/TRA] data and with the temperature variation of average solubility products at 25 and 37°C calculated in this review. However, an overall fit of all [80TOM/NAN] data results in  $\Delta_{\text{sol}} H_{\text{m}}^{\circ} = (17.3 \pm 4.3) \text{ kJ} \cdot \text{mol}^{-1}$ , a value clearly discrepant with all other enthalpies listed in Table VI-15, which has not been included in the final data analysis.

Velich and co-workers published three papers describing an isoperibolic reaction twin calorimeter and measurements of the enthalpy of  $\text{Ca(ox)} \cdot \text{H}_2\text{O(cr)}$  precipitation [92VEL/SOH], [93SOH/COS], [97SOH/KRO]. In the first paper [92VEL/SOH] no characterisation of the precipitating solids is reported. In the second paper [93SOH/COS] they state that “in all experiments crystals of characteristic  $\text{Ca(ox)} \cdot \text{H}_2\text{O(cr)}$  shape were formed”. In the third paper [97SOH/KRO] they state that “ $\text{Ca(ox)} \cdot \text{H}_2\text{O(cr)}$  precipitated as a single solid phase under studied conditions, as determined by X-ray diffraction”. The somewhat discrepant results obtained over time by the

same method are not discussed in [93SOH/COS] or [97SOH/KRO]. Taking the improvements in characterisation of the solid as an indicator of improvement of the quality in experimental procedures, this review considers the results of [97SOH/KRO] as reliable and an unweighted average of reported results (Table 1 in [97SOH/KRO]) with a 95% confidence interval is included in the final data analysis.

Weighted means of the accepted values (Table VI-15) were selected:

$$\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{VI.14}) = (21.5 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{VI.15}) = (25.2 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{VI.16}) = (29.7 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

The temperature dependence of solubility products reported by [74NAN/GAR] and recalculated in this review from data given in [79TOM/NAN2], [80TOM/NAN] and [98STR/TRA] is consistent, within the estimated confidence intervals, with the values calculated using solubility products and solution enthalpies selected in this review (Figure VI-11).

The values selected in this review for Reaction (VI.14),  $\Delta_{\text{sol}}G_{\text{m}}^{\circ}(298.15 \text{ K}) = -R\cdot T^{\circ}\cdot\ln(10)\cdot\log_{10}K_{\text{s},0}^{\circ} = (49.83 \pm 0.34) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_{\text{sol}}H_{\text{m}}^{\circ} = (21.5 \pm 0.5) \text{ kJ}\cdot\text{mol}^{-1}$ , ( $T^{\circ}$  is the reference temperature, 298.15 K), are used to calculate  $\Delta_{\text{sol}}S_{\text{m}}^{\circ} = (\Delta_{\text{sol}}H_{\text{m}}^{\circ} - \Delta_{\text{sol}}G_{\text{m}}^{\circ}) / T^{\circ} = - (95.0 \pm 2.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . From Reaction (VI.14)  $\Delta_{\text{sol}}S_{\text{m}}^{\circ} = S_{\text{m}}^{\circ}(\text{Ca}^{2+}) + S_{\text{m}}^{\circ}(\text{ox}^{2-}) + S_{\text{m}}^{\circ}(\text{H}_2\text{O}, \text{l}) - S_{\text{m}}^{\circ}(\text{Ca}(\text{ox})\cdot\text{H}_2\text{O}, \text{cr})$ , using CODATA values  $S_{\text{m}}^{\circ}(\text{Ca}^{2+}) = - (56.2 \pm 1.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $S_{\text{m}}^{\circ}(\text{H}_2\text{O}, \text{l}) = (69.95 \pm 0.03) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , and  $S_{\text{m}}^{\circ}(\text{Ca}(\text{ox})\cdot\text{H}_2\text{O}, \text{cr}) = (156.4 \pm 2.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  selected in this review, the selected value of the standard molar entropy of the oxalate anion is calculated:

$$S_{\text{m}}^{\circ}(\text{ox}^{2-}, 298.15 \text{ K}) = (47.6 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The standard molar entropy of formation,  $\Delta_{\text{f}}S_{\text{m}}^{\circ} = S_{\text{m}}^{\circ}(\text{ox}^{2-}) - 2\cdot S_{\text{m}}^{\circ}(\text{C}, \text{cr}) - 2\cdot S_{\text{m}}^{\circ}(\text{O}_2, \text{g}) + (n/2)\cdot S_{\text{m}}^{\circ}(\text{H}_2, \text{g})$ , is calculated using the CODATA values  $S_{\text{m}}^{\circ}(\text{C}, \text{cr}) = (5.74 \pm 0.10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ,  $S_{\text{m}}^{\circ}(\text{O}_2, \text{g}) = (205.152 \pm 0.005) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , and  $S_{\text{m}}^{\circ}(\text{H}_2, \text{g}) = (103.680 \pm 0.003) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , where  $n = -2$  is the charge of the oxalate anion,

$$\Delta_{\text{f}}S_{\text{m}}^{\circ}(\text{ox}^{2-}, 298.15 \text{ K}) = - (504.9 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

According to the equation,  $\Delta_{\text{f}}G_{\text{m}}^{\circ}(298.15 \text{ K}) = \Delta_{\text{f}}H_{\text{m}}^{\circ} - T\cdot\Delta_{\text{f}}S_{\text{m}}^{\circ}$ , using  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{ox}^{2-}, 298.15 \text{ K}) = - (830.7 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$  selected in this review (*cf.* Section VI.2.3), the standard molar Gibbs energy of formation of the oxalate anion is selected:

$$\Delta_{\text{f}}G_{\text{m}}^{\circ}(\text{ox}^{2-}, 298.15 \text{ K}) = - (680.1 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}.$$

This value may be combined with  $S_{\text{m}}^{\circ}(\text{ox}^{2-}, 298.15 \text{ K})$  and with the selected equilibrium constants and enthalpy changes for reactions (VI.14), (VI.15) and (VI.16). Using auxiliary data for  $\text{H}_2\text{O}(\text{l})$  and  $\text{Ca}^{2+}$  it is possible to calculate the standard molar free energies of formation, enthalpies of formation and entropies for  $\text{Ca}(\text{ox})\cdot\text{H}_2\text{O}(\text{cr})$ ,

$\text{Ca(ox)}\cdot 2\text{H}_2\text{O(cr)}$  and  $\text{Ca(ox)}\cdot 3\text{H}_2\text{O(cr)}$  at 298.15 K. The results are given in Table VI-16.

Table VI-16: Selected formation data for  $\text{Ca(ox)}\cdot \text{H}_2\text{O(cr)}$ ,  $\text{Ca(ox)}\cdot 2\text{H}_2\text{O(cr)}$  and  $\text{Ca(ox)}\cdot 3\text{H}_2\text{O(cr)}$ .

	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
$\text{Ca(ox)}\cdot \text{H}_2\text{O(cr)}$ ,	$-(1519.9 \pm 2.1)$	$-(1681.0 \pm 1.9)$	$(156.4 \pm 2.0)$
$\text{Ca(ox)}\cdot 2\text{H}_2\text{O(cr)}$	$-(1754.6 \pm 2.1)$	$-(1970.5 \pm 2.2)$	$(205.7 \pm 5.0)$
$\text{Ca(ox)}\cdot 3\text{H}_2\text{O(cr)}$	$-(1991.1 \pm 2.1)$	$-(2260.8 \pm 2.3)$	$(258.4 \pm 5.5)$

The selected formation data for  $\text{ox}^{2-}$  and the selected reaction data for Reaction (VI.9),  $r = 1$  (see Section VI.3.4, page 143) yield:

$$\Delta_f G_m^\circ(\text{Hox}^-, 298.15 \text{ K}) = -(704.4 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

$$S_m^\circ(\text{Hox}^-, 298.15 \text{ K}) = (153.4 \pm 3.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Compounds of the type  $\text{CaM}_2(\text{ox})_2\cdot \text{H}_2\text{O}$  ( $M = \text{K, Rb, Cs}$ ) [27SCH/GAD] and  $\text{CaK(ox)(HCOO)}\cdot \text{H}_2\text{O}$  [27SCH2] have been prepared from boiling solutions in crystalline form, and their stoichiometry has been confirmed by elemental analysis. However, all these compounds do not exhibit congruent equilibrium solubility but rapidly decompose in water by releasing alkali oxalate or formate, respectively, and hence no thermodynamic data are available for any of these compounds.

Synthesis and thermal decomposition studies of  $\text{Ca}[\text{Ca(ox)}_2]\cdot 2\text{H}_2\text{O(cr)}$  have been reported [96DEB/BAR]. However, the authors failed to show, *e.g.*, by X-ray powder diffraction, that the compound they worked with was structurally different from whewellite,  $\text{Ca(ox)}\cdot \text{H}_2\text{O(cr)}$ .

## VI.5.2 Magnesium and calcium oxalate complexes

Complex formation in Mg and Ca oxalate systems has been studied by several investigators by a variety of experimental methods. The equilibrium data found in the literature are summarised in Table VI-17.

Table VI-17: Experimental equilibrium data for the Mg and Ca oxalate systems. The uncertainties are given as reported in the references.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Mg}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Mg(ox)(aq)}$				
con	$\rightarrow 0$	18	3.43	<a href="#">[27DAV]</a> , <a href="#">[32MON/DAV]</a>
ise-H	0.2 M (KCl)	25	2.55	<a href="#">[38CAN/KIB]</a>
sol	0.32 M NaCl	37	2.28	<a href="#">[39PED]</a>
con	$\rightarrow 0$	18	3.41	
pot	1 M KNO <sub>3</sub>	27	1.99	<a href="#">[57LEF]</a>
ise-Hg	0.10 M NaNO <sub>3</sub>	20	(2.76 $\pm$ 0.04)	<a href="#">[57SCH/AND]</a>
sp	0.10 M NaCl	20	(2.76 $\pm$ 0.10)	<a href="#">[60RAA]</a>
(a)	0.2 M KCl + 0.1 M Tris	23	2.61	<a href="#">[62ASA/MOR]</a>
dis	0.1 M KClO <sub>4</sub>	20	(2.39 $\pm$ 0.05)	<a href="#">[63STA]</a>
sp	$\approx$ 0.1 M Tris buffer	25	2.88	<a href="#">[63WAT/TRO]</a>
	$\approx$ 0.1 M Tea buffer		2.90	
gl	0.10 M NaClO <sub>4</sub>	25	(3.10 $\pm$ 0.05)	<a href="#">[75PRA/JON]</a>
sol	0.5 M NaClO <sub>4</sub>	25	1.62	<a href="#">[77FED/KHO]</a>
	1		1.52	
	2		1.44	
	3		1.40	
	4		1.37	
	6		1.34	
	8		1.32	
gl	0.03 M Et <sub>4</sub> NI	37	(3.02 $\pm$ 0.03)	<a href="#">[82DAN/MAR]</a>
	0.05		(2.92 $\pm$ 0.03)	
	0.10		(2.75 $\pm$ 0.04)	
	0.30		(2.54 $\pm$ 0.04)	
	0.50		(2.52 $\pm$ 0.04)	
	$\rightarrow 0$		3.58	
pot	0.10 M KNO <sub>3</sub>	35	4.65	<a href="#">[85RED/RAO]</a>
pot	1.0 M NaClO <sub>4</sub>	30 ?	2.65	<a href="#">[88GHA/MAN]</a>
cou	0.15 M NaCl	25	2.18	<a href="#">[93GLA/MAJ]</a>
		37	2.39	
pot	0.3 m NaCl	25	(2.33 $\pm$ 0.04)	<a href="#">[2001CHO/BON]</a>
	1 m		(2.00 $\pm$ 0.01)	
	2 m		(1.94 $\pm$ 0.02)	
	3 m		(1.77 $\pm$ 0.08)	
	4 m		(1.99 $\pm$ 0.01)	
	5 m		(2.00 $\pm$ 0.06)	

(Continued on next page)



Table VI-17 (continued)

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Mg}^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Mg}(\text{ox})_2^{2-}$				
sol	→ 0	25	4.37	[51BAR/ARG]
ise-ox	0.089 M	25	4.24	[59TEK/VIN2]
	0.049 M		4.54	
	0.031 M		4.54	
pot	0.3 m NaCl	25	(4.00 ± 0.01)	[2001CHO/BON]
	1 m		(3.71 ± 0.01)	
	2 m		(3.73 ± 0.06)	
	3 m		(3.79 ± 0.09)	
	4 m		(4.07 ± 0.08)	
	5 m		(3.99 ± 0.06)	
$\text{Mg}(\text{ox})(\text{aq}) + \text{ox}^{2-} \rightleftharpoons \text{Mg}(\text{ox})_2^{2-}$				
ise-Hg	0.1 M (NaNO <sub>3</sub> )	20	< 1	[57SCH/AND]
$\text{Mg}^{2+} + \text{Hox}^- \rightleftharpoons \text{Mg}(\text{Hox})^+$				
ise-H	0.2 M (KCl)	25	≈ 0.5	[38CAN/KIB]
$\text{Ca}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Ca}(\text{ox})(\text{aq})$				
con	→ 0	18	3.00	[32MON/DAV]
dis	1 M NaClO <sub>4</sub>	25	1.64	[67HAS/MAK]
cix	0.05 M NaCl	25	3.07	[68GOR/FIL]
em	0.1 M (K,H)NO <sub>3</sub>	25	(2.30 ± 0.07)	[70STE/PAZ]
cix	0.02 NaClO <sub>4</sub> -Na <sub>2</sub> ox	25	(2.08 ± 0.04)	[72ARM/DUN]
	0.04		(2.08 ± 0.04)	
	0.06		(2.11 ± 0.03)	
	0.08		(2.20 ± 0.03)	
	0.10		(2.10 ± 0.03)	
	0.20		(2.06 ± 0.04)	
sp	→ 0	38	(3.37 ± 0.01)	[73FIN/SMI]
con	→ 0	25	(3.19 ± 0.01)	[74NAN/GAR]
gl	0.10 M NaClO <sub>4</sub>	25	(3.5 ± 0.05)	[75PRA/JON]
dis	0.5 M NH <sub>4</sub> NO <sub>3</sub>	25	(1.95 ± 0.01)	[76MCD/KEL]
ise-Ca	0.05 M NaCl	25	(2.70 ± 0.03)	[79CRA/MOO]
	0.10		(2.54 ± 0.09)	
	0.15		(1.99 ± 0.04)	
ise-Ca	0.03 M Et <sub>4</sub> NI	37	(2.72 ± 0.04)	[82DAN/MAR]
	0.05		(2.61 ± 0.04)	
	0.10		(2.46 ± 0.05)	
	0.30		(2.23 ± 0.05)	
	0.50		(2.22 ± 0.06)	
	→ 0		3.27	
gl, ise-Ca	0.0015 M	37	(2.24 ± 0.04)	[82RAO/AGA]
pot	0.10 M KNO <sub>3</sub>	35	4.85	[85RED/RAO]
cou	0.15 M NaCl	25	1.46	[93GLA/MAJ]

(Continued on next page)

Table VI-17 (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Ca}^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Ca(ox)}_2^{2-}$				
dis	1 M NaClO <sub>4</sub>	25	2.68	<a href="#">[67HAS/MAK]</a>
sol	$\rightarrow 0$	20	3.49	<a href="#">[71PAZ/STE]</a>
$\text{Ca}^{2+} + \text{Hox}^- \rightleftharpoons \text{Ca(Hox)}^+$				
cix	0.1 M HClO <sub>4</sub> – H <sub>2</sub> ox	25	(1.38 ± 0.09)	<a href="#">[73ARM/DUN]</a>
$\text{Ca}^{2+} + 2 \text{Hox}^- \rightleftharpoons \text{Ca(Hox)}_2(\text{aq})$				
cix	0.1 M HClO <sub>4</sub> – H <sub>2</sub> ox	25	≈ 1.84	<a href="#">[73ARM/DUN]</a>

a: Refractive index measurements with an interferometer.

The stabilities of Mg oxalate 1:1 and 1:2 complexes are in a range suitable for direct determination by alkalimetric titration (Figure VI-12 and Figure VI-13).

Figure VI-12: Simulated titration curves in 0.3 molal NaCl (left) and 3 molal NaCl (right) of  $2 \times 10^{-4}$  molal H<sub>2</sub>ox(aq) (upper curve) and  $2 \times 10^{-4}$  molal H<sub>2</sub>ox(aq) and  $2 \times 10^{-4}$  molal MgCl<sub>2</sub> (lower curve). The dotted lines are calculated neglecting the complex Mg(ox)<sub>2</sub><sup>2-</sup> in the latter case. The symbol  $a$  denotes the moles of base added per moles of ligand present in solution. Stability constants selected in this review have been used to calculate the titration curves.

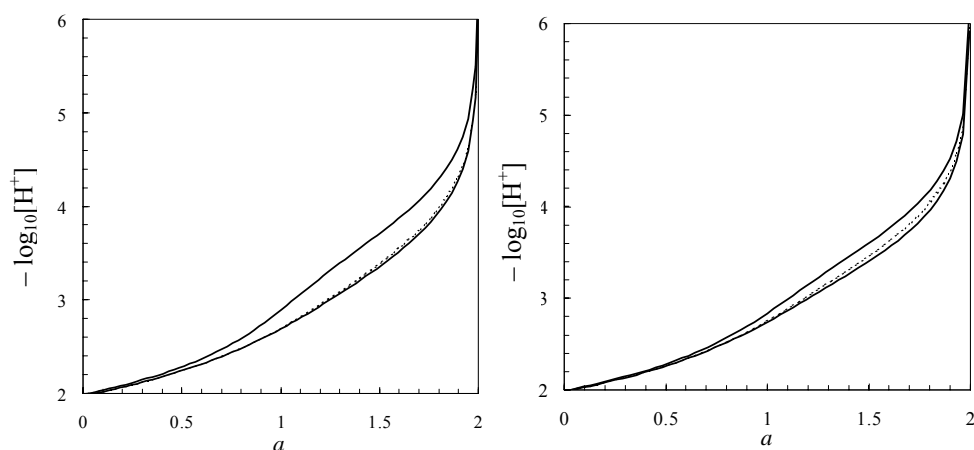
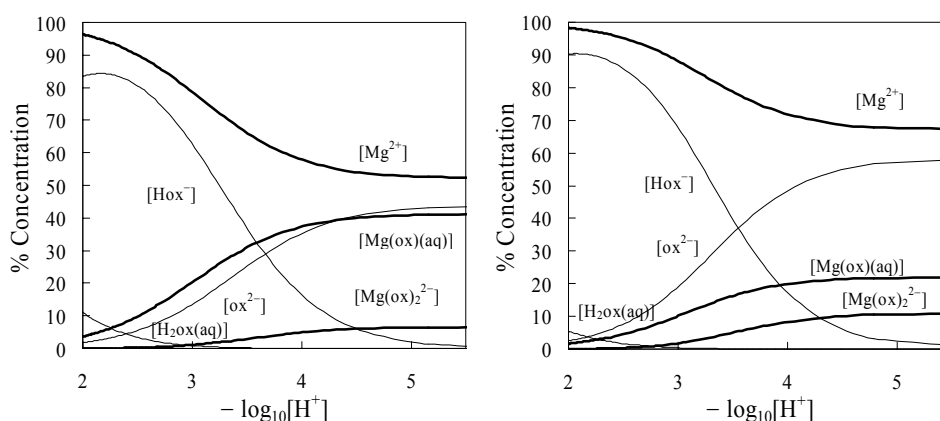


Figure VI-13: Distribution of complex species in the simulated titration of the Mg oxalate system (Figure VI-12) in 0.3 m NaCl (left) and 3 m NaCl (right).



In the concentration range  $[Mg], [ox] < 10^{-3}$  M and low ionic strength the complex  $Mg(ox)_2^{2-}$  is a minor species and its impact on the titration curve is very small (Figure VI-12 and Figure VI-13 left), whereas its relative influence increases with increasing ionic strength (Figure VI-12 and Figure VI-13 right). This behaviour explains why generally in studies carried out at low ionic strength the results were interpreted in terms of  $Mg(ox)(aq)$  only.

The literature data collected in Table VI-17 have been scrutinised in order to select reliable studies, summarised in Table VI-18, on which the evaluation of recommended values is based.

Because of various shortcomings in the experimental procedures or the reporting of the results, the values of [27DAV], [32MON/DAV], [59TEK/VIN2], [62ASA/MOR], [63STA], [63WAT/TRO], [75PRA/JON], [77FED/KHO], [85RED/RAO], [88GHA/MAN], [93GLA/MAJ] have been discarded (see detailed discussions in Appendix A). The values for Mg oxalate complexation derived from  $Mg(ox) \cdot 2H_2O(cr)$  solubility measurements [51BAR/ARG] are not used in the final data analysis because of the uncertainties due to the slow reaction kinetics of magnesium oxalate (see discussion in Section VI.5.1).

The species  $Mg(Hox)^+$  has been postulated in a single titration study [38CAN/KIB], but with the remark that the reported formation constant is “highly tentative”. The existence of protonated Mg oxalate complexes remains to be shown by other techniques, and thus  $Mg(Hox)^+$  is disregarded by this review.

Table VI-18: Accepted equilibrium data for the Mg and Ca oxalate systems. The uncertainties are estimated in this review.

Ionic medium	$t$ (°C)	$\log_{10} K$	$\log_{10} K^o$	Reference
$\text{Mg}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Mg(ox)(aq)}$				
0.2 M (KCl)	25	$(2.55 \pm 0.20)$	$(3.59 \pm 0.20)^a$	<a href="#">[38CAN/KIB]</a>
0.32 M NaCl	37	$(2.28 \pm 0.10)$	$(3.52 \pm 0.10)$	<a href="#">[39PED]</a>
1 M KNO <sub>3</sub>	27	$(1.99 \pm 0.20)$	$(3.38 \pm 0.20)^a$	<a href="#">[57LEF]</a>
0.10 M NaNO <sub>3</sub>	20	$(2.76 \pm 0.08)$	$(3.62 \pm 0.08)^a$	<a href="#">[57SCH/AND]</a>
0.10 M NaCl	20	$(2.76 \pm 0.20)$	$(3.61 \pm 0.20)$	<a href="#">[60RAA]</a>
0.03 M Et <sub>4</sub> NI	37	$(3.02 \pm 0.10)$		<a href="#">[82DAN/MAR]</a>
0.05		$(2.92 \pm 0.10)$		
0.10		$(2.75 \pm 0.10)$		
0.30		$(2.54 \pm 0.10)$		
0.50		$(2.52 \pm 0.10)$	$(3.58 \pm 0.07)^b$	
0.3 m NaCl	25	$(2.33 \pm 0.10)$		<a href="#">[2001CHO/BON]</a>
1 m		$(2.00 \pm 0.10)$		
2 m		$(1.94 \pm 0.10)$		
3 m		$(1.77 \pm 0.16)$		
4 m		$(1.99 \pm 0.10)$		
5 m		$(2.00 \pm 0.12)$	$(3.52 \pm 0.08)^c$	
			$(3.56 \pm 0.04)$	weighted mean
$\text{Mg}^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Mg(ox)}_2^{2-}$				
0.3 m NaCl	25	$(4.00 \pm 0.10)$		<a href="#">[2001CHO/BON]</a>
1 m		$(3.71 \pm 0.10)$		
2 m		$(3.73 \pm 0.12)$		
3 m		$(3.79 \pm 0.18)$		
4 m		$(4.07 \pm 0.16)$		
5 m		$(3.99 \pm 0.12)$	$(5.17 \pm 0.08)^d$	
$\text{Ca}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Ca(ox)(aq)}$				
1 M NaClO <sub>4</sub>	25	$(1.64 \pm 0.20)$	$(3.06 \pm 0.20)^e$	<a href="#">[67HAS/MAK]</a>
0.1 M (K,H)NO <sub>3</sub>	25	$(2.35 \pm 0.10)$	$(3.21 \pm 0.10)^e$	<a href="#">[70STE/PAZ]</a>
→ 0	25	$(3.19 \pm 0.10)$	$(3.19 \pm 0.10)$	<a href="#">[74NAN/GAR]</a>
0.5 M NH <sub>4</sub> NO <sub>3</sub>	25	$(1.83 \pm 0.08)$	$(3.18 \pm 0.13)^{e,f}$	<a href="#">[76MCD/KEL]</a>
			$(3.19 \pm 0.06)$	weighted mean
0.03 M Et <sub>4</sub> NI	37	$(2.72 \pm 0.10)$		<a href="#">[82DAN/MAR]</a>
0.05		$(2.61 \pm 0.10)$		
0.10		$(2.46 \pm 0.10)$		
0.30		$(2.23 \pm 0.10)$		
0.50		$(2.22 \pm 0.12)$	$(3.27 \pm 0.07)^g$	

(Continued on next page)

Table VI-18 (continued)

Ionic medium	<i>t</i> (°C)	$\log_{10} K$	$\log_{10} K^0$	Reference
$\text{Ca(ox)(aq)} + \text{ox}^{2-} \rightleftharpoons \text{Ca(ox)}_2^{2-}$				
1 M NaClO <sub>4</sub>	25	(1.04 ± 0.25)	(0.95 ± 0.29) <sup>e, h</sup>	[67HAS/MAK]
0.5 M NH <sub>4</sub> NO <sub>3</sub>	25	(0.86 ± 0.22)	(0.74 ± 0.25) <sup>e, f, h</sup>	[76MCD/KEL]
			(0.83 ± 0.19)	weighted mean
a: Extrapolated to zero ionic strength assuming that $\varepsilon(\text{Mg(ox)(aq),NaCl}) \approx \varepsilon(\text{Mg(ox)(aq),KCl}) = \varepsilon(\text{Mg(ox)(aq),NaNO}_3) = \varepsilon(\text{Mg(ox)(aq),KNO}_3) = (0.0 \pm 0.1)$ .				
b: Weighted least squares SIT-regression according to Figure VI-14.				
c: Weighted least squares SIT-regression according to Figure VI-15.				
d: Weighted least squares SIT-regression according to Figure VI-16.				
e: Extrapolated to zero ionic strength assuming that $\varepsilon(\text{Mg(ox)(aq),NaCl}) \approx \varepsilon(\text{Ca(ox)(aq),NaClO}_4) = \varepsilon(\text{Ca(ox)(aq),KNO}_3) = \varepsilon(\text{Ca(ox)(aq),NH}_4\text{NO}_3) = (0.0 \pm 0.1)$ .				
f: Extrapolated to zero ionic strength assuming that $\varepsilon(\text{ox}^{2-}, \text{K}^+) \approx \varepsilon(\text{ox}^{2-}, \text{NH}_4^+) = (0.07 \pm 0.20)$ .				
g: Weighted least squares SIT-regression according to Figure VI-17.				
h: Extrapolated to zero ionic strength assuming that $\varepsilon(\text{Mg(ox)}_2^{2-}, \text{Na}^+) \approx \varepsilon(\text{Ca(ox)}_2^{2-}, \text{Na}^+) = \varepsilon(\text{Ca(ox)}_2^{2-}, \text{NH}_4^+) = -(0.15 \pm 0.10)$ .				

A weighted least squares SIT regression plot of the data reported in [2001CHO/BON] for the reaction



reveals that the SIT interaction coefficient for Mg(ox)(aq) actually is zero (Figure VI-14). Hence, it has been assumed that  $\varepsilon(\text{Mg(ox)(aq),NaCl}) \approx \varepsilon(\text{Mg(ox)(aq),KCl}) = \varepsilon(\text{Mg(ox)(aq),NaNO}_3) = \varepsilon(\text{Mg(ox)(aq),KNO}_3) = (0.0 \pm 0.1)$ , and using  $\varepsilon(\text{Mg}^{2+}, \text{Cl}^-) = (0.19 \pm 0.02)$  and  $\varepsilon(\text{Mg}^{2+}, \text{NO}_3^-) = (0.17 \pm 0.01)$  (*cf.* Appendix B), and  $\varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.08 \pm 0.01)$  and  $\varepsilon(\text{ox}^{2-}, \text{K}^+) = (0.07 \pm 0.08)$  selected in this review, the values of [38CAN/KIB], [39PED], [57LEF], [57SCH/AND] and [60RAA] were extrapolated to zero ionic strength (Table VI-18).

Figure VI-14: Weighted least squares SIT-regression plot of equilibrium data from [\[2001CHO/BON\]](#) for the formation of  $\text{Mg}(\text{ox})(\text{aq})$  according to Reaction (VI.17) in  $\text{NaCl}$  at  $25^\circ\text{C}$ . The results are  $\log_{10} K_1^\circ (\text{VI.17}) = (3.52 \pm 0.08)$  and  $\varepsilon(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl}) = (0.00 \pm 0.03)$ .

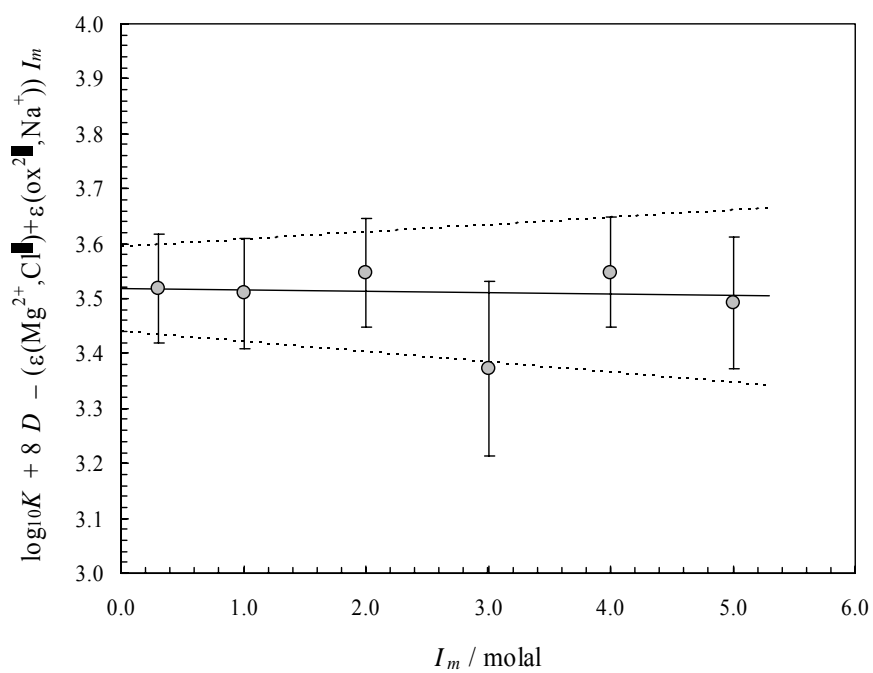
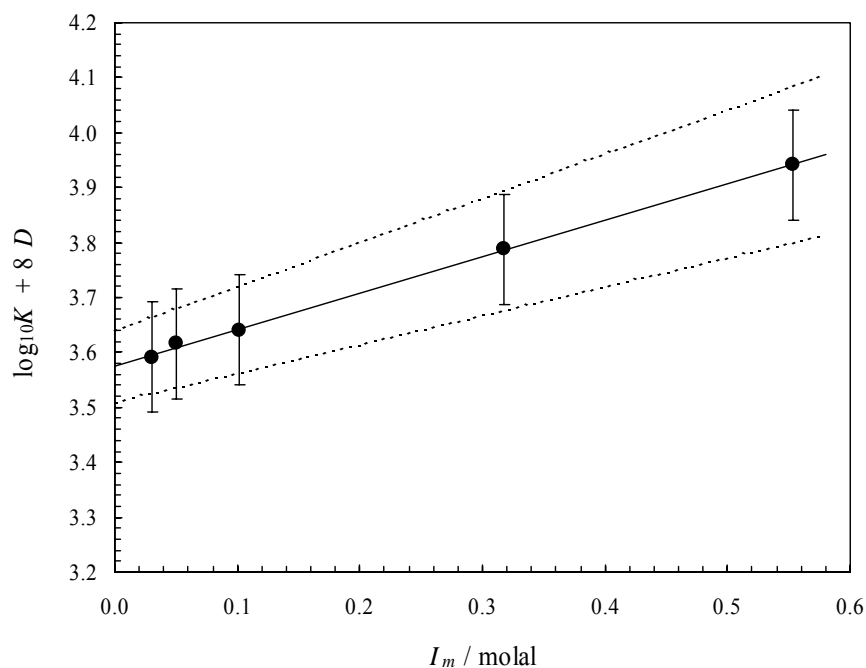


Figure VI-15: Weighted least squares SIT-regression plot of equilibrium data from [82DAN/MAR] for the formation of  $\text{Mg(ox)(aq)}$  according to Reaction (VI.17) in  $\text{Et}_4\text{NI}$  at  $37^\circ\text{C}$ . The results are  $\log_{10} K_1^\circ (\text{VI.17}) = (3.58 \pm 0.07)$  and  $\Delta\varepsilon = -(0.66 \pm 0.22)$ .



No systematic temperature effect can be detected in Table VI-18 for the  $\text{Mg(ox)(aq)}$  values extrapolated to zero ionic strength and hence, a weighted mean is calculated from all data leading to the selected value:

$$\log_{10} K_1^\circ (\text{VI.17}) = (3.56 \pm 0.04).$$

With NEA-TDB selected data and  $\Delta_f G_m^\circ (\text{ox}^{2-}, 298.15 \text{ K})$  selected in this review (Section VI.2.3), this selection yields:

$$\Delta_f G_m^\circ (\text{Mg(ox)}, \text{aq}, 298.15 \text{ K}) = -(1155.83 \pm 2.28) \text{ kJ}\cdot\text{mol}^{-1}.$$

A weighted least squares SIT regression plot of the data reported in [2001CHO/BON] for the reaction:



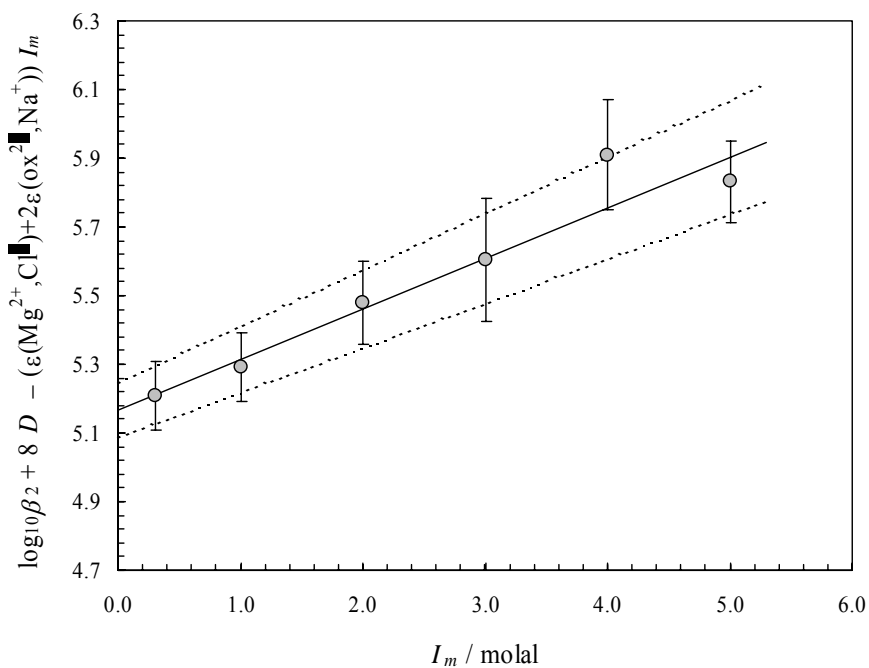
gives the value selected in this review:

$$\log_{10} \beta_2^\circ (\text{VI.18}) = (5.17 \pm 0.08).$$

With NEA-TDB selected data and  $\Delta_f G_m^\circ(\text{ox}^{2-}, 298.15 \text{ K})$  selected in this review (Section VI.2.3), this selection yields:

$$\Delta_f G_m^\circ(\text{Mg}(\text{ox})_2^{2-}, 298.15 \text{ K}) = -(1845.15 \pm 3.92) \text{ kJ} \cdot \text{mol}^{-1}$$

Figure VI-16: Weighted least squares SIT-regression plot of equilibrium data from [2001CHO/BON] for the formation of  $\text{Mg}(\text{ox})_2^{2-}$  according to Reaction (VI.18) in NaCl at 25°C. The results are  $\log_{10} \beta_2^\circ (\text{VI.18}) = (5.17 \pm 0.08)$  and  $\varepsilon(\text{Mg}(\text{ox})_2^{2-}, \text{Na}^+) = -(0.15 \pm 0.03)$ .



The experimental determination of the formation of calcium oxalate complexes is severely hampered by the low solubility of  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}$  (see Section VI.5.1), and as a consequence of these difficulties the values reported in the literature concerning the formation constant of  $\text{Ca}(\text{ox})(\text{aq})$  vary by three orders of magnitude (Table VI-17).

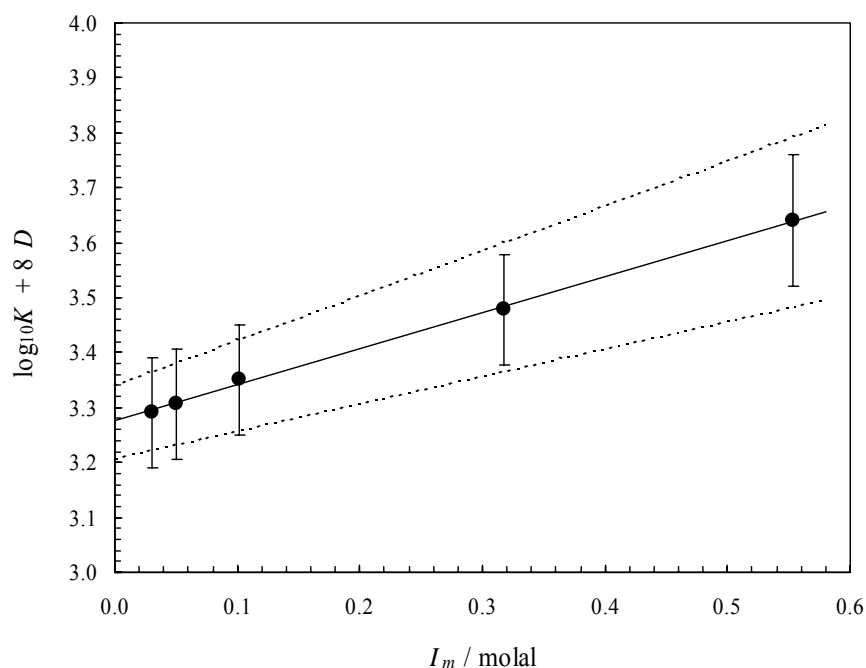


In this review only a few results could be accepted; they were obtained by radiochemical measurements of trace concentrations of Ca in solvent extraction [67HAS/MAK], [76MCD/KEL] and electromigration studies [70STE/PAZ], by using a Ca selective electrode at sufficiently low calcium and oxalate concentrations [82DAN/MAR], or by deriving a complexation constant from conductivity measurements [74NAN/GAR]. All other reported values were rejected [32MON/DAV], [68GOR/FIL], [71PAZ/STE], [72ARM/DUN], [73FIN/SMI], [75PRA/JON], [79CRA/MOO], [82RAO/AGA], [85RED/RAO], [93GLA/MAJ]. For a detailed discussion of all papers see Appendix A.

The existence of the protonated species  $\text{Ca}(\text{Hox})^+$  and  $\text{Ca}(\text{Hox})_2(\text{aq})$  has been postulated in a single study [73ARM/DUN]. However, as discussed in Appendix A, the experiments of [73ARM/DUN] are inconclusive and have been rejected by this review.

Some papers referenced in databases or other papers are erroneous citations, such as [58GEL/HAY] reporting data for oxaloacetic acid, not oxalic acid, and [85KIL] dealing with cadmium oxalate, and not calcium oxalate.

Figure VI-17: Weighted least squares SIT-regression plot of equilibrium data from [82DAN/MAR] for the formation of  $\text{Ca}(\text{ox})(\text{aq})$  according to Reaction (VI.19) in  $\text{Et}_4\text{NI}$  at  $37^\circ\text{C}$ . The results are  $\log_{10} K_1 (\text{VI.19}) = (3.27 \pm 0.07)$  and  $\Delta\varepsilon = -(0.66 \pm 0.25)$ .



For the reaction:



it has been assumed in this review that  $\varepsilon(\text{Mg(ox)(aq),NaCl}) \approx \varepsilon(\text{Ca(ox)(aq),NaClO}_4) = \varepsilon(\text{Ca(ox)(aq),KNO}_3) = \varepsilon(\text{Ca(ox)(aq),NH}_4\text{NO}_3) = (0.0 \pm 0.1)$ , and using  $\varepsilon(\text{Ca}^{2+}, \text{ClO}_4^-) = (0.27 \pm 0.03)$  and  $\varepsilon(\text{Ca}^{2+}, \text{NO}_3^-) = (0.02 \pm 0.01)$  (*cf.* Appendix B), and  $\varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.08 \pm 0.01)$  and  $\varepsilon(\text{ox}^{2-}, \text{K}^+) = (0.07 \pm 0.08)$  selected in this review, as well as assuming  $\varepsilon(\text{ox}^{2-}, \text{K}^+) \approx \varepsilon(\text{ox}^{2-}, \text{NH}_4^+) = (0.07 \pm 0.20)$ , the values of [67HAS/MAK], [70STE/PAZ] and [76MCD/KEL] were extrapolated to zero ionic strength (Table VI-18). A weighted mean is calculated from all data at 25°C leading to the selected value:

$$\log_{10} K_1^\circ (\text{VI.19}) = (3.19 \pm 0.06).$$

This selection yields:

$$\Delta_f G_m^\circ (\text{Ca(ox),aq}, 298.15 \text{ K}) = -(1251.1 \pm 2.1) \text{ kJ}\cdot\text{mol}^{-1}.$$

The value obtained from the SIT regression analysis of equilibrium data from [82DAN/MAR] in Et<sub>4</sub>NI at 37°C,  $\log_{10} K_1^\circ (\text{VI.19}) = (3.27 \pm 0.07)$  seems to indicate a non-zero temperature effect for this reaction. However, considering that the difference of 0.08 log<sub>10</sub>-units is in the same order of magnitude as the uncertainties of the 25°C and 37°C values, no enthalpy of Ca oxalate complex formation is calculated in this review.

For the reaction:



only two reliable studies [67HAS/MAK], [76MCD/KEL] could be identified by this review. It has been assumed that  $\varepsilon(\text{Mg(ox)(aq),NaCl}) \approx \varepsilon(\text{Ca(ox)(aq),NaClO}_4) = \varepsilon(\text{Ca(ox)(aq),NH}_4\text{NO}_3) = (0.0 \pm 0.1)$ , and  $\varepsilon(\text{Mg(ox)}_2^{2-}, \text{Na}^+) \approx \varepsilon(\text{Ca(ox)}_2^{2-}, \text{Na}^+) = \varepsilon(\text{Ca(ox)}_2^{2-}, \text{NH}_4^+) = -(0.15 \pm 0.10)$ , and  $\varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.08 \pm 0.01)$ , as well as assuming  $\varepsilon(\text{ox}^{2-}, \text{K}^+) \approx \varepsilon(\text{ox}^{2-}, \text{NH}_4^+) = (0.07 \pm 0.20)$ , the values of [67HAS/MAK], and [76MCD/KEL] were extrapolated to zero ionic strength (Table VI-18). A weighted mean is calculated leading to the selected value:

$$\log_{10} K_2^\circ (\text{VI.20}) = (0.83 \pm 0.19).$$

This selection yields:

$$\Delta_f G_m^\circ (\text{Ca(ox)}_2^{2-}, 298.15 \text{ K}) = -(1936.0 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

### VI.5.3 Selected values for Mg and Ca oxalate compounds and complexes

The values for magnesium and calcium compounds and complexes selected in this review are summarised in Table VI-19 (see also Table III-1 and III-2 in Chapter III).

Table VI-19: Selected values for Mg and Ca oxalate compounds and complexes.

	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )		$\log_{10} K^\circ$	
	Mg	Ca	Mg	Ca
M(ox), aq	– (1155.8 ± 2.3)	– (1251.1 ± 2.1)		
Mox <sub>2</sub> <sup>2-</sup>	– (1845.2 ± 3.9)	– (1936.0 ± 3.0)		
M <sup>2+</sup> + ox <sup>2-</sup> ⇌ Mox(aq)			(3.56 ± 0.04)	(3.19 ± 0.06)
M <sup>2+</sup> + 2 ox <sup>2-</sup> ⇌ Mox <sub>2</sub> <sup>2-</sup>			(5.17 ± 0.08)	(4.02 ± 0.19)
Ca(ox)·H <sub>2</sub> O(cr),		– (1519.9 ± 2.1)		
Ca(ox)·2H <sub>2</sub> O(cr)		– (1754.6 ± 2.1)		
Ca(ox)·3H <sub>2</sub> O(cr)		– (1991.1 ± 2.1)		
Ca(ox)·H <sub>2</sub> O(cr) ⇌ Ca <sup>2+</sup> + ox <sup>2-</sup> + H <sub>2</sub> O(l)				– (8.73 ± 0.06)
Ca(ox)·2H <sub>2</sub> O(cr) ⇌ Ca <sup>2+</sup> + ox <sup>2-</sup> + 2 H <sub>2</sub> O(l)				– (8.30 ± 0.06)
Ca(ox)·3H <sub>2</sub> O(cr) ⇌ Ca <sup>2+</sup> + ox <sup>2-</sup> + 3 H <sub>2</sub> O(l)				– (8.19 ± 0.04)

## VI.6 Selenium oxalate compounds and complexes

### VI.6.1 Solid selenium oxalates

SeOox was prepared from SeOCl<sub>2</sub> and Ag<sub>2</sub>ox (1:1.1) in tetrahydrofuran and dioxane [66PAE]. No reaction was found with Na<sub>2</sub>ox. The compound crystallises as SeOox·tetrahydrofuran or SeOox·2dioxane.

There are two studies describing the properties of mixed uranium(VI) selenate oxalates in the solid state, (NH<sub>4</sub>)<sub>2</sub>[UO<sub>2</sub>(SeO<sub>4</sub>)ox]·1.5H<sub>2</sub>O [96MIK/GOR2] and Cs<sub>2</sub>[UO<sub>2</sub>(SeO<sub>4</sub>)ox] [2000MIK/GOR2].

No thermodynamic data are available for any of these compounds.

## VI.6.2 Aqueous selenium oxalate complexes

Obradović *et al.* [98OBR/MIT] report pH metric and conductivity measurements in the system  $\text{H}_2\text{Ox} - \text{Na}_2\text{SeO}_3$ , and the authors state that their experimental results indicate the formation of complexes in which the  $\text{ox}^{2-} : \text{SeO}_3^{2-}$  ratio is 2:1. However, a series of simple speciation calculations (*cf.* Appendix A) reveals that most of the effect reported in the figure of this paper is not due to oxalate - selenite complex formation but can be inferred from the acid-base titration data reported by [98OBR/MIT]. The slight deviations from the calculated curve cannot be analysed because the original data are not available.

No further experimental studies involving the thermodynamic properties of selenium oxalates in solution could be identified by this review.

## VI.7 Nickel oxalate compounds and complexes<sup>1</sup>

### VI.7.1 Solid nickel oxalates

The solid that precipitates from aqueous solutions is nickel oxalate dihydrate. Two crystallographic forms of  $\text{Ni}(\text{ox}) \cdot 2\text{H}_2\text{O}$  have been reported: a monoclinic  $\alpha$ -form and an orthorhombic  $\beta$ -form [73DEY/BER]. The structure of the anhydrous nickel(II) oxalate,  $\text{Ni}(\text{ox})(\text{cr})$ , has been described in [82NIK/SHA]. This solid may be obtained by heating the dihydrate. The equilibrium water vapour pressure for the dissociation of  $\text{Ni}(\text{ox}) \cdot 2\text{H}_2\text{O}$  into  $\text{Ni}(\text{ox})(\text{s})$  at 125-177°C is given in [53ALL/SCA]. The thermal decomposition of nickel oxalate has been investigated extensively, see for example [99MAJ/SAR], [2000LVO] and references cited therein.

$\beta$ - $\text{Ni}(\text{ox}) \cdot 2\text{H}_2\text{O}$  is meta-stable and it precipitates initially when solutions of nickel(II) and oxalic acid (or oxalate) are mixed [70DEY/PEN], [73DEY/BER]. This solid transforms into  $\alpha$ - $\text{Ni}(\text{ox}) \cdot 2\text{H}_2\text{O}$  when standing in a boiling solution with excess of oxalate ions [73DEY/BER], although the transformation is inhibited by sulphate ions [70DEY/PEN], [75DEY/CAN].

In the presence of potassium oxalate, a solid solution is apparently formed [09DEA/SCO], [36VOS/ISR] between  $\text{K}_2\text{ox}$  and  $\text{Ni}(\text{ox}) \cdot 2\text{H}_2\text{O}$ . In solutions containing > 12.5 weight-% potassium oxalate the solid  $\text{K}_2\text{Ni}(\text{ox})_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}$  is formed [36VOS/ISR]. The structure of this solid has been analysed by Raman spectroscopy [91BIC/EDW] and by single-crystal X-ray diffraction [93ROM/GUZ]. The solid  $\text{Na}_2\text{Ni}(\text{ox})_2 \cdot 8\text{H}_2\text{O}$  has also been described [11DOD].

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<sup>1</sup> Prof. J. Havel and Dr. P. Lubal (both from the Department of Analytical Chemistry, Masaryk University, Brno, Czech Republic) contributed to this section during the early stages of the review process.

The solubility of  $\text{Ni(ox)} \cdot 2\text{H}_2\text{O}$  may be used to derive the solubility product of the solid, and such data has been reported in several papers. Literature data is available for the solubilities in water [1894NAS], [27SCH3], [37LED/HAU], [51BAR/ARG], [89FEL/TOP] (Table VI-20), in  $\text{H}_2\text{SO}_4$  [70DEY/PEN], [75DEY/CAN] (Table VI-21) and in  $\text{K}_2\text{ox}$  media [51BAR/ARG]. The crystallographic form of the solid studied is not reported in any of the references published before 1970. As discussed in the following, none of the solubility studies in the literature is suitable to recommend a solubility product.

Scholder [27SCH3] observed very slow kinetics for the equilibration, and they had to wait for 100 hours, and therefore it is not surprising that Ledrut and Hauss [37LED/HAU] obtained higher solubilities from their measurements only after 6 hours in initially oversaturated solutions.

Table VI-20: Reported values for the solubility of nickel oxalate in water.

Solid phase	$t$ (°C)	Solubility	Comments	Reference
$\text{Ni(ox)}$	?	$1.8 \times 10^{-2}$ M	See Appendix A	[1894NAS]
$\text{Ni(ox)} \cdot 2\text{H}_2\text{O}$	18	$2.0 \times 10^{-5}$ M ( $10^{-4.69}$ M)	Titration of oxalate with $\text{KMnO}_4$ . From undersaturation after 100 hours. See Appendix A.	[27SCH3]
$\text{Ni(ox)} \cdot 2\text{H}_2\text{O}$	20	$27.7 \times 10^{-5}$ M ( $10^{-3.56}$ M)	Titration of oxalate with $\text{KMnO}_4$ . From oversaturation after 6 hours.	[37LED/HAU]
$\text{Ni(ox)}$	25	$7.15 \times 10^{-5}$ M ( $10^{-4.15}$ M)	Ni: spectrophotometric with dimethylglyoxime. From undersaturation after 96 hours. See also Appendix A.	[51BAR/ARG]
$\text{Ni(ox)} \cdot 2\text{H}_2\text{O}$	20	$1.6 \times 10^{-5}$ M ( $10^{-4.79}$ M)	Not clear how it was measured, or even if it was measured.	[89FEL/TOP]

Solubility data for the two crystallographic forms,  $\alpha$  and  $\beta$ , of  $\text{Ni(ox)} \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{SO}_4$  solutions were used to determine the solubility products in [70DEY/PEN], [75DEY/CAN], and the corresponding enthalpy and entropy changes were obtained from their temperature variation in [75DEY/CAN]. These values, summarised on Table VI-21, were obtained by Deyrieux *et al.* assuming the formation of only the following two complexes in solution:  $\text{Ni(ox)(aq)}$  and  $\text{NiH}_2(\text{ox})\text{SO}_4(\text{aq})$ . However, as discussed in Appendix A, these solubility data are not well suited to unequivocally describe the stoichiometry of the protonated complexes, and the values listed in Table VI-21 are considered unreliable.

Table VI-21: Literature values for the solubility products and thermodynamic data for the reaction:  $\text{Ni(ox)} \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ni}^{2+} + \text{ox}^{2-} + 2\text{H}_2\text{O(l)}$ .

	$\beta\text{-Ni(ox)} \cdot 2\text{H}_2\text{O}$	$\alpha\text{-Ni(ox)} \cdot 2\text{H}_2\text{O}$	Reference
$\log_{10} K_{s,0}^\circ$	$-(9.65 \pm 0.01)$		[70DEY/PEN]
	$-(9.43 \pm 0.14)$	$-(9.68 \pm 0.10)$	[75DEY/CAN]
$\Delta_r H_m^\circ$ (kJ·mol <sup>-1</sup> )	$(22.2 \pm 0.2)$	$(18.3 \pm 0.1)$	[75DEY/CAN]
$\Delta_r S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	$-(106 \pm 3)$	$-(124 \pm 2)$	[75DEY/CAN]

The solubility data as a function of  $\text{K}_2\text{ox}$  in [51BAR/ARG] has serious problems: the authors did not characterise the solid phase properly, and the solubility curve differs substantially with the shape theoretically expected, especially at low values of  $[\text{K}_2\text{ox}]_{\text{added}}$ .

In aqueous solutions in equilibrium with nickel oxalate dihydrate, the following reaction takes place:

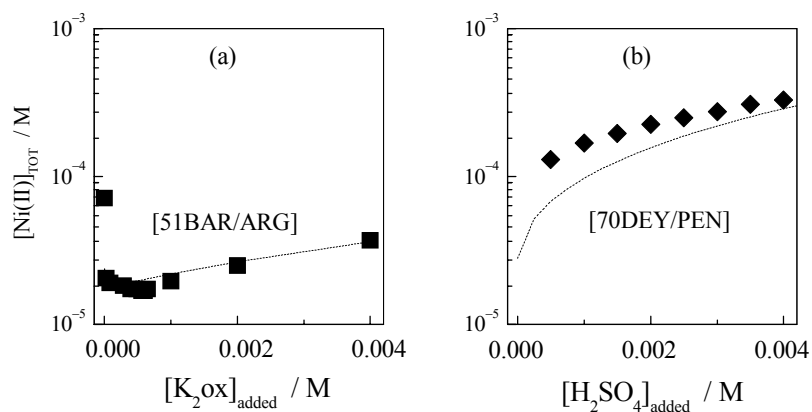
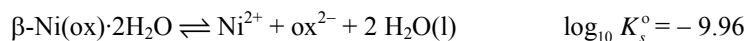


and the concentration of  $\text{Ni(ox)(aq)}$  is almost constant for any medium, as its activity coefficient will be close to unity. The concentration of  $\text{Ni(ox)(aq)}$  corresponds to the minimum possible solubility: any other Ni-species formed will increase the solubility above this concentration. The minimum reported solubility at 25°C is  $[\text{Ni}]_{\text{TOT}} = 10^{-4.77}$  M in  $[\text{K}_2\text{ox}]_{\text{TOT}} = 5.6 \times 10^{-4}$  M [51BAR/ARG]. If it is assumed that this solubility corresponds to the concentration of  $\text{Ni(ox)(aq)}$ , and this is combined with the value of  $\log_{10} K_1^\circ = (5.19 \pm 0.04)$  selected by this review for  $\text{Ni}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Ni(ox)(aq)}$ , then the maximum value for the solubility product may be estimated to be  $\log_{10} K_{s,0}^\circ \leq (-4.77 - 5.19) = -9.96$ . Figure VI-18 shows a comparison between the experimental data from [51BAR/ARG] and [70DEY/PEN] for the solubility of nickel oxalate and curves calculated using this solubility product and the selected values for  $\text{Ni(ox)(aq)}$  and  $\text{Ni(ox)}_2^{2-}$ . The figure shows that the two data sets are discrepant: the value at  $[\text{K}_2\text{ox}]_{\text{added}} = 0$  from [51BAR/ARG] seems to agree with the general trend in the data from [70DEY/PEN], while the other data from [51BAR/ARG] appear to be too low, perhaps because of the formation of a solid solution (see discussion in Appendix A). Although the data from [70DEY/PEN] are more reliable, they are insufficient to establish the protonated species formed in the acid  $\text{H}_2\text{SO}_4$  solutions, and therefore no value is recommended for the solubility product for nickel oxalate.

Calorimetric measurements of the heat of dissolution of “Ni(ox)” in hydrochloric acid [69VAN/PER] or in water [71VAN] have been used to calculate a value of  $\Delta_r H_m^\circ$  (“Ni(ox)”, 298.15 K) =  $-(854 \pm 19)$  kJ·mol<sup>-1</sup> [69VAN/PER] and  $-(882 \pm 1)$  kJ·mol<sup>-1</sup> [71VAN]. These two references contain however almost no details on the experimental and on the data treatment procedures. The enthalpy of formation of  $\text{Ni(ox)}$  is also reported in [56KOR/PET] but this reference is not available to this review.

[75DEY/CAN] reports  $\Delta_f H_m^\circ(\alpha\text{-Ni(ox)}\cdot 2\text{H}_2\text{O}, 298.15\text{ K}) = -(1478.3 \pm 0.1)\text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H_m^\circ(\beta\text{-Ni(ox)}\cdot 2\text{H}_2\text{O}, 298.15\text{ K}) = -(1482.1 \pm 0.2)\text{ kJ}\cdot\text{mol}^{-1}$  calculated from the temperature dependence of the solubility products of these solids in  $\text{H}_2\text{SO}_4$ . However, as mentioned above, these solubility products are considered unreliable by this review, see also the discussion of [75DEY/CAN] in Appendix A. In summary, no reliable value for the enthalpy of formation of any nickel oxalate is available in the literature.

Figure VI-18: Comparison of experimental and calculated values for the solubility of nickel oxalate at 25°C in: (a) potassium oxalate; and (b) sulphuric acid solutions. The curves have been calculated using the selected values for the complex formation between Ni(II) and oxalate, and with the following two constants:



## VI.7.2 Aqueous nickel oxalate complexes

The experimental equilibrium data available on the complex formation of  $\text{Ni}^{2+}$  with oxalate are listed in Table VI-22. Studies on the complex formation between  $\text{Ni}^{2+}$  and  $\text{ox}^{2-}$  have the difficulty of the rather low solubility of nickel oxalate, *cf.* Section VI.7.1, especially if there is no excess of oxalate present in the solutions.

Table VI-22: The stability constants of Ni(II) oxalate complexes reported in literature

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Ni}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Ni}(\text{ox})(\text{aq})$				
con		18	$> 5.3$	[32MON/DAV]
gl, sp	1 M ( $\text{KNO}_3$ )	25	$(4.10 \pm 0.10)$	[60WAT/DEW]
pot	$\rightarrow$ 0 M $\text{NiCl}_2$ ,	0	$(5.179 \pm 0.014)$	[61MCA/NAN]
	$(\text{Na,H})_2\text{ox}$	15	$(5.137 \pm 0.013)$	
		25	$(5.158 \pm 0.009)$	
		35	$(5.173 \pm 0.017)$	
		45	$(5.185 \pm 0.014)$	
dis	0.1 M ( $\text{NaClO}_4$ )	20	$(3.83 \pm 0.05)$	[69MAN/BHA]
sol	$\rightarrow$ 0 M $\text{H}_2\text{SO}_4$	25	$(5.39 \pm 0.03)$	[70DEY/PEN]
sol	$\rightarrow$ 0 M $\text{H}_2\text{SO}_4$	25	$(4.8 \pm 0.3)$	[75DEY/CAN]
dis	1.0 M $\text{Na}(\text{ClO}_4)$	25	3.7	[76MUR/KUR]
pol	0.1 M ( $\text{NaClO}_4$ )	20	4.255	[81URB/BIE2]
pot	0.1 M ( $\text{KNO}_3$ )	35	5.23	[85RED/RAO]
pol	0.1 M ( $\text{NaClO}_4$ )	25	4.16	[88CRO]
pot	0.5 M ( $\text{NaCl}$ )	25	$(4.05 \pm 0.01)$	[89FUE/REB2]
pot	0.1 M ( $\text{KNO}_3$ )	35	$(4.43 \pm 0.05)$	[90RED/SAT]
cix	0.11 M ( $\text{NaClO}_4$ )	25	$(4.27 \pm 0.05)$	[91LOO/KOP]
pot	0.1 M ( $\text{KNO}_3$ )	25	$(4.432 \pm 0.03)$	[93AZA/HAS]
chr	0.1 M ( $\text{NaClO}_4$ )	22	$(4.69 \pm 0.69)$	[93JAN]
pot	0.1 M ( $\text{KNO}_3$ )	30	5.28	[94RED/SHI]
pot	0.1 M ( $\text{NaNO}_3$ )	25	$(3.46 \pm 0.08)$	[98KHA/RAD]
cix	0.1 M ( $\text{NaClO}_4$ )	25	$(4.4 \pm 0.1)$	[2003BAE/BRA]
	0.5 M ( $\text{NaClO}_4$ )		$(3.9 \pm 0.1)$	
	0.3 m ( $\text{NaCl}$ )	20	$(3.98 \pm 0.05)$	[2003BOR/CHO]
	1 m		$(3.72 \pm 0.04)$	
	2 m		$(3.71 \pm 0.05)$	
	3 m		$(3.76 \pm 0.07)$	
	4 m		$(3.87 \pm 0.07)$	
	5 m		$(3.97 \pm 0.04)$	

(Continued on next page)



Table VI-22: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Ni}^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Ni}(\text{ox})_2^{2-}$				
pol	6.2 M LiCl	?	13.7	[34SAR]
sol	var. ( $\leq 0.012$ )	25	6.51	[51BAR/ARG]
cal	(0.25 – 0.8) M $\text{ox}^{2-}$	25	7.2	[54YAT/ZOL]
gl, sp	1 M ( $\text{KNO}_3$ )	25	(7.15 $\pm$ 0.14)	[60WAT/DEW]
?	?	25?	7.64	[63FRI/VER]
dis	0.1 M ( $\text{NaClO}_4$ )	20	(7.88 $\pm$ 0.04)	[63STA]
dis	0.1 M ( $\text{NaClO}_4$ )	20	(7.06 $\pm$ 0.13)	[69MAN/BHA]
dis	1.0 M $\text{Na}(\text{ClO}_4)$	25	6.6	[76MUR/KUR]
em	0.1 M ( $\text{Na}_2\text{HClO}_4$ )	30	6.5	[76YAD/GHO]
pol	0.1 M ( $\text{NaClO}_4$ )	20	7.544	[81URB/BIE2]
pol	0.1 M ( $\text{NaClO}_4$ )	25	7.58	[88CRO]
pot	0.5 M ( $\text{NaCl}$ )	25	(6.01 $\pm$ 0.03)	[89FUE/REB2]
dis	0.3 m ( $\text{NaCl}$ )	20	(6.70 $\pm$ 0.05)	[2003BOR/CHO]
	1 m		(6.49 $\pm$ 0.05)	
	2 m		(6.44 $\pm$ 0.05)	
	3 m		(6.51 $\pm$ 0.05)	
	4 m		(6.72 $\pm$ 0.06)	
	5 m		(6.95 $\pm$ 0.06)	
$\text{Ni}(\text{ox})(\text{aq}) + \text{ox}^{2-} \rightleftharpoons \text{Ni}(\text{ox})_2^{2-}$				
dis	0.25 M ( $\text{NaClO}_4$ )	25	(1.8 $\pm$ 0.2)	[69SUB/COR]
em	0.1 M ( $\text{Na}_2\text{HClO}_4$ )	30	2.2	[92TRI/TRI]
pot	0.1 M ( $\text{NaNO}_3$ )	25	(2.96 $\pm$ 0.05)	[98KHA/RAD]
$\text{Ni}^{2+} + 3 \text{ox}^{2-} \rightleftharpoons \text{Ni}(\text{ox})_3^{4-}$				
gl, sp	1 M ( $\text{KNO}_3$ )	25	(8.51 $\pm$ 0.17)	[60WAT/DEW]
pot	1 M ( $\text{KNO}_3$ )	25	7.2	[68FRI/VER]
$\text{Ni}^{2+} + \text{Hox}^- \rightleftharpoons \text{Ni}(\text{Hox})^+$				
em	0.1 M ( $\text{Na}_2\text{HClO}_4$ )	30	2.3	[76YAD/GHO]
em	0.1 M ( $\text{Na}_2\text{HClO}_4$ )	30	2.3	[92TRI/TRI]
$\text{Ni}^{2+} + \text{Hox}^- + \text{HSO}_4^- \rightleftharpoons \text{Ni}(\text{Hox})(\text{HSO}_4)(\text{aq})$				
sol	$\rightarrow 0$ M $\text{H}_2\text{SO}_4$	25	(6.183 $\pm$ 0.001)	[70DEY/PEN]
sol	$\rightarrow 0$ M $\text{H}_2\text{SO}_4$	25	(6.11 $\pm$ 0.21)	[75DEY/CAN]

Most of the papers deal with the determination of stability constants of complex species  $\text{Ni}(\text{ox})_n^{2-n}$  with  $n=1$  and 2, according to:



The formation of complex species with  $n = 3$  was reported only in two papers: [60WAT/DEW] and [68FRI/VER]. The reason is that such a complex is formed only at high oxalate concentrations, perhaps at  $[\text{ox}]_{\text{TOT}} > 0.1$  M. As discussed in Appendix A these two papers are not recommended because the equilibrium constants were obtained from mixtures containing a fourth component (ethylenediamine or glycine), in experiments where the ionic medium was not constant.

The protonated complex  $\text{Ni}(\text{Hox})^+$  has been postulated from electromigration data, [76YAD/GHO], [92TRI/TRI], but these studies are considered unreliable, see Appendix A. Another protonated species that has been proposed in sulphuric acid solutions is  $\text{Ni}(\text{Hox})(\text{HSO}_4)(\text{aq})$ , [70DEY/PEN], [75DEY/CAN], but it is possible to fit these solubility measurements equally well with several other protonated complexes, see Appendix A.

Even if a rather high number of references with data for the formation of  $\text{Ni}(\text{ox})(\text{aq})$  and  $\text{Ni}(\text{ox})_2^{2-}$  has been found (Table VI-22), only a limited number of studies, listed in Table VI-23, are accepted in this review. All references containing data not considered [32MON/DAV], [34SAR], [51BAR/ARG], [54YAT/ZOL], [60WAT/DEW], [63FRI/VER], [63STA], [68FRI/VER], [69MAN/BHA], [69SUB/COR], [70DEY/PEN], [75DEY/CAN], [76YAD/GHO], [81URB/BIE2], [85RED/RAO], [88CRO], [90RED/SAT], [92TRI/TRI], [93JAN], [94RED/SHI], [98KHA/RAD] are discussed in Appendix A. The interpretation of the selected literature values listed in Table VI-23 according to the SIT model must take into account the different ionic media and temperatures. The data at 20°C from [2003BOR/CHO] were corrected to 25°C using the equations given in Section V.3.6 and the selected  $\Delta_r H_m^\circ$  (VI.21) values for complex formation. However, the interpretation of the calorimetric data requires selected complex formation constants to obtain the enthalpy changes (see below). This interdependency was resolved in an iterative manner. The ionic medium dependence of  $\Delta_r H_m^\circ$  (VI.21) is not known, and Equation (V.58) was used assuming  $\Delta \epsilon_L = (0 \pm 0.010) \text{ kg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . The temperature corrections to the data in [2003BOR/CHO] were small, between  $-0.011$  and  $-0.018$  for  $\log_{10} K_1$ ; and between  $-0.034$  and  $-0.042$  for  $\log_{10} \beta_2$ . The uncertainties in the equilibrium constants were also increased to reflect the uncertainty in the temperature correction, which arises mainly from the uncertainty in  $\Delta \epsilon_L$ . The corrected values are listed in Table VI-23.

The data in Table VI-23, converted to molal units, was treated using a weighted linear least-squares regression procedure with an expression similar to (V.48):

$$\log_{10} K_n(\text{VI.21}) - \Delta z^2 D - (\epsilon(\text{Ni}^{2+}, X^-) + n \epsilon(\text{M}^+, \text{ox}^{2-})) I_m = \log_{10} K_n^\circ(\text{VI.21}) - \Delta \epsilon_n^* I_m$$

In this case  $\Delta z^2 = -8$  for both  $n = 1$  and 2. As the first complex is not electrically charged, the specific ion interaction parameter is expected to be small:  $\Delta \epsilon_1^* = \epsilon(\text{Ni}(\text{ox})(\text{aq}), \text{MX}) \approx 0$ ; while for  $\text{Ni}(\text{ox})_2^{2-}$ :  $\Delta \epsilon_2^* = \epsilon(\text{Na}^+, \text{Ni}(\text{ox})_2^{2-})$  because only data in sodium electrolytes are available. The values of  $\epsilon(\text{Ni}^{2+}, \text{Cl}^-)$  and  $\epsilon(\text{M}^+, \text{ox}^{2-})$  listed in Tables B-4 and B-5 were used for the SIT evaluation. Given the spread of the data, a

minimum uncertainty of  $\pm 0.1 \log_{10}$ -units was assigned to the data sets, *cf.* Table VI-23. The results of the regressions are displayed in Figure VI-19 and Figure VI-20 and the selected stability constants are:

$$\log_{10} K_1^\circ ((\text{VI.21}), n = 1) = (5.19 \pm 0.04)$$

$$\log_{10} \beta_2^\circ ((\text{VI.21}), n = 2) = (7.64 \pm 0.07)$$

with the following specific ion interaction coefficients:  $\varepsilon(\text{Ni}(\text{ox})(\text{aq}), \text{MX}) = -(0.07 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ , and  $\varepsilon(\text{Na}^+, \text{Ni}(\text{ox})_2^{2-}) = -(0.26 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ .

Table VI-23: Accepted stability constants of nickel(II) oxalate complexes at 25°C with the uncertainties assigned in this review.

Method	Ionic medium	<i>t</i> (°C)	$\log_{10} K$	Reference
$\text{Ni}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Ni}(\text{ox})(\text{aq})$				
pot	$\rightarrow 0$	25	$(5.158 \pm 0.10)$	<a href="#">[61MCA/NAN]</a> <sup>a</sup>
dis	1.0 M Na(ClO <sub>4</sub> )	25	$(3.7 \pm 0.2)$	<a href="#">[76MUR/KUR]</a>
pot	0.5 M (NaCl)	25	$(4.05 \pm 0.10)$	<a href="#">[89FUE/REB2]</a>
cix	0.11 M (NaClO <sub>4</sub> )	25	$(4.27 \pm 0.10)$	<a href="#">[91LOO/KOP]</a> <sup>a</sup>
pot	0.1 M (KNO <sub>3</sub> )	25	$(4.432 \pm 0.10)$	<a href="#">[93AZA/HAS]</a>
cix	0.1 M (NaClO <sub>4</sub> )	25	$(4.4 \pm 0.1)$	<a href="#">[2003BAE/BRA]</a>
	0.5 M (NaClO <sub>4</sub> )		$(3.9 \pm 0.1)$	
dis	0.3 m (NaCl)	$\rightarrow 25$	$(3.969 \pm 0.10)$	<a href="#">[2003BOR/CHO]</a> <sup>b</sup>
	1 m		$(3.706 \pm 0.10)$	
	2 m		$(3.694 \pm 0.10)$	
	3 m		$(3.743 \pm 0.10)$	
	4 m		$(3.852 \pm 0.11)$	
	5 m		$(3.952 \pm 0.12)$	
$\text{Ni}^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Ni}(\text{ox})_2^{2-}$				
dis	1.0 M Na(ClO <sub>4</sub> )	25	$(6.6 \pm 0.2)$	<a href="#">[76MUR/KUR]</a>
pot	0.5 M (NaCl)	25	$(6.01 \pm 0.10)$	<a href="#">[89FUE/REB2]</a>
dis	0.3 m (NaCl)	$\rightarrow 25$	$(6.666 \pm 0.10)$	<a href="#">[2003BOR/CHO]</a> <sup>b</sup>
	1 m		$(6.452 \pm 0.10)$	
	2 m		$(6.401 \pm 0.10)$	
	3 m		$(6.470 \pm 0.10)$	
	4 m		$(6.679 \pm 0.11)$	
	5 m		$(6.908 \pm 0.13)$	

a: see comments in Appendix A.

b: the data from [\[2003BOR/CHO\]](#) were corrected to 25°C as described in the text.

Figure VI-19: Weighted least squares SIT-regression plot of equilibrium data for the formation of  $\text{Ni(ox)(aq)}$  according to Reaction (VI.21) with  $n = 1$ .

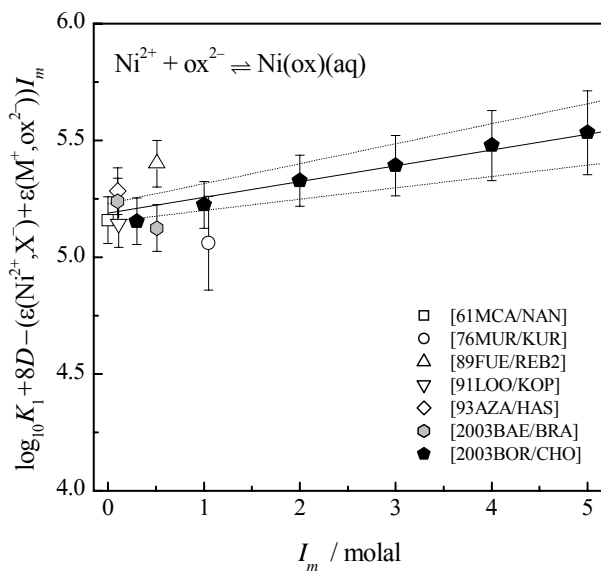
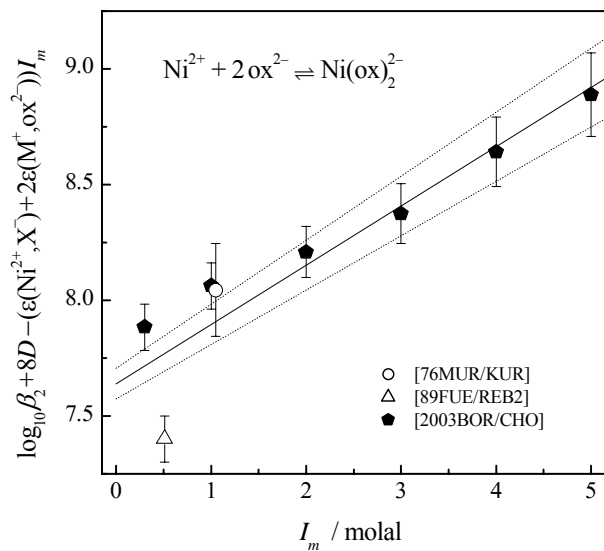


Figure VI-20: Weighted least squares SIT-regression plot of equilibrium data for the formation of  $\text{Ni(ox)}_2^{2-}$  according to Reaction (VI.21) with  $n = 2$ .



### VI.7.2.1 Temperature effects

Enthalpy changes for the complex formation between Ni(II) and oxalate have been determined in four studies. The reported values are listed in Table VI-24.

Table VI-24: Literature values for the enthalpy changes associated with the formation of nickel(II) oxalate complexes at 25°C.

Method	Ionic medium	$\Delta_r H_m$ (kJ·mol <sup>-1</sup> )	Reference
$\text{Ni}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Ni(ox)(aq)}$			
pot	→ 0 M	(0.6 ± 0.4)	[61MCA/NAN]
sol	→ 0 M (H <sub>2</sub> SO <sub>4</sub> )	(51.6 ± 0.2)	[75DEY/CAN] <sup>a</sup>
cal	1 M (KNO <sub>3</sub> )	– (5.4 ± 0.2)	[90LIN/GU] <sup>b</sup>
$\text{Ni}^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Ni(ox)}_2^{2-}$			
cal	(0.25-0.8) M ox <sup>2-</sup>	– 5.15	[54YAT/ZOL]
cal	1 M (KNO <sub>3</sub> )	– (11.0 ± 0.3)	[90LIN/GU] <sup>b</sup>
$\text{Ni}^{2+} + 3 \text{ox}^{2-} \rightleftharpoons \text{Ni(ox)}_3^{4-}$			
cal	1 M (KNO <sub>3</sub> )	– (17.1 ± 0.6)	[90LIN/GU] <sup>b</sup>
$\text{Ni}^{2+} + \text{Hox}^- + \text{HSO}_4^- \rightleftharpoons \text{Ni(Hox)(HSO}_4\text{)(aq)}$			
sol	→ 0 M (H <sub>2</sub> SO <sub>4</sub> )	– (40.8 ± 0.1)	[75DEY/CAN] <sup>a</sup>

a: from the temperature variation of the solubility of  $\alpha$ - and  $\beta$ -Ni(ox)·2H<sub>2</sub>O in H<sub>2</sub>SO<sub>4</sub> solutions.

b: the authors used equilibrium constants from [60WAT/DEW].

The calorimetric study in [54YAT/ZOL] was performed in varying ionic media, and the data cannot be used in this review, see Appendix A.

In [75DEY/CAN] enthalpy data were obtained from the temperature variation of the solubility of  $\alpha$ - and  $\beta$ -Ni(ox)·2H<sub>2</sub>O in H<sub>2</sub>SO<sub>4</sub> solutions. However, these values are unreliable because the authors neglected the formation of NiSO<sub>4</sub>(aq) and the speciation in the solutions studied cannot be pinpointed from the type of measurements performed, see also the discussion in Appendix A.

The calorimetric data in [90LIN/GU] was interpreted by the authors using the equilibrium constants reported in [60WAT/DEW], which are considered unreliable by this review (Appendix A). Therefore, the three calorimetric measurements reported in [90LIN/GU] are re-evaluated in this review, as explained in Appendix A, using selected values for the equilibrium constants, obtaining  $\Delta_r H_m$  ((VI.21),  $n = 1$ ) = – (5.0 ± 0.3) kJ·mol<sup>-1</sup> and  $\Delta_r H_m$  ((VI.21),  $n = 2$ ) = – (12.6 ± 0.3) kJ·mol<sup>-1</sup> at  $I = 1$  M KNO<sub>3</sub> and 25°C. These values are extrapolated to  $I = 0$  using Eq. (V.58) with the same parameters for both  $n = 1$  and 2 in Reaction (VI.7.1):  $\Delta z^2 = -8$  and, lacking additional information,  $\Delta \epsilon_L = 0$ , resulting in the following values:  $\Delta_r H_m^\circ$  ((VI.21),  $n = 1$ ) = – (0.2 ± 0.3) kJ·mol<sup>-1</sup> and  $\Delta_r H_m^\circ$  ((VI.21),  $n = 2$ ) = – (7.8 ± 0.3) kJ·mol<sup>-1</sup>, both at 25°C.

Table VI-25 lists the re-evaluated values from [61MCA/NAN], [90LIN/GU]. For Ni(ox)(aq) the selected enthalpy of reaction is taken as the weighted average of the

value from [61MCA/NAN] and that from [90LIN/GU] extrapolated to zero ionic strength as indicated above, while for  $\text{Ni(ox)}_2^{2-}$  only the value from [90LIN/GU] is available. The selected values become:

$$\Delta_f H_m^\circ (298.15 \text{ K}, (\text{VI.21}), n = 1) = (0.0 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ (298.15 \text{ K}, (\text{VI.21}), n = 2) = -(7.8 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

With these selections, the following formation values and molar entropies are obtained:

$$\Delta_f G_m^\circ (\text{Ni(ox)}, \text{aq}, 298.15 \text{ K}) = -(755.5 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ (\text{Ni(ox)}, \text{aq}, 298.15 \text{ K}) = -(885.7 \pm 1.8) \text{ kJ}\cdot\text{mol}^{-1}$$

$$S_m^\circ (\text{Ni(ox)}, \text{aq}, 298.15 \text{ K}) = (15.2 \pm 3.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

$$\Delta_f G_m^\circ (\text{Ni(ox)}_2^{2-}, 298.15 \text{ K}) = -(1450.0 \pm 3.8) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f H_m^\circ (\text{Ni(ox)}_2^{2-}, 298.15 \text{ K}) = -(1724.1 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$$

$$S_m^\circ (\text{Ni(ox)}_2^{2-}, 298.15 \text{ K}) = (83.5 \pm 6.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

Table VI-25: Selected literature data for the enthalpy changes associated with the formation of nickel(II) oxalate complexes at 25°C.

Method	Ionic medium	$\Delta_f H_m$ (kJ·mol <sup>-1</sup> )	Reference
$\text{Ni}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Ni(ox)(aq)}$			
pot	→ 0 M	$(1.4 \pm 0.8)^a$	[61MCA/NAN]
cal	1 M (KNO <sub>3</sub> )	$-(5.0 \pm 0.3)^a$	[90LIN/GU]
$\text{Ni}^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Ni(ox)}_2^{2-}$			
cal	1 M (KNO <sub>3</sub> )	$-(12.6 \pm 0.3)^a$	[90LIN/GU]

a: re-evaluated by this review, cf. Appendix A

### VI.7.2.2 Ternary complexes

Only ternary complexes between Ni(II), oxalate and either inorganic ligands, or citrate or edta are included in this review. The formation of ternary complexes between Ni(II), edta and oxalate is discussed in Section VIII.7.2. Equilibrium constants for the formation of  $\text{Ni(Hox)(HSO}_4\text{)(aq)}$  have been reported in [70DEY/PEN], [75DEY/CAN]. These values are unreliable because the authors neglected the formation of  $\text{NiSO}_4\text{(aq)}$  and the speciation in the solutions studied cannot be identified from the type of measurements performed, see also the discussion in Appendix A.

## VI.8 Technetium oxalate compounds and complexes

There is very little information in the literature concerning the compounds and aqueous complexes of technetium, and no thermodynamic data has been published.

A few solid phases have been synthesised and characterised, and these are summarised in Table VI-26. There is no information available on the thermodynamic stability of these compounds.

Table VI-26: Technetium oxalate compounds reported in the literature.

Formula	Name	Reference
<b>Tc(II):</b>		
$\text{Tc}(\text{C}_{26}\text{H}_{24}\text{P}_2)_2(\text{ox})\cdot\text{KPF}_6\cdot 1.5\text{H}_2\text{O}$	oxalato-bis(1,2-bis(diphenylphosphino)ethane)-Tc(II) potassium hexafluorophosphate sesquihydrate	<a href="#">[92SEI/MUE]</a>
<b>Tc(IV):</b>		
$(\text{C}_{24}\text{H}_{20}\text{As})_2\text{Tc}(\text{ox})_3$	bis(tetraphenylarsonium) tris(oxalato-O,O')-Tc(IV)	<a href="#">[87COL/WIL]</a>
$\text{K}_4[(\text{ox})_2\text{Tc}(\mu\text{-O})_2\text{Tc}(\text{ox})_2]\cdot 3\text{H}_2\text{O}$	tetra-potassium bis(( $\mu_2$ -oxo)-bis(oxalato-O,O')-Tc(IV)) trihydrate	<a href="#">[90ALB/AND]</a>
<b>Tc(V):</b>		
$(\text{C}_{24}\text{H}_{20}\text{As})_2\text{TcO}(\text{Hox})(\text{ox})_2\cdot 3\text{H}_2\text{O}$	bis(tetraphenylarsonium) (hydrogen oxalato-O)- bis(oxalato-O,O')-oxo-Tc(V) trihydrate	<a href="#">[88BAL/COL]</a>
<b>Tc(VI):</b>		
$(\text{C}_{24}\text{H}_{20}\text{As})_4[(\text{TcN}(\text{ox}))_2\text{O}(\text{ox})]_2$	tetrakis(tetraphenylarsonium) cyclo-bis(( $\mu_2$ -oxalato-O,O',O'',O''')-( $\mu_2$ -oxo)-bis(nitrido-(oxalato-O,O')-Tc(VI)))	<a href="#">[88BAL/COL]</a>
<b>Tc(VII):</b>		
$(\text{C}_{24}\text{H}_{20}\text{As})_2[\text{N}(\text{O}_2)_2\text{Tc}(\text{ox})\text{TcN}(\text{O}_2)_2]$	bis(tetraphenylarsonium) ( $\mu_2$ -oxalato-O,O',O'',O''')- bis(nitrido-bisperoxo-Tc(VII))	<a href="#">[90BAL/COL]</a> <a href="#">[91BAL/COL]</a>

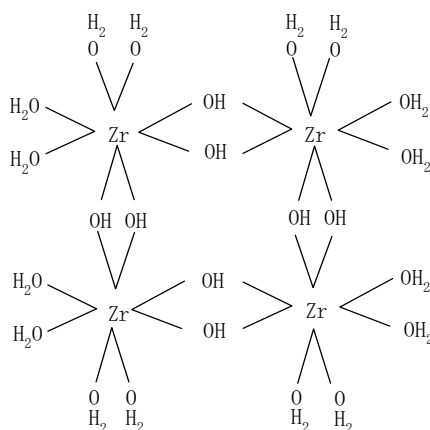
Some qualitative information about the interaction between technetium and oxalate in aqueous solutions has also been published. The stable oxidation state of Tc in contact with air is pertechnetate,  $\text{Tc}^{\text{VII}}\text{O}_4^-$ , and its reduction appears to be facilitated by the presence of ligands that coordinate technetium in lower oxidation states, such as Tc(IV) or perhaps Tc(III). However, in the absence of reducing agents Tc(VII) is relatively stable towards reduction by oxalate [\[2001BER/BAU\]](#). In the presence of nitric and oxalic acids as well as reducing agents, for example Sn(II) or hydrazine, the technetium-oxalate complex formed may be extracted into tributylphosphate (TBP) in dodecane [\[85FRI\]](#), [\[2002SHA\]](#). Although the oxidation state of Tc in the complex(es) has not been established, it is known that Tc(IV) is the most stable oxidation state in reducing conditions [\[99RAR/RAN\]](#). Spectra of the products obtained when reducing Tc(VII) by Sn(II) in oxalate solutions are given in [\[85GRA/FAR\]](#). None of these publications and patents report data that may be used to obtain thermodynamic information for the technetium-oxalate system in aqueous solutions.

## VI.9 Zirconium oxalate compounds and complexes

### VI.9.1 Zirconium oxalate compounds

Since the first report of insoluble zirconium oxalate [1820DUB/SIL], it was generally observed [58BLU] that precipitates formed on adding oxalic acid or oxalate salts to solutions of zirconium salts, and that the precipitates dissolved and very stable soluble complexes were formed when excess amounts of oxalate were added. In an excess amount of oxalate, the solubility of zirconium oxalate has been studied in solution containing variable amounts of alkali (sodium to caesium and ammonium) oxalate ([36BOU], [36BOU2]). Although the solubilities and the solid salts compositions were reported, the results are not credited in this review due to the lack of experimental details. The compositions, structures and preparative conditions for the insoluble compounds formed with relatively small amounts of oxalate are uncertain due to the strong tendency of zirconium to undergo hydrolytic polymerisation even in acidic solutions ([31GAB], [55MOH/SIN], [57ZAI/SHU2], [58BLU], [58BOB/BEN]). By using two phase distribution with TTA, Connick and coworkers ([49CON/MCV], [51CON/REA], [56ZIE/CON]) have shown that monomeric  $\text{Zr}^{4+}$  or  $\text{ZrOH}^{3+}$  can only exist at zirconium concentrations lower than  $5 \times 10^{-4}$  M in 2 M  $\text{HClO}_4$  and lower than  $10^{-4}$  M in 1 M  $\text{HClO}_4$ . Thus, although it was once thought that the simple monomeric “zirconyl” ion,  $\text{ZrO}^{2+}$ , is present in acidic solutions, inferred from the stoichiometry of basic salts such as  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , structural determinations have shown that the solids do not contain such “zirconyl” ions but tetranuclear  $[\text{Zr}_4(\text{OH})_8(\text{OH}_2)_{16}]^{8+}$  moieties, as shown in Figure VI-21 ([76BAE/MES], [97RIC] and the references cited therein).

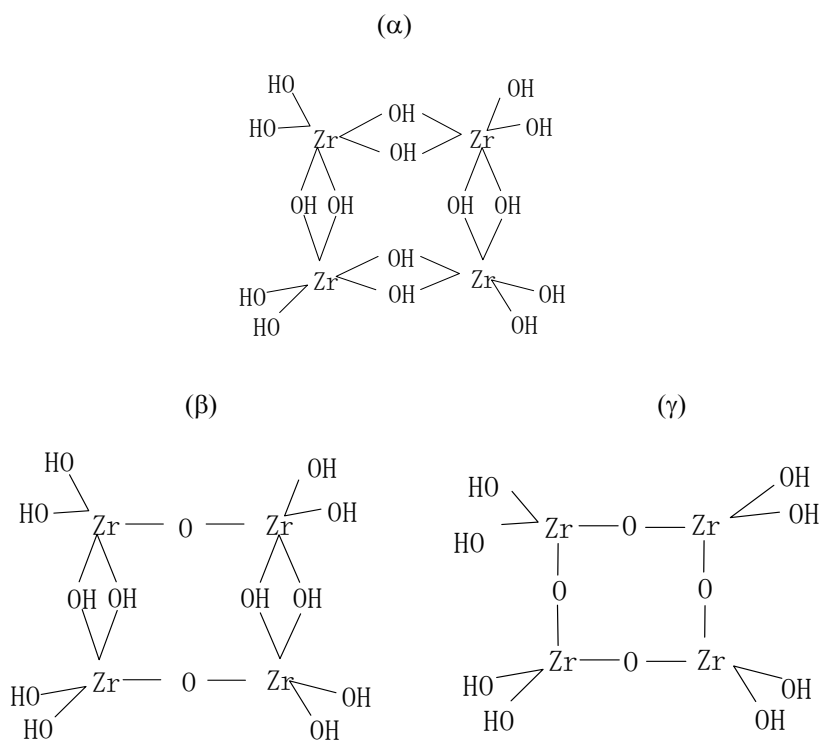
Figure VI-21: Structure of the  $\mu$ -hydroxy bridged tetranuclear cation,  $[\text{Zr}_4(\text{OH})_8(\text{OH}_2)_{16}]^{8+}$ , present in solid  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ .





To obtain information about the degree of polymerisation (change of hydroxide into hydroxo- or oxo-bridged species) in “zirconium hydroxide”, Zaitsev and co-workers ([62ZAI/BOC3], [64ZAI2], [64ZAI3], [65ZAI/BOC], [66ZAI2]) examined by titration in the presence of fluoride the reactivity of variously aged or ignited precipitates for the displacement of OH by fluoride and obtained infrared absorption spectra of these compounds. The result indicated that there were three types of zirconium hydroxides ( $\alpha$ ) freshly prepared precipitate, ( $\beta$ ) precipitate from concentrated “zirconyl chloride” in methanol, and ( $\gamma$ ) precipitate aged by boiling for a long time, each precipitate corresponding to the structure shown in Figure VI-22.

Figure VI-22: Structures of the variously aged “zirconium hydroxides”



Zaitsev [66ZAI2] has also shown that, in the reaction with oxalate, the reactivity of the hydroxide decreases in the order  $\alpha \rightarrow \beta \rightarrow \gamma$ , whereas the  $\beta$ -ring is the most stable, and a small amount of oxalate generally does not alter the tetrameric unit and

only exchange with peripheral hydroxides, and oxalate brings about an increase in the stability of the ring converting the  $\alpha$ -ring into  $\beta$ - or  $\gamma$ -ring. This explains why oxalate forms precipitates (mixed hydroxy-oxalate complexes) when oxalate is deficient and soluble complexes when oxalate is in excess ([64KHA/BOC2], [64KHA/ZAI2]). Based on this fact, Zaitsev and coworkers ([64ZAI/BOC2], [67ZAI/SHU2]) measured the solubilities of these zirconium hydroxides and estimated the apparent solubility products,  $K_{sp}$ , assuming the composition of “zirconyl oxalates” ([67ZAI/SHU2] in Table VI-27). As discussed in the paper [67ZAI/SHU2], values of  $K_{sp}$  were calculated by the authors only for comparing the behavior of these solid compounds. Although these values give some qualitative insight about the solubility of these compounds, they cannot be considered as thermodynamic constants since the solids slowly transform into other forms. At present, no thermodynamic value can be selected for zirconium oxalate compounds.

Crystal structure data are reported for  $\text{Na}_6[\text{ZrOH}(\text{ox})_3]_2 \cdot 7\text{H}_2\text{O}$  [98MOR/ALM],  $[\text{K}_2\{\text{Zr}(\text{ox})_3\}\text{H}_2\text{ox} \cdot \text{H}_2\text{O}]_n$  [97BAG/GAR], and  $\text{K}_6[\{\text{Zr}(\text{ox})_3\}_2(\mu\text{-ox})] \cdot 4\text{H}_2\text{O}$  [97BAG/GAR2], but no thermodynamic data are available for these compounds.

Table VI-27: Literature data on the solubility product of the solid compounds of zirconium with oxalate.

$K_{sp} = [“\text{ZrO}^{2+}”][\text{ox}^{2-}]$  where “ $\text{ZrO}^{2+}$ ” corresponds to the entity given in this table.

Ionic medium	$t$ (°C)	Solid	Definition of $K_{sp}$	$K_{sp}$	Reference
0.01 – 0.06 M $[\text{H}^+]$ $I = 0.1$ M (H, $\text{NH}_4$ ) $\text{ClO}_4$	25		$[\text{Zr}(\text{OH})_2^{2+}][\text{ox}^{2-}]f_{\pm}^2$	$0.98 \times 10^{-10}$	[64ZAI/BOC2]
0.02 – 1.0 M $[\text{H}^+]$ $I = 1$ M (H, $\text{NH}_4$ ) $\text{ClO}_4$	25	$\alpha$	$[\text{Zr}_2(\text{OH})_6^{2+}][\text{ox}^{2-}]$	$(5.0 \pm 1) \times 10^{-10}$	[67ZAI/SHU2]
		$\beta$	$[\text{Zr}_2\text{O}(\text{OH})_4^{2+}][\text{ox}^{2-}]$	$(9.0 \pm 1) \times 10^{-12}$	
		$\gamma$	$[\text{Zr}_2\text{O}_2(\text{OH})_2^{2+}][\text{ox}^{2-}]$	$(4.9 \pm 1) \times 10^{-11}$	

## VI.9.2 Zirconium oxalate complexes

Although it is certain that  $\text{Zr}^{4+}$  forms very stable complexes with oxalate, reliable determination of their stability constants is quite difficult. As discussed in the previous section,  $\text{Zr}^{4+}$  can be predominant only in strongly acidic solutions at low zirconium concentrations ([49CON/MCV], [51CON/REA], [56ZIE/CON]). Even at low concentrations, zirconium undergoes hydrolytic polymerisation at a higher pH. Thus, the experimental determination of the stability of zirconium oxalate complexes can be carried out only in strongly acidic solutions. Moreover, since  $\text{Zr}^{4+}$  usually forms very stable complexes with many substances, the concentration of free  $\text{Zr}^{4+}$  is difficult to be reliably determined. These restrictions, not only concerning the adaptable pH or acidity but also concerning suitable ionic media, are serious obstacles for obtaining reliable speciation and stability constants.

In Table VI-28, experimental equilibrium data found in the literature are presented. Several papers report qualitative information only about zirconium oxalate complexation [59KIR/TAN], [68KOZ], [68POS/ZAI2], [86MAT/PAS], or review original literature [64CAL], [64RYA/MAR], and those are discussed in Appendix A but not included in Table VI-28. As discussed in detail in Appendix A, no paper can be accepted in this review for the selection of the stabilities of zirconium oxalate complexes. Most papers had to be rejected for various reasons [58ERM/BEL], [60BAB/DUB], [61BAB/SHT], [61GRI/AST], [62MAR/RYA2], [62SHV/MAS2], [66KOR/SHE2], [71PYA/KRA2], [71SOL/IVA2], [76TRI/SCH], and only one study [64CAL/KYR] contains reliable experimental data. However, unlike the other metal ions considered in this review, no NEA selected values for Zr hydrolysis were available at the time of the preparation of this section. Thus, a consistent re-evaluation of Zr oxalate complexation based on the data of [64CAL/KYR] has to be postponed until selected hydrolysis data are available.

Table VI-28: Literature data on the formation constants of oxalate complexes of zirconium

Method	Medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Zr}^{4+} + \text{ox}^{2-} \rightleftharpoons \text{Zr(ox)}^{2+}$				
sp	1, 0.5 M HClO <sub>4</sub>	?	9.80	[60BAB/DUB]
1)	1 M HCl	?	9.80	[61BAB/SHT]
em	<i>I</i> = 0.04 M (H <sup>+</sup> , Na <sup>+</sup> , Zr <sup>4+</sup> )(ClO <sub>4</sub> <sup>-</sup> , ox <sup>2-</sup> ) → 0	20	11.13	[62SHV/MAS2]
2)	1 N HNO <sub>3</sub>	?	(11.07 ± 0.2)	[64CAL/KYR]
2)	5 N HNO <sub>3</sub>	?	(11.28 ± 0.2)	[64CAL/KYR]
1)	1 N HCl	?	(10.26 ± 0.12)	[66KOR/SHE2]
$\text{Zr}^{4+} + \text{H}_2\text{ox} \rightleftharpoons \text{Zr(ox)}^{2+} + 2\text{H}^+$				
aix	0.2 M HCl	?	3.85	[58ERM/BEL]
cix	2 M HClO <sub>4</sub>	?	(5.47 ± 0.10)	[62MAR/RYA2]
cix	4 M HClO <sub>4</sub>	?	(5.60 ± 0.12)	[62MAR/RYA2]
$\text{Zr(ox)}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Zr(ox)}_2(\text{aq})$				
sp	1, 0.5 M HClO <sub>4</sub>	?	7.34	[60BAB/DUB]
em	<i>I</i> = 0.04 M (H <sup>+</sup> , Na <sup>+</sup> , Zr <sup>4+</sup> )(ClO <sub>4</sub> <sup>-</sup> , ox <sup>2-</sup> ) → 0	20	9.18	[62SHV/MAS2]
2)	1 N HNO <sub>3</sub>	?	(9.21 ± 0.3)	[64CAL/KYR]
$\text{Zr(ox)}^{2+} + \text{H}_2\text{ox(aq)} \rightleftharpoons \text{Zr(ox)}_2(\text{aq}) + 2\text{H}^+$				
aix	0.2 M HCl	?	4.15	[58ERM/BEL]
cix	4 M HClO <sub>4</sub>	?	(4.21 ± 0.33)	[62MAR/RYA2]

(Continued on next page)

Table VI-28 (continued)

Method	Medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Zr(ox)}_2(\text{aq}) + \text{ox}^{2-} \rightleftharpoons \text{Zr(ox)}_3^{2-}$				
sp	1, 0.5 M HClO <sub>4</sub>	?	3.72	[60BAB/DUB]
em	<i>I</i> = 0.04 M (H <sup>+</sup> , Na <sup>+</sup> , Zr <sup>4+</sup> )(ClO <sub>4</sub> <sup>-</sup> , ox <sup>2-</sup> ) → 0	20	6.66	[62SHV/MAS2]
$\text{Zr(ox)}_2(\text{aq}) + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Zr(ox)}_3^{2-} + 2\text{H}^+$				
aix	0.2 M HCl	?	2.0	[58ERM/BEL]
$\text{Zr(ox)}_3^{2-} + \text{ox}^{2-} \rightleftharpoons \text{Zr(ox)}_4^{4-}$				
sp	1, 0.5 M HClO <sub>4</sub>	?	0.30	[60BAB/DUB]
pot	0.1 M HCl	?	3.89 – 4.10	[61GRI/AST]
em	<i>I</i> = 0.04 M (H <sup>+</sup> , Na <sup>+</sup> , Zr <sup>4+</sup> )(ClO <sub>4</sub> <sup>-</sup> , ox <sup>2-</sup> ) → 0	20	6.07	[62SHV/MAS2]
$\text{Zr(ox)}_3^{2-} + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Zr(ox)}_4^{4-} + 2\text{H}^+$				
aix	0.2 M HCl	?	1.7	[58ERM/BEL]
$\text{ZrO}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{ZrO(ox)}(\text{aq})$				
sp	[H <sup>+</sup> ] = 0.001, 0.5 × 10 <sup>-4</sup> M	?	6.68	[60BAB/DUB]
$\text{ZrO(ox)}(\text{aq}) + \text{ox}^{2-} \rightleftharpoons \text{ZrO(ox)}_2^{2-}$				
sp	[H <sup>+</sup> ] = 0.001, 0.5 × 10 <sup>-4</sup> M	?	3.34	[60BAB/DUB]
$\text{ZrO}^{2+} + 2\text{ox}^{2-} \rightleftharpoons \text{ZrO(ox)}_2^{2-}$				
sol	pH 5.2	?	(8.68 ± 0.10)	[71PYA/KRA2]
$\text{Zr(OH)}_2^{2+} + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Zr(OH)}_2(\text{ox})(\text{aq}) + 2\text{H}^+$				
dis	2 – 4 M HClO <sub>4</sub>	?	6.6	[71SOL/IVA2]
$\text{ZrOH}^{3+} + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Zr(ox)}^{2+} + \text{H}^+$				
dis	<i>I</i> = 4 M (HClO <sub>4</sub> + NaClO <sub>4</sub> )	?	(4.3 ± 0.1)	[76TRI/SCH]

1) Metal indicator method , 2) Sorption on silica gel

## VI.10 Uranium oxalate compounds and complexes

### VI.10.1 Solid uranium oxalates

No structural or thermodynamic data for solid U(III) or U(V) oxalates could be identified in the literature. Thus, only the information on solid U(IV) and U(VI) oxalates is discussed in this review.

#### VI.10.1.1 Solid uranium(IV) oxalates

Seekamp was probably the first to report the formation of a “green crystalline powder” of U(IV) oxalate when a solution of U(VI) nitrate and oxalic acid was exposed to “the sunlight of a July morning” [1862SEE], presumably due to the reduction of U(VI) through photolysis. The first preparation and identification of the chemical composition

of solid U(IV) oxalate compounds were reported in 1901 [01KOH], [01KOH/ROS]. Since then, numerous papers have been published on the preparation of solid U(IV) oxalates, ranging from binary, ternary, quaternary and more complex compounds. Examples of the solid U(IV) oxalates are:  $\text{U(ox)}_2 \cdot n\text{H}_2\text{O(s)}$  ( $n = 1, 2, 6$ ),  $\text{U}_2(\text{ox})_4 \cdot 12\text{H}_2\text{O(s)}$ ,  $\text{M}_i[\text{U}_j(\text{ox})_k] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{H}^+, \text{Na}^+, \text{K}^+, \text{NH}_4^+$ ;  $i = 2, 4, 6, 8$ ;  $j = 1, 2$ ;  $k = 3, 4, 5, 7, 8$ ;  $n = 1, 4, 5, 8, 10$ ),  $\text{M}_i[\text{U(ox)}_k] \cdot n\text{H}_2\text{O(s)}$  ( $\text{M} = \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Cd}^{2+}, \text{Pb}^{2+}$ ;  $i = 2, 4$ ;  $k = 4, 6$ ;  $n = 8, 12$ ),  $\text{M}_2\text{Sr}[\text{U(ox)}_4] \cdot 8\text{H}_2\text{O(s)}$  ( $\text{M} = \text{Na}^+, \text{K}^+, \text{NH}_4^+$ ),  $\text{La}_4[\text{U(ox)}_4]_3 \cdot n\text{H}_2\text{O(s)}$  ( $n = 3, 22$ ),  $\text{MLn}[\text{U(ox)}_4] \cdot 8\text{H}_2\text{O(s)}$  ( $\text{M} = \text{K}^+, \text{NH}_4^+$ ;  $\text{Ln} = \text{La}^{3+}, \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Tb}^{3+}$ ),  $\text{U}_2(\text{ox})_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O(s)}$ ,  $\text{U}_2(\text{ox})_3\text{SO}_4 \cdot 12\text{H}_2\text{O(s)}$  and other mixed ligand U(IV) oxalate compounds containing  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{OH}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SCN}^-$  and  $\text{PO}_4^{3-}$  [66CHE], [87DOL], [91MAT/KAR].

Some of the solid U(IV) oxalates were characterised by chemical analysis, X-ray diffraction and thermal gravimetry and, for a much smaller number of compounds, by solubility measurements. Since this review mainly concerns about the thermodynamic data, Table VI-29 lists only the solid U(IV) oxalates of which the solubilities are reported in the literature. Information on the preparation, structure and properties of thermal decomposition of solid U(IV) oxalates is available in the literature including the review articles [66CHE], [87DOL], [87MEF/KRO] and [91MAT/KAR].

Table VI-29: Solid U(IV) oxalates of which the solubilities are reported in the literature.

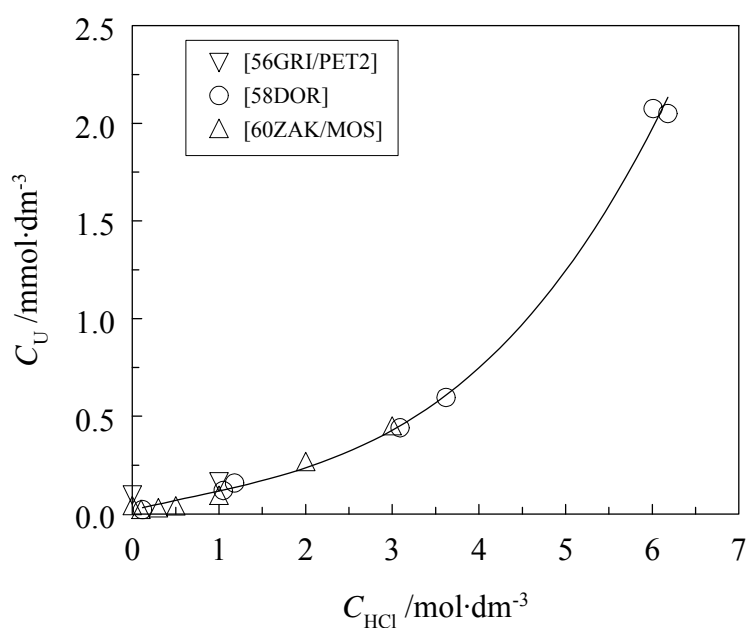
Compound	Reference
$\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$	[56GRI/PET2], [58GRI/PET2], [60ZAK/MOS], [63GRI/PET], [70PET/STE2], [79NIK]
$\text{U(ox)}_2 \cdot \text{H}_2\text{O(s)}$ or $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$	[58DOR]
$\text{K}_4\text{U(ox)}_4 \cdot 8\text{H}_2\text{O(s)}$	[02ORL]
$\text{K}_2\text{U}_2(\text{ox})_5 \cdot 8\text{H}_2\text{O(s)}$	[70PET/STE2]
$\text{KCe}[\text{U(ox)}_4] \cdot 8\text{H}_2\text{O(s)}$	[59GRI/PET]

$\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  is the most frequently studied solid U(IV) oxalate. Upon heating, it dehydrates and eventually decomposes to  $\text{UO}_2(\text{s})$  in nitrogen and  $\text{U}_3\text{O}_8(\text{s})$  in air [63BRE/CLA2], [87DOL]. The stepwise enthalpies of the first and the second dehydration and the decomposition were determined to be 96, 21, and  $-238 \text{ kJ} \cdot \text{mol}^{-1}$ , by differential thermal analysis [69SUB/SIN]. The standard entropy of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  was estimated to be  $S_m^\circ(298.15 \text{ K}) = 385 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  [73MOS].

It is generally agreed in the literature that  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  is sparingly soluble in water [56GRI/PET2], [58DOR], [58GRI/PET2], [60ZAK/MOS], [63GRI/PET], [70PET/STE2], [79NIK]. The solubility increases as the concentrations of mineral acids ( $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$ ) are increased [56GRI/PET2], [58DOR], [58GRI/PET2], [60ZAK/MOS], [63GRI/PET]. Figure VI-23 shows the solubility of

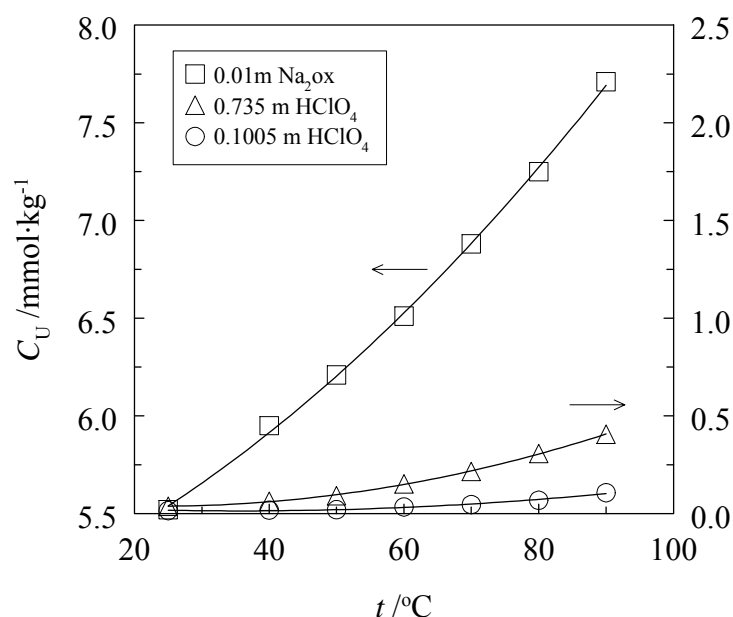
$\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  in HCl and water ( $c_{\text{HCl}} = 0$ ) from [56GRI/PET2], [58DOR] and [60ZAK/MOS]. The temperature for the data from [60ZAK/MOS] is unknown, but there is a good agreement between the data from [58DOR] and [60ZAK/MOS]. However, the solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  in water from [56GRI/PET2] ( $0.097 \text{ mmol} \cdot \text{kg}^{-1}$  U) is more than twice as much as that from [60ZAK/MOS] ( $0.043 \text{ mmol} \cdot \text{kg}^{-1}$  U).

Figure VI-23: Solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  in HCl. Symbols: data from [58DOR] ( $t = 25^\circ\text{C}$ ), [56GRI/PET2] ( $t = 25^\circ\text{C}$ ), and [60ZAK/MOS] ( $t$  unknown); curve: unweighted polynomial fit of the data.



In the solutions of oxalic acid or the salt of oxalate (sodium, ammonium, potassium), the solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  increases significantly due to the formation of aqueous U(IV) oxalate complexes [58DOR], [60ZAK/MOS], [63GRI/PET], [79NIK]. Also, the solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  increases as the temperature is increased. Figure VI-24 shows the data reported in [79NIK].

Figure VI-24: Solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  in  $\text{HClO}_4$  and  $\text{Na}_2\text{ox}$  at different temperatures reported in [79NIK]. Symbols: experimental data; curves: unweighted polynomial fit of the data.



The solubility experiments of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  are usually complicated by the potential oxidation of U(IV) during the experiments and the strong tendency of U(IV) towards hydrolysis. For example, in a study of the solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  in  $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{H}_2\text{SO}_4$  [63GRI/PET], the total concentration of uranium was found to be much higher than the concentration of U(IV) in all the solutions except  $\text{HCl}$ , despite that great care was taken to prevent U(IV) from being oxidised by saturating the solutions with hydrogen and passing nitrogen through the solutions. The difference between the concentrations of total uranium and U(IV) was attributed to the partial oxidation of U(IV) to U(VI) by tracer amounts of oxygen or the product of  $\alpha$ -radiolysis of water [63GRI/PET]. This casts serious doubts on the reliability of the solubility data obtained from the experiments where the analysis of oxidation states of uranium is not performed and/or the equilibrium solid phase is not identified. It should be pointed out that the composition of the equilibrium solid phase was not characterised in any of these solubility experiments, though the formula of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  was given [56GRI/PET2], [58GRI/PET2], [60ZAK/MOS], [63GRI/PET], [70PET/STE2], [79NIK].

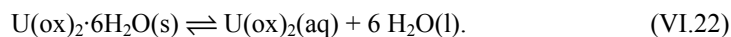
Solubility data from the references where experimental conditions are appropriately described are considered in this review and summarised in Table VI-30. For the references in which the uncertainties of data were not given, or were too optimistic, a value of  $\pm 0.2$  is assigned to the  $\log_{10} K_s$  by this review. The results from [60ZAK/MOS] are included despite that the temperature of the experiment is unknown, because the data appear to agree with the results at 25°C from [58DOR] (see Figure VI-23) and with the data at 25°C from [79NIK] within the uncertainties (Table VI-30). Solubility data from the references with serious faults or without essential experimental conditions (*e.g.*, temperature, ionic strength) are not accepted in this review, including the data for  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  [56GRI/PET2], [58GRI/PET2], [63GRI/PET], [70PET/STE2], for  $\text{K}_4\text{U(ox)}_4\text{(s)}$  [02ORL], for  $\text{K}_2\text{U}_2\text{(ox)}_5 \cdot 8\text{H}_2\text{O(s)}$  [70PET/STE2], and for  $\text{KCe[U(ox)}_4\text{]}\cdot 8\text{H}_2\text{O(s)}$  [59GRI/PET]. The reasons for rejection are provided in Appendix A.

Table VI-30: Solubility constants of solid uranium(IV) oxalates reported in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10} K_s$	Reference
$\text{U(ox)}_2 \cdot \text{H}_2\text{O(s)} \rightleftharpoons \text{U(OH)}^{3+} + 2 \text{ox}^{2-} + \text{H}^+$				
sol	0.118-6.18 M HCl	25	$-(21.91 \pm 0.20)$	<a href="#">[58DOR]</a>
sol	0.26% $\text{H}_2\text{ox}/3.08$ N HCl	25	$-(21.03 \pm 0.20)$	<a href="#">[58DOR]</a>
sol	0.26% $\text{H}_2\text{ox}/6.05$ N HCl	25	$-(22.00 \pm 0.20)$	<a href="#">[58DOR]</a>
$\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)} + 4 \text{H}^+ \rightleftharpoons \text{U}^{4+} + 2 \text{H}_2\text{ox(aq)} + 6 \text{H}_2\text{O(l)}$				
sol	(0-3) M HCl	?	$-(10.82 \pm 0.20)$	<a href="#">[60ZAK/MOS]</a>
$\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)} + 2 \text{H}^+ \rightleftharpoons \text{U(ox)}^{3+} + \text{H}_2\text{ox(aq)} + 6 \text{H}_2\text{O(l)}$				
sol	(0-3) M HCl	?	$-(7.60 \pm 0.20)$	<a href="#">[60ZAK/MOS]</a>
$\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)} \rightleftharpoons \text{U(ox)}_2\text{(aq)} + 6 \text{H}_2\text{O(l)}$				
sol	(0-3) M HCl	?	$-(4.52 \pm 0.20)$	<a href="#">[60ZAK/MOS]</a>
sol	0.1005 m $\text{HClO}_4$	25	$-(4.82 \pm 0.20)$	<a href="#">[79NIK]</a>
		40	$-(4.74 \pm 0.20)$	
		50	$-(4.70 \pm 0.20)$	
		60	$-(4.47 \pm 0.20)$	
		70	$-(4.34 \pm 0.20)$	
		80	$-(4.24 \pm 0.20)$	
		90	$-(4.03 \pm 0.20)$	
$\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)} \rightleftharpoons \text{U}^{4+} + 2 \text{ox}^{2-} + 6 \text{H}_2\text{O(l)}$				
sol	(0-3) M HCl	?	$-(21.37 \pm 0.19)$	<a href="#">[60ZAK/MOS]</a>

The solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  in 0.1005 m  $\text{HClO}_4$  was studied at variable temperatures (25-90°C) (Figure VI-24) [79NIK]. The solubility constant  $\log_{10} K_s$  (VI.22) was found to increase as the temperature was increased (Table VI-30),





From these data, the values of  $\Delta_r H_m$  (VI.22) at variable temperatures were calculated in [79NIK] (Table VI-31). The uncertainties ( $\pm 10\%$ ) are assigned by this review.

Table VI-31: Experimental enthalpy of Reaction (VI.22) reported in [79NIK].

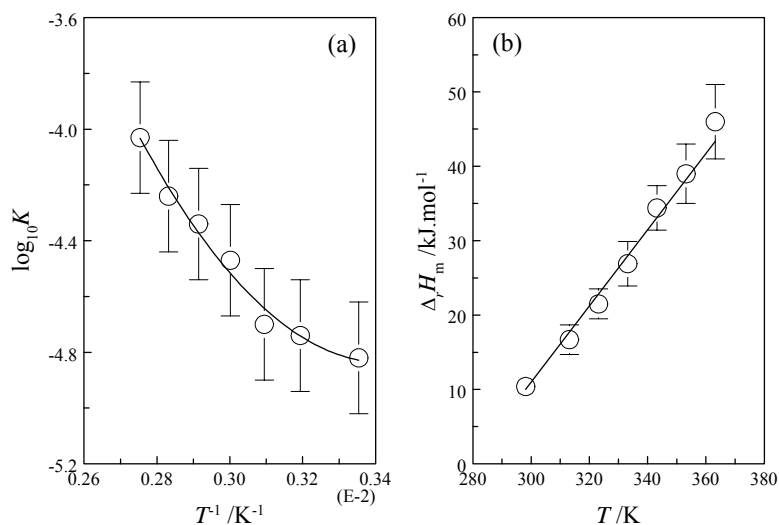
Method	Ionic medium	$t$ (°C)	$\Delta_r H_m$ (kJ·mol <sup>-1</sup> )
$\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)} \rightleftharpoons \text{U(ox)}_2\text{(aq)} + 6 \text{H}_2\text{O(l)}$			
sol	0.1005 m HClO <sub>4</sub>	25	(10.4 ± 1.0)
		40	(16.7 ± 2.0)
		50	(21.5 ± 2.0)
		60	(26.9 ± 3.0)
		70	(34.4 ± 3.0)
		80	(39.0 ± 4.0)
		90	(46.0 ± 5.0)

As pointed out previously and discussed in Appendix A, the equilibrium solid phase in the solubility experiments of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  was not characterised to confirm the composition in any of the references, including [79NIK]. This raises questions on the reliability of the solubility constants in Table VI-30 and the enthalpy of dissolution in Table VI-31. However, the data in Table VI-30 reasonably agree between different references and are consistent with the related stability constants of aqueous U(IV) oxalate complexes from different references (Table VI-36, page 226). The enthalpy values in Table VI-31 are also consistent with the trend of the solubility constants in Table VI-30. The plot of  $\log_{10} K_s$  (VI.22) as a function of  $1/T$  (Figure VI-25-a) indicates that  $\Delta_r H_m$  (VI.22) should be positive in the temperature range because  $d \log_{10} K / d(1/T) < 0$ , that  $\Delta_r H_m$  (VI.22) probably does not remain constant because  $d \log_{10} K / d(1/T) \neq \text{constant}$ , and that  $\Delta_r H_m$  (VI.22) should become increasingly positive as the temperature is increased because  $d \log_{10} K / d(1/T)$  becomes larger as  $T$  increases. A plot of  $\Delta_r H_m$  (VI.22) as a function of the temperature is shown in Figure VI-25-b. A weighted linear regression results in a value of  $\Delta_r C_{p,m}$  (VI.22) = (513 ± 41) J·K<sup>-1</sup>·mol<sup>-1</sup>.

The above discussions show that some of the solubility data reported in the literature agree within experimental uncertainty and appear to be of good quality. Since there are no ionic species involved in Reaction (VI.22), the medium effect on the solubility constant and enthalpy is expected to be small and the correction for ionic strength is probably insignificant compared to the uncertainty of the data. Thus, the values of  $\log_{10} K_s$  (VI.22) in Table VI-30 and  $\Delta_r H_m$  (VI.22) in Table VI-31 may be taken as  $\log_{10} K_s^\circ$  and  $\Delta_r H_m^\circ$  (VI.22). However, taking into consideration various shortcomings

in the experiments, including the lack of characterisation of the equilibrium solid phase and confirmation of the oxidation state of U(IV) and the varied ionic strength, no thermodynamic solubility constants or enthalpy are recommended for  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O(s)}$  by this review.

Figure VI-25: Experimental solubility constants (a) and enthalpy (b) for the Reaction (VI.22), original data from [79NIK].



### VI.10.1.2 Solid uranium(VI) oxalates

#### VI.10.1.2.1 General comments

Preparation and characterisation of many solid U(VI) oxalate compounds were reported in the literature, ranging from binary, ternary and more complex compounds [66CHE]. Examples of the binary and ternary solid U(VI) oxalates are:  $\text{UO}_2(\text{ox}) \cdot n\text{H}_2\text{O}$  ( $n = 0, 1, 3$ ),  $\text{M}[\text{UO}_2(\text{ox})_2] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Sr}^{2+}, \text{Ba}^{2+}; n = 4, 5, 10$ ),  $\text{M}_2[\text{UO}_2(\text{ox})_2] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{Tl}^+, \text{NH}_4^+; n = 0, 2, 3, 4, 5, 6$ ),  $\text{M}_2[\text{UO}_2(\text{ox})_3] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Ba}^{2+}; n = 7$ ),  $\text{M}_4[\text{UO}_2(\text{ox})_3] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{NH}_4^+, \text{Tl}^+; n = ?$ ),  $\text{M}_2[(\text{UO}_2)_2(\text{ox})_3] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{K}^+, \text{Cs}^+, \text{Tl}^+, \text{NH}_4^+; n = 0, 3, 4$ ) and  $\text{M}_6[(\text{UO}_2)_2(\text{ox})_5] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Na}^+, \text{K}^+, \text{Cs}^+, \text{NH}_4^+, \text{N}_2\text{H}_5^+; n = 2, 6, 10, 13$ ) [66CHE]. The quaternary or more complex solid U(VI) oxalates usually contain alkali metals and one or two other ligands such as  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SCN}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SeO}_4^{2-}$ ,  $\text{O}_2^{2-}$  and acetate. Detailed descriptions of the compounds are available in the literature including the review articles [66CHE], [87MEF/KRO], [91MAT/KAR].

Some of the solid U(VI) oxalates were characterised by chemical analysis, X-ray powder diffraction and thermal gravimetry and, for a much smaller number of compounds, by structures from X-ray single crystal data or solubility measurements. Table VI-32 lists only the solid U(VI) oxalates of which either the structural data by X-ray crystallography or the solubilities are reported in the literature.

Table VI-32: Solid U(VI) oxalates of which the structures by X-ray crystallography or the solubilities are reported in the literature.

Compound	Reference	
	Structure by X-ray Crystallography	Solubility
UO <sub>2</sub> ox·3H <sub>2</sub> O	<a href="#">[56STA/CRO3]</a> <a href="#">[72JAY/CHA]</a>	<a href="#">[1842EBE]</a> , <a href="#">[16COL]</a> <a href="#">[17COL]</a> , <a href="#">[17COL2]</a> <a href="#">[25COL]</a> , <a href="#">[34COL]</a> <a href="#">[52AMP/DAV]</a> <a href="#">[57BOL/KOR3]</a> <a href="#">[57BOL/KOR4]</a> <a href="#">[58BOL/KOR]</a> <a href="#">[59MOS/ZAK]</a>
UO <sub>2</sub> ox·H <sub>2</sub> O, UO <sub>2</sub> ox (NH <sub>4</sub> ) <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> ]	<a href="#">[64BRE/CLA]</a> <a href="#">[73ALC2]</a>	
Li <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> ]·5H <sub>2</sub> O, Na <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> ]·4H <sub>2</sub> O	<a href="#">[97DAH/CHA2]</a>	
Na <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> ]·5H <sub>2</sub> O, K <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> ]·3H <sub>2</sub> O		<a href="#">[67SHC/BEL2]</a>
M <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> ]·nH <sub>2</sub> O (M = Rb, Cs, NH <sub>4</sub> , (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> NH <sub>2</sub> ; n = 2 and 4) [(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> (NH)] <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> ]·4H <sub>2</sub> O (CN <sub>3</sub> H <sub>6</sub> ) <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> CO(NH <sub>2</sub> ) <sub>2</sub> ]		<a href="#">[69SHC/BEL]</a>
M <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> CO(NH <sub>2</sub> ) <sub>2</sub> ]·H <sub>2</sub> O <sup>a</sup> (M = K, Rb, Cs, NH <sub>4</sub> )		
Tl <sub>2</sub> [UO <sub>2</sub> (ox) <sub>2</sub> ]·2H <sub>2</sub> O	<a href="#">[73JAY/DIA]</a>	
(NH <sub>4</sub> ) <sub>4</sub> [UO <sub>2</sub> (ox) <sub>3</sub> ]	<a href="#">[73ALC]</a>	
(NH <sub>4</sub> ) <sub>2</sub> [(UO <sub>2</sub> ) <sub>2</sub> (ox) <sub>3</sub> ]	<a href="#">[73ALC3]</a>	
K <sub>2</sub> [(UO <sub>2</sub> ) <sub>2</sub> (ox) <sub>3</sub> ]·4H <sub>2</sub> O	<a href="#">[75JAY/SIN]</a> <a href="#">[2002SZA/FIS]</a>	
K <sub>2</sub> [UO <sub>2</sub> F <sub>2</sub> (ox)], K <sub>4</sub> [UO <sub>2</sub> F <sub>2</sub> (ox) <sub>2</sub> ], K <sub>2</sub> [(UO <sub>2</sub> ) <sub>2</sub> F <sub>4</sub> (ox)]	<a href="#">[78CHA/BHA]</a>	
K <sub>3</sub> [UO <sub>2</sub> F <sub>3</sub> (ox)]·2H <sub>2</sub> O, K <sub>3</sub> [UO <sub>2</sub> F(ox) <sub>2</sub> ]·3H <sub>2</sub> O		<a href="#">[68SHC/BEL]</a>
(CN <sub>3</sub> H <sub>6</sub> ) <sub>3</sub> [UO <sub>2</sub> F <sub>3</sub> (ox)]·H <sub>2</sub> O (CN <sub>3</sub> H <sub>6</sub> ) <sub>3</sub> [UO <sub>2</sub> F(ox) <sub>2</sub> ]·H <sub>2</sub> O		
(NH <sub>4</sub> ) <sub>2</sub> [UO <sub>2</sub> (ox)(SO <sub>3</sub> )]·nH <sub>2</sub> O		<a href="#">[67ZAK/ORL2]</a>
(NH <sub>4</sub> ) <sub>2</sub> [UO <sub>2</sub> (O <sub>2</sub> )ox]·3H <sub>2</sub> O	<a href="#">[64BAS/KRI]</a>	
(N <sub>2</sub> H <sub>5</sub> ) <sub>6</sub> [(UO <sub>2</sub> ) <sub>2</sub> (ox) <sub>5</sub> ]·2H <sub>2</sub> O	<a href="#">[86GOV/PAT]</a>	

(Continued on next page)

Table VI-32: (continued)

Compound	Reference	
	Structure by X-ray Crystallography	Solubility
$K_6[(UO_2)_2(ox)_5] \cdot 10H_2O$	<a href="#">[76LEG/JEA]</a>	<a href="#">[67SHC/BEL]</a>
$Rb_6[(UO_2)_2(ox)_5] \cdot 2H_2O$ , $Cs_6[(UO_2)_2(ox)_5] \cdot 10H_2O$		<a href="#">[67SHC/BEL]</a>
$(CN_3H_6)_6[(UO_2)_2(ox)_5] \cdot 4H_2O^b$		
$[C_2H_4(NH_3)_2]_3[(UO_2)_2(ox)_5] \cdot 3H_2O^c$		
$Cs_2[UO_2(ox)(SeO_4)]$	<a href="#">[2000MIK/GOR2]</a>	
$(NH_4)_2[UO_2(ox)(SeO_4)] \cdot 1.5H_2O$	<a href="#">[96MIK/GOR2]</a>	
$Rb_2[UO_2(ox)(SO_4)] \cdot 4H_2O$	<a href="#">[93MIS/MIK]</a>	

a:  $CO(NH_2)_2$ , urea.

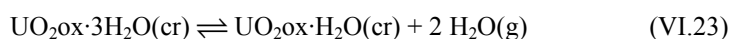
b:  $CN_3H_6^+$ , guanidinium cation.

c:  $[C_2H_4(NH_3)_2]_3^{2+}$ , ethylenediaminium cation.

The crystallographic data from the studies listed in Table VI-32 are not the subject of this review. The solubility data from the studies listed in Table VI-32 for the ternary or more complex solid U(VI) oxalates are not considered in this review, including  $M_6[(UO_2)_2(ox)_5] \cdot nH_2O$  from [\[67SHC/BEL\]](#),  $M_2[UO_2(ox)_2] \cdot nH_2O$  from [\[67SHC/BEL2\]](#) and [\[69SHC/BEL\]](#),  $M_2[UO_2(ox)_2\{CO(NH_2)_2\}] \cdot nH_2O$  from [\[67SHC/BEL2\]](#),  $M_3[UO_2F_3(ox)] \cdot nH_2O$  and  $K_3[UO_2F(ox)_2] \cdot nH_2O$  from [\[68SHC/BEL\]](#),  $(NH_4)_2[UO_2(SO_3)ox] \cdot nH_2O$  from [\[67ZAK/ORL2\]](#). The reasons for rejection are given in Appendix A.

#### VI.10.1.2.2 $UO_2ox \cdot 3H_2O(cr)$

$UO_2ox \cdot 3H_2O$  is the most frequently studied solid U(VI) oxalate. Upon heating, it dehydrates and eventually decomposes to  $UO_2(s)$  in nitrogen and  $U_3O_8(s)$  in air [\[63BRE/CLA2\]](#), [\[87DOL\]](#). The standard enthalpy of the dehydration Reactions (VI.23), (VI.24) are determined to be  $\Delta_f H_m^\circ(VI.23) = (119.9 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_f H_m^\circ(VI.24) = (73.3 \pm 3.5) \text{ kJ} \cdot \text{mol}^{-1}$  at 298.15 K by solution calorimetry [\[77OHA\]](#):



By determining the enthalpies of dissolution of  $H_2ox \cdot 2H_2O(cr)$ ,  $UO_2ox \cdot 3H_2O(cr)$ ,  $UO_2ox \cdot H_2O(cr)$  and  $UO_2ox(cr)$  in a solution of nitric acid and using a thermochemical cycle upon which  $\Delta_f H_m^\circ(UO_2ox \cdot 3H_2O, cr)$  is based, the standard enthalpies of formation,  $\Delta_f H_m^\circ$ , of  $UO_2ox \cdot 3H_2O(cr)$ ,  $UO_2ox \cdot H_2O(cr)$  and  $UO_2ox(cr)$  at 298.15 K were calculated to be  $-(2715.3 \pm 2.4)$ ,  $-(2711.8 \pm 2.4)$ , and  $-(1796.7 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively [\[77OHA\]](#). The value of  $\Delta_f H_m^\circ(UO_2ox \cdot 3H_2O, cr)$  was also calculated to be  $-(2688 \pm 4.1) \text{ kJ} \cdot \text{mol}^{-1}$  from the heat of combustion determined by bomb calorimetry [\[92THA/KUM\]](#), comparable to that reported in [\[77OHA\]](#). The standard

entropy of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  was estimated to be  $S_m^\circ(298.15\text{ K}) = 343\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [73MOS]. This value is consistent with the entropy of formation of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{cr})$ ,  $(347.517 \pm 63.351)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , calculated from reaction data selected by this review (*cf.* Table III-1).

Based on the values of  $\Delta_f H_m^\circ(\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}, \text{cr})$  from [77OHA] and [92THA/KUM], the standard enthalpy of formation of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{cr})$  is selected by this review:

$$\Delta_f H_m^\circ(\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}, \text{cr}, 298.15\text{ K}) = -(2702 \pm 18)\text{ kJ}\cdot\text{mol}^{-1}.$$

The solubility of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  has been studied in water, mineral acids and solutions of oxalates under various conditions [1842EBE], [16COL], [17COL], [17COL2], [25COL], [34COL], [52AMP/DAV], [57BOL/KOR3], [57BOL/KOR4], [58BOL/KOR], [59MOS/ZAK]. Some of the results from these papers are not considered by this review due to various shortcomings associated with the experimental conditions or the lack of information on the experiments. These include the solubility in  $\text{K}_2\text{ox}$  [16COL], in  $\text{Na}_2\text{ox}$  [17COL], in  $(\text{NH}_4)_2\text{ox}$  [17COL2], in  $\text{Mox}$  ( $\text{M} = \text{Ca}, \text{Sr}$  and  $\text{Ba}$ ) [34COL], and the solubility in mixed electrolyte solutions [57BOL/KOR4]. Detailed discussions on the exclusion of the results are provided in Appendix A. Table VI-33 summarises only the studies of which the solubility data of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  are considered by this review.

Table VI-33: Studies of the solubility of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{s})$  considered by this review.

System	$t$ (°C)	Solid phase	Reference
water	14, 100	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ (?)	[1842EBE]
water	11 – 100	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$	[25COL]
$\text{HNO}_3/\text{water}$ (1.8–31% by mass)	20	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$	
$\text{HNO}_3/\text{water}$ (15–70% by mass)	20	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ , $\text{UO}_2\text{ox}$	[52AMP/DAV]
$\text{HNO}_3/\text{water}$ (0–77% by mass)	25, 50	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ , $\text{UO}_2\text{ox}\cdot \text{H}_2\text{O}$ , $\text{UO}_2(\text{NO}_3)_2$	[58BOL/KOR]
$\text{HNO}_3/\text{water}$ (0.5–3.0 mol·dm <sup>-3</sup> )	20	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ (?)	[59MOS/ZAK]
$\text{HClO}_4/\text{water}$ (0.5–3.0 mol·dm <sup>-3</sup> )	20	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ (?)	
$\text{H}_2\text{ox}/\text{water}$ (0–38% by mass)	0–70	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ (?) $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O}$ (?)	[57BOL/KOR3]
$\text{H}_2\text{ox}/\text{HClO}_4/\text{water}$ (0.5 and 1.0 M $\text{HClO}_4$ , 0.08–0.6 M $\text{H}_2\text{ox}$ )	20	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ (?)	[59MOS/ZAK]
$\text{H}_2\text{ox}/\text{HNO}_3/\text{water}$ (0.5, 2.0 and 3.0 M $\text{HNO}_3$ , 0.08–0.6 M $\text{H}_2\text{ox}$ )	20	$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ (?)	

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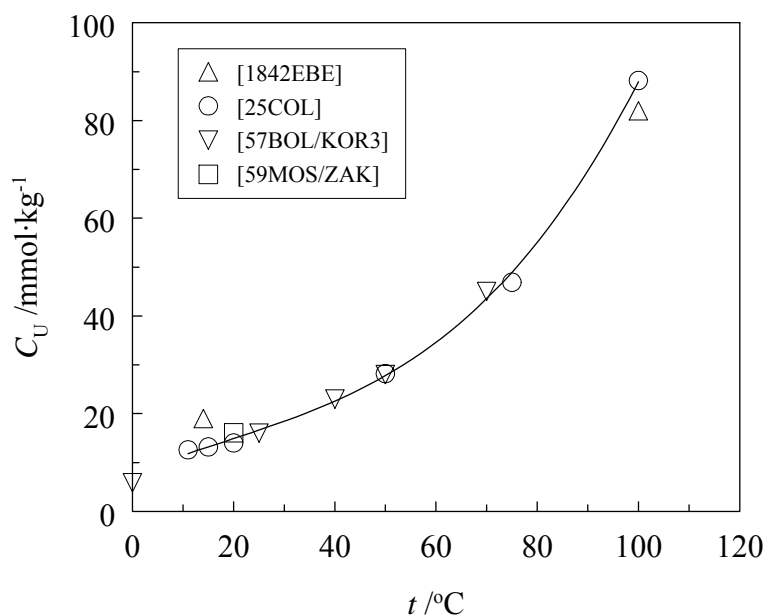
Table VI-33: (continued)

System	$t$ (°C)	Solid phase	Reference
(NH <sub>4</sub> ) <sub>2</sub> ox/HNO <sub>3</sub> /water (0.5 M HNO <sub>3</sub> , 0.07-0.3 M (NH <sub>4</sub> ) <sub>2</sub> ox)	20	UO <sub>2</sub> ox·3H <sub>2</sub> O(?)	[59MOS/ZAK]
(NH <sub>4</sub> ) <sub>2</sub> ox/HClO <sub>4</sub> /water (0.5 and 1.0 M HClO <sub>4</sub> , 0.07-0.3 M (NH <sub>4</sub> ) <sub>2</sub> ox)	20	UO <sub>2</sub> ox·3H <sub>2</sub> O(?)	

#### VI.10.1.2.2.1 Solubilities of UO<sub>2</sub>ox·3H<sub>2</sub>O(s) in water

The solubilities of UO<sub>2</sub>ox·3H<sub>2</sub>O(s) in water at different temperatures (0-100°C) were reported in [1842EBE], [25COL], [57BOL/KOR3] and [59MOS/ZAK]. As shown in Figure VI-26, all the results, except the data at 14°C from [1842EBE] and at 0°C from [57BOL/KOR3], agree with each other very well, suggesting that the values are reproducible and probably reliable. The data at 14°C from [1842EBE] seems erroneously high (> 40% higher than that from [25COL]) and the data at 0°C from [57BOL/KOR3] seems too low compared with the trend demonstrated by all the other data.

Figure VI-26: Solubility of UO<sub>2</sub>ox·3H<sub>2</sub>O(s) in water at different temperatures reported in the literature. Symbols: experimental data; curve: unweighted polynomial fit of the data.

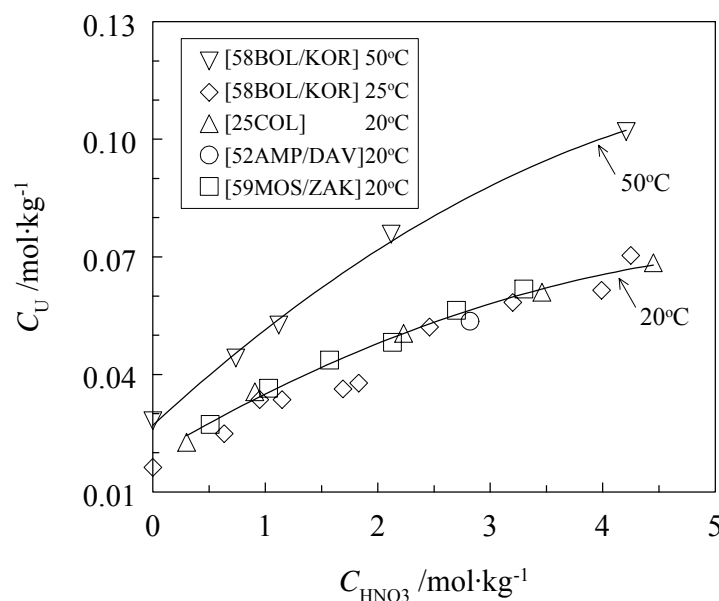


Data in Figure VI-26 show that the solubility of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{s})$  in water increases by six times as the temperature is increased from  $25^\circ\text{C}$  ( $\sim 0.015 \text{ mol}\cdot\text{kg}^{-1}$ ) to  $100^\circ\text{C}$  ( $\sim 0.09 \text{ mol}\cdot\text{kg}^{-1}$ ). By comparison of the solubility in water at the same temperature,  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  is a much more soluble solid than  $\text{U}(\text{ox})_2\cdot 6\text{H}_2\text{O}$ . For example, at  $25^\circ\text{C}$ , the solubility of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  in water ( $\sim 15 \text{ mmol}\cdot\text{kg}^{-1}$ ) is about 300 times as high as that of  $\text{U}(\text{ox})_2\cdot 6\text{H}_2\text{O}$  in water ( $\sim 0.05 \text{ mmol}\cdot\text{dm}^{-3}$ ) (see Figure VI-23, the data point at  $c_{\text{HCl}} = 0$ ).

#### VI.10.1.2.2.2 Solubilities of $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{s})$ in $\text{HNO}_3$

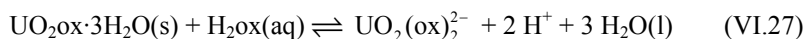
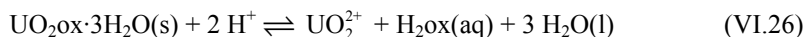
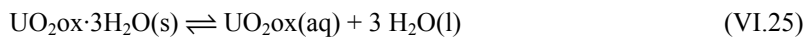
The solubilities of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  in  $\text{HNO}_3$  was reported in [25COL], [52AMP/DAV] and [59MOS/ZAK] at  $20^\circ\text{C}$  and in [58BOL/KOR] at  $25$  and  $50^\circ\text{C}$ . The data obtained from highly concentrated nitric acid solutions from [52AMP/DAV] and [58BOL/KOR] are rejected by this review due to the change of solid phase(s) under these conditions. Detailed discussions are given in Appendix A (Figure A-7 and Figure A-9). The data in solutions with  $[\text{HNO}_3] < 5 \text{ mol}\cdot\text{kg}^{-1}$  from [25COL], [52AMP/DAV], [59MOS/ZAK] and [58BOL/KOR] are shown in Figure VI-27. The data indicate that, at each temperature, the concentration of U(VI) increases as the concentration of nitric acid is increased, that the solubility of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  is higher at  $50^\circ\text{C}$  than  $25$  and  $20^\circ\text{C}$ , and that the data at  $20^\circ\text{C}$  from different studies are in good agreement. This review considered that the data at  $20^\circ\text{C}$  are reproducible and reliable. The data at  $20^\circ\text{C}$  from [59MOS/ZAK] are included in the analysis to calculate the solubility constants for  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ .

Figure VI-27: Solubility of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{s})$  in nitric acid at different temperatures reported in the literature. Symbols: experimental data; curves: unweighted polynomial fit of the data at  $20^\circ\text{C}$  and  $50^\circ\text{C}$ .

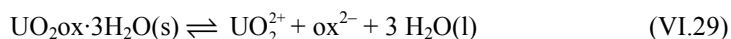


### VI.10.1.2.2.3 Solubility constants of $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{s})$

Based on the comprehensive studies of the solubility of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  at  $(20 \pm 1)^\circ\text{C}$  in a variety of solutions, solubility constants of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  for the following reactions were calculated in [59MOS/ZAK] by solving sets of equations with the solubility data:



$K_s(\text{VI.25})$ ,  $K_s(\text{VI.26})$ ,  $K_s(\text{VI.27})$ , and  $K_s(\text{VI.28})$  are the solubility constants “directly” calculated from the experimental solubility data. Using the dissociation constants of  $\text{H}_2\text{ox}$  ( $K_1 = [\text{H}^+][\text{ox}^{2-}]/[\text{Hox}^-] = 6.4 \times 10^{-5}$  and  $K_2 = [\text{H}^+][\text{Hox}^-]/[\text{H}_2\text{ox}] = 0.108$ ), the authors [59MOS/ZAK] calculated the solubility product of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  for Reaction (VI.29):



where  $K_s(\text{VI.29}) = [\text{UO}_2^{2+}][\text{ox}^{2-}] = K_s(\text{VI.26}) \times (K_1 K_2)$ . The solubility constants  $K_s(\text{VI.25})$ ,  $K_s(\text{VI.26})$ ,  $K_s(\text{VI.27})$ ,  $K_s(\text{VI.28})$  and  $K_s(\text{VI.29})$  from [1842EBE], [25COL], [57BOL/KOR3] and [59MOS/ZAK] are summarised in Table VI-34. Because the uncertainties of data were unavailable or too optimistic in the references, a value of  $\pm 0.2$  is assigned to the  $\log_{10} K$  by this review. Data for Reactions (VI.25), (VI.26), (VI.27), (VI.28) and (VI.29) are discussed as follows.

According to Reaction (VI.25), the solubility of  $\text{UO}_2(\text{ox})\cdot 3\text{H}_2\text{O}(\text{s})$  in water,  $s(\text{mol}\cdot\text{kg}^{-1})$ , obtained in [1842EBE], [25COL] or [57BOL/KOR3] would be equal to or close to  $K_s(\text{VI.25})$  if  $\text{UO}_2\text{ox}(\text{aq})$  is the only species or the dominant species in solution in equilibrium with the solid. To determine if these data can be accepted as  $K_s(\text{VI.25})$ , speciation calculations were performed by this review for a solution of  $0.015 \text{ mol}\cdot\text{kg}^{-1}$   $\text{UO}_2\text{ox}(\text{aq})$  at  $25^\circ\text{C}$  (this is the experimentally observed solubility of  $\text{UO}_2(\text{ox})\cdot 3\text{H}_2\text{O}(\text{s})$ ), using the formation constants of U(VI) oxalate complexes selected by this review (Section VI.10.2.4.1) and the hydrolysis constants of U(VI) in the literature [2003GUI/FAN]. The results indicate that the solution would contain 91%  $\text{UO}_2\text{ox}(\text{aq})$ , 4%  $\text{UO}_2^{2+}$ , 4.5%  $\text{UO}_2(\text{ox})_2^{2-}$ , 0.1%  $\text{UO}_2\text{OH}^+$  and 0.3%  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ , suggesting  $\log_{10} s \approx \log_{10} K_s(\text{VI.25})$  at  $25^\circ\text{C}$ . The speciation calculation also shows that the pcH of the solution would be around 4, which is consistent with the observations in the literature [56GRI/PET2]. It is not clear how the speciation of the solution of  $\text{UO}_2(\text{ox})\cdot 3\text{H}_2\text{O}(\text{s})$  would change at other temperatures because the U(VI) oxalate complex formation constants at other temperatures are unknown. However,  $\text{UO}_2\text{ox}(\text{aq})$  could still be the dominant species in that solution. Therefore, as an approximation, the values of  $K_s(\text{VI.25})$  at variable temperatures are directly calculated from the solubility of  $\text{UO}_2(\text{ox})\cdot 3\text{H}_2\text{O}(\text{s})$  in water reported in [1842EBE], [25COL] and [57BOL/KOR3],



and included in Table VI-34. An uncertainty of  $\pm 0.2$  is assigned to the values of  $\log_{10} K_s$  (VI.25) calculated directly from the solubility in water.

Table VI-34: Solubility constants of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}(\text{s})$  reported in the literature

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i> <sub>s</sub>	Reference
UO <sub>2</sub> ox·3H <sub>2</sub> O(s) ⇌ UO <sub>2</sub> ox(aq) + 3 H <sub>2</sub> O(l)				(VI.25)
sol	(0.5-3.0) M HClO <sub>4</sub>	(20 ± 1)	− (1.92 ± 0.20)	<a href="#">[59MOS/ZAK]</a>
	(0.5-3.0) M HNO <sub>3</sub>	(20 ± 1)	− (1.92 ± 0.20)	
sol	1.0 M HClO <sub>4</sub> /0.08-0.636 M H <sub>2</sub> ox	(20 ± 1)	− (1.92 ± 0.20)	<a href="#">[1842EBE]</a>
	2.0 M HNO <sub>3</sub> /0.08-0.636 M H <sub>2</sub> ox	(20 ± 1)	− (1.89 ± 0.20)	
sol	<i>I</i> → 0	14	− (1.72 ± 0.20)	<a href="#">[1842EBE]</a>
		100	− (1.09 ± 0.20)	
sol	<i>I</i> → 0	15	− (1.88 ± 0.20)	<a href="#">[25COL]</a>
		20	− (1.85 ± 0.20)	
		50	− (1.55 ± 0.20)	
		75	− (1.33 ± 0.20)	
		100	− (1.05 ± 0.20)	
sol	<i>I</i> → 0	0	− (2.23 ± 0.20)	<a href="#">[57BOL/KOR3]</a>
		25	− (1.80 ± 0.20)	
		40	− (1.64 ± 0.20)	
		50	− (1.55 ± 0.20)	
		70	− (1.35 ± 0.20)	
UO <sub>2</sub> ox·3H <sub>2</sub> O(s) + 2 H <sup>+</sup> ⇌ UO <sub>2</sub> <sup>2+</sup> + H <sub>2</sub> ox(aq) + 3 H <sub>2</sub> O(l)				(VI.26)
sol	1.0 M HClO <sub>4</sub> /0.08-0.636 M H <sub>2</sub> ox	(20 ± 1)	− (3.52 ± 0.20)	<a href="#">[59MOS/ZAK]</a>
	2.0 M HNO <sub>3</sub> /0.08-0.636 M H <sub>2</sub> ox	(20 ± 1)	− (3.66 ± 0.20)	
sol	0.5 M HClO <sub>4</sub>	(20 ± 1)	− (3.39 ± 0.20) <sup>a</sup>	<a href="#">[59MOS/ZAK]</a>
	1.0 M HClO <sub>4</sub>	(20 ± 1)	− (3.65 ± 0.20) <sup>a</sup>	
	1.5 M HClO <sub>4</sub>	(20 ± 1)	− (3.39 ± 0.20) <sup>a</sup>	
	2.0 M HClO <sub>4</sub>	(20 ± 1)	− (3.54 ± 0.20) <sup>a</sup>	
	2.5 M HClO <sub>4</sub>	(20 ± 1)	− (3.60 ± 0.20) <sup>a</sup>	
sol	3.0 M HClO <sub>4</sub>	(20 ± 1)	− (3.84 ± 0.20) <sup>a</sup>	<a href="#">[59MOS/ZAK]</a>
	0.5 M HNO <sub>3</sub>	(20 ± 1)	− (3.15 ± 0.20) <sup>a</sup>	
	1.0 M HNO <sub>3</sub>	(20 ± 1)	− (3.31 ± 0.20) <sup>a</sup>	
	1.5 M HNO <sub>3</sub>	(20 ± 1)	− (3.44 ± 0.20) <sup>a</sup>	
	2.0 M HNO <sub>3</sub>	(20 ± 1)	− (3.31 ± 0.20) <sup>a</sup>	
	2.5 M HNO <sub>3</sub>	(20 ± 1)	− (3.38 ± 0.20) <sup>a</sup>	
	3.0 M HNO <sub>3</sub>	(20 ± 1)	− (3.48 ± 0.20) <sup>a</sup>	

(Continued on next page)

Table VI-34: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10}K_s$	Reference
$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{s}) + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{UO}_2\text{ox}_2^{2-} + 2 \text{H}^+ + 3 \text{H}_2\text{O}(\text{l})$				(VI.27)
sol	0.5 M $\text{HClO}_4$ /0.08-0.636 M $\text{H}_2\text{ox}$	$(20 \pm 1)$	$-(1.96 \pm 0.20)$	<a href="#">[59MOS/ZAK]</a>
	0.5 M $\text{HClO}_4$ and 0.07-0.28 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	$-(1.92 \pm 0.20)$	
	1.0 M $\text{HClO}_4$ and 0.07-0.28 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	$-(1.92 \pm 0.20)$	
	0.5 M $\text{HNO}_3$ and 0.07-0.28 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	$-(1.85 \pm 0.20)$	
	1.0 M $\text{HNO}_3$ and 0.07-0.28 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	$-(1.85 \pm 0.20)$	
$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{s}) + 2 \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{UO}_2(\text{ox})_3^{4-} + 4 \text{H}^+ + 3 \text{H}_2\text{O}(\text{l})$				(VI.28)
sol	0.5 M $\text{HClO}_4$ /0.08-0.636 M $\text{H}_2\text{ox}$	$(20 \pm 1)$	$-(1.96 \pm 0.20)$	<a href="#">[59MOS/ZAK]</a>
	0.5 M $\text{HClO}_4$ and 0.07-0.28 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	$-(1.85 \pm 0.20)$	
	1.0 M $\text{HClO}_4$ and 0.07-0.28 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	$-(1.80 \pm 0.20)$	
	0.5 M $\text{HNO}_3$ and 0.07-0.28 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	$-(1.85 \pm 0.20)$	
	1.0 M $\text{HNO}_3$ and 0.07-0.28 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	$-(1.70 \pm 0.20)$	
$\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{UO}_2^{2+} + \text{ox}^{2-} + 3 \text{H}_2\text{O}(\text{l})$				(VI.29)
sol	0.5 M $\text{HClO}_4$	$(20 \pm 1)$	$-(8.55 \pm 0.20)$	<a href="#">[59MOS/ZAK]</a>
	1.0 M $\text{HClO}_4$	$(20 \pm 1)$	$-(8.81 \pm 0.20)$	
	1.5 M $\text{HClO}_4$	$(20 \pm 1)$	$-(8.55 \pm 0.20)$	
	2.0 M $\text{HClO}_4$	$(20 \pm 1)$	$-(8.70 \pm 0.20)$	
	2.5 M $\text{HClO}_4$	$(20 \pm 1)$	$-(8.85 \pm 0.20)$	
	3.0 M $\text{HClO}_4$	$(20 \pm 1)$	$-(9.00 \pm 0.20)$	
	1.0 M $\text{HClO}_4$ and 0.08-0.636 M $\text{H}_2\text{ox}$	$(20 \pm 1)$	$-(8.68 \pm 0.20)$	
	3.0 M $\text{HClO}_4$ and 0.07-0.28 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	$-(8.74 \pm 0.20)$	
sol	0.5 M $\text{HNO}_3$	$(20 \pm 1)$	$-(8.31 \pm 0.20)$	<a href="#">[59MOS/ZAK]</a>
	1.0 M $\text{HNO}_3$	$(20 \pm 1)$	$-(8.47 \pm 0.20)$	
	1.5 M $\text{HNO}_3$	$(20 \pm 1)$	$-(8.60 \pm 0.20)$	
	2.0 M $\text{HNO}_3$	$(20 \pm 1)$	$-(8.47 \pm 0.20)$	
	2.5 M $\text{HNO}_3$	$(20 \pm 1)$	$-(8.54 \pm 0.20)$	
	3.0 M $\text{HNO}_3$	$(20 \pm 1)$	$-(8.64 \pm 0.20)$	
	2.0 M $\text{HNO}_3$ and 0.08-0.636 M $\text{H}_2\text{ox}$	$(20 \pm 1)$	$-(8.82 \pm 0.20)$	
	3.0 M $\text{HNO}_3$ and 0.08-0.476 M $\text{H}_2\text{ox}$	$(20 \pm 1)$	$-(8.55 \pm 0.20)$	

a: Calculated from  $K(\text{VI.29})$  and the “stepwise” dissociation constants of oxalic acid used in [\[59MOS/ZAK\]](#) ( $K_1 = 0.108$  and  $K_2 = 6.4 \times 10^{-5}$ ).

Reaction (VI.25) does not involve ionic species so that the effect of the ionic medium on the equilibrium is expected to be small and probably negligible. As a result, all the values of  $\log_{10} K_s$  (VI.25) from different ionic media in Table VI-34 are treated as for  $I \rightarrow 0$  and plotted as a function of  $1/T$  in Figure VI-28. From the linear regression in Figure VI-28, the value of  $\log_{10} K_s^\circ$  (VI.25) at 298.15 K is calculated to be  $-(1.80 \pm 0.27)$ , identical to that from [\[57BOL/KOR3\]](#). This value is selected by this review:

$$\log_{10} K_s^\circ (\text{VI.25}) = -(1.80 \pm 0.27).$$

From the linear regression of  $\log_{10} K_s$  (VI.25) vs.  $1/T$ , the selected enthalpy of Reaction (VI.25) is calculated to be

$$\Delta_r H_m^\circ (\text{VI.25}) = (20.2 \pm 3.5) \text{ kJ} \cdot \text{mol}^{-1}.$$

Using the value of  $\Delta_f H_m^\circ (\text{UO}_2\text{ox} \cdot 3\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(2702 \pm 18) \text{ kJ} \cdot \text{mol}^{-1}$ , selected in this review (*cf.* Section VI.10.1.2.2), and the  $\Delta_f H_m^\circ (\text{H}_2\text{O}, \text{l}, 298.15 \text{ K}) = -(285.83 \pm 0.04) \text{ kJ} \cdot \text{mol}^{-1}$  from NEA-TDB auxiliary values, the enthalpy of formation of  $\text{UO}_2\text{ox}(\text{aq})$  can be calculated:

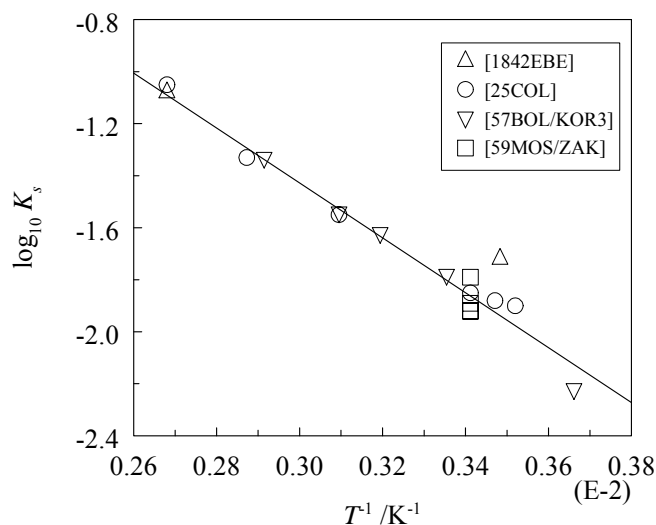
$$\Delta_f H_m^\circ (\text{UO}_2(\text{ox}), \text{aq}, 298.15 \text{ K}) = -(1824.3 \pm 18.3) \text{ kJ} \cdot \text{mol}^{-1}.$$

From the selections for Reaction (VI.25), the following selected values are calculated:

$$\Delta_f G_m^\circ (\text{UO}_2\text{ox} \cdot 3 \text{H}_2\text{O}, \text{aq}, 298.15 \text{ K}) = -(2395.1 \pm 3.1) \text{ kJ} \cdot \text{mol}^{-1}$$

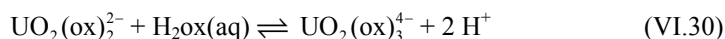
$$S_m^\circ (\text{UO}_2\text{ox} \cdot 3 \text{H}_2\text{O}, \text{aq}, 298.15 \text{ K}) = (347.5 \pm 63.4) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.$$

Figure VI-28:  $\log_{10} K_s$  (VI.25) as a function of  $1/T$ .



The values of  $\log_{10} K_s$  (VI.27) in Table VI-34 appear constant in  $\text{HClO}_4$  or  $\text{HNO}_3$  solutions of different concentrations (0.5 or 1.0 M). Weighted average values were calculated by this review for the media of 0.5-1.0 M  $\text{HClO}_4$  and  $\text{HNO}_3$  with the uncertainties assigned according to the method outlined in Appendix C. The values are shown in Table VI-35.

Subtraction of Reaction (VI.28) by Reaction (VI.27) results in the reaction of the stepwise formation of the  $\text{UO}_2(\text{ox})_3^{4-}$  complex:



From the values of  $\log_{10} K_s$  (VI.27) and  $\log_{10} K_s$  (VI.28) in Table VI-34, the values of  $\log_{10} K$  (VI.30) are calculated by this review to be:  $(0 \pm 0.28)$ ,  $(0.07 \pm 0.28)$ ,  $(0.12 \pm 0.28)$ ,  $(0 \pm 0.28)$  and  $(0.15 \pm 0.28)$  corresponding to the 5 different ionic media for Reactions (VI.27) and (VI.28) shown in Table VI-34.

These values are small and insignificant compared to the uncertainty of the data, suggesting that the formation of the third U(VI) oxalate complex is negligible under the conditions in [59MOS/ZAK], probably because the solution acidity was too high and/or the concentration of oxalate was too low. Consequently, the values of  $\log_{10} K_s$  (VI.28) from [59MOS/ZAK] are considered to be questionable by this review. As a result, the values of  $\log_{10} K_s$  (VI.28) in Table VI-34 are not included in further evaluation.

The values of  $\log_{10} K_s$  (VI.29), in Table VI-34, are not the primary data directly calculated from the experiments. Instead, they were obtained from  $\log_{10} K_s$  (VI.26) in [59MOS/ZAK] by using the dissociation constants of oxalic acid ( $K_1 = [\text{H}^+][\text{ox}^{2-}]/[\text{Hox}^-] = 6.4 \times 10^{-5}$  and  $K_2 = [\text{H}^+][\text{Hox}^-]/[\text{H}_2\text{ox}] = 0.108$ ) that differ from the selected values by this review (Section VI.3). Besides, the dissociation constants should be dependent on the ionic media, but it appears that the same values were erroneously used in [59MOS/ZAK] to calculate  $\log_{10} K_s$  (VI.29) from  $\log_{10} K_s$  (VI.26) in different ionic media. Under the strongly acidic conditions used in [59MOS/ZAK], the oxalate ligand is fully protonated, but the medium effects on the dissociation constants of oxalic acid are not well known. Therefore, the values of solubility product for Reaction (VI.29) that involves the free oxalate ion,  $\text{ox}^{2-}$ , must be regarded with suspicion. The values of  $\log_{10} K_s$  (VI.29) are rejected by this review, but re-evaluated to retrieve two sets of primary data of  $\log_{10} K_s$  (VI.26) for 0.5 – 3.0 M  $\text{HClO}_4$  and 0.5 – 3.0 M  $\text{HNO}_3$  at 20°C (Table VI-34).

The data of  $\log_{10} K_s$  (VI.26) in Table VI-34 obtained in mixed ionic media (1.0 M  $\text{HClO}_4$ /0.08-0.636 M  $\text{H}_2\text{ox}$  or 2.0 M  $\text{HNO}_3$ /0.08-0.636 M  $\text{H}_2\text{ox}$ ) are rejected, but the values of  $\log_{10} K_s$  (VI.26) at  $I = 0.5 - 3.0$  M  $\text{HClO}_4$  and 0.5 – 3.0 M  $\text{HNO}_3$  are accepted by this review. These values are for 20°C and are corrected to 25°C with the following method.

The enthalpy of Reaction (VI.26) is estimated to be  $5.5 \text{ kJ}\cdot\text{mol}^{-1}$  by this review, using the enthalpy of formation  $\Delta_f H_m^\circ(\text{UO}_2(\text{ox})\cdot 3\text{H}_2\text{O}, \text{s}) = -2702 \text{ kJ}\cdot\text{mol}^{-1}$  (selected by this review, Section VI.10.1.2.2),  $\Delta_f H_m^\circ(\text{UO}_2^{2+}) = -1019 \text{ kJ}\cdot\text{mol}^{-1}$  [2003GUI/FAN],  $\Delta_f H_m^\circ(\text{H}_2\text{O}, \text{l}) = -285.83 \text{ kJ}\cdot\text{mol}^{-1}$  [89COX/WAG] and  $\Delta_f H_m^\circ(\text{H}_2\text{ox}, \text{aq}) = -(820.1 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}$  selected in this review (*cf.* Section VI.2.3). Therefore the

change of  $\log_{10} K_s$  (VI.26) from 20°C to 25°C is estimated to be  $\sim 0.02$  by this review using the van't Hoff equation,

$$\log_{10} K_{T_2} - \log_{10} K_{T_1} = \frac{\Delta_r H_m}{2.3023 \cdot R} \times \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

This value is much smaller than the uncertainty of the  $\log_{10} K_s$  (VI.26) in Table VI-34. Therefore, the values of  $\log_{10} K_s$  (VI.26) at 20°C is taken as those at 25°C by this review without correction, but the uncertainties are increased from  $\pm 0.20$  to  $\pm 0.30$  to account for the additional uncertainty the change in temperature could arise.

Some of the  $\log_{10} K_s$  (VI.26) are for nitric acid media and need to be corrected by the complexation of U(VI) by nitrate.

The correction processes are summarised under the entry of [59MOS/ZAK] in Appendix A. The corrected values of  $\log_{10} K_s$  (VI.26) are shown in Table VI-35.

Table VI-35: Solubility constants of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  obtained by re-evaluation of the data in Table VI-34.

Method	Ionic medium	$t$ (°C)	$\log_{10} K_s$	Reference
$\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}(\text{s}) + 2 \text{H}^+ \rightleftharpoons \text{UO}_2^{2+} + \text{H}_2(\text{ox})(\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$				(VI.26)
sol	0.513 m $\text{HClO}_4$	25	$-(3.39 \pm 0.30)^a$	[59MOS/ZAK]
	1.051 m $\text{HClO}_4$	25	$-(3.65 \pm 0.30)^a$	
	1.614 m $\text{HClO}_4$	25	$-(3.39 \pm 0.30)^a$	
	2.204 m $\text{HClO}_4$	25	$-(3.54 \pm 0.30)^a$	
	2.824 m $\text{HClO}_4$	25	$-(3.69 \pm 0.30)^a$	
	3.471 m $\text{HClO}_4$	25	$-(3.84 \pm 0.30)^a$	
sol	0.508 m $\text{HNO}_3$	25	$-(3.25 \pm 0.30)^{a,b}$	[59MOS/ZAK]
	1.032 m $\text{HNO}_3$	25	$-(3.49 \pm 0.30)^{a,b}$	
	1.572 m $\text{HNO}_3$	25	$-(3.70 \pm 0.30)^{a,b}$	
	2.129 m $\text{HNO}_3$	25	$-(3.68 \pm 0.31)^{a,b}$	
	2.707 m $\text{HNO}_3$	25	$-(3.86 \pm 0.31)^{a,b}$	
	3.304 m $\text{HNO}_3$	25	$-(4.09 \pm 0.32)^{a,b}$	
$\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}(\text{s}) + \text{H}_2(\text{ox})(\text{aq}) \rightleftharpoons \text{UO}_2(\text{ox})_2^{2-} + 2 \text{H}^+ + 3 \text{H}_2\text{O}(\text{l})$				(VI.27)
sol	0.5-1.0 M $\text{HClO}_4$	$(20 \pm 1)$	$-(1.93 \pm 0.12)$	[59MOS/ZAK]
	0.5-1.0 M $\text{HNO}_3$	$(20 \pm 1)$	$-(1.85 \pm 0.14)$	

a: The uncertainties are increased by this review from  $\pm 0.20$  to  $\pm 0.30$  to account for the adjustment of the temperature from 20 to 25°C.

b: The constants are corrected for the complexation of nitrate (details are provided in Appendix A).

The values of  $\log_{10} K_s$  (VI.26) in Table VI-35 are used to obtain  $\log_{10} K_s^\circ$  (VI.26) at 298.15 K by the SIT approach outlined in Appendix B. With  $\Delta z^2$  (VI.26) = 2,

$$\log_{10} K_s - 2D = \log_{10} K_s^0 - \Delta\varepsilon(\text{VI.26}) \times I_m \quad (\text{VI.31})$$

where  $D = 0.509\sqrt{I_m} / (1 + 1.5\sqrt{I_m})$  and  $I_m$  is the ionic strength in molality. A plot of  $(\log_{10} K_s - 2D)$  vs.  $I_m$  is shown in Figure VI-29. A weighted linear regression results in the following values:

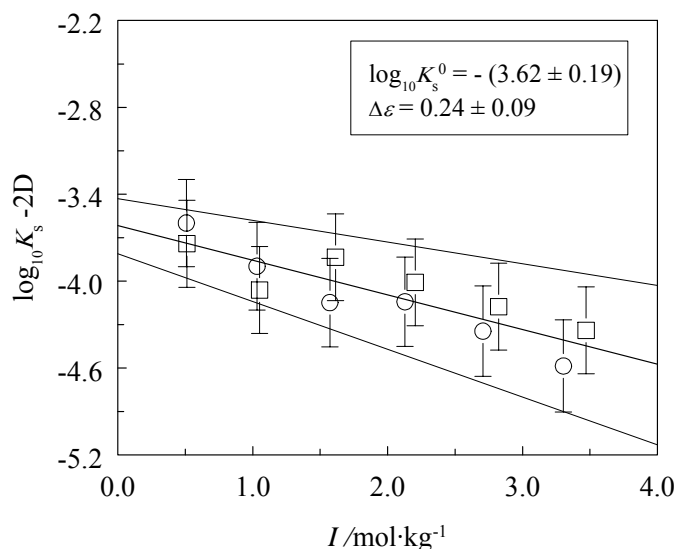
$$\log_{10} K_s^0 (\text{VI.26}) = -(3.62 \pm 0.19),$$

$$\Delta\varepsilon(\text{VI.26}) = (0.24 \pm 0.09) \text{ kg}\cdot\text{mol}^{-1}.$$

The  $\Delta\varepsilon(\text{VI.26})$  calculated from the SIT analysis (Figure VI-29) is in good agreement with the  $\Delta\varepsilon(\text{VI.26})$  calculated from the values of  $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-)$  and  $\varepsilon(\text{H}^+, \text{ClO}_4^-)$  selected by [2003GUI/FAN], if the interaction of the neutral species  $\text{H}_2\text{ox}(\text{aq})$  with the ionic medium is ignored. From [2003GUI/FAN],  $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-)$   $(0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ , thus  $\Delta\varepsilon(\text{VI.26}) = \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - 2\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.18 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ .

Because the value of  $\log_{10} K_s^0 (\text{VI.26})$  can also be calculated from other thermodynamic constants selected by this review, the  $\log_{10} K_s^0 (\text{VI.26})$  obtained from the SIT analysis of the solubility data in Table VI-35,  $-(3.62 \pm 0.19)$ , can be used for a consistency check of the thermodynamic constants selected by this review. From  $\log_{10} K_s^0 (\text{VI.25}) = -(1.80 \pm 0.27)$ ,  $\log_{10} K^0 = (5.65 \pm 0.03)$  for the reaction,  $2\text{H}^+ + \text{ox}^{2-} \rightleftharpoons \text{H}_2\text{ox}(\text{aq})$ , (cf. Section VI.3.5), and  $\log_{10} K^0 = (7.13 \pm 0.06)$  for the reaction,  $\text{UO}_2^{2+} + \text{ox}^{2-} \rightleftharpoons \text{UO}_2\text{ox}(\text{aq})$ , (cf. section VI.10.2.4.1), the solubility constant of Reaction (VI.26) at  $I \rightarrow 0$  and 298.15 K is calculated to be:  $\log_{10} K_s^0 (\text{VI.26}) = -(3.28 \pm 0.28)$ . This value is somewhat higher than that obtained from the SIT analysis of the solubility data in Table VI-35, but the two values overlap within the range of expectancies.

Figure VI-29: SIT plot for Reaction (VI.26). (O)  $\text{HNO}_3$ ; ( $\square$ )  $\text{HClO}_4$



## VI.10.2 Aqueous uranium oxalate complexes

### VI.10.2.1 Aqueous uranium(III) oxalate complexes

U(III) is unstable in aqueous solution and is thermodynamically capable of being oxidised to U(IV) by many anions [63JEZ], [60ALE/ZHD], [70PER/KRO]. The complexation of the anions with U(III) is expected to be weaker than that with U(IV), which could shift the potential of the couple  $U^{IV}/U^{III}$  and facilitate the oxidation of U(III) to U(IV) [70PER/KRO]. Peretrukhin *et al.* observed that, when ammonium oxalate was introduced into a weakly acidic acetate solution of U(III), U(III) was almost instantaneously oxidised to U(IV) while oxalate was reduced to glyoxylic acid (OCHCOOH) [70PER/KRO]. No thermodynamic data for aqueous U(III) oxalates could be identified in the literature by this review.

### VI.10.2.2 Aqueous uranium(IV) oxalate complexes

A few binary aqueous U(IV) oxalates,  $U(ox)^{2+}$ ,  $U(ox)_2(aq)$ ,  $U(ox)_3^{2-}$  and  $U(ox)_4^{4-}$ , are reported in the literature. The stability constants are usually determined in conjunction with the solubility measurements [58GRI/PET2], [60GRI/PET], [60ZAK/MOS], [79NIK]. As discussed previously, the solubility experiments for solid U(IV) oxalates are usually associated with shortcomings including the oxidation of U(IV) during the experiment by oxygen or the product of the radiolysis of water, the strong tendency of U(IV) toward hydrolysis, and lack of the characterisation of the solid phase. Consequently, the assignment of the aqueous U(IV) oxalate complexes and their stability constants based on solubility measurements must be regarded with suspicion, particularly if essential experimental conditions are not provided. The stability constants reported in [58GRI/PET2] and some of the stability constants reported in [60GRI/PET] are rejected by this review. The reasons for rejection are given in Appendix A.

As discussed in Section VI.10.1.1, a variety of stable polynuclear solid U(IV) oxalates have been prepared, *e.g.*,  $U_2(ox)_4 \cdot 12H_2O$ ,  $M_i[U_j(ox)_k] \cdot nH_2O$  ( $M = H^+$ ,  $Na^+$ ,  $K^+$ ,  $NH_4^+$ ;  $i = 2, 4, 6, 8$ ;  $j = 2$ ;  $k = 3, 4, 5, 7, 8$ ;  $n = 1, 4, 5, 8, 10$ ),  $U_2(ox)_2(SO_4)_2 \cdot 6H_2O$  and  $U_2(ox)_3SO_4 \cdot 12H_2O$  [66CHE], [87DOL], [91MAT/KAR].

This may imply that polynuclear U(IV) oxalate complexes could also form in aqueous solutions. For example, in the solubility experiments with  $K_2U_2(ox)_5 \cdot 8H_2O$ , the charge on the anion in solution was found to be  $-2$  by ion exchange and the author assumed that a dimeric U(IV) oxalate species,  $U_2(ox)_5^{2-}$ , was present in the solution [70PET/STE2]. However, this experiment is at fault due to the change in the solid phase during the experiment so that the results are considered unreliable by this review. The presence of  $U_2(ox)_5^{2-}$  remains to be verified. No other experimental evidence is identified in the literature on the formation of polynuclear U(IV) oxalate complexes in aqueous solution.

A ternary complex,  $[U(ox)_2(OH)_2]^{2-}$ , was assumed to form when  $U(ox)_2 \cdot 6H_2O(s)$  was dissolved in solutions of ammonium bicarbonate, but no stability

constant was determined [72GRI/PET2]. The stability constant of a ternary complex,  $\text{Uedta(ox)}^{2-}$ , was reported in [83PER/MIS] but not accepted by this review due to the scarce experimental information (Appendix A). Stability constants considered by this review are summarised in Table VI-36.

Table VI-36: Stability constants of aqueous U(IV) oxalates reported in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{U}^{4+} + \text{ox}^{2-} \rightleftharpoons \text{U(ox)}^{2+}$				
sol	0.5 M HCl and 0.07-0.241 M $(\text{NH}_4)_2\text{ox}$	?	$(8.6 \pm 0.2)$	[60ZAK/MOS]
?	?	?	9.01	[67KUM/SER]
$\text{U(ox)}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{U(ox)}_2(\text{aq})$ (VI.32)				
sol	0.735 m $\text{HClO}_4$	$(25 \pm 0.1)$ $(40 \pm 0.1)$ $(50 \pm 0.1)$ $(60 \pm 0.1)$ $(70 \pm 0.1)$ $(80 \pm 0.1)$ $(90 \pm 0.1)$	$(8.28 \pm 0.20)$ $(8.30 \pm 0.20)$ $(8.36 \pm 0.20)$ $(8.45 \pm 0.20)$ $(8.48 \pm 0.20)$ $(8.55 \pm 0.20)$ $(8.81 \pm 0.20)$	[79NIK] <sup>a</sup>
$\text{U}^{4+} + 2 \text{ox}^{2-} \rightleftharpoons \text{U(ox)}_2(\text{aq})$				
sol	0.5 M HCl and 0.07-0.241 M $(\text{NH}_4)_2\text{ox}$	?	$(16.85 \pm 0.20)$ $(17.40 \pm 0.20)$	[60ZAK/MOS] <sup>b</sup>
$\text{U(ox)}_2(\text{aq}) + \text{ox}^{2-} \rightleftharpoons \text{U(ox)}_3^{2-}$ (VI.33)				
sol	?	?	5.4	[60GRI/PET]
sol	0.01 m $\text{Na}_2\text{ox}$	$(25 \pm 0.1)$ $(40 \pm 0.1)$ $(50 \pm 0.1)$ $(60 \pm 0.1)$ $(70 \pm 0.1)$ $(80 \pm 0.1)$ $(90 \pm 0.1)$	$(5.05 \pm 0.20)$ $(5.14 \pm 0.20)$ $(5.28 \pm 0.20)$ $(5.36 \pm 0.20)$ $(5.52 \pm 0.20)$ $(5.79 \pm 0.20)$ $(6.22 \pm 0.20)$	[79NIK] <sup>a</sup>
$\text{U}^{4+} + 3 \text{ox}^{2-} \rightleftharpoons \text{U(ox)}_3^{2-}$				
sol	0.5 M HCl and 0.07-0.241 M $(\text{NH}_4)_2\text{ox}$	?	$(22.77 \pm 0.20)$ $(22.58 \pm 0.20)$	[60ZAK/MOS] <sup>b</sup>
$\text{U}^{4+} + 4 \text{ox}^{2-} \rightleftharpoons \text{U(ox)}_4^{4-}$				
sol	0.5 M HCl and 0.07-0.241 M $(\text{NH}_4)_2\text{ox}$	?	$(27.24 \pm 0.20)$ $(27.38 \pm 0.20)$	[60ZAK/MOS] <sup>b</sup>
pot	?	?	26	[60GRI/PET]

a: The uncertainties of  $\pm 0.10$  given in the literature are considered to be too optimistic, thus increased to  $\pm 0.20$  by this review.

b: The two values from [60ZAK/MOS] are the results calculated with two different methods from the same experimental data. Details are given in Appendix A.



Despite the shortcomings associated with the solubility experiments, the stability constants in Table VI-36 show general agreement between different references and are internally consistent among the series of species:  $\text{U(ox)}^{2+}$ ,  $\text{U(ox)}_2(\text{aq})$ ,  $\text{U(ox)}_3^{2-}$  and  $\text{U(ox)}_4^{4-}$ . For example, the stepwise stability constants at 25°C follow the order:  $\log_{10}K_1$  ( $8.6 - 9$ )  $> \log_{10}K_2$  ( $8.3$ )  $> \log_{10}K_3$  ( $5$ )  $> \log_{10}K_4$  ( $4.6$ ). The overall stability constants also appear to agree with the sum of stepwise constants from different references within the experimental uncertainty.

The stability constants,  $\log_{10}K(\text{VI.32})$  and  $\log_{10}K(\text{VI.33})$ , determined in 0.735 m  $\text{HClO}_4$  and 0.01 m  $\text{Na}_2\text{ox}$  at variable temperatures (25-90°C), increased as the temperature was increased (Table VI-36). From these data, the values of  $\Delta_r H_m$  (VI.32) and  $\Delta_r H_m$  (VI.33) at variable temperatures were calculated in [79NIK] and shown in Table VI-37. The uncertainties ( $\pm 10\%$ , but no less than  $1 \text{ kJ}\cdot\text{mol}^{-1}$ ) are assigned by this review.

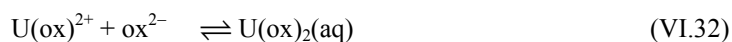


Table VI-37: Experimental enthalpy of Reactions (VI.32) and (VI.33) from [79NIK].

Method	Ionic medium	$t$ (°C)	$\Delta_r H_m$ ( kJ·mol <sup>-1</sup> )
$\text{U(ox)}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{U(ox)}_2(\text{aq})$			(VI.32)
sol	0.735 m HClO <sub>4</sub>	(25 ± 0.1)	(2.8 ± 1.0)
		(40 ± 0.1)	(8.54 ± 1.00)
		(50 ± 0.1)	(13.0 ± 1.0)
		(60 ± 0.1)	(17.9 ± 2.0)
		(70 ± 0.1)	(25.1 ± 2.0)
		(80 ± 0.1)	(29.4 ± 3.0)
		(90 ± 0.1)	(36.0 ± 4.0)
$\text{U(ox)}_2(\text{aq}) + \text{ox}^{2-} \rightleftharpoons \text{U(ox)}_3^{2-}$			(VI.33)
sol	0.01 m Na <sub>2</sub> ox	(25 ± 0.1)	(6.5 ± 1.0)
		(40 ± 0.1)	(18.7 ± 2.0)
		(50 ± 0.1)	(28.0 ± 3.0)
		(60 ± 0.1)	(38.4 ± 4.0)
		(70 ± 0.1)	(53.6 ± 5.0)
		(80 ± 0.1)	(62.6 ± 6.0)
		(90 ± 0.1)	(76.4 ± 8.0)

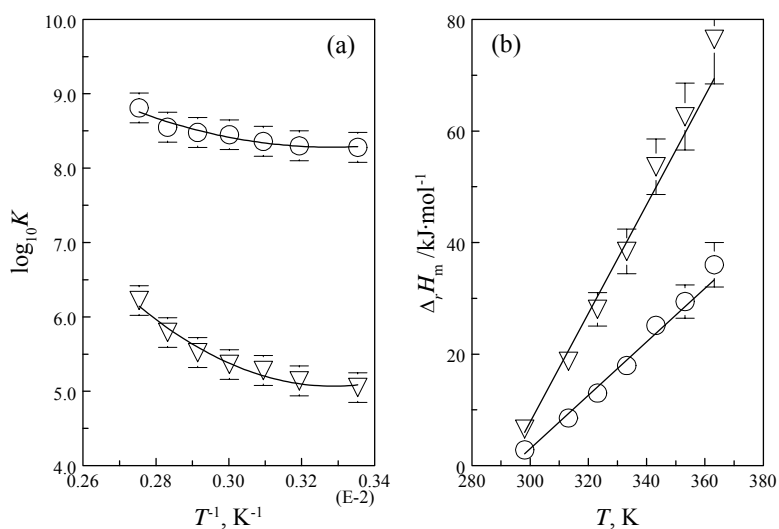
The enthalpy values in Table VI-37 are consistent with the trend of the stability constants in Table VI-36 and Figure VI-30. The plot of  $\log_{10}K(\text{VI.32})$  and  $\log_{10}K(\text{VI.33})$  as a function of  $1/T$  (Figure VI-30-a) indicates that  $\Delta_r H_m$  (VI.32) and  $\Delta_r H_m$  (VI.33) should be positive in the temperature range because  $d \log_{10} K / d(1/T) < 0$ , that  $\Delta_r H_m$  (VI.32) and  $\Delta_r H_m$  (VI.33) probably do not remain constant because

$d \log_{10} K / d(1/T) \neq \text{constant}$ , and that  $\Delta_r H_m$  (VI.32) and  $\Delta_r H_m$  (VI.33) should become increasingly more positive as the temperature is increased because  $d \log_{10} K / d(1/T)$  becomes larger as  $T$  increases.

The plots of  $\Delta_r H_m$  (VI.32) and  $\Delta_r H_m$  (VI.33) as a function of temperature are shown in Figure VI-30-b. A weighted linear regression results in the values of  $\Delta_r C_{p,m}$  (VI.32) =  $(480 \pm 33) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  and  $\Delta_r C_{p,m}$  (VI.33) =  $(976 \pm 56) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

In spite of the self-consistency and the apparent reasonableness of the stability constants in Table VI-36 and the enthalpy of complexation in Table VI-37, further evaluation of the data to derive thermodynamic values with SIT for aqueous U(IV) oxalates is not pursued in this review, due to the previously discussed shortcomings associated with the solubility experiments. No thermodynamic data for aqueous U(IV) oxalates are recommended by this review.

Figure VI-30: Stability constants (a) and enthalpy (b) for Reactions (VI.32): (O) and (VI.33): ( $\nabla$ ), original data from [79NIK].

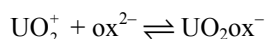


### VI.10.2.3 Aqueous uranium(V) oxalate complexes

Oxalate complexes of U(V) were identified only as reaction intermediates in the electrolytic reduction of U(VI) [46KOL/HAR], [56GRA/GRA], [60ALE/ZHD], [69PER/KRO], [72MAN/VAR], [2002MAK/MER], in the reduction of U(VI) by hydrated electrons generated with pulse radiolysis [81NAS/MUL], or in the photolysis of U(VI) oxalates [76BRI/ELD2], [76BRI/ELD3], [77BRI/ELD]. The presence of oxalate

shifts the potentials of the redox couples  $U^{VI}/U^V$  and  $U^V/U^{IV}$  and facilitates the disproportionation of U(V) [60ALE/ZHD], [72MAN/VAR], [2002MAK/MER], suggesting that the U(V) oxalate complex is weaker than the U(IV) oxalate or U(VI) oxalate complexes due to the lower charge density of  $UO_2^+$  than those of  $UO_2^{2+}$  and  $U^{4+}$ . No experimental stability constants of aqueous U(V) oxalate complexes are identified in the literature.

The value of  $\log_{10}K_1$  of the reaction:



was estimated to be 4.0 in [71MOS6] by “extrapolation”. Neither the temperature nor the ionic strength was specified. The value is rejected in this review.

#### VI.10.2.4 Aqueous uranium(VI) oxalate complexes

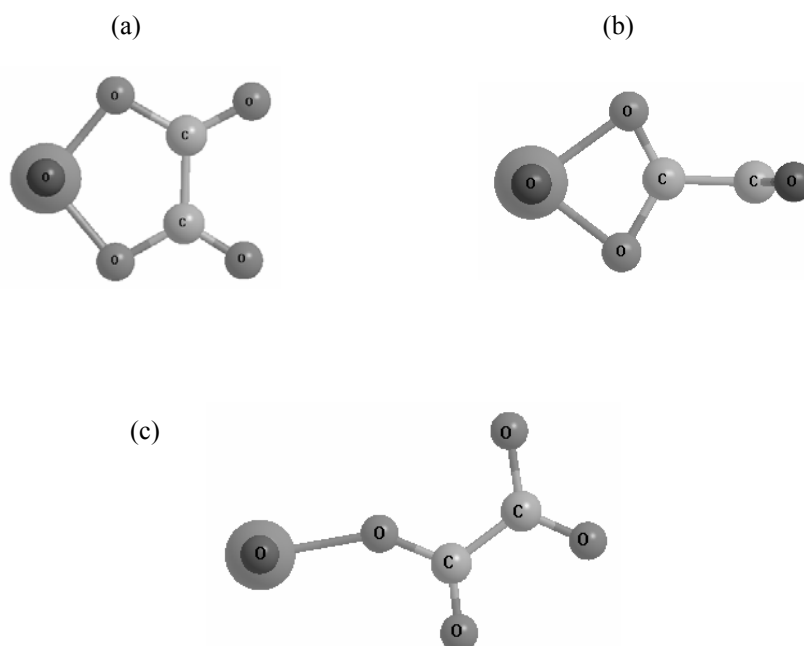
##### VI.10.2.4.1 Binary U(VI) oxalate complexes

It is generally accepted that U(VI) forms the complexes of the type:  $UO_2(ox)_j^{(2-2j)}$  where  $j = 1 - 3$ , in aqueous solutions. Figure VI-31 shows three postulated binding modes of oxalate in U(VI) oxalate complexes, including “side-on” bidentate, “end-on” bidentate and unidentate. Different binding modes are observed in solid U(VI) oxalate compounds, but not confirmed in solution. While the oxalate ligands in  $UO_2ox(aq)$  and  $UO_2(ox)_2^{2-}$  are believed to be “side-on” bidentate with both carboxylate groups coordinating to uranium in the equatorial plane of the linear  $O=U=O$  moiety, there are disagreements about the binding mode of the third oxalate ligand in  $UO_2(ox)_3^{4-}$ . For example, the stepwise formation constants of  $UO_2ox(aq)$ ,  $UO_2(ox)_2^{2-}$  and  $UO_2(ox)_3^{4-}$  from [2000FER/IUL] ( $\log_{10} K_1 = 6.20$ ,  $\log_{10} K_2 = 5.01$  and  $\log_{10} K_3 = 3.69$  at  $I = 2.0$  M  $NaClO_4$ ) suggest that all the three oxalates are identically co-ordinated to uranium in the “side-on” bidentate mode. However, the much smaller third-step constant of  $UO_2(ox)_3^{4-}$  from [69HAV] ( $\log_{10} K_3 = 0.36$  at  $I = 1.0$  M  $NaClO_4$ ) could suggest otherwise. Quantum mechanical calculations [2003VAL/MOL] indicate that the most stable structure of  $UO_2(ox)_3^{4-}$  is a five-coordinate isomer with the third oxalate bonded to uranium with a single carboxylate oxygen (unidentate). The theoretical results seem to agree with the small  $\log_{10} K_3$  from [69HAV] and, are consistent with the results from EXAFS [2003VAL/MOL]. However, since the accuracy of some of the EXAFS results is not particularly high [2003VAL/MOL] and a recent re-investigation of the U(VI) oxalate complexation yields a higher value of the third stepwise constant ( $\log_{10} K_3 = 2.59$  at  $I = 3.0$  M  $NaClO_4$ ) [2002HAV/SOT], the question of the binding modes of oxalate in  $UO_2(ox)_3^{4-}$  in solution remains to be answered. The enthalpy and entropy of complexation that can be determined by calorimetry should help to answer this question.

Oxalate forms the strongest complexes with U(VI) among the unsubstituted alkyldicarboxylates including oxalate, malonate, succinate, glutarate and adipate, mainly

due to an entropy effect. As the carbon chain length increases, the ligand suffers greater loss of rotational and translational freedom upon chelation with U(VI), resulting in a greater entropy loss. A Raman spectroscopic study indicates that the coordination of oxalate and other ligands with  $\text{O}=\text{U}=\text{O}$  weakens the axial U–O bond(s) and shifts its symmetrical stretching vibration frequency [92NGU/BEG]. From the magnitude of the Raman shifts, the binding strength of oxalate with U(VI) was placed between carbonate and fluoride in this order:  $\text{OH}^- > \text{CO}_3^{2-} > \text{ox}^{2-} > \text{F}^- > \text{SO}_4^{2-} > \text{CH}_3\text{CO}_2^- > \text{Cl}^- > \text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{HSO}_4^-$ , which is in good agreement with the order of the formation constants of the complexes obtained by thermodynamic experiments.

Figure VI-31: Postulated binding modes of oxalate in U(VI) complexes. (a) “side-on” bidentate; (b) “end-on” bidentate; (c) unidentate. The large atom represents uranium and the oxalates coordinate to uranium in the equatorial plane. The two axial U=O bonds are perpendicular to the plane.



U(VI) oxalate complexes in solution undergo photochemical reactions when exposed to UV light or the sunlight [1862SEE], [42HEI], [76BRI/ELD2], [76BRI/ELD3], [77BRI/ELD]. The photolysis leads to the reduction of U(VI) to U(IV), accompanied by the release of  $\text{CO}_2$  and  $\text{CO}$  [76BRI/ELD2], [76BRI/ELD3], [77BRI/ELD]. The photosensitive species were found to be  $\text{UO}_2\text{H}_2\text{ox}^{2+}$ ,  $\text{UO}_2\text{ox}(\text{aq})$  and

$\text{UO}_2(\text{ox})_2^{2-}$  in acidic solutions [42HEI],  $\text{UO}_2(\text{Hox})_2(\text{aq})$  in solutions with  $\text{pH} \leq 1.7$  [76BRI/ELD2], [76BRI/ELD3], and  $\text{UO}_2(\text{ox})_2^{2-}$  in solutions with  $\text{pH} = 4.5$  [77BRI/ELD]. The kinetics and mechanism of the photochemical reactions were reported [76BRI/ELD2], [76BRI/ELD3], [77BRI/ELD]. The possibility of photolysis certainly raises concerns on the reliability of the experimental data if the solutions of U(VI) oxalate were exposed to light for a prolonged time. Precautions were taken in some studies to avoid or reduce the exposure of the U(VI) oxalate solutions to sunlight or UV light [67MIY/NUR], [69HAV].

The polynuclear and ternary or quaternary U(VI) oxalate complexes are discussed in Sections VI.10.2.4.2 and VI.10.2.4.3. Table VI-38 lists only the stability constants of the mononuclear binary U(VI) oxalate complexes reported in the literature.

Table VI-38: Stability constants of aqueous U(VI) oxalates reported in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{UO}_2^{2+} + \text{ox}^{2-} \rightleftharpoons \text{UO}_2\text{ox}(\text{aq})$				
sp, pot	$I \approx 0.05, 0.08 \text{ M } \text{UO}_2^{2+} / \text{SO}_4^{2-} / \text{Hox}^-$	25–26	5.82	[42HEI]
sol	$I = 0.5\text{--}1.0 \text{ M } \text{HClO}_4/\text{HNO}_3$	$(20 \pm 1)$	$(6.8 \pm 0.1)$	[59MOS/ZAK]
ise-Ag	$I \rightarrow 0$	$(25.0 \pm 0.1)$	6.0	[59PTI/TEK]
sp	$I = 1.0 \text{ M } \text{NaClO}_4$	$(20 \pm 0.2)$	$(4.63 \pm 0.02)$	[67MIY/NUR]
em	$I = 0.1 \text{ N } \text{KCl}$	25	$(6.7 \pm 0.2)$	[67STE/MAK2]
sp	$I = 0.1 \text{ M } \text{NaClO}_4$	20	$(6.36 \pm 0.07)$	[69HAV]
	$I = 1.0 \text{ M } \text{NaClO}_4$	20	$(5.99 \pm 0.03)$	
pol	$I = 0.2 \text{ M } \text{NaClO}_4$	20	5.0	[72MAN/VAR]
pot	$I = 0.10 \text{ M } \text{KNO}_3$	$(25 \pm 1)$	$(3.97 \pm 0.27)$	[79KUM/CHA]
dis	$I = 4.0 \text{ M } (1 \text{ M } \text{HNO}_3/3 \text{ M } \text{NaNO}_3)$	25	$(6.20 \pm 0.06)$	[83CHO/BOK]
	$I = 4.0 \text{ M } (2 \text{ M } \text{HNO}_3/2 \text{ M } \text{NaNO}_3)$	25	$(6.22 \pm 0.07)$	
	$I = 4.0 \text{ M } (3 \text{ M } \text{HNO}_3/1 \text{ M } \text{NaNO}_3)$	25	$(6.26 \pm 0.09)$	
	$I = 4.0 \text{ M } \text{HNO}_3$	25	$(6.36 \pm 0.06)$	
pot	$I = 0.1 \text{ M } \text{KNO}_3$	25	4.48	[85VEN/SWA]
sp	$I = 0.05 \text{ M } \text{HClO}_4/\text{NaClO}_4$	$(20 \pm 1)$	3.22	[89ABD/ALI]
ix	$I = 0.11 \text{ M } \text{NaClO}_4$ (including 0.01 M acetate)	25?	$(6.10 \pm 0.11)$	[91LOO/KOP]
dis	$I = 3.0 \text{ M } \text{NaClO}_4$	25	$(6.00 \pm 0.05)$	[94ERT/MOH]
	$I = 5.0 \text{ M } \text{NaClO}_4$		$(6.55 \pm 0.28)$	
	$I = 7.0 \text{ M } \text{NaClO}_4$		$(6.55 \pm 0.33)$	
	$I = 9.0 \text{ M } \text{NaClO}_4$		$(7.37 \pm 0.05)$	
dis	$I = 5.0 \text{ m } \text{NaCl}$	25	$(5.50 \pm 0.02)$	[96BOR/LIS]
pot (gl. is-ox)	$I = 2.0 \text{ M } \text{NaClO}_4$	$(25.00 \pm 0.02)$	$(6.20 \pm 0.02)$	[2000FER/IUL]
	$I = 3.0 \text{ M } \text{NaClO}_4$		$(6.39 \pm 0.01)$	

(Continued on next page)

Table VI-38: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{UO}_2^{2+} + \text{ox}^{2-} \rightleftharpoons \text{UO}_2\text{ox}(\text{aq})$				
pot (gl. ise-ox)	$I = 1.0 \text{ M NaClO}_4$	$(25.00 \pm 0.02)$	$(6.03 \pm 0.03)$	[2000VAS/CAR]
dis	$I = 0.3 \text{ m NaCl}$	25	$(5.94 \pm 0.01)$	[2001BOR/MOO]
	$I = 1.0 \text{ m NaCl}$		$(5.92 \pm 0.01)$	
	$I = 2.0 \text{ m NaCl}$		$(5.89 \pm 0.01)$	
	$I = 3.0 \text{ m NaCl}$		$(6.61 \pm 0.02)$	
	$I = 4.0 \text{ m NaCl}$		$(6.70 \pm 0.01)$	
	$I = 5.0 \text{ m NaCl}$		$(5.82 \pm 0.02)$	
sp	$I = 3.0 \text{ M NaClO}_4$	$(25.0 \pm 0.2)$	$(6.31 \pm 0.02)$	[2002HAV/SOT]
$\text{UO}_2^{2+} + 2 \text{ ox}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_2^{2-}$				
sp, pot	$I \approx 0.05, 0.08 \text{ M UO}_2^{2+} / \text{SO}_4^{2-} / \text{Hox}^-$	25–26	10.56	[42HEI]
sol	$I = 0.5\text{--}1.0 \text{ M HClO}_4/\text{HNO}_3$	$(20 \pm 1)$	$(12.0 \pm 0.2)$	[59MOS/ZAK]
ise-Ag	$I \rightarrow 0$	$(25.0 \pm 0.1)$	$(10.8 \pm 0.5)$	[59PTI/TEK]
dis	$I = 0.1 \text{ M NaClO}_4$	?	$(11.08 \pm 0.03)$	[60STA3]
sp	$I = 1.0 \text{ M NaClO}_4$	$(20 \pm 0.2)$	$(8.7 \pm 0.05)$	[67MIY/NUR]
pot	$I = 1.0 \text{ M KNO}_3$	$(25.0 \pm 0.05)$	$(9.1 \pm 0.2)$	[67RAJ/MAR]
em	$I = 0.1 \text{ N KCl}$	25	$(11.8 \pm 0.3)$	[67STE/MAK2]
sp	$I = 0.1 \text{ M NaClO}_4$	20	$(10.59 \pm 0.07)$	[69HAV]
	$I = 1.0 \text{ M NaClO}_4$	20	$(10.64 \pm 0.06)$	
pol	$I = 0.2 \text{ M NaClO}_4$	20	9.8	[72MAN/VAR]
sp, pol	$I = 0.5 \text{ M (H/K)NO}_3$	25	$(9.36 \pm 0.25)$	[76BRI/ELD]
pot	$I = 0.10 \text{ M KNO}_3$	$(25 \pm 1)$	$(9.08 \pm 0.25)$	[79KUM/CHA]
em	$I = 0.1 \text{ M NaClO}_4$	40	6.47	[84SIR]
pot	$I = 0.1 \text{ M KNO}_3$	25	8.43	[85VEN/SWA]
dis	$I = 3.0 \text{ M NaClO}_4$	25	$(11.21 \pm 0.18)$	[94ERT/MOH]
	$I = 5.0 \text{ M NaClO}_4$		$(12.28 \pm 0.11)$	
	$I = 7.0 \text{ M NaClO}_4$		$(12.94 \pm 0.40)$	
	$I = 9.0 \text{ M NaClO}_4$		$(14.08 \pm 0.11)$	
dis	$I = 5.0 \text{ m NaCl}$	25	$(10.60 \pm 0.02)$	[96BOR/LIS]
pot (gl. ise-ox)	$I = 2.0 \text{ M NaClO}_4$	$(25.00 \pm 0.02)$	$(11.21 \pm 0.02)$	[2000FER/IUL]
	$I = 3.0 \text{ M NaClO}_4$		$(11.52 \pm 0.02)$	
pot (gl. ise-ox)	$I = 1.0 \text{ M NaClO}_4$	$(25.00 \pm 0.02)$	$(10.87 \pm 0.07)$	[2000VAS/CAR]
dis	$I = 0.3 \text{ m NaCl}$	25	$(10.1 \pm 0.06)$	[2001BOR/MOO]
	$I = 2.0 \text{ m NaCl}$		$(10.2 \pm 0.08)$	

(Continued on next page)

Table VI-38: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{UO}_2^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_2^{2-}$				
dis	$I = 3.0 \text{ m NaCl}$		$(11.0 \pm 0.07)$	[2001BOR/MOO]
sp	$I = 3.0 \text{ M NaClO}_4$	$(25.0 \pm 0.2)$	$(11.21 \pm 0.07)$	[2002HAV/SOT]
$\text{UO}_2(\text{ox})(\text{aq}) + \text{ox}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_2^{2-}$				
con	$I < 0.1 \text{ mol} \cdot \text{kg}^{-1}$	25	4.46	[56GRI/PTI]
$\text{UO}_2^{2+} + 3 \text{ox}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_3^{4-}$				
sp	$I = 1.0 \text{ M NaClO}_4$	$(20 \pm 0.2)$	$(11.99 \pm 0.11)$	[67MIY/NUR]
sp	$I = 1.0 \text{ M NaClO}_4$	20	$(11.0 \pm 0.2)$	[69HAV]
pot	$I = 0.10 \text{ M KNO}_3$	$(25 \pm 1)$	$(16.40 \pm 0.12)$	[79KUM/CHA]
pot (gl. ise-ox)	$I = 2.0 \text{ M NaClO}_4$	$(25.00 \pm 0.02)$	$(14.9 \pm 0.01)$	[2000FER/IUL]
	$I = 3.0 \text{ M NaClO}_4$		$(15.2 \pm 0.01)$	
pot (gl. ise-ox)	$I = 1.0 \text{ M NaClO}_4$	$(25.00 \pm 0.02)$	$(14.0 \pm 0.3)$	[2000VAS/CAR]
sp	$I = 3.0 \text{ M NaClO}_4$	$(25.0 \pm 0.2)$	$(13.8 \pm 0.04)$	[2002HAV/SOT]
$\text{UO}_2^{2+} + \text{H}^+ + \text{ox}^{2-} \rightleftharpoons \text{UO}_2(\text{Hox})^+$				
dis	$I = 3.0 \text{ M NaClO}_4$	25	$(7.57 \pm 0.06)$	[94ERT/MOH]
	$I = 5.0 \text{ M NaClO}_4$		$(9.22 \pm 0.17)$	
	$I = 7.0 \text{ M NaClO}_4$		$(10.43 \pm 0.07)$	
	$I = 9.0 \text{ M NaClO}_4$		$(10.06 \pm 0.02)$	
$\text{UO}_2^{2+} + \text{Hox}^- \rightleftharpoons \text{UO}_2(\text{Hox})^+$				
ix	$I = 0.16 \text{ M HClO}_4$	$(25 \pm 1)$	3.40	[57LI/WES]
	$I = 1.0 \text{ M HClO}_4$		2.83	
	$I = 2.0 \text{ M HClO}_4$		2.89	
$\text{UO}_2^{2+} + 2 \text{Hox}^- \rightleftharpoons \text{UO}_2(\text{Hox})_2(\text{aq})$				
sp, pol	$I = 0.5 \text{ M (H/K)NO}_3$	25	$(6.00 \pm 0.08)$	[76BRI/ELD]
ix	$I = 0.16 \text{ M HClO}_4$	$(25 \pm 1)$	5.96	[57LI/WES]
	$I = 1.0 \text{ M HClO}_4$		4.67	
	$I = 2.0 \text{ M HClO}_4$		4.73	
$\text{UO}_2^{2+} + 2 \text{H}^+ + 2 \text{ox}^{2-} \rightleftharpoons \text{UO}_2(\text{Hox})_2(\text{aq})$				
dis	$I = 5.0 \text{ M NaClO}_4$	25	$(18.86 \pm 0.15)$	[94ERT/MOH]
	$I = 7.0 \text{ M NaClO}_4$		$(20.04 \pm 0.42)$	
	$I = 9.0 \text{ M NaClO}_4$		$(19.48 \pm 0.59)$	
$\text{UO}_2^{2+} + \text{H}_2(\text{ox})(\text{aq}) \rightleftharpoons \text{UO}_2(\text{H}_2\text{ox})^{2+}$				
sp, pot	$I \approx 0.05, 0.08 \text{ M UO}_2^{2+} / \text{SO}_4^{2-} / \text{Hox}^-$	25–26	2.57	[42HEI]

As the data in Table VI-38 show, the stability constants of  $\text{UO}_2\text{ox}(\text{aq})$ ,  $\text{UO}_2(\text{ox})_2^{2-}$  and  $\text{UO}_2(\text{ox})_3^{4-}$  are quite scattered:  $\log_{10} \beta_1$  from 3.22 to 7.37,  $\log_{10} \beta_2$  from 6.47 to 14.08 and  $\log_{10} \beta_3$  from 11.0 to 16.4. Critical reviews of the papers where the data are reported lead to the following findings:

- i. Systematic errors may be associated with some data, including the  $\log_{10} \beta_1$  from [79KUM/CHA], [85VEN/SWA], [89ABD/ALI], and the  $\log_{10} \beta_2$  from [84SIR] and [67RAJ/MAR]. These data are significantly lower than the majority of the data for the same complexes in the literature. They also seem too low in comparison with the data of relevant systems such as lanthanide oxalate complexes or U(VI) complexes with other dicarboxylates in the literature.
- ii. There are various shortcomings in some studies so that the data (or a portion of the data) are questionable. Examples of the shortcomings are: a) unknown or erroneous dissociation constants of oxalic acid [67MIY/NUR], [67STE/MAK2], [72MAN/VAR], [85VEN/SWA], [89ABD/ALI]; b) lack of experimental details such as the electrode calibration for pH/pcH calibration, [67RAJ/MAR], [72MAN/VAR], [76BRI/ELD], [79KUM/CHA], [85VEN/SWA], [89ABD/ALI]; c) varying ionic strengths or mixed electrolyte media [42HEI], [56GRI/PTI], [59MOS/ZAK], [59PTI/TEK], [72MAN/VAR], [76BRI/ELD], [83CHO/BOK], [89ABD/ALI]; d) incorrect models that either includes questionable species or excludes reasonable species [72MAN/VAR], [76BRI/ELD].
- iii. The existence of the protonated U(VI) oxalate complexes that were assumed to have formed in some experiments,  $\text{UO}_2(\text{Hox})^+$ ,  $\text{UO}_2(\text{Hox})_2(\text{aq})$  and  $\text{UO}_2(\text{H}_2\text{ox})^{2+}$ , is still open for debate. These species, difficult to identify by physical methods, were usually postulated to improve the fitting of potentiometric or spectrophotometric data. If they form, it is most likely to occur in strongly acidic solutions. There are contradictory results in the literature on the protonated U(VI) oxalate complexes. For example, while Heidt and others found the photosensitive species in acidic solutions included  $\text{UO}_2(\text{H}_2\text{ox})^{2+}$  [42HEI], the work by Pitzer *et al.* implies that no hydrogen entered the  $\text{UO}_2\text{ox}(\text{aq})$  and  $\text{UO}_2(\text{ox})_2^{2-}$  complexes [36PIT/GOR]. The results from solvent extraction with TBP indicate that no protonated U(VI) oxalate complexes formed in 1 – 4 M  $\text{HNO}_3$  [83CHO/BOK], but the data from solvent extraction with TTA and HEDHP were fitted with four complexes including  $\text{UO}_2(\text{Hox})^+$  and  $\text{UO}_2(\text{Hox})_2(\text{aq})$  in a pH range of 1.6 to 3.5 [94ERT/MOH]. As the detailed discussions in Appendix A indicate, the stability constants of  $\text{UO}_2(\text{Hox})^+$ ,  $\text{UO}_2(\text{Hox})_2(\text{aq})$  from [94ERT/MOH] are not reliable due to the scarcity and scatter of the experimental data.

Based on these findings, the data in Table VI-38 that are probably associated with systematic errors or various shortcomings are not accepted by this review. These include the data from [42HEI], [56GRI/PTI], [59MOS/ZAK], [59PTI/TEK], [67MIY/NUR], [67RAJ/MAR], [67STE/MAK2], [72MAN/VAR], [79KUM/CHA],



[84SIR], [85VEN/SWA], [89ABD/ALI], and a portion of data from [83CHO/BOK], [94ERT/MOH]. Detailed comments on the individual papers are given in Appendix A.

The reasonableness of the stability constants of the protonated U(VI) oxalate complexes in Table VI-38 can be qualitatively tested by using the combination of the stability constants of  $\text{UO}_2\text{ox}(\text{aq})$  and the dissociation constants of oxalic acid. Such tests indicate that the stability constants for  $\text{UO}_2(\text{Hox})_2(\text{aq})$  from [94ERT/MOH] seem too high, but the data for  $\text{UO}_2(\text{Hox})^+$ ,  $\text{UO}_2(\text{Hox})_2(\text{aq})$  and  $\text{UO}_2(\text{H}_2\text{ox})^{2+}$  from [57LI/WES], [76BRI/ELD] and [42HEI] appear reasonable and self-consistent. However, taking into consideration of the contradictory information in the literature on the presence of these complexes, the stability constants of  $\text{UO}_2(\text{Hox})^+$ ,  $\text{UO}_2(\text{Hox})_2(\text{aq})$  and  $\text{UO}_2(\text{H}_2\text{ox})^{2+}$  in Table VI-38 are not accepted by this review.

In addition, the stability constants in Table VI-38 that are determined at ionic strengths higher than  $5 \text{ mol}\cdot\text{kg}^{-1}$  are not included in the further analysis with SIT by this review.

Table VI-39 shows the stability constants of aqueous U(VI) oxalate complexes that are accepted and used for the SIT analysis by this review. The ionic strengths in molarity are converted into molality based on the information in Appendix B. The stability constants on the molarity scale are also converted to the values on the molality scale according to Eq. (II.37) in Section II.2. New uncertainties are assigned to the data according to the following rules: 1) If the uncertainties are given in the original paper, they are usually doubled to represent  $2\sigma$ . However, if the uncertainties given in the paper appear too optimistic, the uncertainties of  $\log_{10} \beta_1$ ,  $\log_{10} \beta_2$  and  $\log_{10} \beta_3$  are adjusted to be  $\pm 0.1$ ,  $\pm 0.2$ , and  $\pm 0.3$ , respectively. 2) If the uncertainties are not given in the original paper,  $\pm 0.2$ ,  $\pm 0.3$ , and  $\pm 0.4$  are assigned to  $\log_{10} \beta_1$ ,  $\log_{10} \beta_2$  and  $\log_{10} \beta_3$ , respectively.

The stability constants of  $\text{UO}_2\text{ox}(\text{aq})$  and  $\text{UO}_2(\text{ox})_2^{2-}$  from [60STA3] and [69HAV] were originally obtained at temperatures other than  $25^\circ\text{C}$  (Table VI-38). In order to include these data in the SIT analysis, they should be converted to the values at  $25^\circ\text{C}$ , for example, using the van't Hoff equation with the enthalpy of complexation (*cf.* Section VI.10.1.2.2.3).

The enthalpy of complexation for  $\text{UO}_2\text{ox}(\text{aq})$ ,



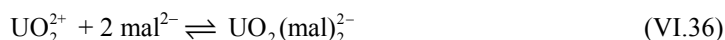
$\Delta_r H_m(\text{VI.34})$  can be estimated from the enthalpy of formation of  $\text{UO}_2\text{ox}(\text{aq})$ ,  $-(1824.3 \pm 18.3) \text{ kJ}\cdot\text{mol}^{-1}$  (*cf.* Section VI.10.1.2.2.3), the enthalpy of formation of  $\text{UO}_2^{2+}$ ,  $-(1019.000 \pm 1.5000) \text{ kJ}\cdot\text{mol}^{-1}$  [2003GUI/FAN], and the enthalpy of formation of  $\text{ox}^{2-}$ ,  $-(830.7 \pm 1.6) \text{ kJ}\cdot\text{mol}^{-1}$  (*cf.* Section VI.3.5):

$$\Delta_r H_m(\text{VI.34}) = (25.4 \pm 18.4) \text{ kJ}\cdot\text{mol}^{-1}.$$

Because of the absence of the enthalpy of complexation for  $\text{UO}_2(\text{ox})_2^{2-}$ ,



it is assumed by this review to be equal to the enthalpy of complexation for the analogous U(VI) malonate complex as an approximation,



Thus,  $\Delta_f H_m$  (VI.35)  $\approx \Delta_f H_m$  (VI.36) =  $(11 \pm 1) \text{ kJ} \cdot \text{mol}^{-1}$  [2002RAO/JIA].

Using the enthalpies of complexation for  $\text{UO}_2\text{ox}(\text{aq})$  and  $\text{UO}_2(\text{ox})_2^{2-}$ , the values of  $\log_{10} \beta_1$  (VI.34) and  $\log_{10} \beta_2$  (VI.35) at other temperatures are converted to those at 25°C. The converted values are shown in Table VI-39. Detailed information on the conversion is provided under the entries of [60STA3] and [69HAV] in Appendix A.

The value of  $\log_{10} \beta_1$  (VI.34) from [83CHO/BOK] was determined in 4 M  $\text{HNO}_3$  and the values of  $\log_{10} \beta_1$  (VI.34) and  $\log_{10} \beta_2$  (VI.35) from [96BOR/LIS] and [2001BOR/MOO] were determined in NaCl of variable ionic strengths. Thus, the values should be corrected for the complexation by nitrate or chloride. Detailed information on the corrections was given under the entries of [83CHO/BOK], [96BOR/LIS] and [2001BOR/MOO] in Appendix A. The corrected stability constants are shown in Table VI-39.

The values of  $\log_{10} \beta_1$  (VI.34) and  $\log_{10} \beta_2$  (VI.35) from [94ERT/MOH] are also re-valuated using the model that excludes the protonated complexes  $\text{UO}_2(\text{Hox})^+$ , and  $\text{UO}_2(\text{Hox})_2(\text{aq})$ , because the latter complexes are unlikely to form in the experiments at pH 1.6 to 3.5 and the data in [94ERT/MOH] are not sufficient to allow the calculation of such complexes. Details on the re-evaluation are given in Appendix A. The values after the re-evaluation are shown in Table VI-39.

Table VI-39: Stability constants of aqueous uranium(VI) oxalates at 25°C accepted by this review.

Method	Ionic medium <sup>a</sup>	$\log_{10} K$	Reference
$\text{UO}_2^{2+} + \text{ox}^{2-} \rightleftharpoons \text{UO}_2\text{ox}(\text{aq})$			
sp	$I = 0.101 \text{ m NaClO}_4$	$(6.42 \pm 0.19)^{\text{b,c}}$	[69HAV]
	$I = 1.05 \text{ m NaClO}_4$	$(6.03 \pm 0.11)^{\text{b,c}}$	
dis	$I = 4.56 \text{ m HNO}_3$	$(7.25 \pm 0.30)^{\text{b,d}}$	[83CHO/BOK]
ix	$I = 0.111 \text{ m NaClO}_4^{\text{e}}$	$(6.10 \pm 0.20)^{\text{b}}$	[91LOO/KOP]
dis	$I = 3.50 \text{ m NaClO}_4$	$(6.06 \pm 0.22)^{\text{b,f}}$	[94ERT/MOH]
dis	$I = 5.0 \text{ m NaCl}$	$(6.92 \pm 0.76)^{\text{g}}$	[96BOR/LIS]
pot (gl. ise-ox)	$I = 2.21 \text{ m NaClO}_4$	$(6.16 \pm 0.10)^{\text{b}}$	[2000FER/IUL]
	$I = 3.50 \text{ m NaClO}_4$	$(6.32 \pm 0.10)^{\text{b}}$	
pot (gl. ise-ox)	$I = 1.05 \text{ m NaClO}_4$	$(6.01 \pm 0.10)^{\text{b}}$	[2000VAS/CAR]

(Continued on next page)

Table VI-39 (continued)

Method	Ionic medium <sup>a</sup>	$\log_{10}K$	Reference
$\text{UO}_2^{2+} + \text{ox}^{2-} \rightleftharpoons \text{UO}_2\text{ox}(\text{aq})$			
dis	$I = 0.3 \text{ m NaCl}$	$(5.99 \pm 0.10)^{\text{e}}$	[2001BOR/MOO]
	$I = 1.0 \text{ m NaCl}$	$(6.05 \pm 0.10)^{\text{e}}$	
	$I = 2.0 \text{ m NaCl}$	$(6.16 \pm 0.10)^{\text{e}}$	
	$I = 3.0 \text{ m NaCl}$	$(7.13 \pm 0.18)^{\text{e}}$	
	$I = 4.0 \text{ m NaCl}$	$(7.60 \pm 0.45)^{\text{e}}$	
	$I = 5.0 \text{ m NaCl}$	$(7.24 \pm 0.76)^{\text{e}}$	
sp	$I = 3.50 \text{ m NaClO}_4$	$(6.24 \pm 0.10)^{\text{b}}$	[2002HAV/SOT]
$\text{UO}_2^{2+} + 2 \text{ ox}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_2^{2-}$			
dis	$I = 0.101 \text{ m NaClO}_4$	$(11.11 \pm 0.11)^{\text{b,c}}$	[60STA3]
sp	$I = 0.101 \text{ m NaClO}_4$	$(10.62 \pm 0.19)^{\text{b,c}}$	[69HAV]
	$I = 1.05 \text{ m NaClO}_4$	$(10.65 \pm 0.17)^{\text{b,c}}$	
dis	$I = 3.50 \text{ m NaClO}_4$	$(10.95 \pm 0.18)^{\text{b,f}}$	[94ERT/MOH]
dis	$I = 5.0 \text{ m NaCl}$	$(12.02 \pm 0.76)^{\text{e}}$	[96BOR/LIS]
pot (gl. ise-ox)	$I = 2.21 \text{ m NaClO}_4$	$(11.12 \pm 0.20)^{\text{b}}$	[2000FER/IUL]
	$I = 3.50 \text{ m NaClO}_4$	$(11.39 \pm 0.20)^{\text{b}}$	
pot (gl. ise-ox)	$I = 1.05 \text{ m NaClO}_4$	$(10.83 \pm 0.14)^{\text{b}}$	[2000VAS/CAR]
dis	$I = 0.3 \text{ m NaCl}$	$(10.15 \pm 0.12)^{\text{e}}$	[2001BOR/MOO]
	$I = 2.0 \text{ m NaCl}$	$(10.47 \pm 0.17)^{\text{e}}$	
	$I = 3.0 \text{ m NaCl}$	$(11.52 \pm 0.22)^{\text{e}}$	
sp	$I = 3.50 \text{ m NaClO}_4$	$(11.08 \pm 0.14)^{\text{b}}$	[2002HAV/SOT]
$\text{UO}_2^{2+} + 3 \text{ ox}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_3^{4-}$			
pot (gl. ise-ox)	$I = 2.21 \text{ m NaClO}_4$	$(14.8 \pm 0.3)^{\text{b}}$	[2000FER/IUL]
	$I = 3.50 \text{ m NaClO}_4$	$(15.0 \pm 0.3)^{\text{b}}$	
pot (gl. ise-ox)	$I = 1.05 \text{ m NaClO}_4$	$(13.9 \pm 0.6)^{\text{b}}$	[2000VAS/CAR]
sp	$I = 3.50 \text{ m NaClO}_4$	$(13.6 \pm 0.3)^{\text{b}}$	[2002HAV/SOT]

a: Converted from molarity to molality following the method in Chapter II.

b: Converted from the units of molarity to the units of molality, following the method in Chapter II.  
The uncertainties are adjusted (Appendix C).

c: Corrected from 20°C to 25°C, see Appendix A.

d: Corrected for the complexation of nitrate, see Appendix A.

e: The medium contains ~ 10% oxalate.

f: Obtained from the recalculation of the values in [94ERT/MOH] by excluding the protonated U(VI) oxalate complexes.

g: Corrected for the complexation of chloride, see Appendix A.

The re-evaluated values in Table VI-39 are used to obtain the stability constants of U(VI) oxalates at  $I = 0$  and 298.15 K with the SIT approach outlined in Appendix B.

The formation of the U(VI) oxalates is represented by the following equilibria:



For Reactions (VI.37) and (VI.38), data in Table VI-39 are fitted with Eq.(VI.40) and (VI.41):

$$\log_{10} \beta_1 + 8D = \log_{10} \beta_1^\circ - \Delta \varepsilon_1 \times I_m \quad (\text{VI.40})$$

$$\log_{10} \beta_2 + 8D = \log_{10} \beta_2^\circ - \Delta \varepsilon_2 \times I_m \quad (\text{VI.41})$$

where  $D = 0.509\sqrt{I_m} / (1 + 1.5\sqrt{I_m})$  and  $I_m$  is the ionic strength in molality.  $\log_{10} \beta_1$  and  $\log_{10} \beta_2$  are the stability constants at  $I_m$  ( $0.1 - 5 \text{ mol}\cdot\text{kg}^{-1}$ ) while  $\log_{10} \beta_1^\circ$  and  $\log_{10} \beta_2^\circ$  are the stability constants at  $I_m = 0$ .  $\Delta \varepsilon_1 = \varepsilon(\text{UO}_2\text{ox}(\text{aq}), \text{Na}^+ + \text{X}^-) - \varepsilon(\text{UO}_2^{2+}, \text{X}^-) - \varepsilon(\text{Na}^+, \text{ox}^{2-})$  and  $\Delta \varepsilon_2 = \varepsilon(\text{UO}_2(\text{ox})_2^{2-}, \text{Na}^+) - \varepsilon(\text{UO}_2^{2+}, \text{X}^-) - 2 \varepsilon(\text{Na}^+, \text{ox}^{2-})$  where  $\text{X}^-$  represents  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ , or  $\text{NO}_3^-$ .

Both weighted (using the uncertainties as the weighing factors) and unweighted linear regressions were performed on the data with Eq.(VI.40) and Eq.(VI.41). Slightly different results are obtained as shown in Table VI-40:

Table VI-40: Calculation of  $\log_{10} \beta_1^\circ$  and  $\log_{10} \beta_2^\circ$  by weighted and unweighted linear regression.

	Weighted	Unweighted
$\log_{10} \beta_1^\circ$ (VI.37)	$(7.16 \pm 0.02)$	$(7.13 \pm 0.16)$
$\Delta \varepsilon_1$	$-(0.41 \pm 0.02)$	$-(0.43 \pm 0.05)$
$\log_{10} \beta_2^\circ$ (VI.38)	$(11.68 \pm 0.07)$	$(11.65 \pm 0.15)$
$\Delta \varepsilon_2$	$-(0.44 \pm 0.03)$	$-(0.48 \pm 0.06)$

The results from the unweighted linear regression are selected by this review because of two reasons: 1) the weighted regression is based on the uncertainties of the individual data points. However, the uncertainties of the data in Table VI-39 are assigned by this review based on very limited or no information in the papers. They do not necessarily reflect the actual uncertainties of the original data. 2) the values of  $\log_{10} \beta^\circ$  and  $\Delta \varepsilon$  obtained by the weighted and unweighted agree within the error limits. The smaller error limits obtained from the weighted regression might be too optimistic. Figure VI-32 and Figure VI-33 show the unweighted regression and the propagation of the error limits from  $I = 0$ .

Figure VI-32: SIT plot of Reaction (VI.37) ( $\log_{10} \beta_1$ ) (+) [69HAV], (+) [83CHO/BOK], (●) [91LOO/KOP], ( $\Delta$ ) [94ERT/MOH], ( $\blacktriangle$ ) [96BOR/LIS], ( $\circ$ ) [2000FER/IUL], ( $\nabla$ ) [2000VAS/CAR], ( $\diamond$ ) [2001BOR/MOO], ( $\square$ ) [2002HAV/SOT].

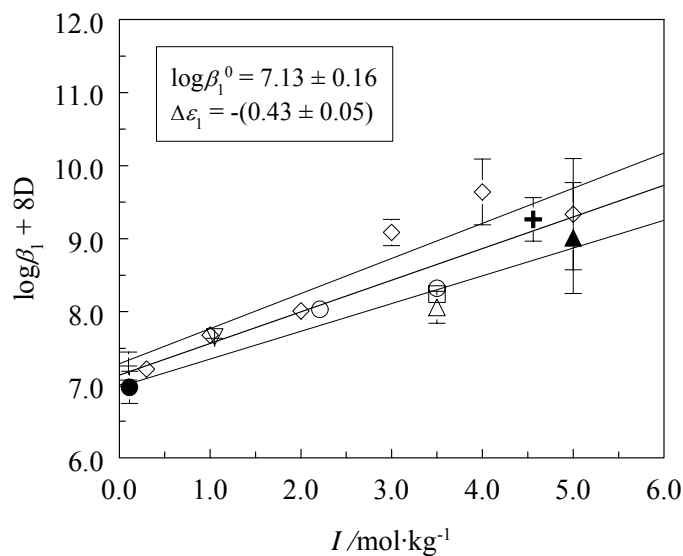
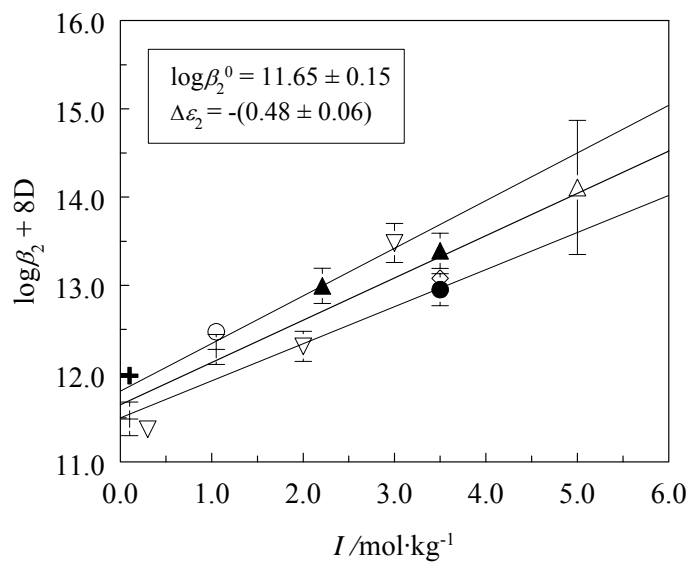


Figure VI-33: SIT plot of Reaction (VI.38) ( $\log_{10} \beta_2$ ) (+) [69HAV], (+) [60STA3], (●) [94ERT/MOH], ( $\Delta$ ) [96BOR/LIS], ( $\blacktriangle$ ) [2000FER/IUL], ( $\circ$ ) [2000VAS/CAR], ( $\nabla$ ) [2001BOR/MOO], ( $\diamond$ ) [2002HAV/SOT].



Since the data used in the SIT analysis include those obtained in different ionic media: perchlorate, chloride and nitrate, the above analysis implies that the ion interaction constants  $\varepsilon(\text{UO}_2^{2+}, \text{X}^-)$  and  $\varepsilon(\text{UO}_2\text{ox}(\text{aq}), \text{Na}^+ + \text{X}^-)$  are the same when  $\text{X}^-$  is  $\text{ClO}_4^-$ ,  $\text{Cl}^-$ , or  $\text{NO}_3^-$ . This implication should be correct for  $\varepsilon(\text{UO}_2^{2+}, \text{X}^-)$  because the complexation of  $\text{UO}_2^{2+}$  with  $\text{Cl}^-$  and  $\text{NO}_3^-$  has been corrected (see Appendix A) so that  $\varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) = \varepsilon(\text{UO}_2^{2+}, \text{NO}_3^-) = \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  [2003GUI/FAN]. It should also be noted that one constant from the  $\text{HNO}_3$  medium [83CHO/BOK] is included in the SIT analysis together with other data from the  $\text{Na}^+$  medium. From the values of  $\Delta\varepsilon_1$  and  $\Delta\varepsilon_2$  in Table VI-40, using  $\varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) = \varepsilon(\text{UO}_2^{2+}, \text{NO}_3^-) = \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  [2003GUI/FAN] and  $\varepsilon(\text{Na}^+, \text{ox}^{2-}) = -(0.08 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$  (cf. Section VI.3.5), two new ion interaction parameters can be derived and selected by this review:

$$\varepsilon(\text{UO}_2\text{ox}(\text{aq}), \text{Na}^+ + \text{X}^-) = -(0.05 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1},$$

where  $\text{X}^- = \text{Cl}^-$ ,  $\text{NO}_3^-$  or  $\text{ClO}_4^-$

$$\varepsilon(\text{UO}_2(\text{ox})_2^{2-}, \text{Na}^+) = -(0.18 \pm 0.07) \text{ kg}\cdot\text{mol}^{-1}.$$

Only four values of the stability constants of  $\text{UO}_2(\text{ox})_3^{4-}$  from the literature are accepted in Table VI-39, with a range of  $I$  from 1.05 to 3.50  $\text{mol}\cdot\text{kg}^{-1}$ . The values seem to be in discrepancy and belong to two parent distributions  $((14.8 \pm 0.3)$  and  $(15.0 \pm 0.3))$ ,  $((13.9 \pm 0.6)$  and  $(13.6 \pm 0.3))$ . Such data do not allow a meaningful regression of Eq.(VI.42) by SIT to derive the  $\log_{10} \beta_3^\circ$  and  $\Delta\varepsilon_3$  for Reaction (VI.39).

$$\log_{10} \beta_3 + 0D = \log_{10} \beta_3^\circ - \Delta\varepsilon_3 \times I_m \quad (\text{VI.42})$$

$$\Delta\varepsilon_3 = \varepsilon(\text{UO}_2(\text{ox})_3^{4-}, \text{Na}^+) - \varepsilon(\text{UO}_2^{2+}, \text{X}^-) - 3 \varepsilon(\text{Na}^+, \text{ox}^{2-})$$

As a result, an analogous approach described below is taken in this review to estimate  $\Delta\varepsilon_3$  and calculate the  $\log_{10} \beta_3^\circ$ . Assuming  $\varepsilon(\text{UO}_2(\text{ox})_3^{4-}, \text{Na}^+) \approx \varepsilon(\text{UO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+) = -(0.01 \pm 0.11) \text{ kg}\cdot\text{mol}^{-1}$  [2003GUI/FAN] and using the values of  $\varepsilon(\text{UO}_2^{2+}, \text{X}^-) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  where  $\text{X}^- = \text{ClO}_4^-$ ,  $\text{Cl}^-$ , or  $\text{NO}_3^-$  [2003GUI/FAN] and  $\varepsilon(\text{Na}^+, \text{ox}^{2-}) = -(0.08 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$  (cf. Section VI.3.5), the value of  $\Delta\varepsilon_3$  is calculated to be  $-(0.23 \pm 0.12) \text{ kg}\cdot\text{mol}^{-1}$ . Thus, values of  $\log_{10} \beta_3^\circ$  are obtained by Eq. (VI.42) from the  $\log_{10} \beta_3$  and summarised in Table VI-41:

Table VI-41: Calculation of  $\log_{10} \beta_3^\circ$  at 298.25 K.

$I (\text{mol}\cdot\text{kg}^{-1})$	$\log_{10} \beta_3$	$\Delta\varepsilon_3 \times I$	$\log_{10} \beta_3^\circ$	Reference
2.21	$(14.8 \pm 0.3)$	$-(0.51 \pm 0.22)$	$(14.3 \pm 0.4)$	[2000FER/IUL]
3.50	$(15.0 \pm 0.3)$	$-(0.80 \pm 0.35)$	$(14.2 \pm 0.5)$	
1.05	$(13.9 \pm 0.6)$	$-(0.24 \pm 0.10)$	$(13.7 \pm 0.6)$	[2000VAS/CAR]
3.50	$(13.6 \pm 0.3)$	$-(0.80 \pm 0.35)$	$(12.8 \pm 0.5)$	[2002HAV/SOT]

An unweighted average of  $\log_{10} \beta_3^\circ$  is  $(13.8 \pm 1.5)$ . A large uncertainty ( $\pm 1.5$ ) was assigned to cover the whole range of expectancy of all the four values.

Based on the accepted stability constants from the literature and the analysis with the SIT approach, the following stability constants of U(VI) oxalates are selected by this review (Table VI-42).

Table VI-42: Selected stability constants of aqueous U(VI) oxalates at 298.15 K.

Reaction	$\log_{10} \beta^\circ$	$\Delta\epsilon, \text{ kg}\cdot\text{mol}^{-1}$
$\text{UO}_2^{2+} + \text{ox}^{2-} \rightleftharpoons \text{UO}_2\text{ox}(\text{aq})$	$(7.13 \pm 0.16)$	$-(0.43 \pm 0.05)$
$\text{UO}_2^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_2^{2-}$	$(11.65 \pm 0.15)$	$-(0.48 \pm 0.06)$
$\text{UO}_2^{2+} + 3 \text{ox}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_3^{4-}$	$(13.8 \pm 1.5)$	$-(0.23 \pm 0.10)$

From the selected reaction data, the following Gibbs energies of formation are calculated:

$$\Delta_f G_m^\circ (\text{UO}_2\text{ox}, \text{aq}, 298.15 \text{ K}) = -(1673.4 \pm 2.7) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ (\text{UO}_2(\text{ox})_2^{2-}, 298.15 \text{ K}) = -(2379.3 \pm 4.1) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ (\text{UO}_2(\text{ox})_3^{4-}, 298.15 \text{ K}) = -(3071.7 \pm 10.3) \text{ kJ}\cdot\text{mol}^{-1}.$$

From the selected  $\Delta_f H_m^\circ (\text{UO}_2\text{ox}, \text{aq}, 298.15 \text{ K})$  and  $\Delta_f G_m^\circ (\text{UO}_2\text{ox}, \text{aq}, 298.15 \text{ K})$ , the following standard molar entropy of this species is calculated:

$$S_m^\circ (\text{UO}_2\text{ox}, \text{aq}, 298.15 \text{ K}) = (171.0 \pm 62.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

#### VI.10.2.4.2 Polynuclear U(VI) oxalate complexes

A few dinuclear U(VI) oxalate complexes were assumed to exist in solutions, including  $(\text{UO}_2)_2(\text{ox})_3^{2-}$  [59TEK/VIN2], [2002HAV/SOT], and  $(\text{UO}_2)_2(\text{ox})_5^{6-}$  [56GRI/PTI], [59TEK/VIN2], [2002HAV/SOT]. The presence of such complexes seems to be supported by the data of electric conductance [56GRI/PTI], [2002HAV/SOT] and the data of vapor pressure osmometry [2002HAV/SOT]. Also, the stability constants of  $(\text{UO}_2)_2(\text{ox})_3^{2-}$  and  $(\text{UO}_2)_2(\text{ox})_5^{6-}$  reported in the literature appear reasonable (Table VI-43). However, the conditions in the vapour pressure and conductance measurements were not identical to those in the spectrophotometric experiments based on which the stability constants of dinuclear species were calculated. The concentrations of oxalate in the spectrophotometric experiments were relatively low. At such concentrations, both the  $(\text{UO}_2)_2(\text{ox})_3^{2-}$  and  $(\text{UO}_2)_2(\text{ox})_5^{6-}$  species are minor ( $< 5\%$ ). The inclusion of such species only slightly improved the overall fit for the spectrophotometric data [2002HAV/SOT]. It is evident that more studies are needed to confirm the presence of such complexes in solution and obtain reliable stability constants. Therefore, the stability constants of dinuclear U(VI) oxalates in Table VI-43 are not accepted by this review.

Table VI-43: Stability constants of dinuclear U(VI) oxalates reported in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$2 \text{UO}_2^{2+} + 3 \text{ox}^{2-} \rightleftharpoons (\text{UO}_2)_2\text{ox}_3^{2-}$				
sp	$I = 3.0 \text{ M NaClO}_4$	$(25.0 \pm 0.2)$	$(18.5 \pm 0.2)$	[2002HAV/SOT]
$2 \text{UO}_2\text{ox}_2^{2-} \rightleftharpoons (\text{UO}_2)_2\text{ox}_3^{2-} + \text{ox}^{2-}$				
ise	$I = 0.022 \text{ M}$	25	1.3	[59TEK/VIN2]
	$I = 0.008 \text{ M}$	25	-0.5	[59TEK/VIN2]
$2 \text{UO}_2^{2+} + 5 \text{ox}^{2-} \rightleftharpoons (\text{UO}_2)_2(\text{ox})_5^{6-}$				
sp	$I = 3.0 \text{ M NaClO}_4$	$(25.0 \pm 0.2)$	$(28.5 \pm 0.1)$	[2002HAV/SOT]
$2 \text{UO}_2(\text{ox})_2^{2-} + \text{ox}^{2-} \rightleftharpoons (\text{UO}_2)_2(\text{ox})_5^{6-}$				
con	$I < 0.1 \text{ mol}\cdot\text{kg}^{-1}$	25	6.30	[56GRI/PTI]
$(\text{UO}_2)_2(\text{ox})_3^{2-} + 2 \text{ox}^{2-} \rightleftharpoons (\text{UO}_2)_2(\text{ox})_5^{6-}$				
ise	$I = 0.069 \text{ M}$	25	4.4	[59TEK/VIN2]

#### VI.10.2.4.3 Ternary U(VI) oxalate complexes

A variety of ternary U(VI) oxalate complexes were assumed to exist in solution, including  $\text{UO}_2(\text{OH})\text{ox}^-$  [56GRI/PTI],  $(\text{UO}_2)_2(\text{OH})_2(\text{ox})_4^{6-}$  and  $(\text{UO}_2)_2(\text{OH})_4(\text{ox})_2^{4-}$  [2000PAL],  $\text{UO}_2\text{F}_3\text{ox}^{3-}$  [68SHC/BEL],  $\text{UO}_2\text{oxSO}_3^{2-}$  and  $\text{UO}_2\text{ox}(\text{SO}_3)_2^{4-}$  [67ZAK/ORL2],  $\text{UO}_2\text{CO}_3\text{ox}^{2-}$ , [61CHE/GOL],  $\text{UO}_2\text{ox}(\text{L})^{2-}$  and  $\text{UO}_2(\text{ox})_2(\text{L})^{4-}$  where  $\text{L}$  = malonate [79KUM/CHA],  $\text{UO}_2\text{ox}(\text{L})^{2-}$  and  $\text{UO}_2\text{ox}(\text{L})_2^{4-}$  where  $\text{L}$  = aminodiacetate [79KUM/CHA],  $\text{UO}_2\text{ox}(\text{L})^{3-}$  where  $\text{L}$  = nitrilotriacetate [84SIR],  $\text{UO}_2\text{ox}(\text{L})^{2-}$  where  $\text{L}$  = phthalate [85VEN/SWA]. However, only a few papers report stability constants for some of these complexes as summarised in Table VI-44.

Quaternary U(VI) oxalate complexes,  $\text{UO}_2\text{ox}(\text{L}'\text{L}'')^{4-}$  where  $\text{L}'$  = malonate and  $\text{L}''$  = iminodiacetate, are also reported in the literature [79KUM/CHA], in conjunction with the data for binary U(VI) oxalate complexes. These data are not accepted by this review because essential experimental conditions are not provided in [79KUM/CHA] and discussions on quaternary complexes containing other organic ligands than ox, cit, edta or isa are beyond the scope of this review. Detailed reasons for the rejection are provided in Appendix A.

As shown in Table VI-44, data on the ternary U(VI) oxalate complexes are rare. Their presence is not confirmed by independent studies or other methods [2000PAL]. Besides, there are a few shortcomings associated with these data. For example, some of the stability constants were determined in conjunction with the preparation of the corresponding solid compounds [67ZAK/ORL2], such as those described in Section VI.10.1.2.1. As a result, the calculated stability constants are correlated to the solubility constants of the solid phases and are associated with high uncertainty if the solid phase is not well defined. The solubility experiments were not conducted in a single ionic medium with constant ionic strength [67ZAK/ORL2]. Experimental condi-



tions are either incorrect or missing [56GRI/PTI], [79KUM/CHA], [84SIR], [85VEN/SWA]. Therefore, the stability constants for the ternary and quaternary U(VI) oxalate complexes are not accepted in this review. Detailed comments on the shortcomings of the references are given in Appendix A.

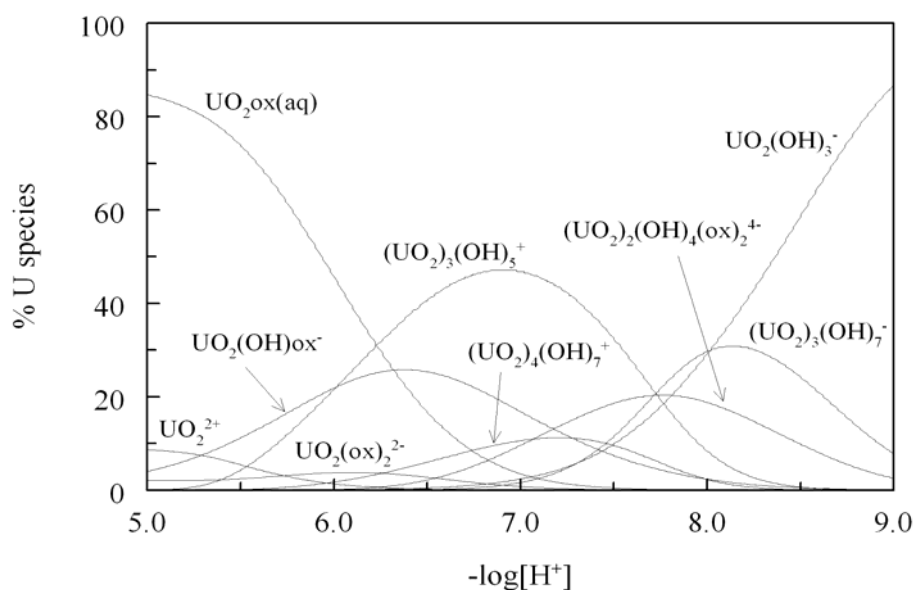
Table VI-44: Stability constants of ternary U(VI) oxalate complexes reported in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{UO}_2\text{ox} \cdot \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{UO}_2\text{ox}(\text{OH})^- + \text{H}^+$				
pot	$I < 0.1 \text{ mol} \cdot \text{kg}^{-1}$	25	$\sim -6.30$	[56GRI/PTI]
$2 \text{UO}_2^{2+} + 2 \text{H}_2\text{O} + 4 \text{ox}^{2-} \rightleftharpoons (\text{UO}_2)_2(\text{OH})_2(\text{ox})_4^{6-} + 2 \text{H}^+$				
pot, cou	$I = 1.0 \text{ M NaClO}_4$	$(25.00 \pm 0.02)$	$(12.48 \pm 0.05)$	[2000PAL]
$2 \text{UO}_2^{2+} + 4 \text{H}_2\text{O} + 2 \text{ox}^{2-} \rightleftharpoons (\text{UO}_2)_2(\text{OH})_4(\text{ox})_2^{4-} + 4 \text{H}^+$				
pot, cou	$I = 1.0 \text{ M NaClO}_4$	$(25.00 \pm 0.02)$	$-(7.15 \pm 0.08)$	[2000PAL]
$\text{UO}_2\text{ox} + \text{SO}_3^{2-} \rightleftharpoons \text{UO}_2\text{oxSO}_3^{2-}$				
sp	$I = ?$	?	4.53	[67ZAK/ORL2]
$\text{UO}_2(\text{SO}_3)\text{ox}^{2-} + \text{SO}_3^{2-} \rightleftharpoons \text{UO}_2\text{ox}(\text{SO}_3)_2^{4-}$				
sol	$I = 2.5 \text{ M NH}_4\text{Cl}$	$(23 \pm 1)$	3.72	[67ZAK/ORL2]
$\text{UO}_2^{2+} + \text{ox}^{2-} + \text{L}^{2-} \rightleftharpoons \text{UO}_2\text{oxL}^{2-}$ , L = malonate				
pot	$I = 0.10 \text{ M KNO}_3$	$(25 \pm 1)$	$(7.67 \pm 0.11)$	[79KUM/CHA]
$\text{UO}_2^{2+} + 2 \text{ox}^{2-} + \text{L}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_2\text{L}^{4-}$ , L = malonate				
pot	$I = 0.10 \text{ M KNO}_3$	$(25 \pm 1)$	$(14.32 \pm 0.24)$	[79KUM/CHA]
$\text{UO}_2^{2+} + \text{ox}^{2-} + \text{L}^{2-} \rightleftharpoons \text{UO}_2\text{oxL}^{2-}$ , L = iminodiacetate				
pot	$I = 0.10 \text{ M KNO}_3$	$(25 \pm 1)$	$(10.07 \pm 0.28)$	[79KUM/CHA]
$\text{UO}_2^{2+} + 2 \text{ox}^{2-} + \text{L}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_2\text{L}^{4-}$ , L = iminodiacetate				
pot	$I = 0.10 \text{ M KNO}_3$	$(25 \pm 1)$	$(13.65 \pm 0.11)$	[79KUM/CHA]
$\text{UO}_2^{2+} + \text{ox}^{2-} + \text{L}^{3-} \rightleftharpoons \text{UO}_2\text{oxL}^{3-}$ , L = nitrilotriacetate				
em	$I = 0.1 \text{ M NaClO}_4$	40	8.98	[84SIR]
$\text{UO}_2^{2+} + \text{ox}^{2-} + \text{L}^{2-} \rightleftharpoons \text{UO}_2\text{oxL}^{2-}$ , L = phthalate				
pot	$I = 0.1 \text{ M KNO}_3$	25	7.24	[85VEN/SWA]

Among the reported ternary complexes, the U(VI)-hydroxyl-oxalato, U(VI)-carbonato-oxalato and U(VI)-fluorido-oxalato complexes are of importance in predicting the chemical behavior of U(VI) in geological environments where the pH, the concentration of carbonate and/or fluoride are high. For example, formation of  $(\text{UO}_2)_2(\text{OH})_2(\text{ox})_4^{6-}$  and  $(\text{UO}_2)_2(\text{OH})_4(\text{ox})_2^{4-}$  [2000PAL] could be significant in solutions with  $\text{pH} > 7$  and change the onset of the hydrolysis of U(VI). Using the data on the U(VI)-hydroxyl-oxalato complexes from [56GRI/PTI] and [2000PAL], the stability constants of U(VI) oxalate complexes selected by this review (Table VI-42), and the

hydrolysis constants of U(VI) [2003GUI/FAN], a speciation diagram (Figure VI-34) is drawn for a solution of  $1 \times 10^{-5}$  M U(VI) and  $1 \times 10^{-5}$  M oxalate at 25°C. As shown in Figure VI-34, assuming the stability constants of  $\text{UO}_2(\text{OH})\text{ox}^-$ ,  $(\text{UO}_2)_2(\text{OH})_2(\text{ox})_4^{6-}$  and  $(\text{UO}_2)_2(\text{OH})_4(\text{ox})_2^{4-}$  are correct, the ternary U(VI)-hydroxyl-oxalato complexes,  $\text{UO}_2(\text{OH})\text{ox}^-$ , and  $(\text{UO}_2)_2(\text{OH})_4(\text{ox})_2^{4-}$  could amount to 20 – 30% of the total U(VI) in the pH regions between 6 and 8, even at such low concentration of oxalate. These two complexes, as well as  $(\text{UO}_2)_2(\text{OH})_2(\text{ox})_4^{6-}$  that is insignificant when [oxalate] is low, could become even more important if the concentration of oxalate is higher. Obviously, it is of great value to conduct further studies and obtain reliable data on ternary U(VI)-hydroxyl-oxalato complexes, so that the effect of oxalate on the hydrolysis of U(VI) can be better evaluated.

Figure VI-34: Speciation of U(VI) at 25°C, using the stability constants of ternary U(VI)-hydroxyl-oxalato complexes in Table VI-44. Formation of solid phases is suppressed.



The formation of U(VI)-carbonato-oxalato complexes was postulated in [61CHE/GOL], but no stability constants were determined. Potentiometric titrations of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}(\text{s})$  with  $(\text{NH}_4)_2\text{CO}_3$  showed pH “plateaus” that suggested the formation of U(VI)-carbonato-oxalato complexes at molar ratios of  $[(\text{NH}_4)_2\text{CO}_3]/[\text{UO}_2(\text{ox})] = 1:1$  and  $2:1$ . Eventually, a precipitate that was assumed to be ammonium tricarbonatouranate formed at a molar ratio of  $[(\text{NH}_4)_2\text{CO}_3]/[\text{UO}_2(\text{ox})] = 3:1$ . Similar observations were made in the titrations of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}(\text{s})$  with  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  [61CHE/GOL]. The first pH plateau appears to correspond to the formation of

$\text{UO}_2\text{CO}_3\text{oxH}_2\text{O}^{2-}$ . Solids with the compositions corresponding to  $\text{M}_2\text{UO}_2\text{CO}_3\text{oxH}_2\text{O}$  ( $\text{M} = \text{NH}_4^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ ) were isolated and the fresh aqueous solutions of such compounds showed electrical conductivities characteristic of three ions, supporting the formula [61CHE/GOL]. Though there is a lack of direct identification of the  $\text{UO}_2\text{CO}_3\text{ox}^{2-}$  complex in solution, its formation could be expected solely based on structural information. The coordination number of  $\text{UO}_2^{2+}$  in its equatorial plane would be five with one bidentate oxalate, one bidentate carbonate and one water. The formation of U(VI)-carbonato-oxalato complexes could affect the concentration of uranium in groundwater where the  $p_{\text{CO}_2}$  is high. To evaluate the importance of the U(VI)-carbonato-oxalato complexes under such conditions, approximation approaches can be taken, in the absence of reliable data, to estimate the stability constants from corresponding binary complexes ( $\text{UO}_2(\text{ox})_2^{2-}$  and  $\text{UO}_2(\text{CO}_3)_2^{2-}$ ) (see Chapter 3 of [97ALL/BAN]). Further discussions on this subject is beyond the scope of this review.

The formation of U(VI)-fluorido-oxalato complexes was postulated, based on the studies of the solubility of  $\text{M}_3\text{UO}_2\text{F}_5$  ( $\text{M} = \text{NH}_4^+$ ,  $\text{K}^+$  and  $\text{CN}_3\text{H}_6^+$ ). Stepwise replacements of fluoride by oxalate, as suggested by the change in solubility as a function of  $[\text{M}_2\text{ox}]$ , could result in species with the formula:  $\text{UO}_2\text{F}_3\text{ox}^{3-}$  and  $\text{UO}_2\text{F}(\text{ox})_2^{3-}$  [68SHC/BEL]. Solids isolated from solutions with corresponding molar ratios of  $\text{M}_3\text{UO}_2\text{F}_5$  and  $\text{M}_2\text{ox}$  appear to be consistent with the formula of ternary U(VI)-fluorido-oxalato compounds, though no evidence was provided to support the existence of such complexes in solution. Similar to the U(VI)-carbonato-oxalato complexes, formation of ternary U(VI)-fluorido-oxalato complexes could also be expected solely based on the structural information of binary U(VI) oxalate and U(VI) fluoride complexes. An equatorial coordination number of five for  $\text{UO}_2^{2+}$  is always satisfied in  $\text{UO}_2\text{F}_5^{3-}$ ,  $\text{UO}_2\text{F}_3\text{ox}^{3-}$  and  $\text{UO}_2\text{F}(\text{ox})_2^{3-}$ . Again, to evaluate the importance of the U(VI)-fluorido-oxalato complexes in groundwater where  $[\text{F}^-]$  is high, approximation approaches can be taken, in the absence of reliable data, to estimate the stability constants from corresponding binary U(VI) fluoride and U(VI) oxalate complexes (see Chapter 3 of [97ALL/BAN]).

## VI.11 Neptunium oxalate compounds and complexes<sup>1</sup>

### VI.11.1 Solid neptunium oxalates

#### VI.11.1.1 Solid neptunium(III) oxalates

Solid Np(III) oxalate, which is unstable to oxidation, was prepared by [71MEF/GEL2], and the composition of the solid was found to correspond to  $\text{Np}_2(\text{ox})_3 \cdot n\text{H}_2\text{O}$ , with  $n \approx 11$ . The standard entropy of this compound was estimated by Moskvin using a Latimer-like method [73MOS]:  $S_m^\circ(298.15 \text{ K}) = 709 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

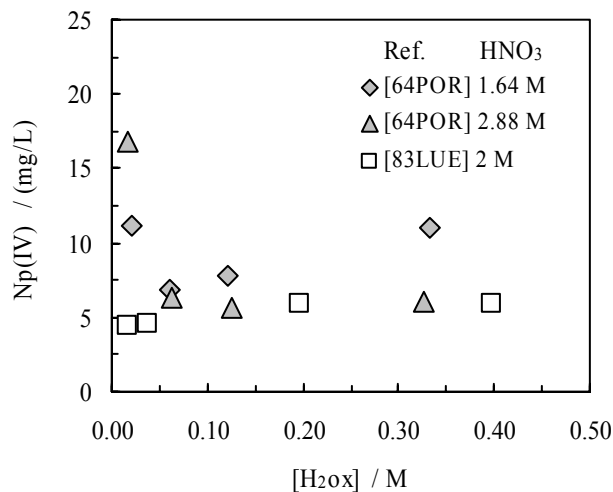
<sup>1</sup> Prof. J. Havel and Dr. P. Lubal (both from the Department of Analytical Chemistry, Masaryk University, Brno, Czech Republic) contributed to this section during the early stages of the review process.

### VI.11.1.2 Solid neptunium(IV) oxalates

The structure of Np(IV) oxalate,  $\text{Np}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$ , was characterised by single crystal X-ray diffraction [97GRI/CHA]. A modified Latimer methodology was used by Moskvin to estimate the standard entropy of this compound:  $S_m^\circ(298.15\text{ K}) = 368\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [73MOS].

Np(IV) oxalate is sparingly soluble in water but in excess of oxalic acid it dissolves forming complexes. In acid media a metastable solid may precipitate when solutions of Np(IV) and oxalic acid are mixed:  $(\text{H}_3\text{O})_2\text{Np}_2(\text{ox})_5 \cdot 7\text{H}_2\text{O}$  (equivalent to  $\text{H}_2\text{Np}_2(\text{ox})_5 \cdot 9\text{H}_2\text{O}$ ). With time this solid is however transformed into  $\text{Np}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$  when standing in the mother liquor [88BYK/KUZ2], [94ZHI/MAT2], [98CHA/KRO]. The solubility of  $\text{Np}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$  was reported in [60KON/GEL], [64BAN/SHA], [64POR], [83LUE]. Unfortunately the solid phase was not characterised in any of these studies, and the presence of  $(\text{H}_3\text{O})_2\text{Np}_2(\text{ox})_5 \cdot 7\text{H}_2\text{O}$  cannot be ruled out. Furthermore the experimental solubilities at  $\approx 22^\circ\text{C}$  reported in [64POR], [83LUE] are in disagreement with each other for solutions with acidities  $< 4\text{ M}$ , cf. Figure VI-35. The solubilities published in [64POR] are not considered in this review, cf. Appendix A.

Figure VI-35: Comparison of some of the experimental solubility data for Np(IV) oxalate in  $\text{HNO}_3$  solutions reported in [64POR], [83LUE] at 23 and  $22^\circ\text{C}$ , respectively. Only the data in the range 1.6 to 2.9 M  $\text{HNO}_3$  have been plotted in the figure, to illustrate the discrepancies between the two sets of data. For these acidities the disagreement is largest at  $[\text{H}_2\text{ox}] < 0.1\text{ M}$ .



Solubility constants have been obtained from solubility measurements of Np(IV) oxalate and reported in [60KON/GEL], [64BAN/SHA], [83LUE], *cf.* Table VI-45. The data from [64POR] were also re-evaluated in [68MOS2], but as already mentioned above, the solubilities published in [64POR] are not considered in this review. Appendix A contains comments on [60KON/GEL], [64BAN/SHA], [64POR], [83LUE]. The earlier study by Kondratov and Gel'man [60KON/GEL] is not considered in this review because of diverse shortcomings described in Appendix A.

High acidities are usually used in studies on aqueous chemistry of  $M^{4+}$  ions in order to avoid the hydrolysis of the metal ion. Under these conditions the oxalate ligand is fully protonated, but the medium effects on the dissociation constants of oxalic acid are not well known in these strongly acidic solutions. Therefore, any published equilibrium constant involving the oxalate ligand,  $ox^{2-}$ , and Np(IV) should be regarded with suspicion. The experimental solubilities reported in [64BAN/SHA], [83LUE] have been analysed by this review using  $H_2ox(aq)$  as a ligand. Details of these re-evaluations are given in the entries of Appendix A. The resulting complex formation constants are discussed in Section VI.11.2.2, while the solubility constants are listed in Table VI-46. There is large disagreement between the complex formation constants derived from these solubilities and those from spectrophotometric or solvent extraction data, *cf.* Section VI.11.2.2. Taking this into account, and considering that the solid phase was not characterised in these studies, no solubility constant is recommended for  $Np(ox)_2 \cdot 6H_2O$ .

Table VI-45: Solubility constants of solid Np(IV) oxalate reported in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10}K_s$	Reference
$Np(ox)_2 \cdot 6H_2O(cr) + 4 H^+ \rightleftharpoons Np^{4+} + 2 H_2ox(aq) + 6 H_2O(l)$				
sol	(1.56 and 2.09) M HCl	16	$-(11.32 \pm 0.03)$	<a href="#">[60KON/GEL]</a>
	(0.41 and 1.08) M HCl	19	$-(11.22 \pm 0.09)$	
$Np(ox)_2 \cdot 6H_2O(cr) \rightleftharpoons Np^{4+} + 2 ox^{2-} + 6 H_2O(l)$				
sol	(1.56 and 2.09) M HCl	16	$-(22.16 \pm 0.03)$	<a href="#">[60KON/GEL]</a>
	(0.41 and 1.08) M HCl	19	$-(22.07 \pm 0.09)$	
	4.1 M HClO <sub>4</sub>	16	$-(22.30 \pm 0.06)$	
sol	1 M HClO <sub>4</sub>	$(26 \pm 2)$	$-(18.89 \pm 0.03)$	<a href="#">[64BAN/SHA]</a>
	1 M (Na, H)ClO <sub>4</sub>		$-(18.89 \pm 0.03)$	
$Np(ox)_2 \cdot 6H_2O(cr) \rightleftharpoons Np(ox)_2(aq) + 6 H_2O(l)$				
sol	(0.4–10) M HNO <sub>3</sub>	22	$-(4.75 \pm 0.07)$	<a href="#">[83LUE]</a>
		45	$-(4.2 \pm 0.2)$	
		60	$-(3.75 \pm 0.05)$	

Ternary neptunium(IV) oxalates with alkali metal ions in an outer coordination sphere are quite soluble in water but they may be precipitated by adding alcohol. In addition to  $(\text{H}_3\text{O})_2\text{Np}_2(\text{ox})_5 \cdot 7\text{H}_2\text{O}$  mentioned above, the following solids have been reported:  $\text{Na}_4\text{Np}(\text{ox})_4 \cdot 3\text{H}_2\text{O}$  and  $\text{K}_4\text{Np}(\text{ox})_4 \cdot 4\text{H}_2\text{O}$  [67MEF/GEL2],  $\text{M}_2\text{Np}_2(\text{ox})_5 \cdot 9\text{H}_2\text{O}$  ( $\text{M} = \text{Na}, \text{K}$ ) and  $(\text{NH}_4)_2\text{Np}_2(\text{ox})_5 \cdot 7\text{H}_2\text{O}$  [88BYK/KUZ2]. The preparation of an ammonium salt reported to be  $(\text{NH}_4)_4\text{Np}(\text{ox})_4 \cdot (\text{NH}_4)_2\text{ox} \cdot n\text{H}_2\text{O}$  was described in [60KON/GEL], [67GEL/MOS].

Table VI-46: Solubility constants for reaction:  $\text{Np}(\text{ox})_2 \cdot 6\text{H}_2\text{O}(\text{cr}) + 4 \text{H}^+ \rightleftharpoons \text{Np}^{4+} + 2 \text{H}_2\text{O}(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$ , obtained from the re-evaluations described in Appendix A of experimental literature solubilities of Np(IV) oxalate at  $\approx 25^\circ\text{C}$ .

Ionic medium	$t$ ( $^\circ\text{C}$ )	$\log_{10}K_s$	Reference to the original data
$I \rightarrow 0$	$(26 \pm 2)$	$-(13.1 \pm 1.0)$	[64BAN/SHA]
1 M $\text{HClO}_4^a$		$-(10.8 \pm 0.9)$	
$I \rightarrow 0$	22	$-(12.2 \pm 0.2)$	[83LUE]

a: The equilibrium constant listed in this line refers to 1 M  $\text{HClO}_4$ , but was obtained by simultaneously analysing solubility data obtained both in 1 M  $\text{NaClO}_4$  and in  $(0.5 \text{ M } \text{HClO}_4 + 0.5 \text{ M } \text{NaClO}_4)$ , cf. Appendix A.

### VI.11.1.3 Solid neptunium(V) oxalates

Binary Np(V) oxalate may be prepared by mixing oxalic acid dissolved in tertiary butyl-alcohol with a solution of Np(V) in 1 M  $\text{HCl}$ . The product was analysed and found to be  $\text{NpO}_2(\text{Hox}) \cdot 2\text{H}_2\text{O}$  [52GIB/GRU], [54GRU/HUT]. This solid is also mentioned in another study [73KHA/MOS2] reporting its IR absorption spectra, but in this case the authors did not give any details on the analysis of the solid. The same synthetic procedure was attempted by [72JON/STO] but a compound with a composition corresponding to  $(\text{NpO}_2)_2\text{ox} \cdot 4\text{H}_2\text{O}$  was isolated instead [72JON/STO]. A similar solid reported to be the monohydrate  $(\text{NpO}_2)_2\text{ox} \cdot \text{H}_2\text{O}$  was prepared by [81ZUB/KRO] and the authors reported that this solid has a slow precipitation rate and a solubility in water at room temperature  $\approx 2.6 \times 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$ . Apparently the number of water molecules in the stoichiometry of Np(V) oxalate depends on the conditions for its synthesis. The molecular structure of  $(\text{NpO}_2)_2\text{ox} \cdot 6\text{H}_2\text{O}$ , obtained from a single-crystal X-ray diffraction study [96GRI/CHA2], shows clearly the presence of  $\text{NpO}_2^+ - \text{NpO}_2^+$  bonds.

Several ternary and quaternary Np(V) oxalate compounds have been reported:  $\text{MNpO}_2\text{ox} \cdot n\text{H}_2\text{O}$ , where  $\text{M} = \text{Na}, \text{K}, \text{Cs}$  or  $\text{NH}_4$  [70GEL/BLO2], [81ZUB/KRO], [87MEF/KRO] and  $\text{Co}(\text{NH}_3)_6\text{NpO}_2(\text{ox})_2 \cdot n\text{H}_2\text{O}$  [91GRI/BAT]. The sodium, ammonium and hexamminecobalt(III) salts have been studied by single-crystal X-ray diffraction [84TOM/VOL], [91GRI/BAT], [91GRI/BES].  $\text{MNpO}_2\text{ox} \cdot n\text{H}_2\text{O}$  compounds have solubilities  $\approx (0.02 \text{ to } 0.04) \text{ M}$ , while  $\text{Co}(\text{NH}_3)_6\text{NpO}_2(\text{ox})_2 \cdot n\text{H}_2\text{O}$  is “almost insoluble” in water [70GEL/BLO2], [76MEF/BLO]. It has been observed that the Np(V) concentration decreases with time in solutions equilibrated with  $\text{MNpO}_2\text{ox} \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Na}, \text{K}$  or

$\text{NH}_4$ ), and this has been explained by assuming that a less soluble compound, probably  $(\text{NpO}_2)_2\text{ox}\cdot\text{H}_2\text{O}$ , is formed [81ZUB/KRO]. For the least soluble caesium salt  $\text{CsNpO}_2\text{ox}\cdot n\text{H}_2\text{O}$  the decrease in  $\text{Np(V)}$ -concentration with time was not observed.

No thermodynamic data is available for any neptunium(V) compound with oxalate.

#### VI.11.1.4 Solid neptunium(VI) oxalates

The redox reactions of neptunyl(VI) with oxalate at room temperature are slow and therefore it is possible to isolate  $\text{Np(VI)}$  oxalate compounds from aqueous solutions for subsequent X-ray analyses or solubility experiments, *e.g.*,  $\text{NpO}_2\text{ox}\cdot 3\text{H}_2\text{O}$ , as well as a series of ternary oxalates of neptunyl(VI) and alkali metals.

The preparation of  $\text{NpO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  was described in [69MEF/KRO2]. In order to avoid reduction of neptunium(VI) to neptunium(V) the synthesis of  $\text{Np(VI)}$  oxalate has to be performed from cold solutions in the presence of an oxidising agent (*e.g.*, 0.05 M  $\text{KBrO}_3$ ). The unit cell parameters for  $\text{NpO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  were reported in [81MEF/GRI].  $\text{NpO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  is slightly soluble in water and in diluted inorganic acid solutions. The solubility of this solid was studied as a function of oxalic acid concentration (up to 0.15 M) in 1 M  $\text{HNO}_3$  at 14°C [69MEF/KRO2], but the reported solubility constant is only of qualitative use, *cf.* Appendix A. The standard entropy of  $\text{NpO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  was estimated by Moskvina [73MOS] using a modified Latimer method:  $S_m^\circ(298.15\text{ K}) = 272\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

Ternary oxalates,  $\text{K}_6(\text{NpO}_2)_2(\text{ox})_5\cdot n\text{H}_2\text{O}$  ( $n = 2$  or 4), were precipitated from cold, slightly acidic, concentrated solutions of neptunium(VI) mixed with saturated  $\text{K}_2\text{ox}$  solutions [81MEF/GRI]. An analogous way of preparation was used for the synthesis of  $\text{Cs}_2(\text{NpO}_2)_2(\text{ox})_3$  and of  $\text{Cs}_2\text{NpO}_2(\text{ox})_2\cdot 2\text{H}_2\text{O}$  [81MEF/GRI]. These compounds are highly soluble in water and they are stable for several days when dried and kept at low temperatures, but they decompose rapidly at temperatures above 100°C [81MEF/GRI].

#### VI.11.1.5 Solid neptunium(VII) oxalates

Neptunium(VII) is readily reduced by oxalate and therefore it is not possible to prepare  $\text{Np(VII)}$  oxalate compounds in the solid state.

### VI.11.2 Aqueous neptunium oxalate complexes

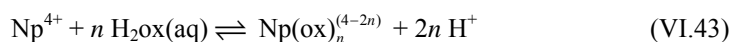
#### VI.11.2.1 Neptunium(III) oxalate complexes

Neptunium(III) is oxidised by oxalate [71MEF/GEL2] and there is no evidence in the literature on the formation of  $\text{Np(III)}$ -oxalate complexes in aqueous solutions.

### VI.11.2.2 Neptunium(IV) oxalate complexes

The complexation of neptunium(IV) with oxalate has been studied mainly by solubility [60KON/GEL], [64BAN/SHA], [83LUE] and by solvent extraction measurements [62ISH/NAK], [64BAN/SHA], [76BAG/RAM3], [77RAM/RAM], [79KUS/GAN]. In addition, spectrophotometry was used in [67MEF/GEL2]. Table VI-47 lists the stability constants reported in the literature. Values of stability constants at temperatures different than 25°C or room temperature were also obtained in [77RAM/RAM], [83LUE].

Species of stoichiometry  $\text{Np}(\text{ox})_n^{(4-2n)}$  ( $n = 1$  to 4) were reported in these references, except for [62ISH/NAK], but this paper is not credited by this review, *cf.* Appendix A. In most cases only the species  $\text{Np}(\text{ox})^{2+}$ ,  $\text{Np}(\text{ox})_2(\text{aq})$  and  $\text{Np}(\text{ox})_3^{2-}$  were assumed to be present in solution. A question not always addressed in these publications is the redox state of the neptunium ions. All the studies on Np(IV) complex formation have to be performed in strongly acidic solution in order to avoid the formation of hydrolysis products such as  $\text{NpOH}^{3+}$ . In these conditions oxalate is fully protonated, but the medium effects on the acidity constants of oxalic acid are not known in *e.g.*,  $\text{HClO}_4$  or  $\text{HNO}_3$  solutions. It is then necessary to evaluate experimental data using oxalic acid as a ligand:



Except for the rejected [62ISH/NAK] (*cf.* Appendix A), the solvent extraction studies may be grouped into two sets: an early investigation [64BAN/SHA] that also reported solubility data; and a series of publications by the same research group [76BAG/RAM3], [77RAM/RAM], [77RAM/RAM2], [79KUS/GAN]. All these reports are discussed in Appendix A, where the re-analysis made by this review of the experimental data at 25°C is described. The equilibrium constants obtained for Reactions (VI.43) are listed in Table VI-48.

Table VI-47: Literature stability constants for neptunium(IV) oxalate complexes.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Np}^{4+} + \text{ox}^{2-} \rightleftharpoons \text{Np}(\text{ox})^{2+}$				
sol	1.0 M HCl	(25 ± 2)	(8.5 ± 0.3)	[60KON/GEL]
sol	1 M $\text{HClO}_4$	(26 ± 2)	(7.47 ± 0.01)	[64BAN/SHA]
	1 M (H, Na) $\text{ClO}_4$		(7.40 ± 0.05)	
dis	1 M $\text{HClO}_4$		(8.19 ± 0.06)	
sp	0.3 M $\text{HClO}_4$	≈20	(8.8 ± 0.1)	[67MEF/GEL2]
dis	1 M $\text{HClO}_4$	25.0	(9.220 ± 0.005)	[76BAG/RAM3]
dis	1 M $\text{HClO}_4$	10	(9.277 ± 0.007)	[77RAM/RAM]
		40	(8.935 ± 0.005)	
dis	1 M $\text{HClO}_4$	25.0	(9.318 ± 0.004)	[77RAM/RAM2]
dis	1 M $\text{H}^+$	25	9.3	[79KUS/GAN]

(Continued on next page)



Table VI-47: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Np}^{4+} + 2 \text{ ox}^{2-} \rightleftharpoons \text{Np}(\text{ox})_2(\text{aq})$				
sol	1.0 M HCl	(25 ± 2)	(17.54 ± 0.01)	<a href="#">[60KON/GEL]</a>
sol	1 M HClO <sub>4</sub>	(26 ± 2)	(13.69 ± 0.02)	<a href="#">[64BAN/SHA]</a>
	1 M (H, Na)ClO <sub>4</sub>		(13.62 ± 0.04)	
dis	1 M HClO <sub>4</sub>		(16.2 ± 0.1)	
sp	0.3 M HClO <sub>4</sub>	≈20	(17.2 ± 0.2)	<a href="#">[67MEF/GEL2]</a>
dis	1 M HClO <sub>4</sub>	25.0	(16.63 ± 0.02)	<a href="#">[76BAG/RAM3]</a>
dis	1 M HClO <sub>4</sub>	10	(16.75 ± 0.03)	<a href="#">[77RAM/RAM]</a>
	1 M HClO <sub>4</sub>	40	(16.23 ± 0.01)	
dis	1 M HClO <sub>4</sub>	25.0	(16.43 ± 0.05)	<a href="#">[77RAM/RAM2]</a>
dis	1 M H <sup>+</sup>	25	16.4	<a href="#">[79KUS/GAN]</a>
$\text{Np}^{4+} + 3 \text{ ox}^{2-} \rightleftharpoons \text{Np}(\text{ox})_3^{2-}$				
sol	1.0 M HCl	(25 ± 2)	(23.96 ± 0.04)	<a href="#">[60KON/GEL]</a>
sol	1 M HClO <sub>4</sub>	(26 ± 2)	(19.37 ± 0.07)	<a href="#">[64BAN/SHA]</a>
	1 M (Na, H)ClO <sub>4</sub>		(19.45 ± 0.05)	
sp	0.3 M HClO <sub>4</sub>	≈20	(24.4 ± 0.2)	<a href="#">[67MEF/GEL2]</a>
dis	1 M HClO <sub>4</sub>	10	(16.64 ± 0.02)	<a href="#">[77RAM/RAM]</a>
dis	1 M HClO <sub>4</sub>	25.0	(23.2 ± 0.2)	<a href="#">[77RAM/RAM2]</a>
dis	1 M H <sup>+</sup>	25	23.2	<a href="#">[79KUS/GAN]</a>
$\text{Np}^{4+} + 4 \text{ ox}^{2-} \rightleftharpoons \text{Np}(\text{ox})_4^{4-}$				
sol	1.0 M HCl	(25 ± 2)	27.4	<a href="#">[60KON/GEL]</a>
sp	0.3 M HClO <sub>4</sub>	≈20	28.4	<a href="#">[67MEF/GEL2]</a>
$\text{Np}^{4+} + 4 \text{ Hox}^- \rightleftharpoons \text{Np}(\text{Hox})_4(\text{aq})$				
dis	(0.5 & 0.9) M HCl	room temperature	3.5	<a href="#">[62ISH/NAK]</a>
$\text{Np}(\text{ox})^{2+} + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Np}(\text{ox})_2(\text{aq}) + 2 \text{ H}^+$				
sol	(0.4 - 10) M HNO <sub>3</sub>	22	(2.15 ± 0.08)	<a href="#">[83LUE]</a>
		45	(1.6 ± 0.2)	
		60	(2.09 ± 0.06)	
$\text{Np}(\text{ox})_2(\text{aq}) + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Np}(\text{ox})_3^{2-} + 2 \text{ H}^+$				
sol	(0.4 - 10) M HNO <sub>3</sub>	22	(0.29 ± 0.08)	<a href="#">[83LUE]</a>
		45	(0.6 ± 0.2)	
		60	(0.02 ± 0.07)	

The solubility studies [60KON/GEL], [64BAN/SHA], [83LUE] are also discussed in Section VI.11.1.2. The earlier study by Kondratov and Gel'man [60KON/GEL] is not considered because of diverse shortcomings described in Appendix A. The solubility data in [64BAN/SHA], [83LUE] and the spectrophotometric measurements in [67MEF/GEL2] were re-analysed by this review using H<sub>2</sub>ox(aq) as the ligand, see Appendix A, and the resulting equilibrium constants are listed in Table VI-48.

While there is a general good agreement for the formation constant of  $\text{Np}(\text{ox})^{2+}$  between the different experimental techniques, this is not so for the second and third complex. In general the solubility values are lower and the spectrophotometric value higher than the two values obtained by solvent extraction, *cf.* Table VI-48. This disagreement is illustrated in the graphs of Figure VI-36. The discrepancies between the different experimental techniques indicate the presence of unknown systematic errors. In addition to the experimental uncertainties in the measurements, the equilibrium constants are not very well defined because of lack of solubility data at low oxalic acid concentrations, and lack of solvent extraction and spectrophotometric data at high oxalic acid concentrations. This review does not select any values for the oxalate complex formation of  $\text{Np}(\text{IV})$ .

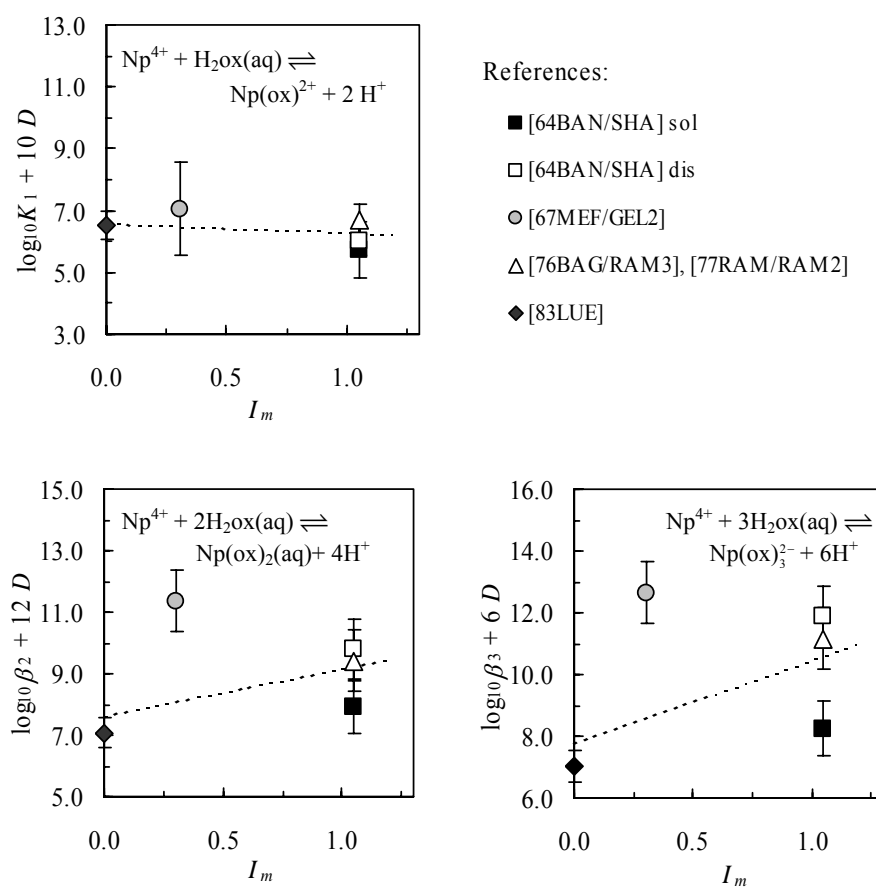
Taking into account the large uncertainty and lack of information on the complexation of  $\text{Np}(\text{IV})$  by oxalic acid at  $\approx 25^\circ\text{C}$  it is of no value to discuss temperature effects. The reported effects are however small [77RAM/RAM], [79KUS/GAN], [83LUE].

Table VI-48: Results from the re-evaluations described in Appendix A of experimental literature data on the complex formation between  $\text{Np}(\text{IV})$  and oxalic acid at  $\approx 25^\circ\text{C}$ .

Method	Ionic medium	$t$ ( $^\circ\text{C}$ )	$\log_{10}K$	Reference to the original data
$\text{Np}^{4+} + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Np}(\text{ox})^{2+} + 2 \text{H}^+$				
dis	1 M $\text{HClO}_4$	$(26 \pm 2)$	$(4.1 \pm 0.2)$	[64BAN/SHA]
sol	(a)		$(3.7 \pm 1.0)$	
sp	0.3 M $\text{HClO}_4$	$\approx 20$	$(5.5 \pm 1.5)$	[67MEF/GEL2]
dis	1 M $\text{HClO}_4$	25.0	$(4.6 \pm 0.1)$	[76BAG/RAM3], [77RAM/RAM2], [79KUS/GAN]
sol	$\rightarrow 0 \text{ M}$	22	$(6.5 \pm 0.5)$	[83LUE]
$\text{Np}^{4+} + 2 \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Np}(\text{ox})_2(\text{aq}) + 4 \text{H}^+$				
dis	1 M $\text{HClO}_4$	$(26 \pm 2)$	$(7.4 \pm 0.4)$	[64BAN/SHA]
sol	(a)		$(5.5 \pm 1.0)$	
sp	0.3 M $\text{HClO}_4$	$\approx 20$	$(9.5 \pm 1.0)$	[67MEF/GEL2]
dis	1 M $\text{HClO}_4$	25.0	$(6.9 \pm 1.0)$	[76BAG/RAM3], [77RAM/RAM2], [79KUS/GAN]
sol	$\rightarrow 0 \text{ M}$	22	$(7.1 \pm 0.3)$	[83LUE]
$\text{Np}^{4+} + 3 \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Np}(\text{ox})_3^{2-} + 6 \text{H}^+$				
dis	1 M $\text{HClO}_4$	$(26 \pm 2)$	$(10.8 \pm 0.4)$	[64BAN/SHA]
sol	(a)		$(7.1 \pm 1.0)$	
sp	0.3 M $\text{HClO}_4$	$\approx 20$	$(11.7 \pm 1.0)$	[67MEF/GEL2]
dis	1 M $\text{HClO}_4$	25.0	$(9.9 \pm 0.7)$	[76BAG/RAM3], [77RAM/RAM2], [79KUS/GAN]
sol	$\rightarrow 0 \text{ M}$	22	$(7.1 \pm 0.3)$	[83LUE]

a: The equilibrium constants listed in these lines refer to 1 M  $\text{HClO}_4$ , but were obtained by simultaneously analysing solubility data obtained both in 1 M  $\text{NaClO}_4$  and in (0.5 M  $\text{HClO}_4$  + 0.5 M  $\text{NaClO}_4$ ), *cf.* Appendix A.

Figure VI-36: Comparison of equilibrium constants for the complex formation between Np(IV) and oxalic acid at  $\approx 25^\circ\text{C}$ . These values were obtained by the re-evaluations of experimental literature data described in Appendix A. The background colour of the symbols indicates the experimental method: black for solubility, white for two phase distribution (solvent extraction) and grey for spectrophotometry. The lines correspond to a weighted linear fit, added to the graphs for illustrative purposes only.



### VI.11.2.3 Neptunium(V) oxalate complexes

Although Np(V) is considered to be stable towards disproportionation ( $2 \text{ NpO}_2^+ + 4 \text{ H}^+ \rightleftharpoons \text{Np}^{4+} + \text{NpO}_2^{2+} + 2 \text{ H}_2\text{O(l)}$ ) in most chemical systems, it has been reported that disproportionation has been observed in the presence of 0.1 M oxalic acid at  $\text{pH} \approx 1.3$  [53GRU/KAT]. The rate of disproportionation of Np(V) in oxalate solutions increases with temperature [67KRO/MEF2], [73SHI/RUM2]. Furthermore, in the presence of molecular oxygen, *e.g.*, from air, Np(V) decomposes catalytically oxalate, edta and other ligands at  $60^\circ\text{C}$  [79SHI/STE2]. The decomposition proceeds through complex formation with the incorporation of molecular oxygen, the oxidation of Np(V) to Np(VI) by the coordinated oxygen, and subsequent reduction of Np(VI) by decomposition of the ligand. At room temperature and moderate acidities the disproportionation of Np(V) is unlikely to be a problem for the experimental studies reviewed below.

Neptunyl(V) complexation by oxalate has been studied by a wide range of experimental techniques: potentiometry, spectrophotometry, solvent extraction, electromigration, ionic exchange and co-precipitation. The reported stability constants are summarised in Table VI-49. Appendix A contains comments on all these studies. The existence of the species  $\text{NpO}_2(\text{ox})_n^{(1-2n)-}$  ( $n = 1$  and  $2$ ) is indicated in these references:



There is no evidence for the formation of higher complexes. A protonated complex,  $\text{NpO}_2\text{Hox(aq)}$ , has also been postulated from ion exchange or solvent extraction data [61ZOL/MAR2], [63ZOL/ALI], [97POK/CHO]. As discussed in the corresponding entries of Appendix A these claims have been rejected by this review. Furthermore, a re-analysis by this review of the spectrophotometric data at acidities up to  $\text{pH} = 1.1$  from [72STO] gave no indication of such a complex, although there were clear indications for the formation of mixed Np(V)-OH<sup>-</sup>-ox<sup>2-</sup> complexes at  $\text{pH} \geq 9$ .

Table VI-49: The stability constants of neptunium(V) oxalate complexes reported in the literature.

Method	Ionic medium	$t$ ( $^\circ\text{C}$ )	$\log_{10} K$	Reference
$\text{NpO}_2^+ + \text{ox}^{2-} \rightleftharpoons \text{NpO}_2\text{ox}^-$				
sp	0.5 M ( $\text{NaClO}_4$ )	room temperature	3.29	[53GRU/KAT]
cix	0.05 M ( $\text{NH}_4\text{ClO}_4$ )	$(20 \pm 2)$	4.0	[61ZOL/MAR2], [63ZOL/ALI]
sp	0.1 M (?)	$(25.0 \pm 0.3)$	3.56	[67KRO/MEF2]
kin	0.23 M ( $\text{HNO}_3$ ?)	57.5	3.48	
gl	1 M ( $\text{NaClO}_4$ )	20	$(3.74 \pm 0.05)$	[72MAG/BIS]
sp	1 M ( $\text{NaClO}_4$ )	$(25.0 \pm 0.2)$	$(4.54 \pm 0.01)$	[72STO]
(a)	0.5 M ( $\text{NH}_4\text{Cl}$ )	$(20 \pm 2)$	$(3.38 \pm 0.11)$	[78MOS/POZ], [79MOS/POZ4]
dis	1 M ( $\text{NaCl}$ )	$(25 \pm 2)$	$(3.42 \pm 0.05)$	[82INO/TOC]

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Table VI-49: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10} K$	Reference
$\text{NpO}_2^+ + \text{ox}^{2-} \rightleftharpoons \text{NpO}_2\text{ox}^-$				
dis	1 M (NaClO <sub>4</sub> )	(25 ± 1)	(3.44 ± 0.03) (3.67 ± 0.01) (3.59 ± 0.01)	<a href="#">[83INO/TOC]</a>
sp	1 M (NaClO <sub>4</sub> )	(23 ± 2)	(3.52 ± 0.06)	<a href="#">[87CAC/NEC]</a>
sp	1 M (H,K)NO <sub>3</sub>	25	4.39	<a href="#">[89NIK/ION2]</a>
em	0.05 M Na(ClO <sub>4</sub> , ox)	(25.0 ± 0.1)	(3.77 ± 0.02)	<a href="#">[89ROS/DIT]</a>
	0.1 M Na(ClO <sub>4</sub> , ox)		(3.90 ± 0.04)	
	0.3 M Na(ClO <sub>4</sub> , ox)		(3.57 ± 0.04)	
	0.1 M Na(NO <sub>3</sub> , ox)		(3.75 ± 0.04)	
sp	1 M (NaClO <sub>4</sub> )	(23 ± 2)	(3.53 ± 0.04)	<a href="#">[89STO/CAC]</a>
dis	0.1 M (NaClO <sub>4</sub> )	(25 ± 1)	(3.7 ± 0.2)	<a href="#">[92TOC/INO]</a>
	1 M (NaClO <sub>4</sub> )		(3.73 ± 0.02) (3.70 ± 0.01)	
dis	5 m (NaCl)	25	(3.04 ± 0.08)	<a href="#">[96BOR/LIS]</a>
dis	0.1 m (NaClO <sub>4</sub> )	25	(3.40 ± 0.04)	<a href="#">[97POK/CHO]</a>
	0.3 m		(3.40 ± 0.04)	
	0.5 m		(3.48 ± 0.05)	
	1 m		(3.35 ± 0.06)	
	3 m		(3.61 ± 0.13)	
	5 m		(3.96 ± 0.04)	
	7 m		(4.23 ± 0.05)	
	9 m		(4.66 ± 0.05)	
dis	0.3 m (NaCl)	25	(3.62 ± 0.03)	<a href="#">[2001BOR/MOO]</a>
	1 m		(3.80 ± 0.02)	<a href="#">[2001CHO/BON]</a>
	2 m		(3.89 ± 0.02)	
	3 m		(4.05 ± 0.02)	
	4 m		(4.18 ± 0.02)	
	5 m		(4.63 ± 0.05)	
$\text{NpO}_2^+ + 2\text{ox}^{2-} \rightleftharpoons \text{NpO}_2(\text{ox})_2^{3-}$				
sp	0.5 M (NaClO <sub>4</sub> )	room temperature	7.06	<a href="#">[53GRU/KAT]</a>
cix	0.05 M (NH <sub>4</sub> ClO <sub>4</sub> )	(20 ± 2)	7.4	<a href="#">[61ZOL/MAR2]</a> , <a href="#">[63ZOL/ALI]</a>
sp	0.1 M (?)	(25.0 ± 0.3)	5.89	<a href="#">[67KRO/MEF2]</a>
kin	0.23 M (HNO <sub>3</sub> ?)	57.5	6.02	
gl	1 M (NaClO <sub>4</sub> )	20	(6.31 ± 0.10)	<a href="#">[72MAG/BIS]</a>
sp	1 M (NaClO <sub>4</sub> )	(25.0 ± 0.2)	(7.86 ± 0.04)	<a href="#">[72STO]</a>

(Continued on next page)

Table VI-49: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10} K$	Reference
$\text{NpO}_2^+ + 2\text{ox}^{2-} \rightleftharpoons \text{NpO}_2(\text{ox})_2^{3-}$				
(a)	0.5 M (NH <sub>4</sub> Cl)	(20 ± 2)	(5.65 ± 0.12)	[78MOS/POZ], [79MOS/POZ4]
dis	1 M (NaCl)	(25 ± 2)	(5.64 ± 0.05)	[82INO/TOC]
dis	1 M (NaClO <sub>4</sub> )	(25 ± 1)	(5.83 ± 0.03)	[83INO/TOC]
			(6.29 ± 0.01)	
			(6.16 ± 0.01)	
sp	1 M (NaClO <sub>4</sub> )	(23 ± 2)	(6.09 ± 0.06)	[87CAC/NEC]
em	0.05 M Na(ClO <sub>4</sub> , ox)	(25.0 ± 0.1)	(5.98 ± 0.20)	[89ROS/DIT]
	0.1 M Na(ClO <sub>4</sub> , ox)		(6.27 ± 0.05)	
	0.3 M Na(ClO <sub>4</sub> , ox)		(5.95 ± 0.13)	
	0.1 M Na(NO <sub>3</sub> , ox)		(6.13 ± 0.06)	
sp	1 M (NaClO <sub>4</sub> )	(23 ± 2)	(6.12 ± 0.05)	[89STO/CAC]
dis	0.1 M (NaClO <sub>4</sub> )	(25 ± 1)	(5.84 ± 0.2)	[92TOC/INO]
	1 M		(6.16 ± 0.02)	
			(6.14 ± 0.01)	
dis	2 m (NaCl)	25	(6.96 ± 0.01)	[2001BOR/MOO],
	3 m		(7.07 ± 0.06)	[2001CHO/BON]
	4 m		(6.99 ± 0.05)	
$\text{NpO}_2^+ + \text{Hox}^- \rightleftharpoons \text{NpO}_2(\text{Hox})(\text{aq})$				
cix	0.05 M (NH <sub>4</sub> ClO <sub>4</sub> )	(20 ± 2)	(2.7 ± 0.2)	[61ZOL/MAR2], [63ZOL/ALI]
$\text{NpO}_2^+ + \text{H}^+ + \text{ox}^{2-} \rightleftharpoons \text{NpO}_2(\text{Hox})(\text{aq})$				
dis	3 m (NaClO <sub>4</sub> )	25	< 7.3	[97POK/CHO]

a: co-precipitation method; (?) ionic medium not reported.

Some of the equilibrium constants reported in Table VI-49 were not included in this review for diverse reasons discussed in the corresponding Appendix A entries: [53GRU/KAT], [61ZOL/MAR2], [63ZOL/ALI], [67KRO/MEF2], [78MOS/POZ], [79MOS/POZ4], [82INO/TOC], [87CAC/NEC], [89NIK/ION2], [89ROS/DIT], [96BOR/LIS]. The remaining data were considered acceptable for further scrutiny, except that the experimental spectrophotometric data in [53GRU/KAT], [72STO] were re-analysed by this review as described in Appendix A. The acceptable stability constants, with their assigned uncertainties, are listed in Table VI-50. The investigations summarised in that table have been performed between 20°C and 25°C. The temperature dependence for the formation of  $\text{NpO}_2\text{ox}^-$  was studied at 10, ≈20, 29 and 47°C [53GRU/KAT] and the authors concluded that the heat of complexation was  $(0 \pm 1.3)$  kJ·mol<sup>-1</sup>. Although this value is not selected by this review, it indicates that all data in Table VI-50 can be included in the final data analysis without explicit temperature corrections to 25°C.

Table VI-50: Accepted stability constants for neptunium(V) oxalate complexation, with the uncertainties assigned by this review.

Method	Ionic medium	$t$ (°C)	$\log_{10} K$	Reference
$\text{NpO}_2^+ + \text{ox}^{2-} \rightleftharpoons \text{NpO}_2\text{ox}^-$				
sp	0.5 M (NaClO <sub>4</sub> )	room temperature	(3.29 ± 0.15)	[53GRU/KAT]
gl	1.0 M (NaClO <sub>4</sub> )	20	(3.74 ± 0.10)	[72MAG/BIS]
sp	1.0 M (NaClO <sub>4</sub> )	(25.0 ± 0.2)	(3.84 ± 0.10) <sup>b</sup>	[72STO]
(a)	0.5 M (NH <sub>4</sub> Cl)	(20 ± 2)	(3.4 ± 0.4)	[78MOS/POZ], [79MOS/POZ4]
dis	1.0 M (NaClO <sub>4</sub> )	(25 ± 1)	(3.62 ± 0.20)	[83INO/TOC]
sp	1.0 M (NaClO <sub>4</sub> )	(23 ± 2)	(3.53 ± 0.10)	[89STO/CAC]
dis	0.1 M (NaClO <sub>4</sub> )	(25 ± 1)	(3.71 ± 0.20)	[92TOC/INO]
	1.0 M		(3.71 ± 0.10)	
dis	0.1 m (NaClO <sub>4</sub> )	25	(3.40 ± 0.20)	[97POK/CHO]
	0.3 m		(3.40 ± 0.20)	
	0.5 m		(3.48 ± 0.20)	
	1.0 m		(3.35 ± 0.20)	
	3.0 m		(3.61 ± 0.20)	
	5.0 m		(3.96 ± 0.20)	
dis	0.3 m (NaCl)	25	(3.62 ± 0.15)	[2001BOR/MOO],
	1.0 m		(3.80 ± 0.15)	[2001CHO/BON]
	2.0 m		(3.89 ± 0.15)	
	3.0 m		(4.05 ± 0.15)	
	4.0 m		(4.18 ± 0.15)	
	5.0 m		(4.63 ± 0.15)	
$\text{NpO}_2^+ + 2\text{ox}^{2-} \rightleftharpoons \text{NpO}_2(\text{ox})_2^{3-}$				
gl	1.0 M (NaClO <sub>4</sub> )	20	(6.31 ± 0.15)	[72MAG/BIS]
sp	1.0 M (NaClO <sub>4</sub> )	(25.0 ± 0.2)	(6.36 ± 0.15) <sup>b</sup>	[72STO]
dis	1.0 M (NaClO <sub>4</sub> )	(25 ± 1)	(6.20 ± 0.20)	[83INO/TOC]
sp	1.0 M (NaClO <sub>4</sub> )	(23 ± 2)	(6.12 ± 0.10)	[89STO/CAC]
dis	0.1 M (NaClO <sub>4</sub> )	(25 ± 1)	(5.84 ± 0.20)	[92TOC/INO]
	1.0 M		(6.15 ± 0.10)	
dis	2 m (NaCl)	25	(6.96 ± 0.15)	[2001BOR/MOO],
	3 m		(7.07 ± 0.15)	[2001CHO/BON]
	4 m		(6.99 ± 0.15)	

a: co-precipitation method. These values, which were obtained in ammonium chloride, were not included in the SIT regression.

b: values obtained from a re-analysis of the original data, see Appendix A.

Most of the studies listed in Table VI-50 were performed in sodium electrolytes, with the exception of [78MOS/POZ], [79MOS/POZ4]. As this review has not been able to examine the effect of ammonium electrolytes on the protonation constants of oxalate, the data from [78MOS/POZ], [79MOS/POZ4] is not considered any further.

Only two studies report data at  $I > 1$  M, namely [97POK/CHO] in  $\text{NaClO}_4$ , and [2001BOR/MOO], [2001CHO/BON] in  $\text{NaCl}$ . The medium effect might be interpreted as a weak complex formation between  $\text{NpO}_2^+$  and  $\text{Cl}^-$ , or as a difference in activity coefficients. According to the SIT model described in Appendix B the activity coefficients of  $\text{NpO}_2^+$  in chloride media are smaller than in perchlorate media: Equation (B.4) with  $\varepsilon(\text{NpO}_2^+, \text{Cl}^-) = (0.09 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{NpO}_2^+, \text{ClO}_4^-) = (0.25 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  [2001LEM/FUG]. This requires that the stability constants in perchlorate media should be larger than in chloride media:

$$\log_{10} \beta_1 = \log_{10} \beta_1^o + \log_{10} \gamma_{\text{NpO}_2^+} + \log_{10} \gamma_{\text{ox}^{2-}} - \log_{10} \gamma_{\text{NpO}_2\text{ox}^-}.$$

If the alternative model of weak complex formation with anions from the background electrolyte is analysed, the same effect should be observed, a smaller constant should be observed in chloride media. Following a similar discussion to that given in Section V.4, one may write:

$$\log_{10} \beta_1^* = \log_{10} \beta_1 - \log_{10} (1 + K(\text{NpO}_2\text{Cl}) \cdot [\text{Cl}^-])$$

where  $\beta_1^*$  is the equilibrium constant in chloride media;  $\beta_1$  is the same constant in the absence of chloride, but at the same ionic strength; and  $K(\text{NpO}_2\text{Cl})$  is the equilibrium constant for the weak complex formation between  $\text{NpO}_2^+$  and  $\text{Cl}^-$ , also at the same ionic strength. It must be noted in this context that the NEA-TDB reviews have chosen to interpret medium effects of  $\text{Np(V)}$  in chloride solutions as arising from changes in activity coefficients, rather than from weak complex formation which is difficult to demonstrate experimentally at moderate concentrations of chloride ions.

In any case it is clear that equilibrium constants for complex formation between  $\text{Np(V)}$  and any ligand should be larger in perchlorate media than in chloride media. However, the two sets of data for oxalate, [97POK/CHO] in  $\text{NaClO}_4$  and [2001BOR/MOO], [2001CHO/BON] in  $\text{NaCl}$ , show a reverse trend. [97POK/CHO] contains data also on acetate and citrate and a comparison with the results listed in [2001CHO/BON] shows that for acetate the equilibrium constants in  $\text{NaCl}$  media are also larger than those in  $\text{NaClO}_4$  (with one exception: the values at background electrolyte 0.3 molal). On the other hand the citrate data show the expected trend: the values of  $\beta_1$  in  $\text{NaClO}_4$  are larger than those in  $\text{NaCl}$  media. There is no clear reason for the disagreement between the  $\text{Np(V)}$ -oxalate (and -acetate) equilibrium constants in [97POK/CHO] on one hand and in [2001BOR/MOO], [2001CHO/BON] on the other. A possible explanation might be that the interpretation of the data in [97POK/CHO] should have included the formation of  $\text{NpO}_2(\text{ox})_2^{3-}$ , although Pokrovsky and Choppin reported not to have found evidence for it. Nevertheless, because of this unresolved



disagreement the data from these two studies at  $I_m > 1$  molal are not considered acceptable, while the data at  $I_m \leq 1$  molal are included in the selection procedure, with an increased uncertainty of  $\pm 0.2 \log_{10}$ -units.

Therefore, all the values listed in Table VI-50, except the  $\beta_1$  values from [78MOS/POZ], [79MOS/POZ4], and all values at  $I_m > 1$  molal from [97POK/CHO], [2001BOR/MOO], [2001CHO/BON] were converted to molal units and they were extrapolated to zero ionic strength using the SIT methodology:

$$\log_{10} \beta_n - \frac{\Delta z^2 \cdot 0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} - \varepsilon(\text{NpO}_2^+, X^-) I_m = \log_{10} \beta_n^\circ - \Delta \varepsilon'_n I_m$$

where  $X^-$  is either  $\text{Cl}^-$  or  $\text{ClO}_4^-$ ;  $\Delta \varepsilon'_n = \varepsilon(\text{Na}^+, \text{NpO}_2(\text{ox})_n^{(n-2n)}) - n \varepsilon(\text{Na}^+, \text{ox}^{2-})$ ; and  $\Delta z^2 = -4$  and  $0$  for  $n = 1$  and  $2$ , respectively. The SIT extrapolations are illustrated in Figure VI-37 and Figure VI-38, and they resulted in the following selected values:

$$\begin{aligned} \log_{10} \beta_1^\circ (\text{VI.44}) &= (3.9 \pm 0.1), & \Delta \varepsilon'_1 (\text{VI.44}) &= -(0.3 \pm 0.1) \text{ kg} \cdot \text{mol}^{-1} \\ \log_{10} \beta_2^\circ (\text{VI.45}) &= (5.8 \pm 0.2), & \Delta \varepsilon'_2 (\text{VI.45}) &= -(0.1 \pm 0.2) \text{ kg} \cdot \text{mol}^{-1} \end{aligned}$$

Using the interaction coefficient  $\varepsilon(\text{ox}^{2-}, \text{Na}^+) = -(0.08 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}$  selected by this review (Section VI.3), the interaction coefficients  $\varepsilon(\text{Na}^+, \text{NpO}_2\text{ox}^-) = -(0.4 \pm 0.1) \text{ kg} \cdot \text{mol}^{-1}$  and  $\varepsilon(\text{Na}^+, \text{NpO}_2(\text{ox})_2^{3-}) = -(0.3 \pm 0.2) \text{ kg} \cdot \text{mol}^{-1}$  are obtained. These values may be compared with the data for Np(V)-carbonate complexes [2001LEM/FUG]:  $\log_{10} \beta_1^\circ (\text{NpO}_2\text{CO}_3^-) = (4.96 \pm 0.06)$ ,  $\varepsilon(\text{Na}^+, \text{NpO}_2\text{CO}_3^-) = -(0.18 \pm 0.15) \text{ kg} \cdot \text{mol}^{-1}$ ; and  $\log_{10} \beta_2^\circ (\text{NpO}_2(\text{CO}_3)_2^{3-}) = (6.53 \pm 0.10)$ ,  $\varepsilon(\text{Na}^+, \text{NpO}_2(\text{CO}_3)_2^{3-}) = -(0.33 \pm 0.17) \text{ kg} \cdot \text{mol}^{-1}$ . It can be seen that the stability constants for neptunium(V)-oxalate at zero ionic strength are lower than analogous complexes of Np(V)-carbonate.

The selected equilibrium constants yield:

$$\begin{aligned} \Delta_f G_m^\circ (\text{NpO}_2\text{ox}^-, 298.15 \text{ K}) &= -(1610.2 \pm 5.9) \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta_f G_m^\circ (\text{NpO}_2(\text{ox})_2^{3-}, 298.15 \text{ K}) &= -(2301.1 \pm 6.8) \text{ kJ} \cdot \text{mol}^{-1}. \end{aligned}$$

Figure VI-37: Extrapolation of data for reaction  $\text{NpO}_2^+ + \text{ox}^{2-} \rightleftharpoons \text{NpO}_2\text{ox}^-$  listed in Table VI-50 according to the SIT model described in Appendix B. Symbols with white background correspond to NaCl ionic medium, all other data were obtained in  $\text{NaClO}_4$  media.

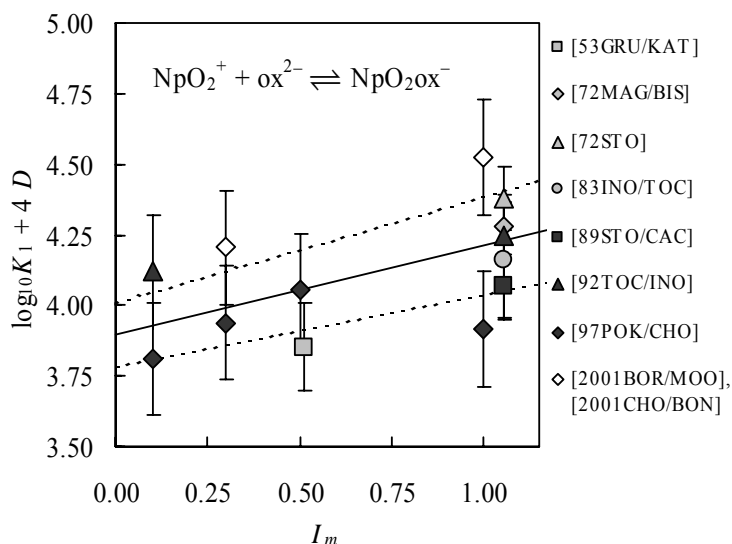
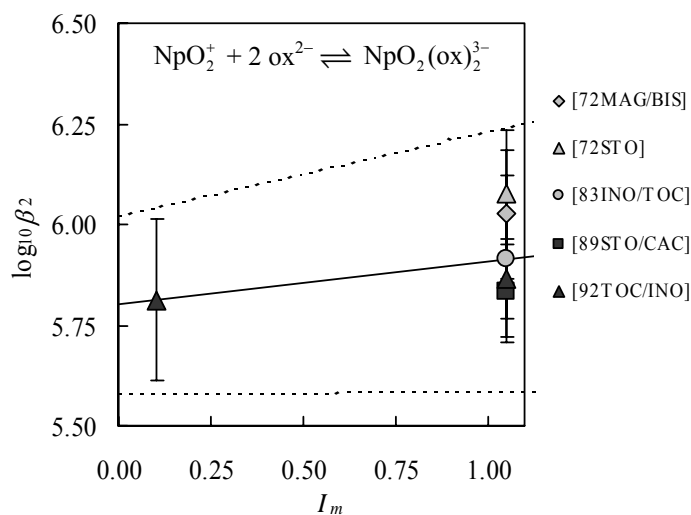


Figure VI-38: Extrapolation of data for reaction  $\text{NpO}_2^+ + 2 \text{ox}^{2-} \rightleftharpoons \text{NpO}_2(\text{ox})_2^{3-}$  listed in Table VI-50 according to the SIT model described in Appendix B.



#### VI.11.2.4 Neptunium(VI) oxalate complexes

The study of  $\text{NpO}_2^{2+}$  complexation with oxalate is complicated by redox reactions where  $\text{Np(VI)}$  is reduced by oxalate to  $\text{Np(V)}$  which is somewhat stabilised by oxalate complexation [67KRO/MEF2], [69MEF/KRO2], [69SHA/AMI], [84RAO/CHO], [98REE/WYG]. At acid concentrations above 3 M ( $\text{HClO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ) the reduction of  $\text{Np(VI)}$  is fast.

Mefod'eva *et al.* [69MEF/KRO2] studied the  $\text{Np(VI)}$ -oxalate system at temperatures below 20°C. These authors determined approximate values of complex formation using spectrophotometry and solubility measurements. The complexes  $\text{NpO}_2\text{ox(aq)}$  and  $\text{NpO}_2(\text{ox})_2^{2-}$  were proposed, and their formation constants were reported, *cf.* Appendix A. These values are only of qualitative significance for laboratory studies. For any application modelling the long term behaviour of neptunium, *e.g.*, for nuclear waste disposal, the unstable  $\text{Np(VI)}$  oxalate complexes are unimportant as was pointed out in [98REE/WYG].

#### VI.11.2.5 Neptunium(VII) oxalate complexes

In acidic medium  $\text{Np(VII)}$  is rapidly reduced both by water [2001LEM/FUG] and by oxalate [70SHI/KRO]. For example the half-life of  $\text{Np(VII)}$  is about 0.01 seconds at 25°C in solutions with  $[\text{Np}]_{\text{TOT}} = 0.08$  M,  $[\text{ox}]_{\text{TOT}} = 9.2 \times 10^{-4}$  M,  $[\text{H}^+] = 0.059$  M, and  $I = 1.0$  M [78COO/WOO]. In basic medium  $\text{Np(VII)}$  is more stable, and the reduction by water to  $\text{Np(VI)}$  takes place over a period of hours to weeks at room temperature [2001LEM/FUG].

Because of the instability of  $\text{Np(VII)}$  no equilibrium constants for  $\text{Np(VII)}$ -oxalate species have been determined. However, for nuclear waste disposal applications, often involving long term perspectives, equilibrium constants for highly unstable neptunium(VII)-oxalate species are not needed anyway.

### VI.12 Plutonium oxalate compounds and complexes

#### VI.12.1 Solid plutonium oxalates

Solid plutonium oxalates have been widely used and investigated because of their usefulness, *e.g.*, in Pu-separation from other actinides. The solids reported in the literature are listed in Table VI-51.

Although there is a large amount of information concerning the temperature stability of several of these oxalates and their conversion into plutonium oxide, these properties are not discussed in this review. Information concerning the thermal stabilities may be found in several monographs [54CUN], [67GEL/MOS], [79CLE], [86WEI/KAT], [87MEF/KRO], [91MAT/KAR].

It should be kept in mind when discussing the properties of plutonium compounds and solutions that there is, as an additional difficulty, the problem of radiation damages and water radiolysis, especially for  $^{238}\text{Pu}$ , but also to a lesser extent for  $^{239}\text{Pu}$  [56FOM/KAR], [58GEL/SOK], [60SOK/GEL], [86KAN/KIM].

#### VI.12.1.1 Solid plutonium(III) oxalates

The precipitation of solid Pu(III) oxalate was reported quite early in the history of plutonium chemistry [49PAT2], [49PAT]. The solubility of Pu(III)-oxalate in water is given to be  $4.32 \times 10^{-6}$  and  $1.88 \times 10^{-5}$  M at 20 and 70°C, respectively [57GEL/MAT2], [57GEL/MAT3], [67GEL/MOS]. The extent of the hydration of this compound has been subject to discussion [79CLE], but most probably the correct formula is  $\text{Pu}_2(\text{ox})_3 \cdot 10\text{H}_2\text{O}$  [63CHA], [65JEN/MOO]. In some earlier papers the formula is given with nine water molecules, *e.g.*, in [57GEL/MOS]. The standard entropy of  $\text{Pu}_2(\text{ox})_3 \cdot 9\text{H}_2\text{O}$  was estimated by Moskvina using a Latimer-like method:  $S_m^\circ$  (298.15 K) =  $651 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  [73MOS].

The references reporting the solubility of Pu(III)-oxalate are summarised in Table VI-52. These studies fall into two categories: those in near-neutral solutions, where the total concentration of oxalate was varied, and those in acid media, where either the total acidity or total oxalic acid was varied.

In acid media oxalic acid remains protonated and the extent of complex formation is expected to be limited or negligible. Under such conditions a solubility product may be determined from the solubility data. On the other hand, solubility determinations in near-neutral solutions with varying ligand concentration would allow the determination of equilibrium constants for complex formation. In both cases several requirements must be fulfilled: proper phase separation after the equilibration time; checks that the solutions are not over- or undersaturated; characterisation of the solid phase and verification that it does not change with varying conditions such as acidity and ligand concentration. All studies on the Pu(III)-oxalate system are deficient in one or several of these requirements. In addition, the instability of Pu(III) towards oxidation in oxalate solutions, especially in nitric acid media, requires the presence of reductants increasing the uncertainty of these studies.

The data in near-neutral solutions of oxalate are reported in [57GEL/MAT2], [57GEL/MAT3], [67GEL/MOS]. Data at several temperatures have also been reported in these publications. In addition solubilities in  $\text{K}_2\text{ox}$  solutions at  $\text{pH} \approx 4$  are given in [58FOM/VOR]. The authors of these studies derived equilibrium constants for the complex formation between  $\text{Pu}^{3+}$  and oxalate, see Table VI-57. All these values are rejected in this review, see details for these publications in Appendix A. Likewise the enthalpy changes reported in [57GEL/MAT2], [57GEL/MAT3] are not recommended by this review.

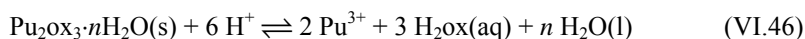
Table VI-51: Pu-oxalate compounds reported in the literature.

Compound	Reference(s)
<b>Pu(III)</b>	
$\text{Pu}_2(\text{ox})_3 \cdot 10\text{H}_2\text{O}$	[63CHA], [65JEN/MOO], [67BUR/POR], [69SUB/SIN], [94ZHI/MAT4]
$\text{Pu}_2(\text{ox})_3 \cdot 9\text{H}_2\text{O}$	[57GEL/MOS]
$\text{LiPu}(\text{ox})_2 \cdot 3.5\text{H}_2\text{O}$	[84ZUB/KRO]
$\text{NaPu}(\text{ox})_2 \cdot 3.5\text{H}_2\text{O}$	[84ZUB/KRO]
$\text{KPu}(\text{ox})_2 \cdot 3.5\text{H}_2\text{O}$	[84ZUB/KRO]
$\text{CsPu}(\text{ox})_2 \cdot 0.5\text{H}_2\text{O}$	[83ZUB/KRO3], [84ZUB/KRO]
$\text{NH}_4\text{Pu}(\text{ox})_2 \cdot \text{H}_2\text{O}$	[83ZUB/KRO3], [84ZUB/KRO]
<b>Pu(IV)</b>	
$\text{Pu}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$	[61MAN/FRA], [65JEN/MOO2], [69SUB/SIN], [80NIS], [94ZHI/MAT3]
$\text{Pu}(\text{ox})_2 \cdot 2\text{H}_2\text{O}$	[65JEN/MOO2]
$\text{H}_2\text{Pu}_2(\text{ox})_5 \cdot 9\text{H}_2\text{O}$	[84KHA/AND]
$(\text{NH}_4)_6\text{Pu}(\text{ox})_5 \cdot n\text{H}_2\text{O}$	[58GEL/SOK], [91MAT/KAR] p.51
$\text{Na}_4\text{Pu}(\text{ox})_4 \cdot 5\text{H}_2\text{O}$	[58GEL/SOK], [91MAT/KAR] p.51
$\text{K}_4\text{Pu}(\text{ox})_4 \cdot 4\text{H}_2\text{O}$	[58GEL/SOK], [91MAT/KAR] p.52
$\text{K}_6\text{Pu}(\text{ox})_5 \cdot 4\text{H}_2\text{O}$	[58GEL/SOK]
$\text{K}_3\text{Pu}(\text{CO}_3)_2\text{ox} \cdot n\text{H}_2\text{O}$	[58GEL/ZAI3]
$\text{K}_4\text{Pu}(\text{CO}_3)_3\text{ox} \cdot n\text{H}_2\text{O}$	[58GEL/ZAI3]
$\text{Na}_4\text{Pu}(\text{CO}_3)_2(\text{ox})_2 \cdot 3\text{H}_2\text{O}$	[58GEL/ZAI3]
$\text{Na}_4\text{Pu}(\text{CO}_3)_3\text{ox} \cdot n\text{H}_2\text{O}$	[58GEL/ZAI3]
$\text{Pu}(\text{ox})_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$	[84AND/KIR]
$(\text{Co}(\text{en})_3)_4(\text{Pu}(\text{ox})_4)_3 \cdot n\text{H}_2\text{O}$	[77HOS/UEN2]
$(\text{Cr}(\text{en})_6)_4(\text{Pu}(\text{ox})_4)_3 \cdot n\text{H}_2\text{O}$	[77HOS/UEN2]
$(\text{Cr}(\text{CO}(\text{NH}_2)_2)_6)_4(\text{Pu}(\text{ox})_4)_3 \cdot n\text{H}_2\text{O}$	[72HOS/UEN]
<b>Pu(V)</b>	
$\text{NH}_4\text{PuO}_2\text{ox} \cdot n\text{H}_2\text{O}$	[64GEL/ZAI], [73ZAI/ALE]
<b>Pu(VI)</b>	
$\text{PuO}_2\text{ox} \cdot 3\text{H}_2\text{O}$	[58GEL/DRA3], [65JEN/MOO], [69SUB/SIN], [96BES/KRO]
$\text{PuO}_2\text{ox} \cdot \text{H}_2\text{O}$	[96BES/KRO]
$\text{BaPuO}_2(\text{ox})_2 \cdot n\text{H}_2\text{O}$	[91MAT/KAR] p.74
$(\text{NH}_4)_2(\text{PuO}_2)_2(\text{ox})_3$	[96BES/KRO]
$(\text{NH}_4)_2\text{PuO}_2(\text{ox})_2$	[96BES/KRO]
$\text{K}_2(\text{PuO}_2)_2(\text{ox})_3 \cdot 4\text{H}_2\text{O}$	[96BES/KRO]

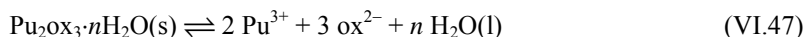
Table VI-52: Literature studies reporting the solubility of Pu(III)-oxalate.

Ref.	Reported solid phase	<i>t</i> (°C)	Ionic Media	Comments
a	Pu <sub>2</sub> (ox) <sub>3</sub> ·9H <sub>2</sub> O		[H <sup>+</sup> ] = 0.22 to 3.7 M; [H <sub>2</sub> ox] = 0.14 to 0.5 M	Experimental details not available.
b	Pu(III) oxalate		[H <sup>+</sup> ] = 0.22 to 3.7 M	Experimental details not available. $K = \frac{[\text{Pu}^{3+}]^2[\text{H}_2\text{ox}]^3}{[\text{H}^+]^6} \approx 2 \times 10^{-10}$
c	Pu <sub>2</sub> (ox) <sub>3</sub> ·9H <sub>2</sub> O	20	≤ 3 M K <sub>2</sub> ox, <i>I</i> not constant; and ≤ 2.4 M K <sub>2</sub> ox at <i>I</i> = constant (KCl)	Sodium formaldehyde sulfoxylate used as reductant in N <sub>2</sub> atm. Ionic strength not specified. 4-6 hours equilibration. Solid not characterised.
		70	up to 0.7 M (NH <sub>4</sub> ) <sub>2</sub> ox	
d	Pu <sub>2</sub> (ox) <sub>3</sub> ·9H <sub>2</sub> O	20	<ul style="list-style-type: none"> <li>0.3 M K<sub>2</sub>ox and 0.1-2 M of either HNO<sub>3</sub>, HCl or H<sub>2</sub>SO<sub>4</sub>.</li> <li>0.1-2 M HNO<sub>3</sub> and 0.28 M (NH<sub>4</sub>)<sub>2</sub>ox.</li> <li>0.5-2 M HNO<sub>3</sub> and 0.64 M H<sub>2</sub>ox</li> </ul>	Experimental details not available. Presumably the same conditions as for <a href="#">[57GEL/MAT2]</a> .
		20-90	[K <sub>2</sub> ox] = 1.8 and 2.4 M	
e	Pu <sub>2</sub> (ox) <sub>3</sub> ·9H <sub>2</sub> O	25	0.17 to 0.87 M K <sub>2</sub> ox, pH 2.7 to 4.2. Some data also at <i>I</i> = 3 (KCl), 0.35 to 0.95 K <sub>2</sub> ox, pH ≈ 4.	[Pu <sup>3+</sup> ] measured polarographically “immediately” after precipitation. Solid not characterised.
f	Pu <sub>2</sub> (ox) <sub>3</sub> ·10H <sub>2</sub> O	21	0.09 to 0.3 M H <sub>2</sub> ox and 0.5 to 3.1 HNO <sub>3</sub>	Ascorbic acid as reductant. Equilibration from under-saturation. Filtered samples. Solid not characterised.
g	Pu <sub>2</sub> (ox) <sub>3</sub> ·10H <sub>2</sub> O	23	0.6 to 2 M HNO <sub>3</sub> and 0.12 and 0.18 M H <sub>2</sub> ox	Hydrazine or ascorbic acid as reductant. Precipitation, 0.5 to 3 hour equilibration, and paper filtration. Solid not characterised.
		30-68	1.45 M HNO <sub>3</sub> , 0.2 M H <sub>2</sub> ox and 0.18 M N <sub>2</sub> H <sub>4</sub>	
h	Pu(III) oxalate	21	0.02 to 0.45 M H <sub>2</sub> ox and 0.2-2 M HNO <sub>3</sub> , with NaNO <sub>3</sub> added to constant <i>I</i> = 2.3 M; also 0.02 to 0.45 M H <sub>2</sub> ox and 3 M HNO <sub>3</sub>	Hydrazine and hydroxylamine nitrate as reductants. Precipitation and 50 hour equilibration followed by centrifugation. Solid not characterised.
		50	0.02 to 0.45 M H <sub>2</sub> ox and 0.5 & 1 M HNO <sub>3</sub> , with NaNO <sub>3</sub> added to constant <i>I</i> = 2.3 M	
i	Pu <sub>2</sub> (ox) <sub>3</sub> ·10H <sub>2</sub> O	≈25	0.02 to 0.2 M H <sub>2</sub> ox and HCl or HNO <sub>3</sub> 0.5-2 M	Ascorbic acid used as reductant. Both precipitation experiments (0.5 hour equilibration) and equilibration from under-saturation (1 hour shaking and 0.5 hour settling). Separation by centrifuge. Solid not characterised.
a:	Thomas & Warner, eds., 1944 (ref.5, p.421 in <a href="#">[54CUN]</a> )			e: <a href="#">[58FOM/VOR]</a>
b:	Reas & Connick 1946 (ref.156, p.335 in <a href="#">[54HIN]</a> )			f: <a href="#">[67BUR/POR]</a>
c:	<a href="#">[57GEL/MAT2]</a> , <a href="#">[57GEL/MAT3]</a> , <a href="#">[67GEL/MOS]</a>			g: <a href="#">[71CHE2]</a>
d:	Moskvin 1957 (ref.34, p.31 in <a href="#">[67GEL/MOS]</a> )			h: <a href="#">[87SUE/HU]</a>
				i: <a href="#">[94HAS/KHE]</a> , <a href="#">[95HAS/KHE]</a>

Two values for the solubility constant of Pu(III)-oxalate have been reported. A value of  $\log_{10} K_s = -9.7$  for:



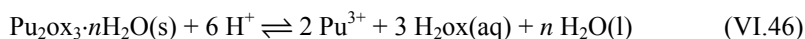
was reported in [54HIN] originating from a technical report by Reas and Connick (1946), *cf.* Table VI-52. It is probable that this value was calculated from the four solubilities tabulated in p.421 of [54CUN]. It has not been possible for this review to retrieve the original reports, and it is not clear if this constant refers to standard conditions (zero ionic strength). The other value was reported in [67GEL/MOS],  $\log_{10} K_s$  (VI.46) =  $-9.44$  for the reaction given above, which was recalculated in [57GEL/MAT2], [57GEL/MAT3], [67GEL/MOS] to be  $\log_{10} K_s$  (VI.47) =  $-24.79$  for reaction:



Corresponding values at 70°C were also reported. The authors used the data at all ionic strengths without applying activity coefficient corrections when evaluating these constants. All literature values for the solubility constants (Reactions (VI.46) and (VI.47)) and the derived enthalpy changes are rejected by this review.

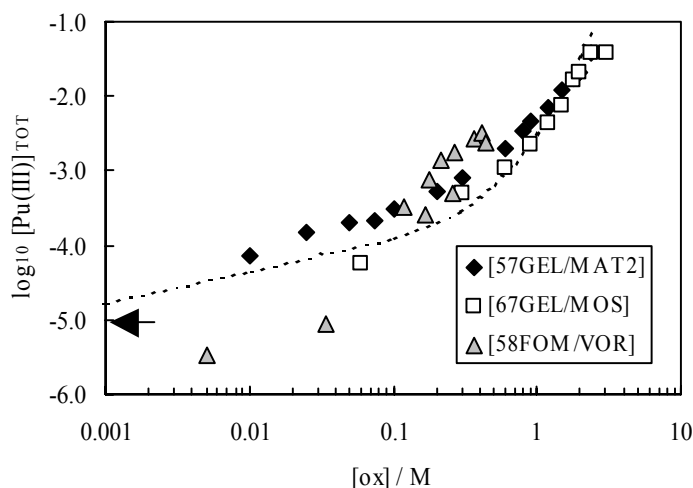
The original solubility data available in the literature was examined by this review in order to try to find a qualitative chemical model. A simple model would consist of the complexes  $\text{Pu(ox)}_n^{3-2n}$  with  $n = 0$  to 4. There are no other reliable studies based on independent experimental techniques to establish the composition of the complexes in the aqueous phase, *cf.* Section VI.12.2.1. The formation of oxalate complexes is constrained by the solubility data at varying concentration of  $\text{ox}^{2-}$ , that is, at low acidities. The model is compared to some of the experimental data in Figure VI-39 and Figure VI-40, which show that although there is a relatively large spread in the solubilities, the data display a consistent pattern, suggesting that probably the same solid phase was present in all these studies. No difference is apparent in systems containing either HCl or  $\text{HNO}_3$  or different reducing agents (ascorbic acid, hydrazine, *etc.*).

By varying the equilibrium constants of the model it is possible to see that, given the spread of the experimental data, it is not necessary to include  $\text{Pu(ox)}_4^{5-}$  in the model. Furthermore, the calculations show that protonated complexes are not required. The dotted curves in Figure VI-39 and Figure VI-40 were obtained using the following equilibrium reactions:



with the NEA-selected value for Reaction (VI.48) [2003GUI/FAN], and the following approximate values:  $\log_{10} K_s^\circ$  (VI.46) =  $-7.5$ ;  $\log_{10} \beta_1^\circ$  (VI.49) =  $8.5$ ;  $\log_{10} \beta_2^\circ$  (VI.50) =  $12.7$ ; and  $\log_{10} \beta_3^\circ$  (VI.51) =  $12.1$ . Furthermore, the SIT model described in Appendix B was used with parameters that included the possible weak complex formation between  $\text{Pu}^{3+}$  and either chloride or nitrate<sup>1</sup>.

Figure VI-39: Comparison of experimental Pu(III) concentrations in solutions in contact with Pu(III)-oxalate and varying concentrations of the oxalate ligand. All data were obtained at  $\text{pH} \geq 2$ . The dotted line has been calculated using the model described in the text. The arrow shows the value corresponding to the solubility of Pu(III)-oxalate in water [57GEL/MAT2].



There are a few caveats to the model described above: the experimental data it tries to describe has several deficiencies; the solid phase was not characterised in any of the investigations; and  $\beta_3$ (VI.51) <  $\beta_2$ (VI.50). The unexpectedly weak formation constant of  $\text{Pu}(\text{ox})_3^{3-}$  might indicate that either there are serious systematic deviations in the experimental data, or the model is inadequate: for example other species are perhaps formed that have not been considered, or the assumptions in the values of the  $\epsilon$ -parameters are erroneous. A study on the  $\text{Yb}^{3+}$ -oxalate system [2000GAM/WOO] showed that the possibility of formation of ternary solid oxalates with alkali metals cannot be excluded, adding further uncertainty to the interpretation of the  $\text{Pu}^{3+}$ -data.

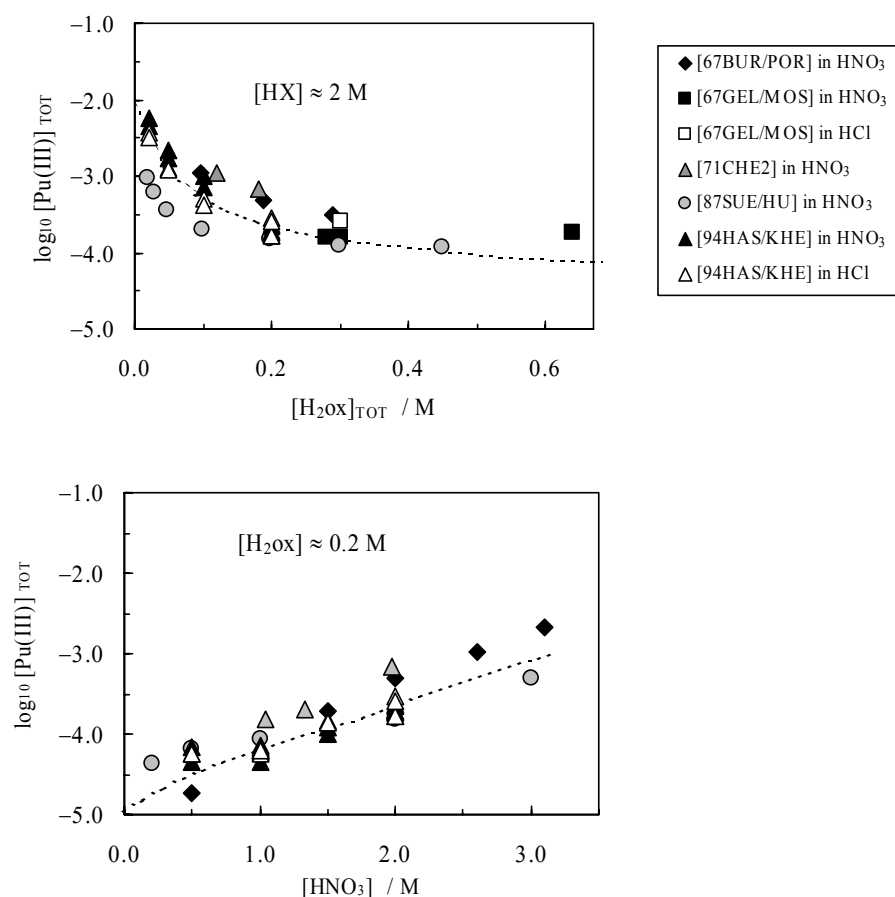
<sup>1</sup> The following specific ion-interaction coefficients were used:  $\epsilon(\text{Pu}^{3+}, \text{Cl}^-) = \epsilon(\text{Pu}^{3+}, \text{NO}_3^-) = 0.23 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\epsilon(\text{PuOH}^{2+}, \text{Cl}^-) = \epsilon(\text{PuOH}^{2+}, \text{NO}_3^-) = 0.39 \text{ kg} \cdot \text{mol}^{-1}$ ,  $\epsilon(\text{K}^+, \text{ox}^{2-}) = 0.07 \text{ kg} \cdot \text{mol}^{-1}$ , and  $\epsilon(\text{K}^+, \text{Hox}^-) = -0.01 \text{ kg} \cdot \text{mol}^{-1}$ . For all other ions the following approximation was used:  $\epsilon(\text{M}^{Z_M}, \text{X}^{Z_X}) = 0.15 + 0.15 \times ((Z_M - 1) + (Z_X + 1))$ , giving for example  $\epsilon(\text{H}^+, \text{Pu}(\text{ox})_2^-) = 0.15 \text{ kg} \cdot \text{mol}^{-1}$ .



In summary, the available studies on the solubility of Pu(III)-oxalate have several shortcomings, and although a simple model may be used to describe the data qualitatively, no thermodynamic values are recommended by this review.

Solids of composition  $\text{MPu}(\text{ox})_2 \cdot n\text{H}_2\text{O}$  where M is an alkali metal or ammonium ion have been reported, *cf.* Table VI-51. No thermodynamic data are available for these solids.

Figure VI-40: Comparison of the experimental solubility data for Pu(III) oxalate: *a*) in solutions containing ammonium oxalate and nitric acid; and *b*) in solutions containing oxalic and nitric acids. The dotted lines have been calculated using the model described in the text.



### VI.12.1.2 Solid plutonium(IV) oxalates

Pu(IV) oxalate is relatively insoluble and may be used to separate plutonium from industrial aqueous streams or as a precursor for the preparation of plutonium oxide, see for example [86WEI/KAT]. The precipitate is a hexahydrate,  $\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$ , and X-ray powder data for this solid is reported in [65JEN/MOO2]. A modified Latimer methodology was used by Moskvin to estimate the standard entropy of  $\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$ :  $S_m^\circ(298.15\text{ K}) = 372\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [73MOS].

The solubility of  $\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$  has been studied and reported by many groups, cf. Table VI-53. Although an effort has been made by this review to retrieve all the literature on this subject, it is quite possible that some technical reports have been missed.

Table VI-53: Literature studies reporting the solubility of Pu(IV)-oxalate.

Reference	Reported solid phase	$t$ (°C)	Ionic media	Comments
[44OCO2]	Pu(IV) oxalate	25	$[\text{HNO}_3] = 0.1$ to $6\text{ M}$ ; $[\text{H}_2\text{ox}] = 0.05$ to $0.2\text{ M}$	Precipitation of the solid in $0.06\text{ cm}^3$ . 2 days equilibration. Sampling and analytical method not reported.
[49REA]	$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$	25	$[\text{HNO}_3] = 0.75\text{ M}$ ; $[\text{H}_2\text{ox}] = 0$ to $0.4\text{ M}$	10 days equilibration. Sampling method not reported. Data analysed to retrieve equilibrium constants. See Appendix A.
[58GEL/MOS2], [58MOS/GEL]	$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$	20	$[\text{HNO}_3] = 1\text{ M}$ ; $[(\text{NH}_4)_2\text{ox}] = 0$ to $0.35\text{ M}$	4-6 hours equilibration. Sampling method not reported. Data analysed to retrieve equilibrium constants. See Appendix A.
[58MOS/GEL3]	$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$	20	$[\text{HNO}_3] = 3.8\text{ M}$ ; $[(\text{NH}_4)_2\text{ox}] = 0$ to $0.35\text{ M}$	The same experimental method as in [58MOS/GEL]. Data analysed to retrieve equilibrium constants. See Appendix A.
[58MOS/GEL]	$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$	20	$[(\text{NH}_4)_2\text{ox}] = 0$ to $0.26\text{ M}$	4-6 hours equilibration. Sampling method not reported. Data analysed to retrieve equilibrium constants. See Appendix A.

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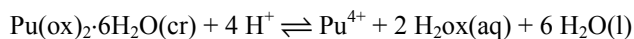
Table VI-53 (continued)

Reference	Reported solid phase	<i>t</i> (°C)	Ionic Media	Comments
<a href="#">[58GEL/MOS2]</a> , <a href="#">[58MOS/GEL3]</a>	Pu(ox) <sub>2</sub> ·6H <sub>2</sub> O	20	[HNO <sub>3</sub> ] or [H <sub>2</sub> SO <sub>4</sub> ] or [HClO <sub>4</sub> ] ≤ 1M	The same experimental method as in <a href="#">[58MOS/GEL]</a> . Data analysed to retrieve equilibrium constants. See Appendix A.
<a href="#">[61MAN/FRA]</a>	Pu(IV) oxalate	27	[HNO <sub>3</sub> ] = 0 to 3.52 M; [H <sub>2</sub> ox] = 0 to 0.6 M	14-21 days equilibration. Sampling method not reported.
<a href="#">[67ABR]</a>	Pu(IV) oxalate	≈24	[HNO <sub>3</sub> ] = 0.6 to 5.3 M; [ox <sup>2-</sup> ] = 0.1 and 0.25 M	18 hours equilibration. Paper rejected, see Appendix A.
<a href="#">[67RIC]</a>	Pu(ox) <sub>2</sub> ·6H <sub>2</sub> O	≈21	[HNO <sub>3</sub> ] = 0 to 3.5 M; [H <sub>2</sub> ox] = 0 to 0.3 M	15 minutes equilibration. Data disregarded because of too short reaction time.
		22 to 95	[HNO <sub>3</sub> ] = 3 M; [H <sub>2</sub> ox] = 0.05 to 0.3 M	
<a href="#">[83CHH/GOP]</a>	Pu(ox) <sub>2</sub> ·6H <sub>2</sub> O	?	[HNO <sub>3</sub> ] = 1 to 6 M; [H <sub>2</sub> ox] = 0 to 0.5 M	20 hours equilibration. Data reported only in a graph.
<a href="#">[86RAO/PIU]</a>	Pu(ox) <sub>2</sub> ·6H <sub>2</sub> O	?	[HNO <sub>3</sub> ] = 0.5 to 4 M; [H <sub>2</sub> ox] = 0, 0.1, or 0.2 M	20 hours equilibration. Data reported only in a graph. Not clear if the data is reported as mg-Pu·L <sup>-1</sup> or as mg-solid·L <sup>-1</sup> .
<a href="#">[2001GUO/LIA]</a>	Pu(IV) oxalate	25	[HNO <sub>3</sub> ] = 0.2 to 1 M; [H <sub>2</sub> ox] = 0.05 to 0.7 M	40 hours equilibration. Not clear if the data is reported as mg-Pu·L <sup>-1</sup> or as mg-solid·L <sup>-1</sup> .

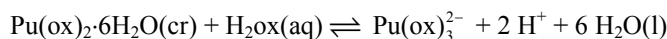
Most of the publications reviewed are oriented towards the parameterisation of industrial separation processes, and attainment of correct equilibrium conditions or a careful description of the experimental methodology was not prioritised. The references where the data have been analysed in terms of equilibrium constants are indicated in Table VI-53. The rest of the studies are of technical type, and in some of them the solubilities are reported in mg·L<sup>-1</sup> and it is not clear if the data are given as mass of Pu(IV)-oxalate per litre or as mg-Pu·L<sup>-1</sup> (this is indicated in Table VI-53); the difference is a factor of ≈ 2.2, *i.e.*, 0.34 log<sub>10</sub>-units in Pu-concentration. References [\[67ABR\]](#), [\[67RIC\]](#) are not considered reliable, see comments in Appendix A, and the data from the other publications aiming to technical characterisation of Pu-separation processes are of qualitative interest only [\[44OCO2\]](#), [\[61MAN/FRA\]](#), [\[83CHH/GOP\]](#), [\[86RAO/PIU\]](#), [\[2001GUO/LIA\]](#).

The majority of the solubility data have been obtained in strong acids (mainly HNO<sub>3</sub>) because both disproportionation (for example: 3 Pu<sup>4+</sup> + 2 H<sub>2</sub>O(l) ⇌ 2 Pu<sup>3+</sup> + PuO<sub>2</sub><sup>2+</sup> + 4 H<sup>+</sup>) and hydrolysis (Pu<sup>4+</sup> + H<sub>2</sub>O(l) ⇌ PuOH<sup>3+</sup> + H<sup>+</sup>) are suppressed at high

acidities. In the absence of added oxalic acid the solubility of the solid increases with acidity:



Already from the earliest solubility experiments [44OCO2] it could be deduced that the complex formation between  $\text{Pu}^{4+}$  and  $\text{ox}^{2-}$  is strong: even in solutions containing  $\geq 1 \text{ M H}^+$  the solubility is increased by adding  $\text{H}_2\text{ox}$ :



The references where the data have been analysed in terms of equilibrium constants are considered to be most reliable [49REA], [58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL], and the corresponding solubility and complex formation constants are listed in Table VI-54 and Table VI-58. However, in none of these publications is the solid state characterised, neither before nor after the experiments. Therefore, these solubility data may not be recommended by this review. In addition it has been reported that Pu(IV) oxidises oxalic acid, at least in acid solutions. The process is relatively slow at room temperature [49REA] but it is quite fast at  $\approx 100^\circ\text{C}$  [67RIC], [88NIK/DZY]. In nitric acid solutions the Pu(III) formed is oxidised back to Pu(IV), *cf.* Section VI.12.2.2. The relative decrease in oxalic acid concentration may be quite large in solutions where Pu(IV)-oxalate is allowed to dissolve without added oxalic acid, with increased measured solubilities as a consequence. It is therefore not surprising that there is a large variety of reported solubilities in solutions where neither oxalate nor oxalic acid has been added, sometimes larger than a factor of ten, as shown in Figure VI-41.

Nevertheless, it is deemed that it may be useful for the reader to have the experimental solubilities re-evaluated in order to obtain approximate values of equilibrium constants, for example as a guide when planning future experiments, *etc.* The data tabulated in [49REA] at  $0.75 \text{ M HNO}_3$ , and in [58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL] at  $1 \text{ M HNO}_3$  have therefore been reanalysed by this review using  $\text{H}_2\text{ox}(\text{aq})$  as a ligand, assuming that the solid phase in these studies was  $\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$  and using the SIT model, see the descriptions in Appendix A. The results of these evaluations are summarised in Table VI-55. The agreement between the equilibrium constants obtained from the two sets of data is relatively good, but the agreement between the model results and other data reported in [58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL] is less satisfactory, see the comments in Appendix A for [58MOS/GEL3]. Taking into account that none of these publications reported a characterisation of the solid phase, the values listed in Table VI-55 should be regarded as qualitative. The other published solubilities, considered to be less accurate, are compared in Figure VI-41 with values calculated using averages of the re-evaluations listed in Table VI-55. The figure illustrates the spread of the solubilities obtained for technical applications. Figure VI-41 and the figure in Appendix A for [58MOS/GEL3] show that the agreement between the model and the majority of the experimental data is qualitatively correct, but the low quality of the published results prevents any data selection.

Figure VI-41: Experimental Pu(IV) concentrations (converted to molal units) measured in solutions in contact with Pu(IV)-oxalate. The upper diagram shows data in strong acids (up to 2 M) without added oxalic acid or excess oxalate (black squares are data in  $\text{HClO}_4$ , all other data were obtained in  $\text{HNO}_3$ ). The lower diagram shows data in 1 M  $\text{HNO}_3$  (except for [49REA] which is at 0.75 M) as a function of added oxalic acid (except for [58GEL/MOS2], [58MOS/GEL] where ammonium oxalate was added). The curves were calculated assuming the formation of complexes according to:  $\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O(cr)} + (n-2) \text{H}_2\text{ox(aq)} \rightleftharpoons \text{Pu(ox)}_n^{4-2n} + (2n-4) \text{H}^+ + 6 \text{H}_2\text{O(l)}$ ; with the following equilibrium constants:  $\log_{10} K_s^\circ (n = 0) = -13$ ;  $\log_{10} K_s^\circ (n = 1) = -8.0$ ;  $\log_{10} K_s^\circ (n = 2) = -4.6$ ;  $\log_{10} {}^*K_s^\circ (n = 3) = -4.3$ ;  $\log_{10} {}^*K_s^\circ (n = 4) = -8.4$ , cf. Table VI-55. In the lower diagram the continuous and dashed lines corresponds to calculated solubilities as a function of added  $\text{H}_2\text{ox}$  and  $(\text{NH}_4)_2\text{ox}$ , respectively.

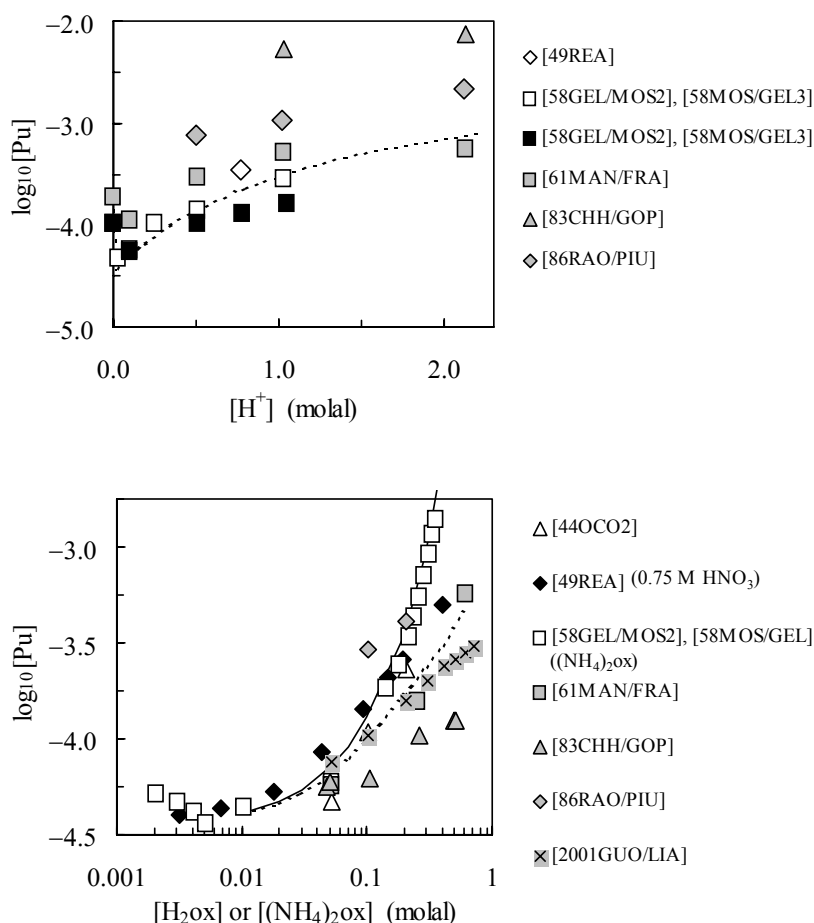


Table VI-54: Literature solubility constants involving solid Pu(IV) oxalate.

Ionic Medium	<i>t</i> (°C)	$\log_{10}K_s$	References
$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O(cr)} \rightleftharpoons \text{Pu}^{4+} + 2 \text{ox}^{2-} + 6 \text{H}_2\text{O(l)}$			
1 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{ox}$	20	– 21.4	<a href="#">[58GEL/MOS2]</a> , <a href="#">[58MOS/GEL]</a>
0.5 to 1 M $\text{HClO}_4$		– 21.3	
3.8 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{ox}$		– 20.1	
$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O(cr)} + 4 \text{H}^+ \rightleftharpoons \text{Pu}^{4+} + 2 \text{H}_2\text{ox(aq)} + 6 \text{H}_2\text{O(l)}$			
0.5 to 1 M $\text{HClO}_4$	20	– 11	<a href="#">[58MOS/GEL3]</a>
$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O(cr)} + 2 \text{H}^+ \rightleftharpoons \text{Pu(ox)}^{2+} + \text{H}_2\text{ox(aq)} + 6 \text{H}_2\text{O(l)}$			
0.75 M $\text{HNO}_3$ + 0 to 0.4 $\text{H}_2\text{ox}$	25	– 7.51	<a href="#">[49REA]</a>
1 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{ox}$	20	– 7.51	<a href="#">[58MOS/GEL]</a>
$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O(cr)} \rightleftharpoons \text{Pu(ox)}_2\text{(aq)} + 6 \text{H}_2\text{O(l)}$			
0.75 M $\text{HNO}_3$ + 0 to 0.4 $\text{H}_2\text{ox}$	25	– 4.52	<a href="#">[49REA]</a>
1 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{ox}$	20	– 4.49	<a href="#">[58MOS/GEL]</a>
0.5 to 1 M $\text{HClO}_4$	20	– 4.49	<a href="#">[58MOS/GEL3]</a>
$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O(cr)} + \text{H}_2\text{ox(aq)} \rightleftharpoons \text{Pu(ox)}_3^{2-} + 2 \text{H}^+ + 6 \text{H}_2\text{O(l)}$			
0.75 M $\text{HNO}_3$ + 0 to 0.4 $\text{H}_2\text{ox}$	25	– 3.12	<a href="#">[49REA]</a>
1 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{ox}$	20	– 3.17	<a href="#">[58MOS/GEL]</a>
$\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O(cr)} + 2 \text{H}_2\text{ox(aq)} \rightleftharpoons \text{Pu(ox)}_4^{4-} + 4 \text{H}^+ + 6 \text{H}_2\text{O(l)}$			
1 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{ox}$	20	– (4.15 ± 0.02)	<a href="#">[58MOS/GEL]</a>

Several ternary Pu(IV) oxalates have been reported, *cf.* Table VI-51. No thermodynamic data are available for any of these compounds. The precipitation of plutonium(IV) oxalate using the ions tris(ethylenediamine) Co(III), hexamine Cr(III) and hexaurea Cr(III) has been reported in [\[72HOS/UEN\]](#), [\[77HOS/UEN2\]](#).

Mixed oxalate-carbonate compounds have also been synthesised [\[58GEL/ZAI3\]](#): these solids are reported to be readily soluble in water.

Table VI-55: Results from re-analysis performed by this review of literature data on Pu(IV) oxalate solubility. All equilibrium constants are in molal units, in standard conditions (zero ionic strength) and at the temperature of the original experiments. Corrections for hydrolysis ( $\text{PuOH}^{3+}$  and  $\text{Pu}(\text{OH})_2^{2+}$ ) and nitrate complexation ( $\text{PuNO}_3^{3+}$ ) are included in the equilibrium constants. See Appendix A for more details on the calculations.

Background electrolyte used in the experiments <sup>†</sup>	<i>t</i> (°C)	$\log_{10}K_s^\circ$	Original references
$\text{Pu}(\text{ox})_2 \cdot 6\text{H}_2\text{O}(\text{cr}) + 4 \text{H}^+ \rightleftharpoons \text{Pu}^{4+} + 2 \text{H}_2\text{ox}(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$			
0.75 M $\text{HClO}_4$ (and 0.001 to 0.4 $\text{H}_2\text{ox}$ )	25	$\leq -13$	<a href="#">[49REA]</a>
1 M $\text{HNO}_3$ (and up to 0.35 M $(\text{NH}_4)_2\text{ox}$ )	20	$\leq -13$	<a href="#">[58GEL/MOS2]</a> , <a href="#">[58MOS/GEL3]</a> , <a href="#">[58MOS/GEL]</a>
$\text{Pu}(\text{ox})_2 \cdot 6\text{H}_2\text{O}(\text{cr}) + 2 \text{H}^+ \rightleftharpoons \text{Pu}(\text{ox})^{2+} + \text{H}_2\text{ox}(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$			
0.75 M $\text{HClO}_4$ (and 0.001 to 0.4 $\text{H}_2\text{ox}$ )	25	$-(8.1 \pm 0.3)$	<a href="#">[49REA]</a>
1 M $\text{HNO}_3$ (and up to 0.35 M $(\text{NH}_4)_2\text{ox}$ )	20	$-(7.9 \pm 0.1)$	<a href="#">[58GEL/MOS2]</a> , <a href="#">[58MOS/GEL3]</a> , <a href="#">[58MOS/GEL]</a>
$\text{Pu}(\text{ox})_2 \cdot 6\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{Pu}(\text{ox})_2(\text{aq}) + 6 \text{H}_2\text{O}(\text{l})$			
0.75 M $\text{HClO}_4$ (and 0.001 to 0.4 $\text{H}_2\text{ox}$ )	25	$-(4.58 \pm 0.04)$	<a href="#">[49REA]</a>
1 M $\text{HNO}_3$ (and up to 0.35 M $(\text{NH}_4)_2\text{ox}$ )	20	$-(4.6 \pm 0.1)$	<a href="#">[58GEL/MOS2]</a> , <a href="#">[58MOS/GEL3]</a> , <a href="#">[58MOS/GEL]</a>
$\text{Pu}(\text{ox})_2 \cdot 6\text{H}_2\text{O}(\text{cr}) + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Pu}(\text{ox})_3^{2-} + 2 \text{H}^+ + 6 \text{H}_2\text{O}(\text{l})$			
0.75 M $\text{HClO}_4$ (and 0.001 to 0.4 $\text{H}_2\text{ox}$ )	25	$-(4.26 \pm 0.03)$	<a href="#">[49REA]</a>
1 M $\text{HNO}_3$ (and up to 0.35 M $(\text{NH}_4)_2\text{ox}$ )	20	$-(4.37 \pm 0.05)$	<a href="#">[58GEL/MOS2]</a> , <a href="#">[58MOS/GEL3]</a> , <a href="#">[58MOS/GEL]</a>
$\text{Pu}(\text{ox})_2 \cdot 6\text{H}_2\text{O}(\text{cr}) + 2 \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Pu}(\text{ox})_4^{4-} + 4 \text{H}^+ + 6 \text{H}_2\text{O}(\text{l})$			
0.75 M $\text{HClO}_4$ (and 0.001 to 0.4 $\text{H}_2\text{ox}$ )	25	$-(8.2 \pm 0.5)$	<a href="#">[49REA]</a>
1 M $\text{HNO}_3$ (and up to 0.35 M $(\text{NH}_4)_2\text{ox}$ )	20	$-(9 \pm 1)$	<a href="#">[58GEL/MOS2]</a> , <a href="#">[58MOS/GEL3]</a> , <a href="#">[58MOS/GEL]</a>

<sup>†</sup>: The equilibrium constants reported here correspond to  $I = 0$ .

### VI.12.1.3 Solid plutonium(V) oxalates

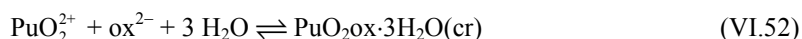
The preparation of  $\text{NH}_4\text{PuO}_2\text{ox} \cdot n\text{H}_2\text{O}$ , with  $n = 3$  and 6, has been described in [\[64GEL/ZAI\]](#), [\[73ZAI/ALE\]](#). These solids are apparently quite soluble in aqueous media but can be prepared by adding alcohol to solutions containing 4-6 g of Pu per litre. No studies reporting solubility or thermodynamic data have been found for Pu(V) oxalate compounds.

#### VI.12.1.4 Solid plutonium(VI) oxalates

$\text{PuO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  was synthesised and analysed in [58GEL/DRA3], where it is reported that this solid decomposes explosively when heated over  $180^\circ\text{C}$ . The standard entropy of this solid was estimated by Moskvin [73MOS] using a modified Latimer method:  $S_m^\circ(298.15\text{ K}) = 290\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

The solubility of Pu(VI) oxalate has only been reported in acid media [58DRA/MOS2], [58GEL/DRA2], [58GEL/DRA3], [59MOS], possibly because in neutral solutions the reduction of Pu(VI) by oxalate is expected to be faster, *cf.* Section VI.12.2.2. The solubility values were originally published by Gel'man and Drabkina [58GEL/DRA3], and later modelled by the same authors in collaboration with Moskvin [58DRA/MOS2], [58GEL/DRA2]. The formation of  $\text{PuO}_2\text{ox}(\text{aq})$  and  $\text{PuO}_2(\text{ox})_2^{2-}$  was assumed. The reported values for equilibrium constants involving  $\text{PuO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  are listed in Table VI-56. The experimental methodology is not systematically described in these papers, for example it is not stated how the solution was separated from the solid after the equilibration time (filtration or centrifugation?). The solid phase was characterised only once by chemical analysis before the dissolution experiments, and the equilibration time used, two hours, might have been too short: the authors state that equilibrium was “almost complete” after this time. The interpretation of the data is also doubtful: solubilities at several ionic strengths are generally mixed and there is no description of any activity coefficient correction. The oxalate protonation constants used by the authors were  $\log_{10} K_1 = 4.19$  and  $\log_{10} K_2 = 0.97$ , and the value of  $K_1$  seems too large for  $I \approx 1\text{ M}$  (see Table VI-8). Because of these deficiencies, the equilibrium constants in Table VI-56 are disregarded by this review.

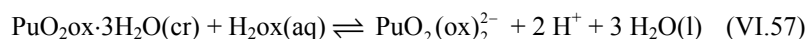
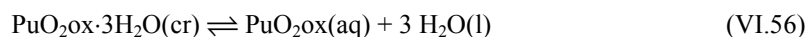
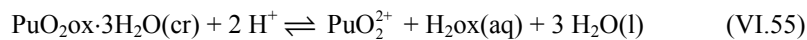
An approximate chemical equilibrium model is obtained in this review by fitting calculated Pu(VI) oxalate solubilities to the experimental data [58DRA/MOS2], [58GEL/DRA2], [58GEL/DRA3]. The calculations involve the SIT model for activity coefficients described in Appendix B and the following equilibrium reactions:



A reasonably good fit (see Figure VI-42) is found using  $\log_{10} K_s^\circ(\text{VI.52}) = 10$ ,  $\log_{10} \beta_1^\circ(\text{VI.53}) = 7.2$ , and  $\log_{10} \beta_2^\circ(\text{VI.54}) = 11.6$ ; together with  $\varepsilon(\text{PuO}_2^{2+}, \text{NO}_3^-) \approx \varepsilon(\text{UO}_2^{2+}, \text{NO}_3^-) = (0.24 \pm 0.03)\text{ kg}\cdot\text{mol}^{-1}$  (which requires neglecting the Pu(VI)-nitrate complex formation), and  $\varepsilon(\text{H}^+, \text{Hox}^-) = \varepsilon(\text{H}^+, \text{ox}^{2-}) = \varepsilon(\text{H}^+, \text{PuO}_2(\text{ox})_2^{2-}) = \varepsilon(\text{PuO}_2\text{ox}(\text{aq}), \text{HNO}_3) = \varepsilon(\text{H}_2\text{ox}(\text{aq}), \text{HNO}_3) = 0\text{ kg}\cdot\text{mol}^{-1}$ . In these acid solutions  $\text{ox}^{2-}$  is not an important species, and the results are not sensitive to  $\varepsilon(\text{H}^+, \text{ox}^{2-})$ . However, the modelled solubilities in this system depend on the evaluated  $[\text{H}_2\text{ox}(\text{aq})]/[\text{Hox}^-]$  ratio, and the calculated de-protonation of oxalic acid varies somewhat with  $\varepsilon(\text{H}^+, \text{Hox}^-)$ , as it is assumed that  $\varepsilon(\text{H}_2\text{ox}(\text{aq}), \text{HNO}_3) \approx 0$ . Nevertheless, practically the same results are



obtained with  $\varepsilon(\text{H}^+, \text{Hox}^-)$  in the range (+ 0.3 to – 0.3)  $\text{kg}\cdot\text{mol}^{-1}$ . The equilibrium constants given above may be recombined with the selected protonation constants to give:



$\log_{10} K_s^\circ$  (VI.55) = – 4.35,  $\log_{10} K_s^\circ$  (VI.56) = – 2.8 and  $\log_{10} K_s^\circ$  (VI.57) = – 4.05. These approximate equilibrium constants (for  $I = 0$ ) agree within expected uncertainties with those reported in [58DRA/MOS2], [58GEL/DRA2] (for an unknown ionic strength) and they may be used to describe qualitatively the reported solubilities for the Pu(VI)-oxalate system in nitric acid. There are however several reservations, expressed above, on the quality of the experimental data and therefore no equilibrium constants derived from these solubilities are recommended. However, the importance of Pu(VI) in oxalate solutions is marginal taking into account the instability of Pu(VI) towards reduction by radiolysis produced by  $\alpha$ -radiation and the reduction of Pu(VI) by oxalate and oxalic acid in aqueous solutions.

Other oxalate solids of Pu(VI) have been reported, *cf.* Table VI-51. No thermodynamic data are available for these compounds.

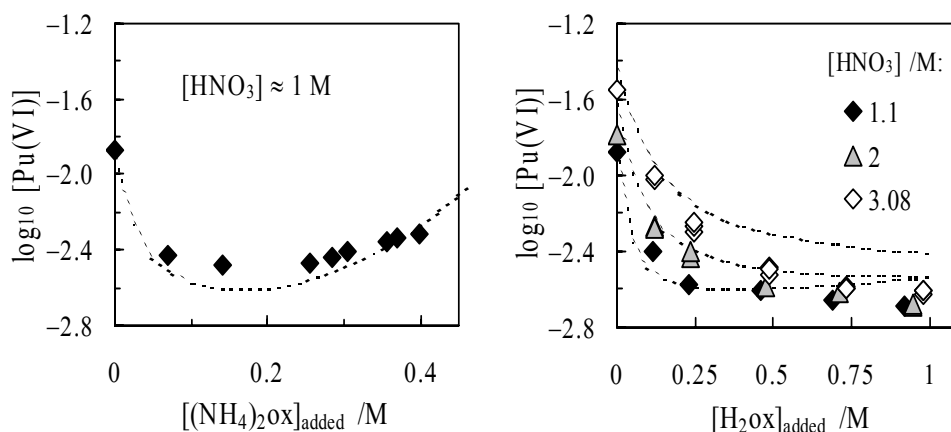
Table VI-56: Literature solubility constants involving solid Pu(VI) oxalate.

Ionic Medium	$t$ (°C)	$\log_{10} K_s$	Reference
$\text{PuO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{PuO}_2^{2+} + \text{ox}^{2-} + 3\text{H}_2\text{O}(\text{l})$			
1.1 to 3.1 M $\text{HNO}_3$	(20 ± 1)	– 9.20	[58DRA/MOS2]
1 M $\text{HNO}_3$ + 0 to 0.4 M $(\text{NH}_4)_2\text{ox}$	(20 ± 1)	– 9.85	[58DRA/MOS2] <sup>a</sup>
$\text{PuO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{cr}) + 2\text{H}^+ \rightleftharpoons \text{PuO}_2^{2+} + \text{H}_2\text{ox}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$			
1.1 to 3 M $\text{HNO}_3$ + 0 to 0.75 M $\text{H}_2\text{ox}$	(20 ± 1)	– 4.07 <sup>b</sup>	[58DRA/MOS2]
$\text{PuO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{PuO}_2\text{ox}(\text{aq}) + 3\text{H}_2\text{O}(\text{l})$			
1.1 to 3 M $\text{HNO}_3$ + 0 to 0.75 M $\text{H}_2\text{ox}$	(20 ± 1)	– 2.66	[58DRA/MOS2]
1 M $\text{HNO}_3$ + 0 to 0.4 M $(\text{NH}_4)_2\text{ox}$	(20 ± 1)	– 2.57	[58GEL/DRA2]
$\text{PuO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{cr}) + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{PuO}_2(\text{ox})_2^{2-} + 2\text{H}^+ + 3\text{H}_2\text{O}(\text{l})$			
1 M $\text{HNO}_3$ + 0 to 0.4 M $(\text{NH}_4)_2\text{ox}$	(20 ± 1)	– 2.95	[58GEL/DRA2]

a: using their own exp. data in [58GEL/DRA2].

b: using literature values for the protonation constants of oxalate, the authors converted this value into  $\log_{10} K_s = -9.23$  for the solubility product of  $\text{PuO}_2\text{ox}\cdot 3\text{H}_2\text{O}(\text{cr})$ .

Figure VI-42: Comparison of some of the experimental solubility data [58DRA/MOS2], [58GEL/DRA2], [58GEL/DRA3] for Pu(VI) oxalate in solutions containing nitric acid. The dotted line has been calculated using the model described in the text.



## VI.12.2 Aqueous plutonium oxalate complexes

### VI.12.2.1 Plutonium(III) oxalate complexes

The oxidation of Pu(III) in oxalate solutions is fast [57GEL/MOS], [67GEL/MOS], [83ZUB/KRO3]. Therefore, studies on the complex formation between Pu(III) and oxalate require the presence of reducing agents in the solutions, *e.g.*, hydrazine, and this introduces some uncertainty to all experimental studies of this system.

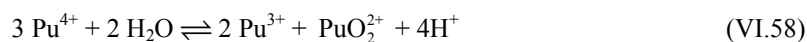
Several Pu(III)-oxalate complexes have been proposed in the literature: a protonated complex, Pu(Hox)<sub>4</sub><sup>-</sup>, as well as Pu(ox)<sub>n</sub><sup>3-2n</sup> with *n* = 2 to 4. The equilibrium constants reported in the literature for this system are listed in Table VI-57. Except for a cation-exchange study [58GEL/MAT], all values were obtained from solubility investigations, see also the discussion of the solubility of Pu(III) oxalate in Section VI.12.1.1. The formation of Pu(Hox)<sub>4</sub><sup>-</sup> reported in the cation-exchange study [58GEL/MAT] is not substantiated by the experimental data, see Appendix A. None of the other equilibrium constants reported are accepted in this review, see details in Appendix A. Likewise the enthalpy changes derived in [57GEL/MAT2], [57GEL/MAT3] are not recommended by this review either. Approximate values of equilibrium constants for qualitative modeling of this system may be found in Section VI.12.1.1.

Table VI-57: Literature stability constants for Pu(III) oxalate complexes.

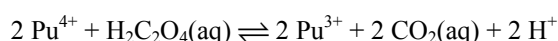
Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Pu}^{3+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Pu}(\text{ox})_2^-$				
sol	4.5? M KCl	20	9.31	<a href="#">[57GEL/MAT2]</a> , <a href="#">[57GEL/MAT3]</a>
	0-0.7 M (NH <sub>4</sub> ) <sub>2</sub> ox	70	7.94	
cix	1 M NH <sub>4</sub> Cl	20±1	9.15	<a href="#">[57GEL/MAT3]</a> , <a href="#">[58GEL/MAT]</a>
$\text{Pu}^{3+} + 3 \text{ox}^{2-} \rightleftharpoons \text{Pu}(\text{ox})_3^{3-}$				
sol	4.5? M KCl	20	18.7	<a href="#">[57GEL/MAT2]</a> , <a href="#">[57GEL/MAT3]</a>
	0-0.7 M (NH <sub>4</sub> ) <sub>2</sub> ox	70	16.2	
pol	3 M KCl	25±1	10.66	<a href="#">[58FOM/VOR]</a>
$\text{Pu}^{3+} + 4 \text{ox}^{2-} \rightleftharpoons \text{Pu}(\text{ox})_4^{5-}$				
sol	4.5? M KCl	20	27.6	<a href="#">[57GEL/MAT2]</a> , <a href="#">[57GEL/MAT3]</a>
	0-0.7 M (NH <sub>4</sub> ) <sub>2</sub> ox	70	24.8	
sol, pol	3 M KCl	25±1	11.62	<a href="#">[58FOM/VOR]</a>
$\text{Pu}^{3+} + 4 \text{Hox}^- \rightleftharpoons \text{Pu}(\text{Hox})_4^-$				
cix	1 M NH <sub>4</sub> Cl	20±1	10.95	<a href="#">[57GEL/MAT3]</a> , <a href="#">[58GEL/MAT]</a>

### VI.12.2.2 Plutonium(IV) oxalate complexes

In aqueous solutions not containing ligands the disproportionation of Pu(IV) is enhanced by low acidities, *e.g.*:



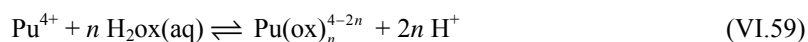
Due to its high electric charge, Pu<sup>4+</sup> is expected to form stronger complexes with most ligands as compared with the other valences of plutonium. Therefore it is to be expected that the tetravalent state of plutonium is stabilised against disproportionation by the presence of oxalate and other ligands. There is however the potential risk of oxalic acid being oxidised by Pu(IV):



$$\Delta_r G_m^\circ = -(261 \pm 8) \text{ kJ} \cdot \text{mol}^{-1}.$$

In nitric acid solutions the Pu(III) ions produced are easily oxidised back to Pu(IV) in a complex set of reactions (see *e.g.*, p.269 in [\[54CON\]](#) or p.76 [\[79CLE\]](#)):  $2 \text{Pu}^{3+} + \text{NO}_3^- + 3 \text{H}^+ \rightleftharpoons 2 \text{Pu}^{4+} + \text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$ ;  $\text{Pu}^{3+} + \text{HNO}_2(\text{aq}) + \text{H}^+ \rightleftharpoons \text{Pu}^{4+} + \text{H}_2\text{O}(\text{l}) + \text{NO}(\text{aq})$ ; *etc.* The oxidation of oxalic acid is relatively slow at room temperature [\[49REA\]](#) but it is quite fast at ≈100°C [\[88NIK/DZY\]](#).

The potential risk for disproportionation (Reaction (VI.58)) and the strong hydrolysis of this cation imposes that studies of complex formation are performed in acid media where oxalate is fully protonated. Under these conditions the reactions of complex formation may be written:



Data has been presented in the literature supporting the existence of complexes  $\text{Pu}(\text{ox})_n^{4-2n}$  with  $n = 1$  to 4, see Table VI-58.

Table VI-58: Literature stability constants for Pu(IV) oxalate complexes.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	References
$\text{Pu}^{4+} + \text{ox}^{2-} \rightleftharpoons \text{Pu}(\text{ox})^{2+}$				
sol	1 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{Ox}$	20	8.74	[58GEL/MOS2], [58MOS/GEL]
sol	0.3 M $\text{HNO}_3$	$(18 \pm 3)$	10.7	[69MIK]
dis	1 M $\text{HClO}_4$	10	$(9.75 \pm 0.01)$	[77RAM/RAM]
dis	1 M $\text{HClO}_4$	25	$(9.73 \pm 0.01)$	[76BAG/RAM3]
dis	1 M $\text{HClO}_4$	25	$(9.425 \pm 0.008)$	[77RAM/RAM2]
dis	0.1 M $\text{HNO}_3$ + 3.9 M $\text{NaNO}_3$	25	$(7.84 \pm 0.08)$	[83CHO/BOK]
	1 M $\text{HNO}_3$ + 3 M $\text{NaNO}_3$		$(8.24 \pm 0.05)$	
	2 M $\text{HNO}_3$ + 2 M $\text{NaNO}_3$		$(8.32 \pm 0.05)$	
	3 M $\text{HNO}_3$ + 1 M $\text{NaNO}_3$		$(8.33 \pm 0.04)$	
	3.9 M $\text{HNO}_3$ + 0.1 M $\text{NaNO}_3$		$(8.30 \pm 0.09)$	
	4 M $\text{HNO}_3$		$(8.29 \pm 0.05)$	
$\text{Pu}^{4+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Pu}(\text{ox})_2(\text{aq})$				
sol	1 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{Ox}$	20	16.92	[58GEL/MOS2], [58MOS/GEL]
dis	1 M $\text{HClO}_4$	10	$(17.64 \pm 0.01)$	[77RAM/RAM]
dis	1 M $\text{HClO}_4$	25	$(17.37 \pm 0.03)$	[76BAG/RAM3]
dis	1 M $\text{HClO}_4$	25	$(16.5 \pm 0.2)$	[77RAM/RAM2]
dis	1 M $\text{HNO}_3$ + 3 M $\text{HNaNO}_3$	25	$(15.02 \pm 0.09)$	[83CHO/BOK]
	2 M $\text{HNO}_3$ + 2 M $\text{HNaNO}_3$		$(14.71 \pm 0.08)$	
	3 M $\text{HNO}_3$ + 1 M $\text{HNaNO}_3$		$(14.56 \pm 0.05)$	
	4 M $\text{HNO}_3$		$(15.17 \pm 0.08)$	
$\text{Pu}^{4+} + 3 \text{ox}^{2-} \rightleftharpoons \text{Pu}(\text{ox})_3^{2-}$				
sol	1 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{Ox}$	20	23.40	[58GEL/MOS2], [58MOS/GEL]
sol	0.02 to 0.14 M $(\text{NH}_4)_2\text{Ox}$	20	20.6	[58MOS/GEL]
dis	1 M $\text{HClO}_4$	25	$(24.1 \pm 0.2)$	[77RAM/RAM2]
$\text{Pu}^{4+} + 4 \text{ox}^{2-} \rightleftharpoons \text{Pu}(\text{ox})_4^{4-}$				
sol	1 M $\text{HNO}_3$ + 0 to 0.35 M $(\text{NH}_4)_2\text{Ox}$	20	27.5	[58GEL/MOS2], [58MOS/GEL]
pol	3 M $\text{KCl}$	$(25 \pm 1)$	27.48	[58FOM/VOR]

(Continued on next page)

Table VI-58 (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	References
$\text{Pu(IV)} + \text{H}_2\text{ox(aq)} \rightleftharpoons \text{Pu(ox)}^{2+} + 2 \text{H}^+$				
kin	5 M (H,Na)NO <sub>3</sub>	98	(2.34 ± 0.09)	<a href="#">[88NIK/DZY]</a>
	5 M ? HCl		(2.0 ± 0.2)	
$\text{Pu(ox)}^{2+} + \text{H}_2\text{ox(aq)} \rightleftharpoons \text{Pu(ox)}_2\text{(aq)} + 2 \text{H}^+$				
sol	0.75 M HNO <sub>3</sub> + 0 to 0.4 M H <sub>2</sub> ox	25	2.98	<a href="#">[49REA]</a>
$\text{Pu(ox)}_2\text{(aq)} + \text{H}_2\text{ox(aq)} \rightleftharpoons \text{Pu(ox)}_3^{2-} + 2 \text{H}^+$				
sol	0.75 M HNO <sub>3</sub> + 0 to 0.4 M H <sub>2</sub> ox	25	1.40	<a href="#">[49REA]</a>
$\text{PuOH}^{3+} + \text{H}_2\text{ox(aq)} \rightleftharpoons \text{PuOH(ox)}^+ + 2 \text{H}^+$				
dis	0.1, 2 and 4 M HNO <sub>3</sub>	20-25	7.38	<a href="#">[72SOL/IVA]</a> , <a href="#">[74SOL]</a>

No evidence has been found in the literature for the formation of protonated complexes such as  $\text{PuHox}^{3+}$ . The existence of  $\text{Pu(ox)}_5^{6-}$  is suggested by the solid  $\text{K}_6\text{Pu(ox)}_5 \cdot 4\text{H}_2\text{O}$  (Table VI-51). Data from ion-exchange experiments for solutions at  $\text{pH} \approx 6$  with  $\text{K}_2\text{ox}$  concentration varying between 0.065 and 0.74 M suggested the stoichiometry  $\text{Pu(ox)}_5^{6-}$  [\[59ERM/BEL2\]](#). Ionic strength effects were however not taken into account, and the results are therefore inconclusive. Measurements of solubilities of Pu(IV) oxalate,  $\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$  (references listed in Section VI.12.1.2), and of sodium oxalate,  $\text{Na}_2\text{ox}$  [\[68MAT/KRO\]](#), give no evidence for such a complex, although these studies extend only to oxalate concentrations below 0.4 M, and the solid phase was not characterised in any of the solubility studies. The complex  $\text{PuOH(ox)}^+$  was proposed in [\[72SOL/IVA\]](#), [\[74SOL\]](#), but these references are considered unreliable, see the discussion in Appendix A.

The studies on the stability of the  $\text{Pu(ox)}_n^{4-2n}$  complexes (Table VI-58) are based on either solubility or solvent extraction data. The only exceptions are the investigation on the rate of oxidation of oxalic acid at  $\approx 100^\circ\text{C}$  [\[88NIK/DZY\]](#) which is of no interest here, and a polarographic study [\[58FOM/VOR\]](#) which is not credited by this review. See comments in Appendix A on these two references.

The references using solvent extraction techniques have been discussed in Appendix A. The data from [\[72SOL/IVA\]](#), [\[74SOL\]](#) cannot be accepted. The results at  $25^\circ\text{C}$  from [\[76BAG/RAM3\]](#), [\[77RAM/RAM2\]](#) have been re-evaluated in this review (*cf.* Appendix A), but the data from [\[77RAM/RAM2\]](#) are considered less reliable. The stepwise equilibrium constants obtained by this re-evaluation are listed in Table VI-59 together with the stepwise equilibrium constants from [\[83CHO/BOK\]](#), which have been converted to molal units and corrected for Pu(IV)-nitrate complexation.

The papers where the solubility of Pu(IV) oxalate has been studied are discussed in Section VI.12.1.2. The reported solubility data are considered to be only of qualitative nature because the solid phase was not characterised in the original references [49REA], [58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL]. The data has been re-evaluated in this review to provide the readers with qualitative values that support the solvent extraction data, see Table VI-59. These qualitative data may also be useful for provisional modelling calculations. In [69MIK] the solubility of arylarsonates was used to estimate the complex formation between Pu(IV) and several ligands, but as discussed in Appendix A, the reported data is not considered to be reliable.

Figure VI-43 illustrates the ionic strength dependence of the equilibrium constants for  $\text{Pu}(\text{ox})^{2+}$ ,  $\text{Pu}(\text{ox})_2(\text{aq})$  and  $\text{Pu}(\text{ox})_3^{2-}$  listed in Table VI-59. Given the large uncertainties in most of the data, and the qualitative nature of the equilibrium constants derived from the solubility studies, no value is recommended.

Mixed oxalate-carbonate compounds of Pu(IV) have been synthesised [58GEL/ZAI3] but there is no information available on the stability of mixed Pu(IV) complexes in aqueous solutions with both  $\text{CO}_3^{2-}$  and  $\text{ox}^{2-}$ .

Table VI-59: Stepwise stability constants for Pu(IV) oxalate complexes converted to molal units and corrected for the formation of  $\text{PuOH}^{3+}$ , and when necessary for  $\text{PuNO}_3^{3+}$ .

Method	Ionic medium	<i>t</i> (°C)	$\log_{10}K$	Reference
$\text{Pu}^{4+} + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Pu}(\text{ox})^{2+} + 2 \text{H}^+$				
sol	$I \rightarrow 0$	25	$\geq 4.9$ <sup>a,b</sup>	[49REA]
sol	$I \rightarrow 0$	20	$\geq 5.1$ <sup>b,c</sup>	[58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL]
dis	1 M $\text{HClO}_4$	25	$(5.3 \pm 0.3)$ <sup>d</sup>	[76BAG/RAM3]
dis	$I = 4 \text{ M (H,Na)NO}_3$	25	$(4.7 \pm 0.8)$	[83CHO/BOK]
$\text{Pu}(\text{ox})^{2+} + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Pu}(\text{ox})_2(\text{aq}) + 2 \text{H}^+$				
sol	$I \rightarrow 0$	25	$(3.5 \pm 0.3)$ <sup>a,b</sup>	[49REA]
sol	$I \rightarrow 0$	20	$(3.3 \pm 0.1)$ <sup>b,c</sup>	[58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL]
dis	1 M $\text{HClO}_4$	25	$(2.8 \pm 0.7)$ <sup>d</sup>	[76BAG/RAM3]
dis	$I = 4 \text{ M (H,Na)NO}_3$	25	$(1.7 \pm 1.1)$	[83CHO/BOK]
$\text{Pu}(\text{ox})_2(\text{aq}) + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Pu}(\text{ox})_3^{2-} + 2 \text{H}^+$				
sol	$I \rightarrow 0$	25	$(0.32 \pm 0.05)$ <sup>a,b</sup>	[49REA]
sol	$I \rightarrow 0$	20	$(0.2 \pm 0.1)$ <sup>b,c</sup>	[58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL]
dis	1 M $\text{HClO}_4$	25	$(2.9 \pm 0.9)$ <sup>d</sup>	[76BAG/RAM3]

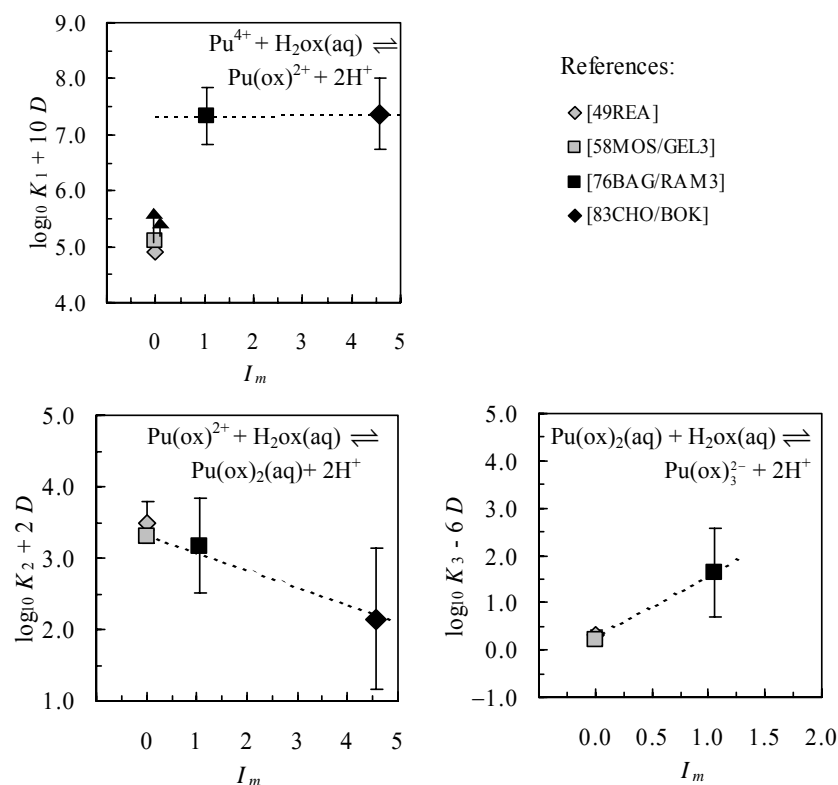
(Continued on next page)

Table VI-59 (continued)

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Pu}(\text{ox})_3^{2-} + \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Pu}(\text{ox})_4^{4-} + 2 \text{H}^+$				
sol	$I \rightarrow 0$	25	$-(3.9 \pm 0.5)^{\text{a,b}}$	[49REA]
sol	$I \rightarrow 0^{\text{b}}$	20	$-(4.6 \pm 1.0)^{\text{b,c}}$	[58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL]

- a: Equilibrium constants obtained by re-evaluating the original solubility data at 0.75 M HClO<sub>4</sub>, see Table VI-55 and Appendix A.
- b: As the solid phase was not characterised in the original reference these equilibrium constants are considered to be of qualitative nature.
- c: Equilibrium constants obtained by re-evaluating the original solubility data at 1 M HNO<sub>3</sub>, see Table VI-55 and Appendix A.
- d: Results from a reanalysis of the original solvent-extraction data, see Appendix A.

Figure VI-43: Overview of the equilibrium constants at  $\approx 25^\circ\text{C}$  listed in Table VI-59 for the Pu(IV) complexes  $\text{Pu}(\text{ox})_n^{4-2n}$  with  $n = 1$  to 3. The background colour of the symbols indicates the experimental method: black for two phase distribution (solvent extraction) and grey for solubility. The solubility data are considered to be qualitative because the solid phase was not characterised. The lines correspond to a weighted linear fit, added to the graphs for illustrative purposes only.



### VI.12.2.3 Plutonium(V) oxalate complexes

The disproportionation of Pu(V) is enhanced in oxalate solutions because of the stronger complexes formed with  $\text{PuO}_2^{2+}$  and  $\text{Pu}^{4+}$  and oxalate as compared with  $\text{PuO}_2^+$  [58COO/FOR], [67ERM/KRO2]. Pu(III) is not formed as a disproportionation product because it is quickly oxidised in oxalate media. Even Pu(VI) is unstable in oxalate media, but the reduction proceeds more slowly.

Two Pu(V)-oxalate complexes with 1:1 and 1:2 stoichiometry have been proposed in this system, as well as a protonated complex:  $\text{PuO}_2\text{Hox}(\text{aq})$ . Table VI-60 lists the equilibrium constants reported in the literature, which correspond to four independent studies,

- The data from Kondrashova *et al.*, cited in the book of Gel'man *et al.* [67GEL/MOS], has not been published elsewhere and will not be discussed any further.
- The coprecipitation (or sorption) method is judged to have too many uncertainties and the data obtained using this method [78MOS/POZ], [79MOS/POZ4], [79MOS/POZ] are not credited in this review, see the discussion of [79MOS/POZ] in Appendix A.
- The remaining studies [67ERM/KRO2], [73ZAI/ALE] were performed in conditions where the disproportionation reactions of Pu(V) competed with the oxalate complexation, see also the comments on these two papers in Appendix A.

In summary, Pu(V) disproportionates strongly in oxalate solution, and there are indications on the formation of Pu(V) oxalate complexes. However, the stoichiometry and stability of these complexes has not been acceptably determined.

Table VI-60: Literature stability constants for Pu(V) oxalate complexes.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	References
$\text{PuO}_2^+ + \text{ox}^{2-} \rightleftharpoons \text{PuO}_2\text{ox}^-$				
kin	$(\text{NH}_4)_2\text{ox}$ ; $I \approx 0.1$	25	3.88	[67ERM/KRO2]
	$(\text{NH}_4)_2\text{ox}$ ; $I \approx 0.2$		3.85	
ix	0.05	?	4.5	Kondrashova <i>et al.</i> <sup>b</sup>
sp	$\approx 0.15 \text{ NH}_4\text{ClO}_4$	?	3.7	[73ZAI/ALE]
(a)	0.5 M $\text{NH}_4\text{Cl}$	$(20 \pm 2)$	$(3.95 \pm 0.12)$	[78MOS/POZ]
$\text{PuO}_2^+ + 2 \text{ox}^{2-} \rightleftharpoons \text{PuO}_2(\text{ox})_2^{3-}$				
kin	$(\text{NH}_4)_2\text{ox}$ ; $I \approx 0.1$	25	6.7	[67ERM/KRO2]
	$(\text{NH}_4)_2\text{ox}$ ; $I \approx 0.2$		6.8	
ix	?	?	7.4	Kondrashova <i>et al.</i> <sup>b</sup>
(a)	0.5 M $\text{NH}_4\text{Cl}$	$(20 \pm 2)$	$(6.43 \pm 0.25)$	[78MOS/POZ]

(Continued on next page)



Table VI-60 (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	References
$\text{PuO}_2^+ + \text{ox}^{2-} + \text{H}^+ \rightleftharpoons \text{PuO}_2\text{Hox}(\text{aq})$				
kin	$(\text{NH}_4)_2\text{ox}$ ; $I \approx 0.1$	25	2.32	<a href="#">[67ERM/KRO2]</a>
	$(\text{NH}_4)_2\text{ox}$ ; $I \approx 0.2$		2.27	

a: co-precipitation method.

b: cited in section "Formation of acido complexes by Pu(V)" and in Table 22 of [\[67GEL/MOS\]](#).**VI.12.2.4 Plutonium(VI) oxalate complexes**

Pu(VI) in solution is prone to reduction caused by the radiolysis products of water produced by self-radiation [\[86WEI/KAT\]](#). In addition to this instability, the presence of an excess of oxalic acid in acid solutions induces the reduction of Pu(VI) to Pu(IV) [\[59DRA/GEL\]](#). The stability of Pu(VI) increases with the concentration of  $\text{HNO}_3$ , but it decreases with increasing HCl concentration. In neutral ammonium oxalate solutions (of unreported concentration) this process is quite fast [\[59DRA/GEL\]](#). The kinetics of Pu(VI) reduction in oxalate solutions in 1 M  $(\text{Na,H})\text{ClO}_4$  have also been studied at temperatures 70 to 90°C [\[73ZAK/ORL\]](#). However, at room temperature the reduction induced by oxalate is relatively slow: in the order of days [\[59DRA/GEL\]](#), [\[96BES/KRO\]](#), [\[98REE/WYG\]](#).

The complexes  $\text{PuO}_2\text{ox}(\text{aq})$  and  $\text{PuO}_2(\text{ox})_2^{2-}$  have been proposed in two studies, one based on solubility and the other using potentiometry. The equilibrium constants reported are summarised in Table VI-61.

The solubility of plutonium(VI) oxalate,  $\text{PuO}_2\text{ox} \cdot 3\text{H}_2\text{O}$ , was reported by Drabkina, Gel'man and Moskvina [\[58GEL/DRA2\]](#), [\[58GEL/DRA3\]](#), [\[58GEL/MOS2\]](#), [\[67GEL/MOS\]](#). These papers are discussed in Section VI.12.1.4, where approximate equilibrium constants at  $I = 0$  are proposed to describe qualitatively the reported solubilities.

The potentiometric study of [\[73POR/PAO\]](#) appears to be well performed. The authors used freshly prepared Pu(VI) to avoid self-reduction by radiolysis, and the oxidation state was checked spectrophotometrically both before and after each titration. An uncertainty of  $\pm 0.5 \log_{10}$ -units should cover all possible errors in this redox-unstable system. The value  $\log_{10} \beta_2 = (9.35 \pm 0.50)$  at  $I = 1 \text{ M}$  agrees with the values obtained from solubility measurements, see Section VI.12.1.4, within their expected uncertainties (perhaps  $\pm 1 \log_{10}$ -units or more).

No equilibrium constants are recommended for the Pu(VI)-oxalate system because of several factors: the instability of Pu(VI) in oxalate solutions; the uncertainties concerning the accuracy of the solubility data; and that there is only a single additional study reporting only data for  $\text{PuO}_2(\text{ox})_2^{2-}$ , but not for  $\text{PuO}_2\text{ox}(\text{aq})$ .

Table VI-61: Literature stability constants for Pu(VI) oxalate complexes.

Method	Ionic medium	$t$ (°C)	$\log_{10} K$	Reference
$\text{PuO}_2^{2+} + \text{ox}^{2-} \rightleftharpoons \text{PuO}_2\text{ox}(\text{aq})$				
sol	1 M $\text{HNO}_3$ 0 to 0.4 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	6.64 <sup>a</sup>	[58GEL/DRA2]
$\text{PuO}_2^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{PuO}_2(\text{ox})_2^{2-}$				
sol	1 M $\text{HNO}_3$ 0 to 0.4 M $(\text{NH}_4)_2\text{ox}$	$(20 \pm 1)$	11.5 <sup>a</sup>	[58GEL/DRA2]
pot	1 M $\text{NaClO}_4$	20	$(9.35 \pm 0.50)$	[73POR/PAO]

a: value obtained by the authors from a least-squares fitting of the experimental solubility data, using  $\log_{10} K_s = -9.23$  for the solubility product of  $\text{PuO}_2\text{ox} \cdot 3\text{H}_2\text{O}(\text{cr})$  published elsewhere [58DRA/MOS2]. See also comments in Section VI.12.1.4.

## VI.13 Americium oxalate compounds and complexes

### VI.13.1 Solid americium oxalates

#### VI.13.1.1 Am(III) compounds

Among possible oxidation states, Am(III), Am(IV), Am(V) and Am(VI), solid oxalate compounds of Am(III) and Am(V) have been prepared and some of their properties were investigated. For Am(III),  $\text{Am}_2(\text{ox})_3 \cdot n\text{H}_2\text{O}$  is known to be formed as an insoluble solid in weakly acidic or neutral solutions and was used for the isolation of americium from solution. However, TGA ([58MAR2]), DTA ([89VAS/KAL], [90VAS/KAL2]) and XRD ([67WEI/MEE]) of  $\text{Am}_2(\text{ox})_3 \cdot n\text{H}_2\text{O}$  indicate that  $n$  changes from 11 to 0 depending on the experimental conditions. In air, it loses its hydrated water and changes into  $\text{Am}_2(\text{ox})_3$  by 240°C. It begins to decompose at 270°C and the conversion into  $\text{Am}_2\text{O}_3$  completes at ~ 420°C. It was observed that solid  $^{241}\text{Am}_2(\text{ox})_3(\text{s})$  is self-destroyed by  $\alpha$ -radiation of the  $^{241}\text{Am}$  isotope and the compound is transformed into  $\text{Am}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$  liberating gaseous  $\text{CO}_2$  within 50-60 days [62LEB/PIR2]. The experiments were usually carried out under the conditions to avoid this effect of  $\alpha$ -radiolysis. Although attempts were made to measure the solubility [60LEB/PIR2], [67BUR/POR], [77ZAK/KOR], [87PAZ/KRI] and to determine the solubility product of  $\text{Am}_2(\text{ox})_3 \cdot n\text{H}_2\text{O}$ , as shown in Table VI-62, the present review could not select any value due to the problems in the references, as discussed in Appendix A. These are mainly the uncertainties in identifying the dissolved species and the solid phase in equilibrium with the solutions. Some ternary oxalates  $\text{MAm}(\text{ox})_2 \cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{Na}, \text{K}, \text{NH}_4, \text{Cs}$ ) have been isolated and their properties were examined ([83ZUB/KRO], [83ZUB/KRO2]), but no thermodynamic data are available for these compounds.

Table VI-62: Literature data on the solubility product of the solid compounds of Am(III) with oxalate.

$n$	Ionic medium	$t$ (°C)	$\log_{10} K_{s,0}$	Reference
$\text{Am}_2(\text{ox})_3 \cdot n\text{H}_2\text{O} \rightleftharpoons 2\text{Am}^{3+} + 3\text{ox}^{2-} + n\text{H}_2\text{O}$				
9	0.2 ~ 0.3 M $\text{HClO}_4 \rightarrow 0$	25	- 30.66	[60LEB/PIR2]
	0.1 ~ 1 M nitric acid $\rightarrow 0$	14	- 29 ~ -31	[77ZAK/KOR]
	water $\rightarrow 0$	14	- 19.2	

**VI.13.1.2 Am(V) compounds**

Although  $\text{MAmO}_2(\text{ox}) \cdot x\text{H}_2\text{O}$  ( $\text{M} = \text{K}, \text{Cs}$ ) has been isolated and their properties were examined [82ZUB/KRO], no thermodynamic data are available for Am(V) compounds.

**VI.13.2 Aqueous americium oxalate complexes****VI.13.2.1 Am(III) oxalate complexes**

A literature search by this review on the complex formation of americium-oxalate systems revealed information concerning the aqueous complexes of Am(III) and Am(V). As shown in Table VI-63, there are many papers dealing with  $\text{Am}(\text{ox})_n^{3-2n}$ , where  $n = 1$  and 2. Higher values of  $n$  may be possible, but their existence is not well established since the concentration range of oxalate in the experiments is not wide enough. Several papers [60LEB/PIR2], [65SEK4], [66STA], [74BYK/PET2], [87PAZ/KRI] report the stability of  $\text{Am}(\text{ox})_3^{3-}$ , and its existence is fairly probable since there is no steric or other reason to exclude this species. Although the complexes with  $\text{Hox}^-$  may be possible, their stabilities are expected to be much smaller than those with  $\text{ox}^{2-}$ . Based on the discussion of the references in Appendix A, this review does not select any values for the complexes of Am(III) of the type  $\text{Am}(\text{Hox})_n^{3-n}$  due to the lack of reliability of all papers which report values for Am(III) complexes with  $\text{Hox}^-$ .

Table VI-63: Literature data on the formation constants of oxalate complexes of Am(III).

Method	Ionic medium	$t(^{\circ}\text{C})$	$\log_{10}K$	Reference
$\text{Am}^{3+} + \text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})^+$				
cix	0.2 M $\text{NH}_4\text{Cl} \rightarrow 0$	20-25	5.99	[60LEB/PIR]
sol	$I = 0.2 \sim 0.7 \text{ M } (\text{H}^+, \text{K}^+, \text{ClO}_4^-, \text{ox}^{2-}, \text{Hox}^-) \rightarrow 0$	25	$(7.30 \pm 0.06)$	[60LEB/PIR2]
dis	1 M $\text{NaClO}_4$	25	$(4.63 \pm 0.08)$	[64SEK], [65SEK4]
em	$I = 0.1 \sim 0.3 \text{ M } (\text{H}^+, \text{NH}_4^+, \text{Cl}^-, \text{ox}^{2-}, \text{Hox}^-)$	25	$(6.15 \pm 0.16)$	[65STE/MAK]
cix	0.5 M $\text{NaClO}_4$	25	$(4.82 \pm 0.03)$	[68AZI/LYL]
em	0.1 M	25	$(5.25 \pm 0.10)$	[71STE]
dis	0.7 M $\text{NaCl}$	21	$(4.58 \pm 0.05)$	[83CAC/CHO]
sol	$\rightarrow 0$	25	6.89	[87PAZ/KRI]
em	0.10 Na(H)ClO <sub>4</sub>	25	$(5.01 \pm 0.13)$	[90ROS/REI]
	0.05 Na(H)ClO <sub>4</sub>		$(5.11 \pm 0.13)$	
	0.01 Na(H)ClO <sub>4</sub>		$(5.38 \pm 0.18)$	
dis	1.0 M $\text{NaClO}_4$	25	$(4.66 \pm 0.02)$	[96CHO/CHE]
	3.0 M $\text{NaClO}_4$		$(4.64 \pm 0.03)$	
	5.0 M $\text{NaClO}_4$		$(4.83 \pm 0.06)$	
dis	0.3 m $\text{NaCl}$	25	$(4.53 \pm 0.01)$	[2001BOR/MOO]
	1 m $\text{NaCl}$		$(4.17 \pm 0.05)$	
	2 m $\text{NaCl}$		$(4.40 \pm 0.04)$	
	3 m $\text{NaCl}$		$(4.56 \pm 0.04)$	
	4 m $\text{NaCl}$		$(4.63 \pm 0.04)$	
	5 m $\text{NaCl}$		$(4.57 \pm 0.06)$	
$\text{Am}^{3+} + 2\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_2^-$				
cix	0.2 M $\text{NH}_4\text{Cl} \rightarrow 0$	20-25	10.15	[60LEB/PIR]
sol	$I = 0.2 \sim 0.7 \text{ M } (\text{H}^+, \text{K}^+, \text{ClO}_4^-, \text{ox}^{2-}, \text{Hox}^-) \rightarrow 0$	25	$(11.46 \pm 0.10)$	[60LEB/PIR2]
cix	1 M $\text{NH}_4\text{Cl}$		$(9.7-10.0)$	[60MOS/KHA]
dis	1 M $\text{NaClO}_4$	25	$(8.35 \pm 0.09)$	[64SEK], [65SEK4]
em	$I = 0.1 \sim 0.3 \text{ M } (\text{H}^+, \text{NH}_4^+, \text{Cl}^-, \text{ox}^{2-}, \text{Hox}^-)$	25	$(10.54 \pm 0.19)$	[65STE/MAK]
dis	0.1 M $\text{NH}_4\text{Cl}$	20	8.3	[66STA]
cix	0.5 M $\text{NaClO}_4$	25	$(8.60 \pm 0.04)$	[68AZI/LYL]
em	0.1 M	25	$(8.85 \pm 0.10)$	[71STE]
dis	0.7 M $\text{NaCl}$	21	$(7.91 \pm 0.10)$	[83CAC/CHO]
sol	$\rightarrow 0$	25	9.73	[87PAZ/KRI]

(Continued on next page)

Table VI-63 (continued)

Method	Ionic medium	$t(^{\circ}\text{C})$	$\log_{10}K$	Reference
$\text{Am}^{3+} + 2\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_2^-$				
em	0.10 Na(H)ClO <sub>4</sub>	25	$(8.16 \pm 0.20)$	<a href="#">[90ROS/REI]</a>
	0.05 Na(H)ClO <sub>4</sub>		$(8.30 \pm 0.19)$	
	0.01 Na(H)ClO <sub>4</sub>		$(8.96 \pm 0.34)$	
dis	1.0 M NaClO <sub>4</sub>	25	$(8.35 \pm 0.02)$	<a href="#">[96CHO/CHE]</a>
	3.0 M NaClO <sub>4</sub>		$(8.56 \pm 0.09)$	
	5.0 M NaClO <sub>4</sub>		$(9.24 \pm 0.09)$	
dis	0.3 m NaCl	25	$(8.22 \pm 0.02)$	<a href="#">[2001BOR/MOO]</a>
	1 m NaCl		$(7.77 \pm 0.08)$	
	2 m NaCl		$(8.22 \pm 0.03)$	
	3 m NaCl		$(8.42 \pm 0.07)$	
	4 m NaCl		$(8.46 \pm 0.02)$	
	5 m NaCl		$(8.6 \pm 0.1)$	
$\text{Am}^{3+} + 3\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_3^{3-}$				
sol	$I = 0.2 \sim 0.7 \text{ M } (\text{H}^+, \text{K}^+, \text{ClO}_4^-, \text{ox}^{2-}, \text{Hox}^-) \rightarrow 0$	25	$(12.3 \pm 0.2)$	<a href="#">[60LEB/PIR2]</a>
dis	1 M NaClO <sub>4</sub>	25	$(11.15 \pm 0.07)$	<a href="#">[64SEK]</a> , <a href="#">[65SEK4]</a>
dis	0.1 M NH <sub>4</sub> Cl	20	11.8	<a href="#">[66STA]</a>
sol	$\rightarrow 0$	25	11.58	<a href="#">[87PAZ/KRI]</a>
$\text{Am}^{3+} + \text{Hox}^- \rightleftharpoons \text{Am}(\text{Hox})^{2+}$				
sol	$\rightarrow 0$	25	4.64	<a href="#">[87PAZ/KRI]</a>
$\text{Am}^{3+} + 3\text{Hox}^- \rightleftharpoons \text{Am}(\text{Hox})_3(\text{aq})$				
cix	1 M NH <sub>4</sub> Cl		9.64	<a href="#">[60MOS/KHA]</a>
$\text{Am}^{3+} + 4\text{Hox}^- \rightleftharpoons \text{Am}(\text{Hox})_4^-$				
cix	1 M NH <sub>4</sub> Cl		11	<a href="#">[60MOS/KHA]</a>

Table VI-64: Accepted formation constants for oxalate complexes of Am(III) at 25°C used to derive the selected values.

Method	Ionic medium	$\log_{10}K^{a,b}$	Reference
$\text{Am}^{3+} + \text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})^+$			(VI.60)
dis	1.1 <i>m</i> NaClO <sub>4</sub>	(4.61 ± 0.20)	[65SEK4]
dis	0.7 <i>m</i> NaCl	(4.61 ± 0.10)	[83CAC/CHO]
dis	1.1 <i>m</i> NaClO <sub>4</sub>	(4.64 ± 0.10)	[96CHO/CHE]
	3.5 <i>m</i> NaClO <sub>4</sub>	(4.57 ± 0.10)	
	6.6 <i>m</i> NaClO <sub>4</sub>	(4.71 ± 0.20)	
dis	0.3 <i>m</i> NaCl	(4.55 ± 0.10)	[2001BOR/MOO]
	1 <i>m</i> NaCl	(4.21 ± 0.10)	
	2 <i>m</i> NaCl	(4.44 ± 0.15)	
	3 <i>m</i> NaCl	(4.61 ± 0.20)	
	4 <i>m</i> NaCl	(4.70 ± 0.20)	
	5 <i>m</i> NaCl	(4.66 ± 0.30)	
$\text{Am}^{3+} + 2\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_2^-$			(VI.61)
dis	1.1 <i>m</i> NaClO <sub>4</sub>	(8.31 ± 0.20)	[65SEK4]
dis	0.7 <i>m</i> NaCl	(7.93 ± 0.15)	[83CAC/CHO]
dis	1.1 <i>m</i> NaClO <sub>4</sub>	(8.30 ± 0.20)	[96CHO/CHE]
	3.5 <i>m</i> NaClO <sub>4</sub>	(8.42 ± 0.20)	
	6.6 <i>m</i> NaClO <sub>4</sub>	(9.00 ± 0.30)	
dis	0.3 <i>m</i> NaCl	(8.24 ± 0.20)	[2001BOR/MOO]
	1 <i>m</i> NaCl	(7.81 ± 0.20)	
	2 <i>m</i> NaCl	(8.26 ± 0.30)	
	3 <i>m</i> NaCl	(8.47 ± 0.30)	
	4 <i>m</i> NaCl	(8.53 ± 0.40)	
	5 <i>m</i> NaCl	(8.7 ± 0.5)	
$\text{Am}^{3+} + 3\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_3^{3-}$			(VI.62)
dis	1.1 <i>m</i> NaClO <sub>4</sub>	(11.15 ± 0.40)	[65SEK4]

a: Refers to the reactions indicated, the ionic strength given in the table. Uncertainties are estimated by this review.

b: The values of  $\log_{10}K$  are those converted into molality unit, and corrected for chloride complex formation if ionic strength is controlled by NaCl.

Figure VI-44: Fitting of the values of  $\log_{10} K$  (VI.60) at each ionic strength (Table VI-63) to the SIT equation. The solid line is drawn by using the result of the fitting given below. Solid line:

$$\log_{10} K - \Delta z^2 D = \log_{10} K^o - \Delta \varepsilon I_m \quad \text{where} \quad D = \frac{0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad \text{and} \quad \Delta z^2 = -12$$

$$\log_{10} K^o = 6.51$$

$$\Delta \varepsilon = \varepsilon(\text{Am}(\text{ox})^+, X^-) - \varepsilon(\text{Am}^{3+}, X^-) - \varepsilon(\text{Na}^+, \text{ox}^{2-}) = -0.33 \text{ kg} \cdot \text{mol}^{-1}$$

$$\text{dotted line: } \Delta(\log_{10} K) = \pm 0.07, \Delta(\Delta \varepsilon) = \pm 0.04 \text{ kg} \cdot \text{mol}^{-1} \text{ (from fitting)}$$

$$\text{broken line: } \Delta(\log_{10} K) = \pm 0.15, \Delta(\Delta \varepsilon) = \pm 0.10 \text{ kg} \cdot \text{mol}^{-1} \text{ (selected)}$$

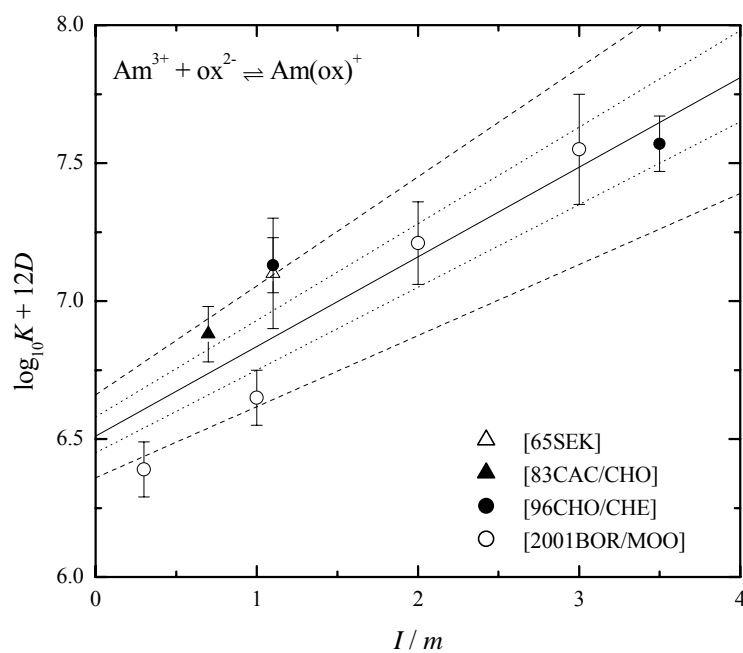


Figure VI-45: Plot of  $\log_{10} K$  (VI.60) against  $I_m$ . The solid line is drawn by using the result of the fitting given below. Solid line:

$$\log_{10} K - \Delta z^2 D = \log_{10} K^\circ - \Delta \varepsilon I_m \quad \text{where} \quad D = \frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \quad \text{and} \quad \Delta z^2 = -12$$

$$\log_{10} K^\circ = 6.51$$

$$\Delta \varepsilon = \varepsilon(\text{Am}(\text{ox})^+, \text{X}^-) - \varepsilon(\text{Am}^{3+}, \text{X}^-) - \varepsilon(\text{Na}^+, \text{ox}^{2-}) = -0.33 \text{ kg}\cdot\text{mol}^{-1}$$

$$\text{dotted line: } \Delta(\log_{10} K) = \pm 0.07, \Delta(\Delta \varepsilon) = \pm 0.04 \text{ kg}\cdot\text{mol}^{-1} \text{ (from fitting)}$$

$$\text{broken line: } \Delta(\log_{10} K) = \pm 0.15, \Delta(\Delta \varepsilon) = \pm 0.10 \text{ kg}\cdot\text{mol}^{-1} \text{ (selected)}$$

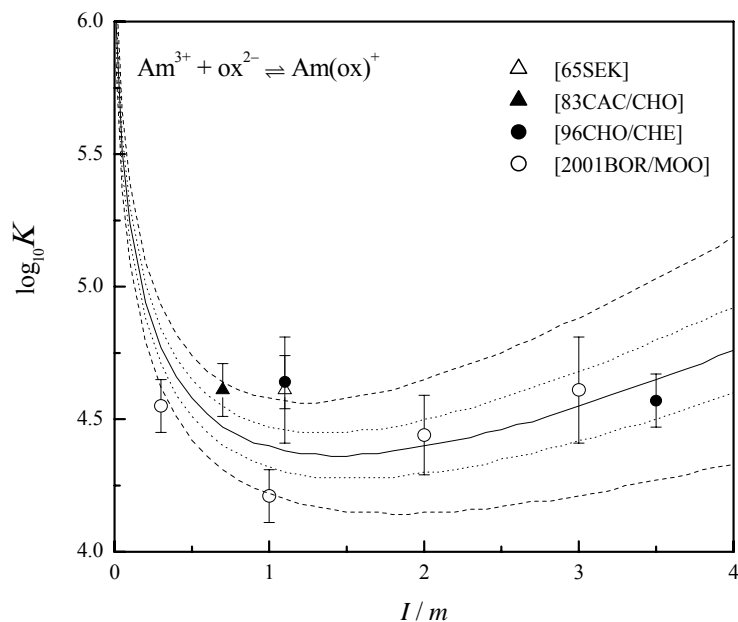




Figure VI-46: Fitting of the values of  $\log_{10} K$  (VI.61) at each ionic strength (Table VI-63) to the SIT equation. The solid line is drawn by using the result of the fitting given below.

$$\log_{10} K - \Delta z^2 D = \log_{10} K^o - \Delta \varepsilon I_m \quad \text{where} \quad D = \frac{0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad \text{and} \quad \Delta z^2 = -16$$

$$\log_{10} K^o = 10.71$$

$$\Delta \varepsilon = \varepsilon(\text{Am}(\text{ox})_2^-, \text{Na}^+) - \varepsilon(\text{Am}^{3+}, \text{X}^-) - 2\varepsilon(\text{Na}^+, \text{ox}^{2-}) = -0.54 \text{ kg} \cdot \text{mol}^{-1}$$

$$\text{dotted line: } \Delta(\log_{10} K) = \pm 0.12, \Delta(\Delta \varepsilon) = \pm 0.07 \text{ kg} \cdot \text{mol}^{-1} \text{ (from fitting)}$$

$$\text{broken line: } \Delta(\log_{10} K) = \pm 0.20, \Delta(\Delta \varepsilon) = \pm 0.10 \text{ kg} \cdot \text{mol}^{-1} \text{ (selected)}$$

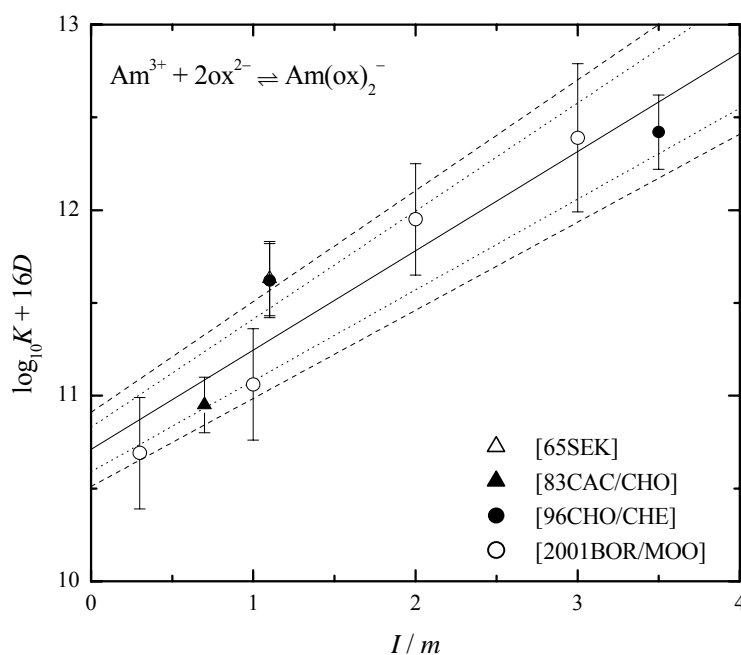


Figure VI-47: Plot of  $\log_{10} K$  (VI.61) against  $I_m$ . The solid line is drawn by using the result of the fitting given below. Solid line:

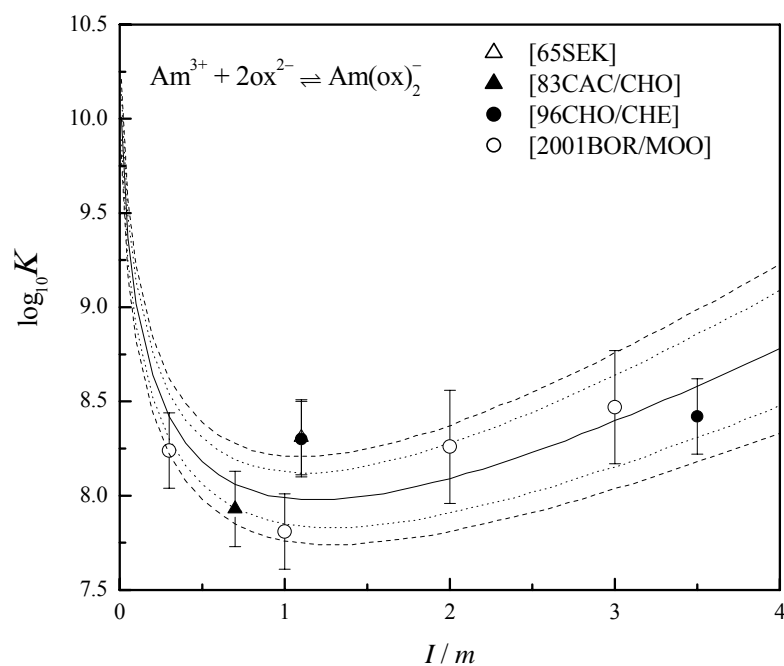
$$\log_{10} K - \Delta z^2 D = \log_{10} K^o - \Delta \varepsilon I_m \quad \text{where} \quad D = \frac{0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad \text{and} \quad \Delta z^2 = -16$$

$$\log_{10} K^o = 10.71$$

$$\Delta \varepsilon = \varepsilon(\text{Am}(\text{ox})_2^-, \text{Na}^+) - \varepsilon(\text{Am}^{3+}, \text{X}^-) - 2\varepsilon(\text{Na}^+, \text{ox}^{2-}) = -0.54 \text{ kg} \cdot \text{mol}^{-1}$$

dotted line:  $\Delta(\log_{10} K) = \pm 0.12$ ,  $\Delta(\Delta \varepsilon) = \pm 0.07 \text{ kg} \cdot \text{mol}^{-1}$  (from fitting)

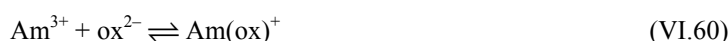
broken line:  $\Delta(\log_{10} K) = \pm 0.20$ ,  $\Delta(\Delta \varepsilon) = \pm 0.10 \text{ kg} \cdot \text{mol}^{-1}$  (selected)



Based on the discussion for the literature studies on Appendix A, the constants listed in Table VI-64 are accepted in this review. The values in Table VI-64 are those converted into molality units and corrected for chloride complex formation when necessary. By assuming  $\varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) = \varepsilon(\text{Am}^{3+}, \text{Cl}^-) = (0.49 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ , the analyses are conducted for the data at  $I_m < 4 \text{ m}$  in the form of:

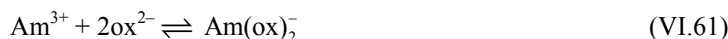
$$\log_{10} K - \Delta z^2 D = \log_{10} K^\circ - \Delta \varepsilon I_m \quad \text{where } D = \frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}}$$

For the reaction:



$$\Delta z^2 = -12 \text{ and } \Delta \varepsilon = \varepsilon(\text{Am}(\text{ox})^+, \text{ClO}_4^-) - \varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) - \varepsilon(\text{Na}^+, \text{ox}^{2-}),$$

and for the reaction,



$$\Delta z^2 = -16 \text{ and } \Delta \varepsilon = \varepsilon(\text{Na}^+, \text{Am}(\text{ox})_2^-) - \varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) - 2 \varepsilon(\text{Na}^+, \text{ox}^{2-}).$$

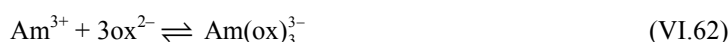
Figure VI-44 to Figure VI-47 show the result of the fittings. The obtained values are:

$$\log_{10} K (\text{VI.60}) = (6.51 \pm 0.07), \Delta \varepsilon = -(0.33 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$$

$$\log_{10} K (\text{VI.61}) = (10.71 \pm 0.12), \Delta \varepsilon = -(0.54 \pm 0.07) \text{ kg} \cdot \text{mol}^{-1}.$$

As shown in the Figures, the values at the ionic strength lower than around 1.0  $m$  show somewhat large deviations probably due to some overlooked systematic errors. If we use  $\varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.03)$  and  $\varepsilon(\text{Na}^+, \text{ox}^{2-}) = -(0.08 \pm 0.01)$ , the obtained values of  $\Delta \varepsilon$  give  $\varepsilon(\text{Am}(\text{ox})^+, \text{ClO}_4^-) = (0.08 \pm 0.05)$  and  $\varepsilon(\text{Na}^+, \text{Am}(\text{ox})_2^-) = -(0.21 \pm 0.08)$ , which seem reasonable. Taking these details of the results in consideration, this review selects values for these reactions but with larger uncertainties as given in Table VI-65.

For the reaction,



there is only one value which is considered reliable as is given in Table VI-64. If we want to obtain  $\log_{10} K^\circ$  by using the equation,

$$\log_{10} K^\circ = \log_{10} K - \Delta z^2 D \quad (\text{VI.63})$$

where  $\Delta z^2 = -12$ ,  $\log_{10} K^\circ$ , the value of  $\Delta \varepsilon = \varepsilon(\text{Na}^+, \text{Am}(\text{ox})_3^{3-}) - \varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) - 3\varepsilon(\text{Na}^+, \text{ox}^{2-})$  is necessary. If we assume  $\varepsilon(\text{Na}^+, \text{Am}(\text{ox})_3^{3-}) = \varepsilon(\text{Na}^+, \text{Am}(\text{CO}_3)_3^{3-}) = -(0.23 \pm 0.10)$ ,  $\Delta \varepsilon = -(0.48 \pm 0.11)$  is estimated. This would give  $\log_{10} K^\circ (\text{VI.62}) = 13.04$ . Considering the large uncertainty coming from the assumption for the ion interaction term and scarcity of the available data, this review selects the value of 13.0 with a large uncertainty of 1.0 as is given in Table VI-65.

Table VI-65: Selected formation constants for the oxalate complexes of  $\text{Am}^{3+}$  at 25°C.

Reaction	$\log_{10} K^o$	$\Delta\epsilon / \text{kg}\cdot\text{mol}^{-1}$
$\text{Am}^{3+} + \text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})^+$	$(6.51 \pm 0.15)$	$-(0.33 \pm 0.10)$
$\text{Am}^{3+} + 2\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_2^-$	$(10.71 \pm 0.20)$	$-(0.54 \pm 0.10)$
$\text{Am}^{3+} + 3\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_3^{3-}$	$(13.0 \pm 1.0)$	$-(0.48 \pm 0.50)$

The selected values reported in Table VI-65 yield:

$$\Delta_f G_m^o (\text{Am}(\text{ox})^+, 298.15 \text{ K}) = -(1316.0 \pm 5.2) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^o (\text{Am}(\text{ox})_2^-, 298.15 \text{ K}) = -(2020.1 \pm 6.1) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^o (\text{Am}(\text{ox})_3^{3-}, 298.15 \text{ K}) = -(2713.3 \pm 9.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

### VI.13.2.2 Am(V) oxalate complexes

At room temperature, americium(V) is relatively stable in oxalate solutions ( $\text{Am}(\text{V})$  at the concentration level of 1 mM is reduced by 0.1 M oxalate by about 2 % within 1 hour). The process is independent of oxalate concentration, but strongly depends on proton concentration or temperature ([74SHI/NIK2], [82ZUB/KRO]). Qualitatively,  $\text{AmO}_2^+$  forms oxalate complexes with similar stabilities as  $\text{NpO}_2^+$  complexes. Two papers were found for the reactions of  $\text{Am}(\text{V})$  with oxalates (Table VI-66):



These papers give qualitative information about the stabilities of oxalate complexes of  $\text{Am}(\text{V})$ . However, because of the instability of  $\text{Am}(\text{V})$  in the presence of oxalate, their values may only be of importance in short term laboratory studies, and could not be selected due to the experimental problems in the reports, as discussed in Appendix A.

Table VI-66: Literature data on the formation constants of  $\text{Am}(\text{V})$  oxalate complexes

Method	Ionic medium	$t$ (°C)	$\log_{10} K$	Reference
$\text{AmO}_2^+ + \text{ox}^{2-} \rightleftharpoons \text{AmO}_2(\text{ox})^-$				
sp	$I = 0.25 \text{ M } (\text{K}^+, \text{ox}^{2-}, \text{Hox}^-, \text{NO}_3^-)$	25	$(3.27 \pm 0.05)$	[74SHI/NIK2]
(a)	$I = 0.5 \text{ M } \text{NH}_4\text{Cl}$		$(3.08 \pm 0.08)$	[79MOS/POZ4]
$\text{AmO}_2^+ + 2\text{ox}^{2-} \rightleftharpoons \text{AmO}_2(\text{ox})_2^{3-}$				
sp	$I = 0.25 \text{ M } (\text{K}^+, \text{ox}^{2-}, \text{Hox}^-, \text{NO}_3^-)$	25	$(5.36 \pm 0.09)$	[74SHI/NIK2]

a: co-precipitation method

**VI.13.2.3 Am(VI) oxalate complexes**

In solutions with excess  $\text{H}_2\text{Ox}$ , Am(VI) was found to be reduced by oxalate and mainly to disproportionate into Am(III) and Am(V) ([\[85SHI\]](#)). No thermodynamic data are available for these highly unstable Am(VI) complexes.



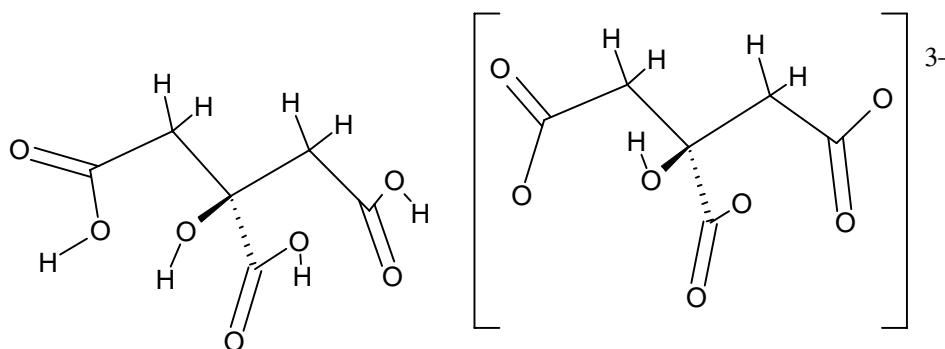
## Chapter VII

# Discussion of data selection for citrate compounds and complexes

### VII.1 Introduction

Citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid) has the chemical formula,  $\text{HOOC-CH}_2\text{-C(OH)-COOH-CH}_2\text{-COOH}$  ( $\text{C}_6\text{H}_8\text{O}_7$ ; molecular weight:  $192.123 \text{ g} \cdot \text{mol}^{-1}$ ; CAS Registry Number: 77-92-9). The three carboxylic groups may dissociate in aqueous solutions at acidities that are perhaps most common in nature. In reactions and formulae in this review citric acid will be denoted as  $\text{H}_3\text{cit}$ , and the citrate ligand in aqueous solutions will be denoted as  $\text{cit}^{3-}$ . The structures of citric acid and of citrate are shown in Figure VII-1.

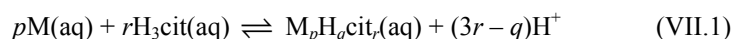
Figure VII-1: The structures of citric acid in  $\text{H}_3\text{cit} \cdot \text{H}_2\text{O}(\text{cr})$  [72ROE/KAN] and of citrate in  $\text{Na}_3\text{cit} \cdot 5.5\text{H}_2\text{O}(\text{cr})$  [86VIO/ROD].



Citrate has four functional groups, three carboxylates and one hydroxy group, all of which are potential coordination sites. As a result, citrate is a strong complexing

agent because it may easily form chelate complexes. The hydroxyl group in organic ligands is, in general, a very weak acid and only deprotonates at  $\text{pH} > 12$  in the absence of metal-ions. Furthermore the configuration of these four functional groups imposes steric constraints on the coordination and more than three groups cannot bind to the same metal ion. The non-bonded functional group(s) can be used as a bridge to a second metal ion, and polynuclear complexes are therefore abundant in metal – citrate systems. Especially for citrate complexes, there is some evidence ([\[78STR/KAR\]](#), [\[83BAK/BAK\]](#), [\[98MAT/RAP\]](#)) that, depending on the size and charge density of the metal ion, only two carboxylates and the hydroxyl group can bind to the same metal ion. In this case, it is expected that the strong interaction between the metal ion and the hydroxyl oxygen would lead to the deprotonation of the hydroxyl group at much lower pH.

The polyprotic citric acid can form a number of ternary complexes of the type  $\text{M}_p\text{H}_q\text{cit}_r$ . Hence, the general stoichiometric equation for the complex formation in metal – citrate systems using M and  $\text{H}_3\text{cit}$  as components is:



where charges have been omitted for simplicity. It is in general straightforward to determine the stoichiometry of the complexes formed in Equation (VII.1), but it is *not* the case for their constitution that describes how the different functional groups are bonded.

There are two types of problem to consider: one is the isomers formed which relate to the number of functional groups that are bonded in a certain complex, *e.g.*,  $\text{M}(\text{cit})$ . The magnitude of the equilibrium constant provides an indication on this number: the strength of the complex increases with the number of functional groups coordinated. Comparison of the equilibrium constants in the citrate system with those found in ligands with fewer functional groups (acetate, glycolate, oxalate, *etc.*) provide useful hints on the actual coordination. However, such comparisons are outside the scope of this review.

The second type of problem has its origin in the so-called “proton ambiguity” that arises in many “standard” solution chemical methods such as potentiometry. With these methods it is in general not possible to determine the origin of the protons released in Equation (VII.1), they may come from the ligand  $\text{H}_n\text{cit}^{3-n}$ ,  $n = 3, 2, 1, 0, -1$  or from coordinated water. Hence the thermodynamic equilibrium constants are the same for complexes such as  $\text{M}(\text{cit})$  and  $\text{M}(\text{OH})(\text{Hcit})$ , because they result in the same number of protons on the right hand side of Equation (VII.1). A second example is the complexes  $\text{M}(\text{OH})(\text{cit})$  and  $\text{M}(\text{H}_{-1}\text{cit})$ , where  $\text{H}_{-1}\text{cit}^{4-}$  is the fully deprotonated ligand. In this review, we generally use the simpler notations  $\text{M}(\text{cit})$  and  $\text{M}(\text{H}_{-1}\text{cit})$  unless we have clear evidence for a different constitution.

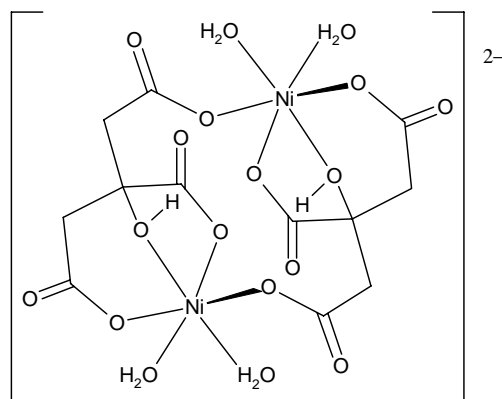
The deduction of the constitution is facilitated if one has information from NMR [\[78STR/KAR\]](#) and other spectroscopic methods, but the structural data obtained



from metal citrate compounds provide also useful information. Some examples are shown in Figure VII-2 and Figure VII-3. The second one shows the structure of a complex involving two different metal ions. In the case of sodium, citrate coordination occurs with a protonated carboxylic group, and two bridging oxygen atoms belonging to deprotonated carboxylic and hydroxy groups.

Figure VII-2: The structures of: (a)  $[\text{Ni}(\text{cit})(\text{H}_2\text{O})_2]_2^{2-}$  [\[83BAK/BAK\]](#), and (b)  $\text{Fe}(\text{cit})_2^{5-}$  [\[98MAT/RAP\]](#).

a)



b)

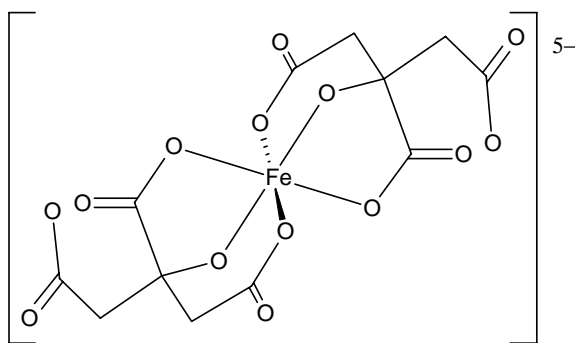
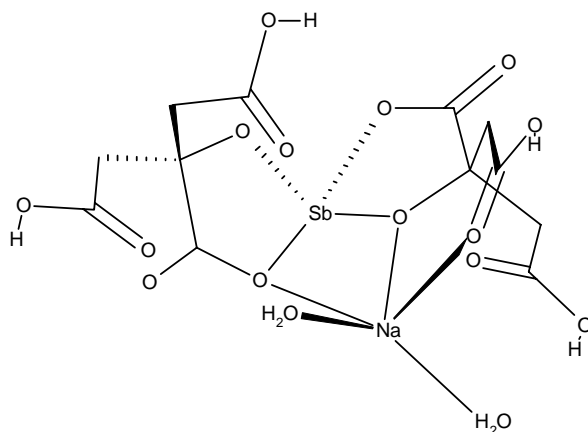


Figure VII-3: The structure of  $\text{SbNa}(\text{cit})_2(\text{H}_2\text{O})_2$  [91HAR/SMI].

### VII.1.1 Metal ion citrates

Several metal-ion salts with citrate have been reported in the literature. The solubilities of these citrates might be of interest when modelling natural systems containing metal ions and citrate. The available information in the literature concerning the solubility of Ni, Zr, Tc, U, Np, Pu and Am is discussed in this section. No information was found for selenium citrate compounds. The thermodynamic properties of magnesium and calcium citrates are reviewed in Section VII.5. Information on the solubility of other metal-ion citrates is also briefly mentioned in this section to help the reader in estimating the possible importance of citrate salts in any given system.

It must be borne in mind that the solubility of all citrates is pH-dependent. The protonation of the citrate ligand at  $\text{pH} \leq 6$  will increase the solubility of these salts, see for example Figure VII-4. In the alkaline region mixed metal-hydroxo-citrate complexes may be formed, and the possibility of the precipitation of other solids must be taken into account, such as oxides, hydroxides, hydroxocitrates, *etc.* The formation of metal-citrates with different numbers of water molecules must also be considered when interpreting solubility data, and the fact that hydration might be dependent on factors such as ionic strength (*i.e.*, activity of water), temperature, *etc.*

The solubility of citrates of  $\text{M}^+$  ions is probably quite high, for example the reported solubility for  $\text{KH}_2\text{cit}(\text{cr})$  in water at  $25^\circ\text{C}$  is 0.94 M [91AUK]. However, the

solubility of Ag(I) citrate at 25°C is  $0.284 \text{ g} \cdot (1000 \text{ g water})^{-1}$ , *i.e.*,  $\approx 0.6 \text{ mM}$  (*cf.* [\[59VIN/GET\]](#) and references therein).

$M^{2+}$ -citrate have solubilities that vary by several orders of magnitude, depending on the metal cation. The solubility of Mg, Ca, Zn and Cd citrates is reported in [\[69SKO/KUM\]](#) as a function of pH. The solubility is found to follow the trend  $\text{Mg} > \text{Ca} > \text{Cd} > \text{Zn}$ . At  $\text{pH} \approx 4.2$  the solubility of Mg-citrate is 0.04 M (corresponding to  $[\text{Mg}]_{\text{TOT}} = 0.12 \text{ M}$ ), while for Ca and Zn the solubilities at the same pH are only 0.005 and 0.0006 M, respectively. In pure water the solubility of magnesium and calcium citrates is found to be  $\approx 0.05 \text{ M}$  and  $\approx 0.0015 \text{ M}$ , respectively [\[93APE\]](#), [\[95ROB/GIA2\]](#), [\[2001CIA/TOM\]](#). There is no information in the literature about the solubility of  $\text{Ni}^{2+}$  and  $\text{UO}_2^{2+}$  citrate compounds. However, the preparation procedure for  $\text{K}_2[\text{Ni}(\text{cit})(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}$  suggests that the citrates of nickel are quite soluble [\[83BAK/BAK\]](#). Similarly the studies on the complex formation between citrate and  $\text{Ni}^{2+}$  and  $\text{UO}_2^{2+}$  in aqueous solution indicate that it is possible to prepare solutions containing several  $\text{mmol} \cdot \text{L}^{-1}$  of these ions, *e.g.*, [\[78KER/CHU\]](#) and [\[80VAN/KUC\]](#). Smaller solubility limits for U(VI)-citrate may be achieved by using  $\text{Co}(\text{NH}_3)_6^{3-}$  as precipitating agent [\[77HOS/UEN\]](#).

$M^{3+}$ -citrate compounds have been obtained with rare-earth elements, Al(III), Fe(III), *etc.* Citrates of lanthanides have been prepared by Skorik *et al.* [\[65SKO/SER\]](#), [\[66SKO/SER\]](#), [\[69SKO/MAM\]](#). The solubilities of the rare-earth citrates are reported for  $I = 0.1 \text{ M}$  to be in the range (0.3 – 3) mM at  $\text{pH} \approx (3.0 \pm 0.2)$  [\[65SKO/SER\]](#), [\[66SKO/SER\]](#), [\[69SKO/MAM\]](#). At  $\text{pH} \approx 6$  these solubilities decrease slightly (to 0.2 – 1 mM). For Fe(III)-citrate the solubility is reported to be  $\approx 0.025 \text{ M}$  [\[93APE\]](#). The solubility of actinide(III) citrates has not been reported, although millimolar concentrations of reactants have been used in several of the studies concerning the complexation of Am(III) and Pu(III) with citrate, *e.g.*, [\[72EBE/MOA\]](#), [\[84BOU/GUI\]](#) and [\[89POC\]](#).

Thorium citrate may be used as an example of a  $M^{4+}$ -citrate. The solubility of Th(IV) citrate at  $I = 0.1 \text{ M}$  has been reported to be  $\approx 0.03 \text{ mM}$  [\[67SKO/KUM\]](#). The experimental studies on the complex formation between Zr(IV) and citrate have also been conducted with solutions  $< 0.1 \text{ mM}$ , *e.g.*, [\[66KOR/SHE2\]](#) and [\[75ZAI/NIK\]](#). On the other hand, for  $\text{Pu}^{4+}$  solutions in the millimolar range have been used [\[66NEB\]](#), [\[66NEB2\]](#). This is also the case for the Tc(IV)-citrate system [\[77MUN2\]](#). Somewhat lower solubility limits for the Th(IV)- and Pu(IV)-citrate systems may be achieved by using  $\text{Co}(\text{NH}_3)_6^{3-}$  as precipitating agent [\[77HOS/UEN\]](#).

In conclusion, for most applications related to modelling the fate of metal ions in natural systems it is unlikely that the solubility limits of the corresponding citrate salts are reached. This is due to the fact that the concentrations of metal ions in such systems are in general too low, with the exception, perhaps, of calcium and to a lesser extent magnesium. In particular, for judging the safety of nuclear waste disposal facilities, the solubilities of radionuclide citrate salts appear to be too high to be used as a

source-term limitation of either citrate or of radionuclides. However, high levels of calcium might impose limits on the maximum levels of citrate.

As an example, the calculated citrate concentrations needed to reach the solubility limit of  $\text{Ca}_3(\text{cit})_2 \cdot 4\text{H}_2\text{O}$  in  $\text{CaCl}_2$  solutions are presented in Figure VII-4. The figure shows:

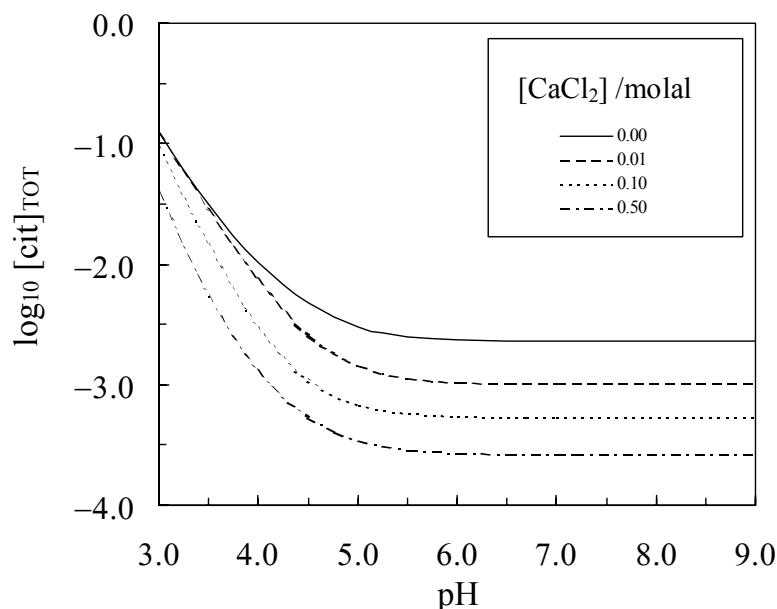
- The common-ion effect: an increased  $\text{Ca}^{2+}$  concentration decreases the solubility of calcium citrate;
- The effect of side reactions: rising  $\text{H}^+$ -concentrations (decreasing pH) increase the protonation of the ligand ( $\text{Hcit}^{2-}$ ,  $\text{H}_2\text{cit}^-$  and  $\text{H}_3\text{cit}(\text{aq})$ ) and the formation of protonated complexes ( $\text{Ca}(\text{Hcit})(\text{aq})$  and  $\text{Ca}(\text{H}_2\text{cit})^+$ ).

There is no evidence for side reactions in alkaline conditions such as the formation of hydroxocitrate complexes with calcium, *etc.*, and therefore the solubilities shown in Figure VII-4 remain constant at  $\text{pH} > 6$ .

Figure VII-4 was drawn using equilibrium constants selected by this review for protonation, complex formation and solubility. The activity of water was estimated with equations (B.9), (B.10) and (B.11) using the value of  $\epsilon(\text{Ca}^{2+}, \text{Cl}^-)$  in Table B.4. The activity coefficients of ions were calculated using equation (B.4) and the specific ion interaction parameters in Table B.4 ( $\epsilon(\text{Ca}^{2+}, \text{Cl}^-)$  and  $\epsilon(\text{H}^+, \text{Cl}^-)$ ). As there is no information about the  $\epsilon$ -values for other ion pairs, *e.g.*, for  $\epsilon(\text{Ca}^{2+}, \text{Ca}(\text{cit})^-)$ , a crude relationship between the values of  $\epsilon$  and the charge of the interacting ions was used:  $\epsilon(\text{M}, \text{X}) = 0.15 + 0.15 \times ((Z_{\text{M}} - 1) + (Z_{\text{X}} + 1)) \text{ kg} \cdot \text{mol}^{-1}$ . The following specific ion interaction coefficients (in  $\text{kg} \cdot \text{mol}^{-1}$ ) were obtained using this rough estimation method:  $\epsilon(\text{Ca}^{2+}, \text{cit}^{3-}) = 0.00$ ,  $\epsilon(\text{Ca}^{2+}, \text{Hcit}^{2-}) = 0.15$ ,  $\epsilon(\text{Ca}^{2+}, \text{H}_2\text{cit}^-) = 0.30$ ,  $\epsilon(\text{Ca}^{2+}, \text{Ca}(\text{cit})^-) = 0.30$ , and  $\epsilon(\text{Ca}(\text{H}_2\text{cit})^+, \text{Cl}^-) = 0.15$ . Neutral species,  $\text{H}_3\text{cit}(\text{aq})$  and  $\text{Ca}(\text{Hcit})(\text{aq})$ , were assumed to behave ideally.

The results shown in Figure VII-4 indicate that even in saline Ca-rich waters substantial concentrations of citrate may occur without the precipitation of calcium citrate. The citrate levels appear to be high enough to be able to affect the transport of trace metals in natural waters. The results shown in Figure VII-4 also illustrate the capabilities of the SIT model.

Figure VII-4: The total concentration of citrate at equilibrium with  $\text{Ca}_3\text{cit}_2\cdot 4\text{H}_2\text{O}$  in calcium chloride solutions as a function of pH at 25°C.



## VII.2 Citric acid

At temperatures below 36°C the solid formed at equilibrium in the system citric acid-water is the monohydrate,  $\text{H}_3\text{cit}\cdot\text{H}_2\text{O}(\text{cr})$ . Above this temperature  $\text{H}_3\text{cit}(\text{cr})$  is formed instead [37DAL]. The crystal structure for anhydrous citric acid has been reported by Glusker *et al.* [69GLU/MIN].

### VII.2.1 $\text{H}_3\text{cit}\cdot\text{H}_2\text{O}(\text{cr})$

The standard heat capacity has been determined in [62EVA/HOA], [82KRU/MIL]. From these data, the following values are selected:

$$C_{p,m}^\circ(\text{H}_3\text{cit}\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (268.05 \pm 0.10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$S_m^\circ(\text{H}_3\text{cit}\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (283.6 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The selected heat of combustion of citric acid monohydrate has been determined by Chappel and Hoare [58CHA/HOA] and the value re-evaluated by Domalski [72DOM] is:

$$\Delta_f H_m^\circ(\text{H}_3\text{cit}\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(1838.46 \pm 2.00) \text{ kJ}\cdot\text{mol}^{-1}.$$

This value agrees with the calculation made in this review using the auxiliary data in Table IV-1. The standard Gibbs energy of formation is calculated to be:

$$\Delta_f G_m^\circ (\text{H}_3\text{cit}\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = - (1473.3 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

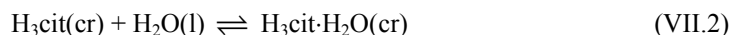
### VII.2.2 H<sub>3</sub>cit(cr)

The standard molar heat capacity and entropies determined by de Kruif *et al.* [82KRU/MIL] are adopted in this review, with the following assigned uncertainties,

$$C_{p,m}^\circ (\text{H}_3\text{cit}, \text{cr}, 298.15 \text{ K}) = (225.4 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1},$$

$$S_m^\circ (\text{H}_3\text{cit}, \text{cr}, 298.15 \text{ K}) = (252.1 \pm 0.2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

The enthalpy of formation of H<sub>3</sub>cit(cr) may be calculated using the enthalpy change for the reaction:



which has been determined calorimetrically to be  $\Delta_r H_m^\circ (\text{VII.2}) = - (11.3 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$  [82KRU/MIL] and  $- (10.85 \pm 0.19) \text{ kJ}\cdot\text{mol}^{-1}$  [86APE]. Using the weighted average,  $- (10.9 \pm 0.2) \text{ kJ}\cdot\text{mol}^{-1}$ , with the auxiliary data for H<sub>2</sub>O(l), and  $\Delta_f H_m^\circ (\text{H}_3\text{cit}\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$  selected in Section VII.2.1, this review obtains the following selected value for the standard enthalpy of formation of H<sub>3</sub>cit(cr) at 25°C:

$$\Delta_f H_m^\circ (\text{H}_3\text{cit}, \text{cr}, 298.15 \text{ K}) = - (1541.7 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

This agrees with value calculated by Domalski [72DOM] from early determinations of the heat of combustion of this solid [64WIL/SHI], namely  $\Delta_f H_m^\circ (\text{H}_3\text{cit}, \text{cr}, 298.15 \text{ K}) = - (1543.8 \pm 8.0) \text{ kJ}\cdot\text{mol}^{-1}$ .

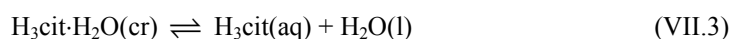
The standard Gibbs energy of formation is calculated from the values of the standard entropy and of the enthalpy of formation selected above:

$$\Delta_f G_m^\circ (\text{H}_3\text{cit}, \text{cr}, 298.15 \text{ K}) = - (1236.7 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

The enthalpy of solution of H<sub>3</sub>cit(cr) has been evaluated calorimetrically  $\Delta_{\text{sol}} H_m^\circ = (19.3 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$  by [93BAL/BAR].

### VII.2.3 H<sub>3</sub>cit(aq)

The solubility of citric acid may be used to calculate the value of  $\Delta_f G_m^\circ (\text{H}_3\text{cit}, \text{aq}, 298.15 \text{ K})$  from the following reaction,



$$\Delta_r G_m^\circ (\text{VII.3}) = \Delta_f G_m^\circ (\text{H}_3\text{cit}(\text{aq})) + \Delta_f G_m^\circ (\text{H}_2\text{O}(\text{l})) - \Delta_f G_m^\circ (\text{H}_3\text{cit}\cdot\text{H}_2\text{O}(\text{cr}))$$

$$\log_{10} K^\circ (\text{VII.3}) = - \Delta_r G_m^\circ (\text{VII.3}) / (R T \ln (10)) = \log_{10} a_{\text{H}_3\text{cit}} + \log_{10} a_{\text{H}_2\text{O}}.$$

At 25°C, the solubility of the monohydrate,  $\text{H}_3\text{cit}\cdot\text{H}_2\text{O}(\text{cr})$ , is quite high:  $(8.45 \pm 0.03)$  molal [37DAL], [55LEV], [76LAG/AUB], [82KRU/MIL], [87APE/MAN]. The results of Laguerie *et al.* [76LAG/AUB] are discarded: these authors determined the solubility of the monohydrate as a function of temperature, and their data give 207.5 g of monohydrate in 100 g of  $\text{H}_2\text{O}$ , which corresponds to 9.88 molal, in disagreement with all other studies.

The osmotic coefficient of the saturated solution (8.45  $m$ ) at 25°C is  $\phi = (1.625 \pm 0.005)$  [55LEV], [95APE/DOV2], *i.e.*,  $\log_{10} a_{\text{H}_2\text{O}} = -(0.108 \pm 0.001)$ . Apelblat *et al.* obtained expressions for the osmotic and activity coefficients of  $\text{H}_3\text{cit}(\text{aq})$ -solutions [95APE/DOV2], using a correction for the limited dissociation of the acid into  $\text{H}^+$  and  $\text{H}_2\text{cit}^{2-}$ . From these equations, the values for the saturated solution are  $\phi = 1.615$  and  $\log_{10} \gamma_{\text{H}_3\text{cit}(\text{aq})} = (0.509 \pm 0.004)$ .

Under equilibrium conditions then,  $\log_{10} a_{\text{H}_3\text{cit}} = \log_{10} m_{\text{H}_3\text{cit}} + \log_{10} \gamma_{\text{H}_3\text{cit}(\text{aq})} = \log_{10} (8.45 \pm 0.03) + (0.509 \pm 0.004) = (1.436 \pm 0.004)$ . Therefore:

$$\log_{10} K^\circ (\text{VII.3}) = (1.328 \pm 0.004).$$

This gives  $\Delta_r G_m^\circ (\text{VII.3}) = -(7.58 \pm 0.02) \text{ kJ}\cdot\text{mol}^{-1}$ , and results in the following selected value:

$$\Delta_f G_m^\circ (\text{H}_3\text{cit}, \text{aq}, 298.15 \text{ K}) = -(1243.7 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

The enthalpy change for reaction (VII.3) may be determined either calorimetrically or from the temperature dependence of the solubility of the saturated solutions. The values found in the literature are given in Table VII-1.

Table VII-1: Literature values for  $\Delta_r H_m^\circ (\text{VII.3})$ .

Method	Enthalpy changes at 298.15 K ( $\text{kJ}\cdot\text{mol}^{-1}$ )	Reference
$\text{H}_3\text{cit}(\text{cr})$		
cal	$\Delta_{\text{sol}} H_m (m \approx 0.01) = (18.47 \pm 0.09)^a$	[82KRU/MIL]
cal	$\Delta_{\text{sol}} H_m (m = 0.0200) = (18.21 \pm 0.07)$	[86APE]
$\text{H}_3\text{cit}\cdot\text{H}_2\text{O}(\text{cr})$		
$\partial m_{\text{sat}}/\partial T$	$\Delta_{\text{sol}} H_m (m_{\text{sat}}) = 29.8$	[55LEV]
cal	$\Delta_{\text{sol}} H_m (m \approx 0.01) = (29.25 \pm 0.20)^a$	[82KRU/MIL]
cal	$\Delta_{\text{sol}} H_m (m = 0.0203) = (29.06 \pm 0.12)$	[86APE]
$\partial m_{\text{sat}}/\partial T$	$\Delta_{\text{sol}} H_m (m_{\text{sat}}) = 26.0$	[87APE/MAN]
$\partial m_{\text{sat}}/\partial T$	$\Delta_{\text{sol}} H_m (m_{\text{sat}}) = 28.98$	[95APE/DOV]

a: These values are given with negative sign in Table 6 of [82KRU/MIL], apparently a misprint.

The calorimetric values in dilute solutions should be more accurate than the values derived from the temperature dependency of concentration of saturated solutions. Selecting the average of the two values determined from solution calorimetry for  $\text{H}_3\text{cit}\cdot\text{H}_2\text{O}(\text{cr})$  leads to the selected values:

$$\Delta_{\text{sol}}H_{\text{m}}^{\circ} = \Delta_{\text{r}}H_{\text{m}}^{\circ}(\text{VII.3}) = (29.11 \pm 0.11) \text{ kJ}\cdot\text{mol}^{-1}.$$

In addition, Dobrogowska *et al.* [90DOB/HEP] have determined the enthalpy of dilution of aqueous citric acid. Their data may be extrapolated to a saturated solution, giving an enthalpy of dilution  $\Delta_{\text{dil}}H_{\text{m}}(298.15 \text{ K}, m_{\text{sat}}) = (2.8 \pm 0.2) \text{ kJ}\cdot\text{mol}^{-1}$ . Therefore, the average of the data at saturated conditions ( $\Delta_{\text{sol}}H_{\text{m}}(m_{\text{sat}}) = (28.3 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$ ) may be extrapolated to infinite dilution to give  $\Delta_{\text{sol}}H_{\text{m}} = (31.0 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$ , which agrees with the calorimetric value within the uncertainties.

Using the value of  $\Delta_{\text{r}}H_{\text{m}}^{\circ}(\text{VII.3})$  determined calorimetrically and  $\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{H}_3\text{cit}\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$  selected above leads to:

$$\Delta_{\text{f}}H_{\text{m}}^{\circ}(\text{H}_3\text{cit}, \text{aq}, 298.15 \text{ K}) = -(1523.5 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}.$$

The standard entropy for aqueous citric acid may be calculated from the changes in entropy for Reaction (VII.3) and the standard entropies of  $\text{H}_3\text{cit}\cdot\text{H}_2\text{O}(\text{cr})$  (selected in Section VII.2.1) and  $\text{H}_2\text{O}(\text{l})$  (*cf.* Table IV-1):

$$S_{\text{m}}^{\circ}(\text{H}_3\text{cit}, \text{aq}, 298.15 \text{ K}) = (336.7 \pm 0.4) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

As a consistency check, the enthalpy change for the reaction:



is calculated to be  $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{VII.4}) = (18 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$ , in agreement with the value  $\Delta_{\text{sol}}H_{\text{m}}^{\circ}(\text{VII.4}) = (19.3 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$  obtained calorimetrically [93BAL/BAR].

The partial molar heat capacity at infinite dilution for undissociated citric acid has been reported to be  $C_{p,\text{m}}^{\circ}(\text{H}_3\text{cit}, \text{aq}, 298.15 \text{ K}) = (322.5 \pm 1.6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  [89SIJ/ROS].

The partial molar volume of the undissociated acid in water is  $V_{\text{m}}^{\circ}(\text{H}_3\text{cit}, 298.15 \text{ K}) = (113.5 \pm 1.5) \text{ cm}^3\cdot\text{mol}^{-1}$  [55LEV], [89MAN/APE], [89SIJ/ROS], [90APE/MAN]. For the citrate ions Apelblat and Manzurola [90APE/MAN] determined  $V_{\text{m}}^{\circ}(\text{Hcit}^{2-}, 298.15 \text{ K}) = (88.5 \pm 0.5) \text{ cm}^3\cdot\text{mol}^{-1}$  and  $V_{\text{m}}^{\circ}(\text{cit}^{3-}, 298.15 \text{ K}) = (72 \pm 1) \text{ cm}^3\cdot\text{mol}^{-1}$ , and estimated  $V_{\text{m}}^{\circ}(\text{H}_2\text{cit}^{-}, 298.15 \text{ K}) = (99.7 \pm 1.0) \text{ cm}^3\cdot\text{mol}^{-1}$  (uncertainty assigned by this review).

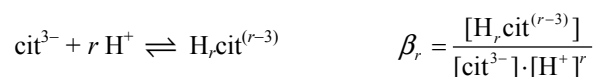
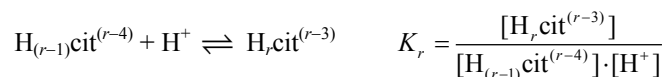


## VII.3 Protonation constants for citrate

### VII.3.1 Introduction

Citric acid normally behaves as a triprotic acid. The hydroxy-group has been found to dissociate only at high pH-values ( $> 12$ ), although it might dissociate at substantially lower pH values to participate in the co-ordination of metal cations. In this review citric acid is denoted as  $\text{H}_3\text{cit}$ , and the citrate ion with the hydroxy-group dissociated is denoted as  $\text{H}_{-1}\text{cit}^{4-}$ .

The standard TDB nomenclature is used for the protonation of a ligand:



Using this nomenclature, the equilibrium constant for the deprotonation of the hydroxy-group is denoted as follows,



and the protonation of  $\text{H}_{-1}\text{cit}^{4-}$  is expressed as:



Therefore,  $\beta_{-1} = (K_0)^{-1}$ .

A large number of references ( $\approx 130$ ) were found from a literature search for the acid-base equilibria of citrate. The majority of these references contain studies on metal complexation, where the authors needed values for the dissociation constants of citric acid under the same experimental conditions as the metal-complexation study.

Because of the large number of references, it was advantageous to judge the quality of the experimental details quite rigorously. The following criteria were considered when discarding references within the screening process:

- Clear indication must be given that the acid-base constants were determined experimentally in the actual study, and not taken from another publication.
- The calibration method for the pH-electrodes must be indicated. They must have been calibrated in the concentration scale, and not with standard pH-buffers. That is, “pH” must refer to  $-\log_{10}[\text{H}^+]$ . References were discarded when they reported mixed equilibrium constants, *i.e.*, involving both proton activities and ligand concentrations:

$$K_r^{\text{mixed}} = \frac{[\text{H}_r \text{cit}^{(r-3)}]}{[\text{H}_{(r-1)} \text{cit}^{(r-4)}] a_{\text{H}^+}}.$$

In some cases it is reported that the glass electrodes were calibrated with standard buffers, and  $[\text{H}^+]$  calculated from pH, for example with the Davies equation. This procedure is not accepted in this review.

- The total ligand concentration, the temperature, the ionic strength, and the nature of the background electrolyte must be given.
- A background electrolyte providing a constant ionic medium must be used. For studies where  $I \leq 0.1$  M this is quite difficult to achieve. For example, pH values below 2 can not be reached at  $I < 0.1$  M without disturbing substantially the composition of the ionic medium. In the case of citrate, with a charge of  $-3$ , the total concentration that can be used is limited, otherwise the ionic strength is substantially increased. For example, if the background electrolyte is 0.1 M then  $[\text{cit}^{3-}]_{\text{TOT}}$  should be  $\leq 4$  mM. In this review equilibrium constants at  $I < 0.1$  M were not considered because of the large junction potentials and the difficulties in keeping constant both the ionic strength and the nature of the electrolyte at such low concentrations. Studies were also rejected if they had been performed with  $[\text{cit}^{3-}]_{\text{TOT}}$  that was clearly too high for the constant ionic media concept.

The dissociation constants of citric acid reported in the following references were discarded from the review procedure because they did not fulfil one or more of the criteria indicated above: [\[28KOL/BOS\]](#), [\[28SIM\]](#), [\[29BJE/UNM\]](#), [\[49BAT/PIN\]](#), [\[51HEI\]](#), [\[52ELL2\]](#), [\[53WAR/WEB\]](#), [\[57LEF4\]](#), [\[59LI/LIN\]](#), [\[61LI/TAN\]](#), [\[62RYA/MAR\]](#), [\[63FUR/GIU\]](#), [\[63MAT\]](#), [\[65TAT/GRZ\]](#), [\[66NEB\]](#), [\[68SPI/MAR\]](#), [\[69LIT/PUR\]](#), [\[70BAR/BRI\]](#), [\[70GRZ/TAT\]](#), [\[71SKO/KUM\]](#), [\[72BEL/KAZ\]](#), [\[73GOR/KHU\]](#), [\[73HUB/HUS\]](#), [\[73KHA/PET\]](#), [\[73RAM/MAN2\]](#), [\[74MEY\]](#), [\[74PET/KHA\]](#), [\[75BRI/STU\]](#), [\[75DAN/OST\]](#), [\[75PEA/CRE\]](#), [\[76NOW/CAN\]](#), [\[76VAN/KUC\]](#), [\[77ROO/WIL\]](#), [\[77WIL\]](#), [\[78FLY/KOR\]](#), [\[78USS/BOS\]](#), [\[81BOU\]](#), [\[81MAL/SEN\]](#), [\[82GAR/RAM\]](#), [\[82INO/TOC\]](#), [\[84BOU/GUI\]](#), [\[84BOU/PET\]](#), [\[85RIZ/ANT\]](#), [\[86BAR/HAV\]](#), [\[86CAP/ROB\]](#), [\[86SAL/ZHU\]](#), [\[87FIN/DUF\]](#), [\[87HYN/ODO\]](#), [\[87KIT/ITO\]](#), [\[87RAY/DUF\]](#), [\[88GHA/MAN\]](#), [\[88MEL/BAR\]](#), [\[89MAN/APE\]](#), [\[89PAP/ZIO\]](#), [\[89YAD/GHO\]](#), [\[90FIN/DUF\]](#), [\[90WAN/YAN\]](#), [\[91APE/BAR\]](#), [\[91CHR/CUM\]](#), [\[92DAN/ROB\]](#), [\[92MIL/DOB\]](#), [\[92POG/KAP\]](#), [\[95PAP/ZIO\]](#), [\[96SAE/KHA\]](#), [\[96SCH/CON\]](#), [\[2000YOS/OKA\]](#), [\[2001JAN/HAR\]](#). These references are *not* discussed in Appendix A.

For other references a more detailed discussion is given in Appendix A [\[80ARE/CAL\]](#), [\[80DAN/RIG\]](#), [\[81CUC/DAN\]](#), [\[83DAN/RIG\]](#), [\[84DAN/OST\]](#), [\[85DAN/ROB\]](#), [\[86CRU/WAT\]](#), [\[90DAN/ROB\]](#), [\[90DAN/ROB2\]](#), [\[91BAP\]](#), [\[95LIS/CHO\]](#), [\[96BOR/LIS\]](#), [\[96XUE/TRA\]](#), [\[99ROB/STE\]](#), [\[2001SAR\]](#).

The data reported in the remaining references for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and tetraalkylammonium ionic media are listed in Table VII-2. A number of other ionic media have been used in literature studies:

- $\text{NH}_4\text{Cl}$  [81AMI/DAN]
- $\text{RbCl}$  and  $\text{CsCl}$  [90DAN/ROB2]
- Sea water [99STE/GIA], [2000ROB/STE]

However, the number of studies performed with these salts is scarce, and the corresponding protonation constants were not included in this review.

The uncertainties reported in the original publications were multiplied by a factor (1.96) to obtain error limits closer to a 95% total uncertainty level, *i.e.*, including random and possible systematic deviations. In cases where no uncertainty limits were reported in the original publication, a value of  $\pm 0.1 \log_{10}$ -units was used in the least-squares regression. Reported uncertainties below  $\pm 0.01$  in  $\log_{10} K$  in the original papers were increased to  $\pm 0.02$  ( $\approx \pm 0.01 \times 1.96$ ) in the data processing.

When applying the SIT model described in Appendix B to the activity coefficients of tetraalkylammonium halides, it may be shown that the specific ion-interaction coefficient,  $\varepsilon(\text{R}_4\text{N}^+, \text{X}^-)$ , depends on the ionic strength. A proper representation of the data is achieved by setting  $\varepsilon(\text{R}_4\text{N}^+, \text{X}^-) = \varepsilon_1(\text{R}_4\text{N}^+, \text{X}^-) + \varepsilon_2(\text{R}_4\text{N}^+, \text{X}^-) \cdot \log_{10} [\text{R}_4\text{N}^+]$ . Because of this, the protonation constants of citrate in tetraalkylammonium salts was fitted to the SIT equations by setting  $\varepsilon(\text{R}_4\text{N}^+, \text{H}_r\text{cit}^{(r-3)}) = \varepsilon_1(\text{R}_4\text{N}^+, \text{H}_r\text{cit}^{(r-3)}) + \varepsilon_2(\text{R}_4\text{N}^+, \text{H}_r\text{cit}^{(r-3)}) \cdot \log_{10} [\text{R}_4\text{N}^+]$ .

Several references report data at other temperatures than  $25^\circ\text{C}$ . Those references that reported only data at another temperature in the range  $(18 \text{ to } 37)^\circ\text{C}$  were also included in the review procedure, and these  $\log_{10} K$  values were extrapolated to  $25^\circ\text{C}$ . The corrections were obtained from reaction enthalpies selected in section VII.3.7. Ionic media corrections to the reaction enthalpies consist of two parts (*cf.* Section V.3.6): a Debye-Hückel expression, and a specific ion interaction ( $\Delta\varepsilon_L$ ) term. In cases where no data was available,  $\Delta\varepsilon_L$  was set equal to  $(0 \pm 5) \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1}$ . The resulting reaction enthalpies are all relatively small, and because of the limited temperature interval involved ( $\leq \pm 12^\circ\text{C}$ ), the calculated corrections for  $\log_{10} K_r$  were always  $\leq 0.07 \log_{10}$ -units. If needed the uncertainties in the adjusted protonation constants were also increased following the error-propagation rules described in Appendix C for the additional uncertainty in the value of  $\Delta_r H_m$ .

Table VII-2: Literature data on the protonation constants for citrate considered in this review. Data in *italics* were reported in molal units.

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_0$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$	Reference
pot	1	Na(Cl)	18	10.82	5.135	4.092	2.778	<a href="#">[40ADE]</a> <sup>a</sup>
	1.5				5.082	4.077	2.788	
	2				5.077	4.091	2.811	
	2.5				5.101	4.139	2.857	
	3				5.124	4.178	2.91	
pot	0.1	(KCl)	19	10.82	5.67	4.40	2.95	<a href="#">[59OKA/KOL]</a>
pot	0.5	(NaClO <sub>4</sub> )	25		5.26	4.10	2.74	<a href="#">[62FUR/CER]</a>
pot	0.1	(NaClO <sub>4</sub> )	20		5.68	4.35	2.87	<a href="#">[64CAM/OST]</a>
pot	0.1	(NaClO <sub>4</sub> )	20		(5.68 ± 0.02)	(4.38 ± 0.02)	(2.96 ± 0.03)	<a href="#">[64TIM]</a>
pot	0.1	(KNO <sub>3</sub> )	25		5.65	4.30	2.79	<a href="#">[65RAJ/MAR]</a>
	1				5.34	4.11	2.63	
sp	1	NaCl	25			4.168		<a href="#">[67FIS2]</a>
	2					4.188		
	3					4.284		
	4					4.420		
sp	1	NaBr	25			4.223		
	2					4.276		
	3					4.396		
	4					4.542		
sp	1	NaNO <sub>3</sub>	25			4.173		
	2					4.168		
	3					4.231		
	4					4.328		
sp	1	NaClO <sub>4</sub>	25			4.237		
	2					4.314		
	3					4.434		
	4					4.601		
sp	1	KCl	25			4.240		
	2					4.307		
	3					4.435		
sp	1	KBr	25			4.282		
	2					4.400		
	3					4.536		
sp	1	KNO <sub>3</sub>	25			4.261		
	2					4.297		

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Table VII-2: (continued)

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_0$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$	Reference
pot	3	LiClO <sub>4</sub>	25		4.7	4.2	2.8	[68GUI]
pot	0.1	KCl	25		(5.685 ± 0.017)	(4.375 ± 0.013)	(2.892 ± 0.013)	[72KAN]
pot	1	(LiClO <sub>4</sub> )	25		5.00	3.90	2.70	[72MET/GUI3]
pot	2	Na(ClO <sub>4</sub> )	25	>13	(5.18 ± 0.03)	(4.16 ± 0.05)	(2.90 ± 0.07)	[73BOT/VIC1], [73BOT/VIC2]
pot	0.1	KNO <sub>3</sub>	25		(5.70 ± 0.02)	(4.36 ± 0.03)	(2.81 ± 0.08)	[74FIE/MCC]
pot	1	(KNO <sub>3</sub> )	25		(5.33 ± 0.05)	(4.13 ± 0.03)	(2.83 ± 0.04)	[74VAN/GEN]
pot	0.1	KCl	25		(5.646 ± 0.024)	(4.387 ± 0.006)	(2.871 ± 0.003)	[75MAT/HIR]
pot	0.1	(KNO <sub>3</sub> )	25		(5.74 ± 0.01)	(4.36 ± 0.01)	(2.91 ± 0.01)	[76HAR/MAR]
pot	0.15	Na(ClO <sub>4</sub> )	37		(5.539 ± 0.003)	(4.236 ± 0.004)	(2.869 ± 0.006)	[78BER/MAY]
pot	1	NaClO <sub>4</sub>	25		5.05	4.05	2.71	[78KER/CHU]
pot	0.12	(NaCl)	25	(13.8±0.3)	(5.70 ± 0.05)	(4.32 ± 0.01)	(2.94 ± 0.05)	[78RAJ/MAI]
pot	0.15	(KNO <sub>3</sub> )	37		(5.62 ± 0.02)	(4.29 ± 0.04)	(2.87 ± 0.06)	[79AMI/DAN]
pot	1	Na(ClO <sub>4</sub> )	25		(5.171 ± 0.002)	(4.097 ± 0.003)	(2.811 ± 0.003)	[79EKS/OLI]
pot	0.1	(Me <sub>4</sub> NBr)	25		5.78	4.32	2.89	[79HEU/POP]
pot	0.14	KCl	37		(5.652 ± 0.005)	(4.302 ± 0.007)	(2.88 ± 0.01)	[80DAN/RIG]
	0.3				(5.472 ± 0.005)	(4.190 ± 0.007)	(2.78 ± 0.01)	
	1				(5.292 ± 0.007)	(4.098 ± 0.008)	(2.84 ± 0.01)	
pot	0.1	(KCl)	25		(5.72 ± 0.02)	(4.37 ± 0.01)	(2.94 ± 0.01)	[80HED/LID]
pot	0.12	(NaCl)	25	(13.0±0.3)	(5.70 ± 0.06)	(4.32 ± 0.01)	(2.92 ± 0.06)	[81RAJ/MAI]
pot	0.2	(KNO <sub>3</sub> )	25		(5.69 ± 0.02)	(4.38 ± 0.02)	(2.92 ± 0.03)	[82AVD/KEA]
pot	0.15	(NaCl)	37		(5.468 ± 0.002)	(4.187 ± 0.003)	(2.775 ± 0.005)	[82JAC]
pot	0.1	(Et <sub>4</sub> NI)	37		(5.86 ± 0.02)	(4.40 ± 0.02)	(2.92 ± 0.02)	[83DAN/RIG]
	0.3				(5.82 ± 0.02)	(4.37 ± 0.02)	(2.915 ± 0.002)	
	1				(6.07 ± 0.01)	(4.505 ± 0.008)	(3.065 ± 0.015)	
pot	0.6	Na(Cl)	25		(5.217 ± 0.005)	(4.081 ± 0.004)	(2.769 ± 0.003)	[83OHM/SJO], [83OHM/SJO2]
pot	0.25	(Et <sub>4</sub> NBr)	25		(5.82 ± 0.01)	(4.38 ± 0.02)	(2.95 ± 0.04)	[84DAN/OST]
pot	2	Na(ClO <sub>4</sub> )	25		(5.02 ± 0.02)	(4.03 ± 0.03)	(2.75 ± 0.03)	[84GRE/WIK]
pot	0.1	(KNO <sub>3</sub> )	25		(5.710 ± 0.002)	(4.389 ± 0.002)	(3.025 ± 0.002)	[84MOT/MAR]
pot	1	(Na)Cl	25		(5.12 ± 0.01)	(4.05 ± 0.01)	(2.77 ± 0.01)	[86CRU/WAT]
pot	0.1	(KCl)	25		(5.70 ± 0.02)	(4.35 ± 0.01)	(2.91 ± 0.02)	[86GRE/POW]

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Table VII-2: (continued)

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_0$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$	Reference
pot	0.5	NaNO <sub>3</sub>	25		(5.32 ± 0.01)	(4.16 ± 0.01)	(2.81 ± 0.01)	[89RIB/SAL], [89RIB/SAL2]
pot	0.15	NaCl	37		(5.539 ± 0.001)	(4.248 ± 0.001)	(2.856 ± 0.002)	[89VEN/BER]
pot	0.1	(KNO <sub>3</sub> )	25		(5.69 ± 0.02)	(4.35 ± 0.04)	(2.90 ± 0.07)	[90ARE/CON]
pot	0.16	(NaCl)	25		5.545	4.267	2.879	[90DAN/ROB] <sup>b</sup> , [90DAN/ROB2]
	0.36				5.315	4.162	2.824	
	0.64				5.169	4.090	2.783	
	1				5.093	4.017	2.739	
	0.16	(KCl)	25		5.595	4.297	2.900	
	0.36				5.433	4.219	2.857	
	0.64				5.349	4.167	2.804	
	1				5.311	4.097	2.723	
	0.16	(LiCl)	25		5.487	4.247	2.889	
	0.36				5.210	4.127	2.846	
	0.64				5.033	4.047	2.824	
	1				4.963	3.981	2.806	
pot	0.16	Et <sub>4</sub> N(I)	25		(5.848 ± 0.015)	(4.396 ± 0.01)	(2.953 ± 0.011)	[90ROB/STE] <sup>b</sup>
	0.36				(5.858 ± 0.015)	(4.396 ± 0.01)	(2.973 ± 0.011)	
	0.64				(5.958 ± 0.015)	(4.454 ± 0.01)	(3.029 ± 0.011)	
	1				(6.099 ± 0.015)	(4.536 ± 0.01)	(3.106 ± 0.011)	
pot	0.15	(NaCl)	25		(5.540 ± 0.005)	(4.240 ± 0.008)	(2.867 ± 0.010)	[91JAC/TOI]
pot	0.1	(NaClO <sub>4</sub> )	25		5.70			[92GLA/HUL]
pot	0.15	(NaCl)	25		5.71	4.38	2.92	[93GLA/MAJ] <sup>c</sup>
pot	0.2	(KCl)	25		(5.57 ± 0.02)	(4.27 ± 0.02)	(2.87 ± 0.03)	[95KIS/BUG], [96KIS/JEZ]
pot	0.5	(NaClO <sub>4</sub> )	25		(5.317 ± 0.007)	(4.147 ± 0.010)	(2.832 ± 0.011)	[95PII/LAJ]
pot	0.1	NaClO <sub>4</sub>	25		(5.70 ± 0.01)	(4.42 ± 0.01)	(2.99 ± 0.01)	[96CHO/ERT] <sup>d</sup> , [2001CHO/BON]
	0.3				(5.41 ± 0.01)	(4.19 ± 0.01)	(2.72 ± 0.01)	
	0.5				(5.33 ± 0.01)	(4.26 ± 0.01)	(2.92 ± 0.02)	
	1				(5.25 ± 0.01)	(4.24 ± 0.01)	(2.95 ± 0.01)	
	3.5				(5.22 ± 0.01)	(4.29 ± 0.02)	(2.96 ± 0.01)	
	6.5				(5.56 ± 0.01)	(4.63 ± 0.01)	(3.27 ± 0.01)	
	0.1	NaCl	25		(5.63 ± 0.01)	(4.36 ± 0.01)	(2.93 ± 0.01)	
	0.3				(5.38 ± 0.01)	(4.25 ± 0.01)	(2.88 ± 0.02)	
	0.5				(5.27 ± 0.01)	(4.23 ± 0.01)	(2.90 ± 0.02)	

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Table VII-2: (continued)

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_0$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$	Reference
pot	<i>I</i>	NaCl	25		(5.20 ± 0.02)	(4.18 ± 0.01)	(2.88 ± 0.05)	<a href="#">[96CHO/ERT]</a> <sup>d</sup> , <a href="#">[2001CHO/BON]</a>
	2				(5.12 ± 0.01)	(4.19 ± 0.01)	(2.87 ± 0.01)	
	3				(5.17 ± 0.01)	(4.28 ± 0.01)	(2.98 ± 0.03)	
	5				(5.35 ± 0.01)	(4.49 ± 0.01)	(3.13 ± 0.02)	
pot	0.1	Me <sub>4</sub> NCl	25		5.84	4.40	2.94	<a href="#">[96XUE/TRA]</a>
pot	0.1	(NaCl)	25		(5.643 ± 0.02)	(4.280 ± 0.015)	(2.901 ± 0.002)	<a href="#">[97BEN/PAL]</a> <sup>e</sup>
	0.3				(5.373 ± 0.02)	(4.176 ± 0.022)	(2.822 ± 0.002)	
	0.6				(5.251 ± 0.02)	(4.081 ± 0.024)	(2.752 ± 0.006)	
	1.0				(5.132 ± 0.02)	(4.066 ± 0.024)	(2.742 ± 0.008)	
pot	0.300	Me <sub>4</sub> N(Cl)	25		(5.741 ± 0.01)			<a href="#">[97FOT/GIA]</a>
	0.301				(5.737 ± 0.01)			
	0.523				(5.678 ± 0.01)			
	1.014				(5.679 ± 0.01)			
	1.014				(5.674 ± 0.01)			
	1.475				(5.687 ± 0.01)			
	1.479				(5.717 ± 0.01)			
	2.139				(5.73 ± 0.01)			
	2.141				(5.76 ± 0.01)			
	2.982				(5.803 ± 0.01)			
	2.988				(5.856 ± 0.01)			
	0.271					(4.314 ± 0.01)		
	0.271					(4.312 ± 0.01)		
	0.506					(4.265 ± 0.01)		
	1.02					(4.251 ± 0.01)		
	1.019					(4.249 ± 0.01)		
	1.509					(4.254 ± 0.01)		
	1.512					(4.276 ± 0.01)		
	2.214					(4.294 ± 0.01)		
	2.215					(4.313 ± 0.01)		
	3.114					(4.352 ± 0.01)		
	3.113					(4.388 ± 0.01)		
	0.259						(2.894 ± 0.01)	
	0.259						(2.892 ± 0.01)	
	0.505						(2.876 ± 0.01)	
	1.051						(2.885 ± 0.01)	

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Table VII-2: (continued)

Method	<i>I</i> (M)	Electrolyte	<i>t</i> (°C)	$\log_{10} K_0$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$	Reference
pot	1.051	Me <sub>4</sub> N(Cl)	25				(2.888 ± 0.01)	<a href="#">[97FOT/GIA]</a>
	1.571						(2.928 ± 0.01)	
	1.576						(2.926 ± 0.01)	
	2.325						(2.987 ± 0.01)	
	2.328						(2.991 ± 0.01)	
	3.291						3.069 ± 0.01)	
	3.298						3.082 ± 0.01)	
pot	0.3	Na(Cl)	25	(5.464 ± 0.008)	(4.25 ± 0.01)	(2.92 ± 0.04)		<a href="#">[99MIZ/BON]</a>
	1			(5.179 ± 0.005)	(4.11 ± 0.02)	(2.87 ± 0.02)		
	2			(5.076 ± 0.006)	(4.09 ± 0.01)	(2.84 ± 0.04)		
	3			(5.084 ± 0.006)	(4.116 ± 0.002)	(2.79 ± 0.01)		
	4			(5.20 ± 0.04)	(4.24 ± 0.02)	(2.93 ± 0.06)		
	5			(5.22 ± 0.04)	(4.32 ± 0.03)	(2.96 ± 0.07)		
pot	0.5	Na(Cl)	25	(5.412 ± 0.003)	(4.137 ± 0.003)	(2.817 ± 0.005)		<a href="#">[99ROB/STE]</a> <sup>f</sup>
	1			(5.275 ± 0.003)	(4.079 ± 0.003)	(2.794 ± 0.005)		
	2			(5.190 ± 0.003)	(4.093 ± 0.003)	(2.818 ± 0.005)		
	3			(5.189 ± 0.003)	(4.167 ± 0.003)	(2.880 ± 0.005)		
	5			(5.287 ± 0.003)	(4.397 ± 0.003)	3.065 ± 0.005)		
	0.5	K(Cl)	25	(5.439 ± 0.003)	(4.151 ± 0.003)	(2.822 ± 0.005)		
	1			(5.327 ± 0.003)	(4.106 ± 0.003)	(2.803 ± 0.005)		
	2			(5.288 ± 0.003)	(4.142 ± 0.003)	(2.833 ± 0.005)		
	3			(5.324 ± 0.003)	(4.233 ± 0.003)	(2.898 ± 0.005)		
	4.5			(5.432 ± 0.003)	(4.415 ± 0.003)	(3.030 ± 0.005)		
pot	1	NaClO <sub>4</sub>	25	(5.162 ± 0.003)	(4.089 ± 0.007)	(2.799 ± 0.012)		<a href="#">[2001CIA/TOM2]</a>
pot	0.2	(KCl)	25	(5.57 ± 0.02)	(4.27 ± 0.02)	(2.87 ± 0.03)		<a href="#">[2001LAK/BAN]</a>

- a: Large citrate concentrations were used in [\[40ADE\]](#), and only data at  $I \geq 1$  M are considered in this review.
- b: Protonation constants were also determined at other temperatures (10, 20, 30, 40 and 50°C) in [\[90DAN/ROB2\]](#) and [\[90ROB/STE\]](#).
- c: Results at 37°C were also reported in [\[93GLA/MAJ\]](#).
- d: Protonation constants were also determined at higher ionic strengths in [\[96CHO/ERT\]](#).
- e: Protonation constants were also determined at other temperatures (between 5 and 150°C) in [\[97BEN/PAL\]](#).
- f: Large citrate concentrations were used in [\[99ROB/STE\]](#), and only data at  $I \geq 0.5$  M are considered in this review.



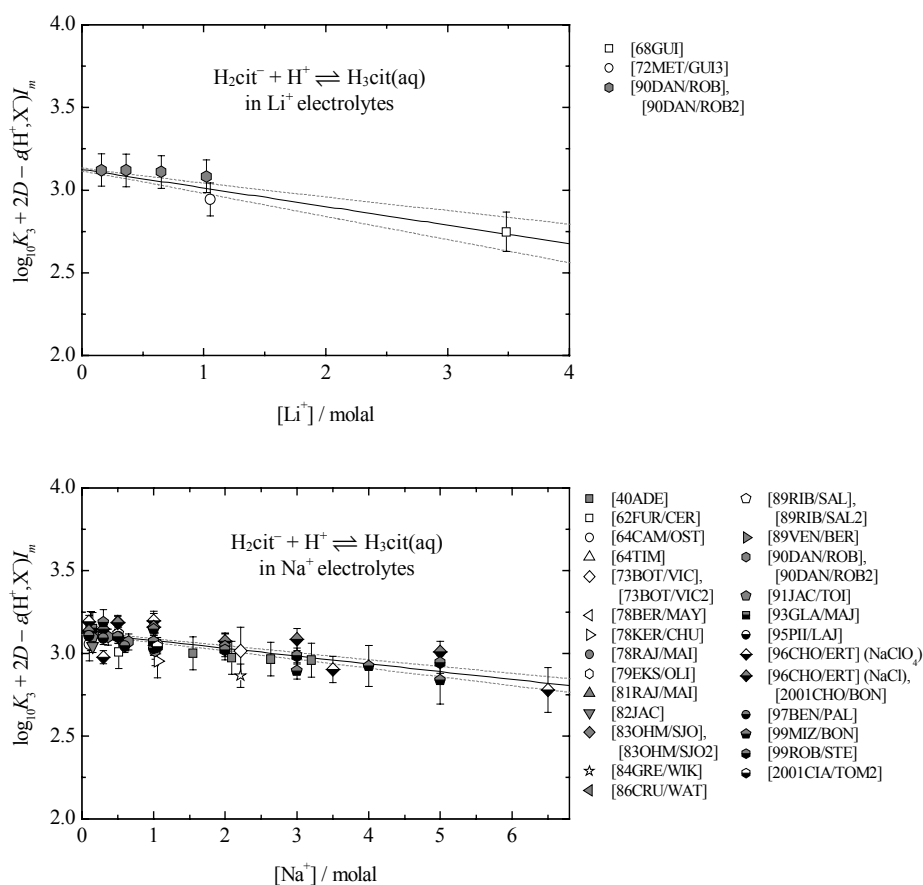
### VII.3.2 Analysis of $K_3$

The data in Table VII-2 for the third protonation of citrate,



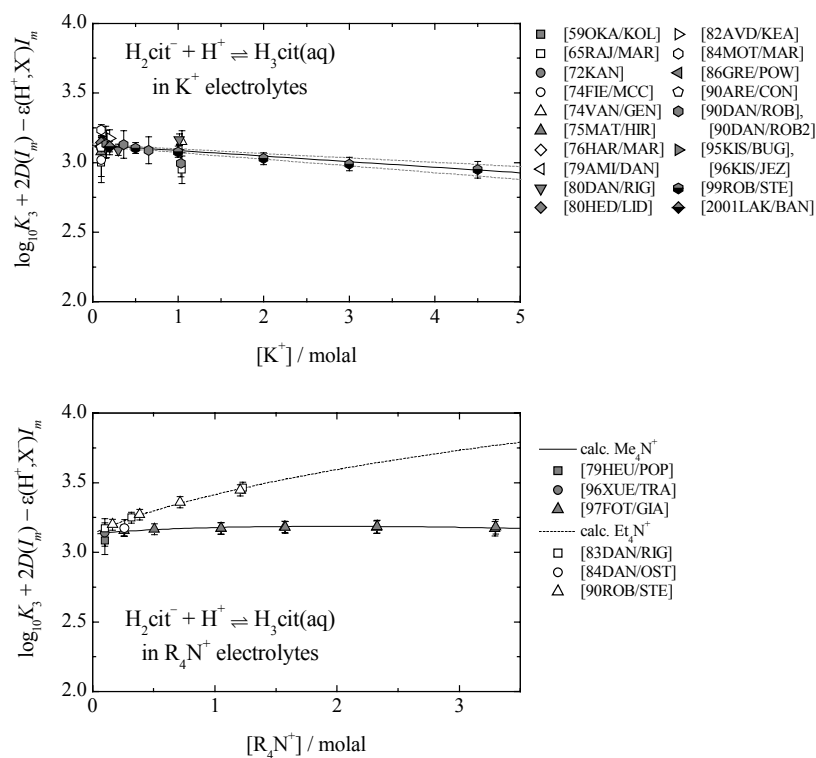
were treated with the SIT methodology described in Appendix B, using a weighted multi-linear least-squares regression procedure. This procedure assumes that a common value of  $\log_{10} K_3^\circ$  should fit all the data. For this reaction  $\Delta\epsilon_3^*(\text{VII.5}) = \epsilon(\text{H}_3\text{cit}, \text{MX}) - \epsilon(\text{H}_2\text{cit}^-, \text{M}^+)$ , where  $\text{X}^-$  and  $\text{M}^+$  are the anion and cation, respectively, of the background electrolyte, and  $\Delta z^2 = -2$ . The regression plots are shown in Figure VII-5, and the results are reported in Table VII-3.

Figure VII-5: Multi-linear least-squares SIT regression plots for the reaction:  $\text{H}_2\text{cit}^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{cit}(\text{aq})$ . Data from Table VII-2 were extrapolated to 25°C and converted to molal units in the plots.



(Continued on next page)

Figure VII-5 (Continued)

Table VII-3: Selected values of  $\log_{10} K_3^\circ$  (VII.5) and  $\Delta\varepsilon_3^*$  at 25°C.

$\log_{10} K_3^\circ$ (VII.5) = $(3.13 \pm 0.01)$	
Medium <sup>a</sup>	$\Delta\varepsilon_3^*$ (VII.5) / ( $\text{kg} \cdot \text{mol}^{-1}$ )
$\text{Li}^+$	$(0.11 \pm 0.03)$
$\text{Na}^+$	$(0.05 \pm 0.01)$
$\text{K}^+$	$(0.04 \pm 0.01)$
$\text{Me}_4\text{N}^+$	$-(0.05 \pm 0.02) + (0.07 \pm 0.04) \log_{10} [\text{Me}_4\text{N}^+]$
$\text{Et}_4\text{N}^+$	$-(0.29 \pm 0.02) + (0.2 \pm 0.1) \log_{10} [\text{Et}_4\text{N}^+]$

a:  $\text{Me}_4\text{N}^+$  and  $\text{Et}_4\text{N}^+$  represent tetramethyl- and tetraethylammonium, respectively

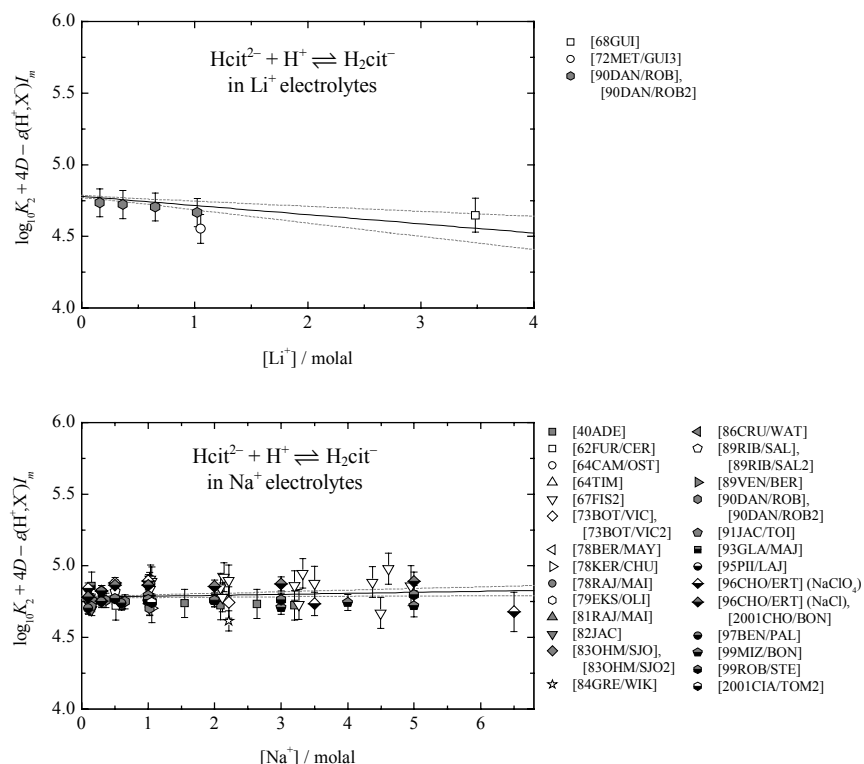
### VII.3.3 Analysis of $K_2$

The data in Table VII-2 for the second protonation of citrate:



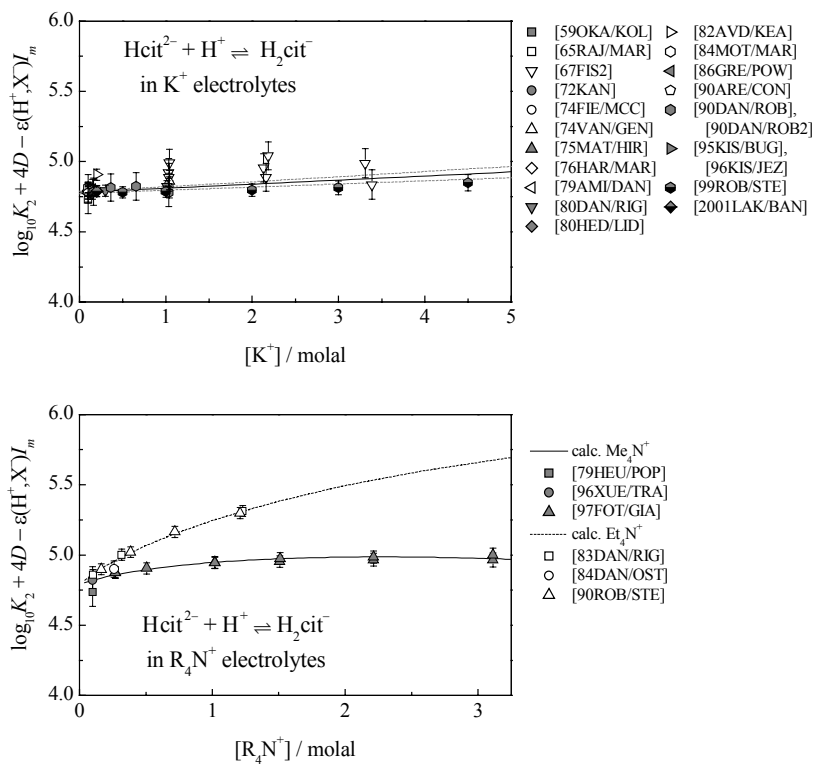
were treated with the SIT methodology described in Appendix B, using a weighted multi-linear least-squares regression procedure. This procedure assumes that a common value of  $\log_{10} K_2^\circ$  should fit all the data. For this reaction  $\Delta\epsilon_2^*(\text{VII.6}) = \epsilon(\text{H}_2\text{cit}^-, \text{M}^+) - \epsilon(\text{Hcit}^{2-}, \text{M}^+)$ , where  $\text{M}^+$  is the cation of the background electrolyte, and  $\Delta z^2 = -4$ . The regression plots are shown in Figure VII-6, and the results, with the values selected in this review, are reported in Table VII-4.

Figure VII-6: Multi-linear least-squares SIT regression plots for the reaction:  $\text{Hcit}^{2-} + \text{H}^+ \rightleftharpoons \text{H}_2\text{cit}^-$ . Data from Table VII-2 were extrapolated to 25°C and converted to molal units in the plots.



(Continued on next page.)

Figure VII-6 (Continued)

Table VII-4: Selected values of  $\log_{10} K_2^o$  (VII.6) and  $\Delta\varepsilon_2^*$  at 25°C.

$\log_{10} K_2^o$ (VII.6) = $(4.78 \pm 0.01)$	
Medium <sup>a</sup>	$\Delta\varepsilon^*$ (VII.6) / $(kg \cdot mol^{-1})$
$Li^+$	$(0.06 \pm 0.03)$
$Na^+$	$-(0.01 \pm 0.01)$
$K^+$	$-(0.03 \pm 0.01)$
$Me_4N^+$	$-(0.16 \pm 0.02) + (0.21 \pm 0.05) \log_{10} [Me_4N^+]$
$Et_4N^+$	$-(0.46 \pm 0.02) + (0.4 \pm 0.1) \log_{10} [Et_4N^+]$

a:  $Me_4N^+$  and  $Et_4N^+$  represent tetramethyl- and tetraethylammonium, respectively

### VII.3.4 Analysis of $K_1$

The values listed in Table VII-2 for the first protonation of citrate:



were plotted using the SIT methodology described in Appendix B. For the first protonation constant of citrate,  $\Delta\epsilon_1^* = \epsilon(\text{M}^+, \text{Hcit}^{2-}) - \epsilon(\text{M}^+, \text{cit}^{3-})$ , where  $\text{M}^+$  is the cation of the background electrolyte, and  $\Delta z^2 = -6$ . Regressions of the data for individual background cations ( $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and tetraalkylammonium ions) resulted in slightly different values for  $\log_{10} K_1^\circ$ , *cf.* Table VII-5.

Table VII-5: Results from regressions of experimental data obtained with each of the background cations at 25°C.

Background cation	$\log_{10} K_1^\circ$ value obtained at $I_m = 0$	$\Delta\epsilon_1^*$ / (kg·mol <sup>-1</sup> )
$\text{Li}^+$	$(6.22 \pm 0.11)$	$(0.16 \pm 0.07)$
$\text{Na}^+$	$(6.28 \pm 0.02)$	$(0.02 \pm 0.01)$
$\text{K}^+$	$(6.37 \pm 0.02)$	$-(0.01 \pm 0.02)$
$\text{Me}_4\text{N}^+$ and $\text{Et}_4\text{N}^+$	$(6.41 \pm 0.06)$	$-(0.37 \pm 0.05) + (0.43 \pm 0.08) \log_{10} [\text{Me}_4\text{N}^+]$ $-(0.77 \pm 0.05) + (0.5 \pm 0.2) \log_{10} [\text{Et}_4\text{N}^+]$

These would be the expected results if alkali-cation complexes were formed with citrate, *cf.* Section V.3 and Section VII.4. The values extrapolated to  $I_m = 0$  in the different ionic media indicated that weak complex formation perhaps takes place in  $\text{Li}^+$ -media, and to a lesser extent in  $\text{Na}^+$  electrolytes. Further data on the complex formation between citrate and alkali cations is discussed in section VII.4.

The results in potassium and  $\text{R}_4\text{N}^+$  electrolytes agreed within the uncertainties and they indicated that the value of  $\log_{10} K_1^\circ$  should be between 6.35 and 6.47. A weighted multi-linear least-squares regression of the data in  $\text{K}^+$  and  $\text{R}_4\text{N}^+$  media gave as a result  $\log_{10} K_1^\circ = (6.36 \pm 0.01)$ .

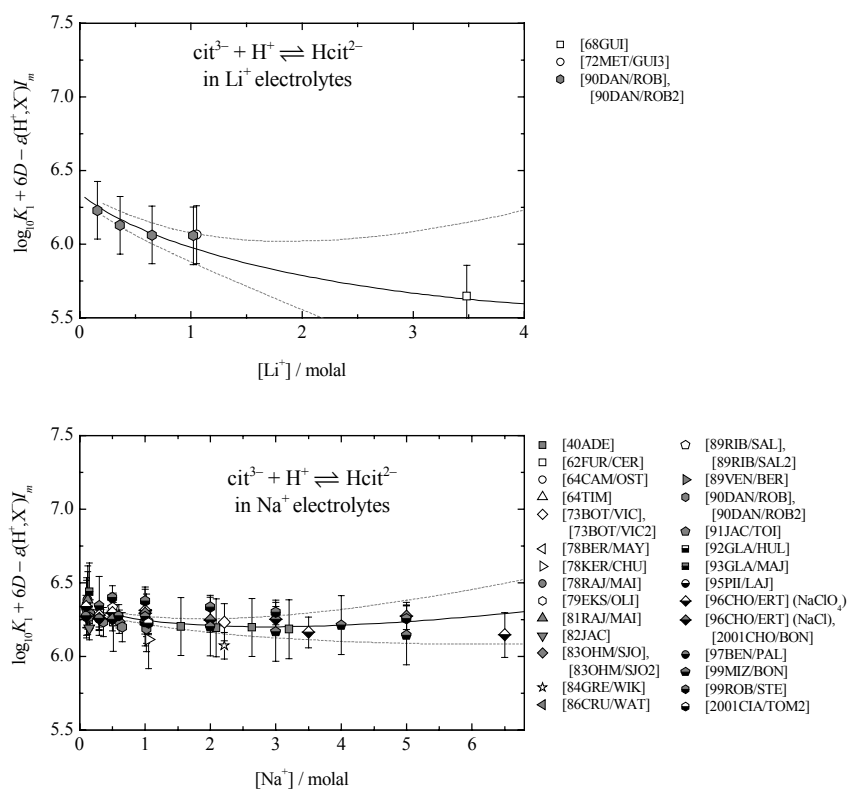
A similar weighted multi-linear least-squares regression but with the whole data set, assuming a common value of  $\log_{10} K_1^\circ$  for all ionic media, could be performed successfully by assuming that  $\Delta\epsilon_1^*$  was not independent of ionic strength in  $\text{Li}^+$ ,  $\text{Na}^+$  as well as  $\text{R}_4\text{N}^+$  electrolytes. The weights of the data in lithium and sodium media were decreased by a factor of 4 (uncertainties multiplied by  $\sqrt{4}$ ) because of the larger number of data in  $\text{Li}^+$  and  $\text{Na}^+$  media (62 values) as compared with those in  $\text{K}^+$  and  $\text{R}_4\text{N}^+$  salts (50 values). This also gave less importance to data where complex formation with background cations could introduce an unknown bias. This modified weighting is indicated in the error bars of Figure VII-7 that shows a comparison of the data with the results of the regression. Table VII-6 reports the values selected in this review, where the limits in  $\log_{10} K_1^\circ$  have been increased to reflect the uncertainties in this system.

Table VII-6: Selected values of  $\log_{10} K_1^\circ$  (VII.7) and  $\Delta\epsilon_1^*$  at 25°C.

$\log_{10} K_1^\circ = (6.36 \pm 0.02)$	
Medium <sup>a</sup>	$\Delta\epsilon_1^*/(\text{kg} \cdot \text{mol}^{-1})$
$\text{Li}^+$	$(0.38 \pm 0.10) - (0.3 \pm 0.2) \log_{10} [\text{Li}^+]$
$\text{Na}^+$	$(0.11 \pm 0.02) - (0.13 \pm 0.03) \log_{10} [\text{Na}^+]$
$\text{K}^+$	$-(0.03 \pm 0.01)$
$\text{Me}_4\text{N}^+$	$-(0.43 \pm 0.02) + (0.52 \pm 0.05) \log_{10} [\text{Me}_4\text{N}^+]$
$\text{Et}_4\text{N}^+$	$-(0.82 \pm 0.02) + (0.8 \pm 0.1) \log_{10} [\text{Et}_4\text{N}^+]$

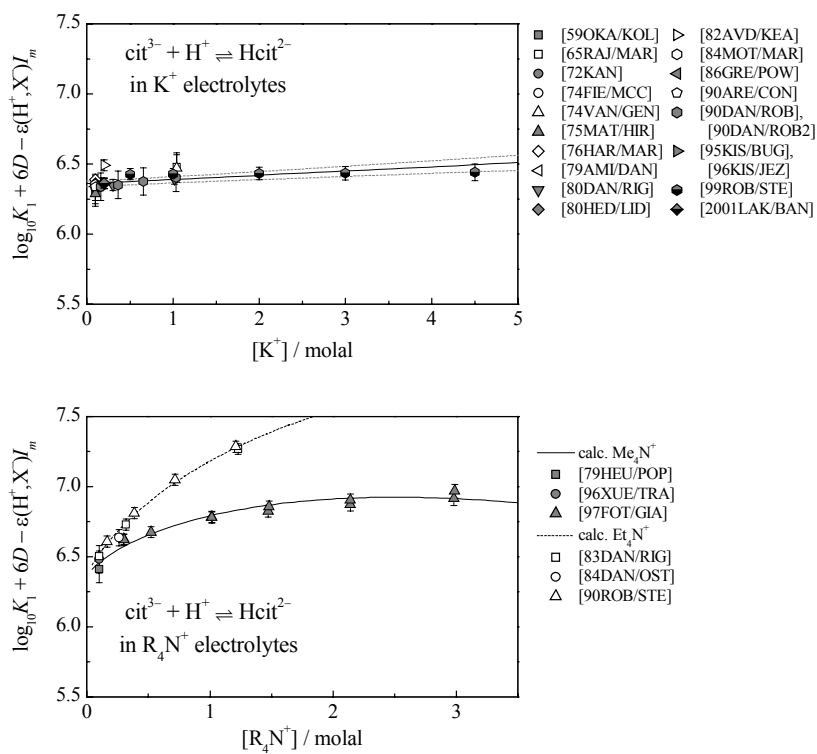
a:  $\text{Me}_4\text{N}^+$  and  $\text{Et}_4\text{N}^+$  represent tetramethyl- and tetraethylammonium, respectively

Figure VII-7: Equilibrium constants for Reaction (VII.7). Data from Table VII-2 were extrapolated to 25°C and converted to molal units and plotted according to the SIT methodology (see text for details).



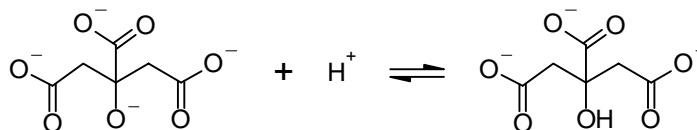
(Continued on next page)

Figure VII-7 (continued)

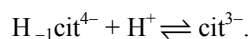


### VII.3.5 Analysis of $K_0$

The protonation of the hydroxy-group,



may be schematically written as:



The equilibrium constant for this reaction,  $K_0$ , has been reported in a few papers. Most of these studies have been made in  $\text{Na}^+$  media (Table VII-7). In contradiction with these determinations Bottari and Vicedomini found no evidence for this dissociation in  $[\text{OH}^-] \leq 0.2 \text{ M}$  using a hydrogen electrode in  $2 \text{ M NaClO}_4$  media [73BOT/VIC2].

Table VII-7: Literature data on the protonation constant for  $\text{H}_1\text{cit}^{4-}$  included in the review process.

Method	$I$	Electrolyte	$t$ ( $^\circ\text{C}$ )	$\log_{10}K_0$	Reference
pot	0.1	KCl	19	10.82	[59OKA/KOL]
pot	2	$\text{NaClO}_4$	25	$>13$	[73BOT/VIC2], [73BOT/VIC]
pot	0.12	NaCl	25	$(13.8 \pm 0.3)$	[78RAJ/MAI]
pot	0.12	NaCl	25	$(13.0 \pm 0.3)$	[81RAJ/MAI]

The experimental determination of  $K_0$  is associated with special difficulties, mainly due to the high alkalinity of the solutions ( $\log_{10}[\text{H}^+] \leq -12$ ). Under these conditions the response of the glass electrode may be affected by the sodium effect and by changes in the junction potentials. The solutions might also be unnoticeably contaminated by atmospheric  $\text{CO}_2$ . Substantial changes in the composition of the ionic media also take place for experiments conducted at  $I \lesssim 1$ , when a substantial amount of sodium hydroxide replaces the background electrolyte. Owing to all these factors, no value for  $\log_{10} K_0^\circ$  may be recommended, although it is expected to be larger than that for the protonation of  $\text{HO}^-$  (*i.e.*,  $\log_{10} K_0^\circ > 14$ ). Because of this  $\text{H}_1\text{cit}^{4-}$  can not be used as a component when calculating equilibrium constants, as done in [58HEI/FRI]. The equilibrium constant, from [57PAT/PAN2] and [65PAT/PAN2] for the reaction:



indicates a very large inductive effect on the dissociation constant of the OH-group in  $\text{cit}^{3-}$  upon coordination to Ni(II); the dissociation constant increases more than six orders of magnitude. The complex formation between Ni(II) and citrate is discussed in detail in Section VII.7.

### VII.3.6 Selected protonation constants for citrate

Summarising the results from sections VII.3.2 to VII.3.5, the selected standard values for the protonation constants of citrate are:

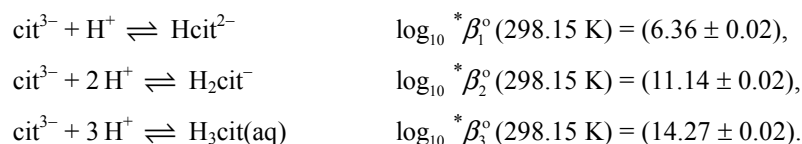
$$\log_{10} K_1^\circ ((\text{VII.7}), 298.15 \text{ K}) = (6.36 \pm 0.02),$$

$$\log_{10} K_2^\circ ((\text{VII.6}), 298.15 \text{ K}) = (4.78 \pm 0.01),$$

$$\log_{10} K_3^\circ ((\text{VII.5}), 298.15 \text{ K}) = (3.13 \pm 0.01).$$



These values correspond to the following global standard protonation constants:



In a few studies the protonation of citrate has been investigated in solutions of weak ionic strengths, and the authors used Debye-Hückel expressions for activity coefficients to obtain values for  $\log_{10} K_r^\circ$  [28KOL/BOS], [28SIM], [29BJE/UNM], [49BAT/PIN], [51HEI], [69LIT/PUR], [78FLY/KOR], [78USS/BOS], [89PAP/ZIO], [89YAD/GHO], [91APE/BAR], [96SAE/KHA]. The data from [51HEI], [96SAE/KHA] are discrepant and were not considered. The averages of the remaining data ( $\log_{10} K_r^\circ = (3.12 \pm 0.09)$ ,  $(4.77 \pm 0.08)$  and  $(6.38 \pm 0.11)$  for  $r = 3$  to 1, respectively) agree well with the values selected by this review.

Protonation constants for citrate for different ionic media may be calculated using the SIT model described in Appendix B, and the selected standard protonation constants and specific ion interaction coefficients. In Table VII-8 the results from such calculations are reported for some ionic media commonly used in chemical equilibrium studies. The distribution of the different protonated forms of citrate as a function of pH in 1 M NaCl is shown in Figure VII-8.

Figure VII-8: Calculated distribution of citrate species as a function of pH in 1 M NaCl at 25°C. The equilibrium constants listed in Table VII-8 were used to draw the curves.

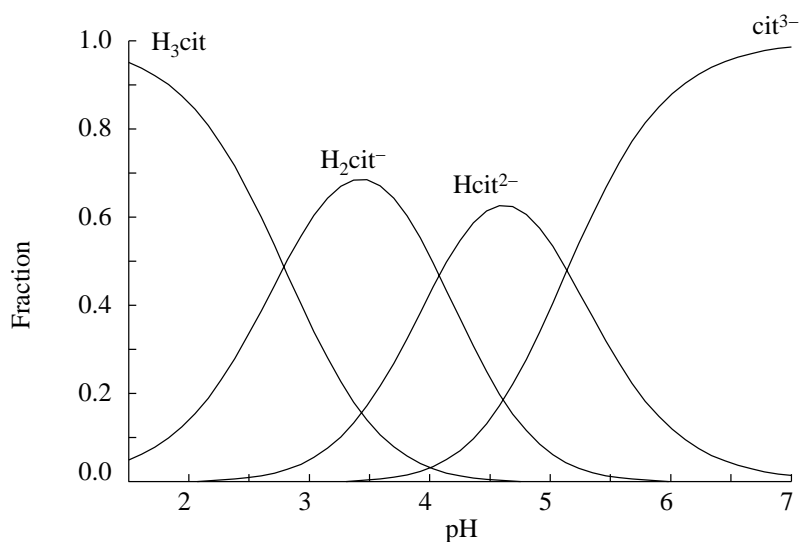


Table VII-8: Calculated equilibrium constants *in Molar units* for some  $\text{cit}^{3-} / \text{H}^+ / \text{Na}^+ / \text{K}^+$  systems at 25°C. The SIT model for activity coefficients has been used with the  $\Delta\epsilon_n$  obtained in this review. Other parameters from Appendix B were used as appropriate. Care should be exercised when using values at highest ionic strengths, because they are confirmed by few experimental data only, as indicated in the figures of Sections VII.3.2 to VII.3.4.

NaClO <sub>4</sub>				
<i>I</i> (M)	<i>I<sub>m</sub></i> (molal)	log <sub>10</sub> <i>K</i> <sub>1</sub>	log <sub>10</sub> <i>K</i> <sub>2</sub>	log <sub>10</sub> <i>K</i> <sub>3</sub>
0	0.000	(6.36 ± 0.02)	(4.78 ± 0.01)	(3.13 ± 0.01)
0.1	0.101	(5.70 ± 0.01)	(4.36 ± 0.01)	(2.92 ± 0.01)
0.25	0.254	(5.48 ± 0.01)	(4.24 ± 0.01)	(2.87 ± 0.01)
0.5	0.513	(5.31 ± 0.02)	(4.17 ± 0.02)	(2.84 ± 0.02)
0.75	0.779	(5.23 ± 0.03)	(4.14 ± 0.02)	(2.83 ± 0.02)
1	1.05	(5.18 ± 0.03)	(4.14 ± 0.03)	(2.84 ± 0.03)
2	2.21	(5.16 ± 0.07)	(4.22 ± 0.05)	(2.90 ± 0.05)
3	3.50	(5.28 ± 0.11)	(4.37 ± 0.08)	(3.01 ± 0.08)
4	4.95	(5.48 ± 0.18)	(4.57 ± 0.11)	(3.15 ± 0.11)
5	6.58	(5.76 ± 0.25)	(4.81 ± 0.15)	(3.30 ± 0.15)

NaNO <sub>3</sub>				
<i>I</i> (M)	<i>I<sub>m</sub></i> (molal)	log <sub>10</sub> <i>K</i> <sub>1</sub>	log <sub>10</sub> <i>K</i> <sub>2</sub>	log <sub>10</sub> <i>K</i> <sub>3</sub>
0	0.000	(6.36 ± 0.02)	(4.78 ± 0.01)	(3.13 ± 0.01)
0.1	0.101	(5.69 ± 0.02)	(4.35 ± 0.01)	(2.92 ± 0.01)
0.25	0.253	(5.46 ± 0.02)	(4.22 ± 0.01)	(2.85 ± 0.01)
0.5	0.509	(5.28 ± 0.02)	(4.13 ± 0.01)	(2.80 ± 0.01)
0.75	0.769	(5.17 ± 0.03)	(4.08 ± 0.01)	(2.77 ± 0.01)
1	1.03	(5.11 ± 0.03)	(4.06 ± 0.02)	(2.76 ± 0.02)
2	2.14	(5.00 ± 0.06)	(4.05 ± 0.03)	(2.74 ± 0.03)
3	3.33	(5.01 ± 0.09)	(4.10 ± 0.05)	(2.74 ± 0.05)
4	4.61	(5.08 ± 0.14)	(4.18 ± 0.07)	(2.77 ± 0.07)
5	6.02	(5.21 ± 0.20)	(4.27 ± 0.09)	(2.80 ± 0.09)

(Continued on next page)

Table VII-8 (continued)

NaCl				
$I$ (M)	$I_m$ (molal)	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$
0	0.000	(6.36 $\pm$ 0.02)	(4.78 $\pm$ 0.01)	(3.13 $\pm$ 0.01)
0.1	0.100	(5.69 $\pm$ 0.02)	(4.36 $\pm$ 0.01)	(2.92 $\pm$ 0.01)
0.25	0.252	(5.47 $\pm$ 0.02)	(4.23 $\pm$ 0.01)	(2.86 $\pm$ 0.01)
0.5	0.506	(5.30 $\pm$ 0.02)	(4.15 $\pm$ 0.01)	(2.82 $\pm$ 0.01)
0.75	0.762	(5.21 $\pm$ 0.03)	(4.12 $\pm$ 0.01)	(2.81 $\pm$ 0.01)
1	1.02	(5.15 $\pm$ 0.03)	(4.10 $\pm$ 0.02)	(2.80 $\pm$ 0.02)
2	2.09	(5.09 $\pm$ 0.06)	(4.14 $\pm$ 0.03)	(2.83 $\pm$ 0.03)
3	3.20	(5.15 $\pm$ 0.09)	(4.24 $\pm$ 0.05)	(2.89 $\pm$ 0.05)
4	4.37	(5.26 $\pm$ 0.13)	(4.36 $\pm$ 0.06)	(2.96 $\pm$ 0.06)
5	5.61	(5.42 $\pm$ 0.18)	(4.50 $\pm$ 0.08)	(3.04 $\pm$ 0.08)
KCl				
$I$ (M)	$I_m$ (molal)	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$
0	0.000	(6.36 $\pm$ 0.02)	(4.78 $\pm$ 0.01)	(3.13 $\pm$ 0.01)
0.1	0.101	(5.72 $\pm$ 0.02)	(4.36 $\pm$ 0.01)	(2.92 $\pm$ 0.01)
0.25	0.252	(5.53 $\pm$ 0.02)	(4.24 $\pm$ 0.01)	(2.86 $\pm$ 0.01)
0.5	0.509	(5.39 $\pm$ 0.02)	(4.16 $\pm$ 0.01)	(2.83 $\pm$ 0.01)
0.75	0.769	(5.33 $\pm$ 0.02)	(4.13 $\pm$ 0.01)	(2.82 $\pm$ 0.01)
1	1.03	(5.30 $\pm$ 0.02)	(4.13 $\pm$ 0.02)	(2.82 $\pm$ 0.02)
2	2.13	(5.31 $\pm$ 0.04)	(4.20 $\pm$ 0.03)	(2.86 $\pm$ 0.03)
3	3.31	(5.41 $\pm$ 0.05)	(4.33 $\pm$ 0.05)	(2.94 $\pm$ 0.05)
4	4.58	(5.55 $\pm$ 0.07)	(4.49 $\pm$ 0.07)	(3.04 $\pm$ 0.07)
KNO <sub>3</sub>				
$I$ (M)	$I_m$ (molal)	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$
0	0.000	(6.36 $\pm$ 0.02)	(4.78 $\pm$ 0.01)	(3.13 $\pm$ 0.01)
0.1	0.101	(5.72 $\pm$ 0.02)	(4.36 $\pm$ 0.01)	(2.92 $\pm$ 0.01)
0.25	0.253	(5.51 $\pm$ 0.02)	(4.23 $\pm$ 0.01)	(2.85 $\pm$ 0.01)
0.5	0.512	(5.37 $\pm$ 0.02)	(4.14 $\pm$ 0.01)	(2.80 $\pm$ 0.01)
0.75	0.776	(5.29 $\pm$ 0.02)	(4.10 $\pm$ 0.01)	(2.78 $\pm$ 0.01)
1	1.05	(5.25 $\pm$ 0.02)	(4.08 $\pm$ 0.02)	(2.77 $\pm$ 0.02)
2	2.19	(5.21 $\pm$ 0.04)	(4.10 $\pm$ 0.03)	(2.77 $\pm$ 0.03)
3	3.44	(5.27 $\pm$ 0.05)	(4.19 $\pm$ 0.05)	(2.79 $\pm$ 0.05)

It is expected that the value of  $\varepsilon(\text{H}_3\text{cit}, \text{MX})$  will be small. In this review the approximation is made that  $\varepsilon(\text{H}_3\text{cit}, \text{MX}) = (0.00 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ . Table VII-9 contains selected specific ion interaction coefficients based on this approximation and on the  $\Delta\varepsilon_n^*$  listed in previous subsections. These  $\varepsilon$ -values agree within the uncertainties with experimental water activities in  $\text{Na}_3\text{cit}$  solutions and in mixtures of  $\text{H}_3\text{cit}$ - $\text{NaCl}$ : see the discussion in Appendix A for [\[2004SCH/MAU\]](#).

Table VII-9: Selected specific ion interaction coefficients ( $\text{kg}\cdot\text{mol}^{-1}$ ) for citrate and its protonated forms in  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and tetramethylammonium electrolytes.

	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{Me}_4\text{N}^+$
$\varepsilon(\text{M}^+, \text{cit}^{3-})$	$-(0.55 \pm 0.11)$ $+ (0.3 \pm 0.2) \log_{10} I_m$	$-(0.15 \pm 0.03)$ $+ (0.13 \pm 0.03) \log_{10} I_m$	$(0.02 \pm 0.02)$	$(0.64 \pm 0.04)$ $-(0.80 \pm 0.08) \log_{10} I_m$
$\varepsilon(\text{M}^+, \text{Hcit}^{2-})$	$-(0.17 \pm 0.04)$	$-(0.04 \pm 0.02)$	$-(0.01 \pm 0.02)$	$(0.21 \pm 0.03)$ $-(0.28 \pm 0.07) \log_{10} I_m$
$\varepsilon(\text{M}^+, \text{H}_2\text{cit}^-)$	$-(0.11 \pm 0.03)$	$-(0.05 \pm 0.01)$	$-(0.04 \pm 0.01)$	$(0.05 \pm 0.02)$ $-(0.07 \pm 0.04) \log_{10} I_m$
$\varepsilon(\text{H}_3\text{cit}, \text{MX})$	$(0.00 \pm 0.01)$	$(0.00 \pm 0.01)$	$(0.00 \pm 0.01)$	$(0.00 \pm 0.01)$

### VII.3.7 Temperature effects

Temperature effects on the equilibrium constants for the protonation of citrate have been determined both calorimetrically and by the determination of the protonation constants at different temperatures. The data found in the literature are listed in Table VII-10. In addition some heats of dilution and neutralisation were presented in [29RIC/MAI].

Table VII-10: Literature data on the enthalpy changes for citrate protonation, with assigned uncertainties.

Method <sup>a</sup>	Medium <sup>b</sup>	$t$ (°C)	$\Delta_r H_m$ ((VII.8),) ( $\text{kJ}\cdot\text{mol}^{-1}$ )			Reference
			$r=1$	$r=2$	$r=3$	
$\partial pK_a / \partial T$	$\rightarrow 0$ NaCl	18 - 37	$(2.51 \pm 2.5)^c$	$-(2.18 \pm 2.5)^c$	$-(4.27 \pm 2.5)^c$	[29BJE/UNM]
$\partial pK_a / \partial T$	$\rightarrow 0$ KCl	0 - 50	$(3.36 \pm 0.64)^c$	$-(2.44 \pm 0.64)^c$	$-(4.17 \pm 0.64)^c$	[49BAT/PIN]
cal	$\approx 1$ M $(\text{H}_3\text{Na})_3\text{cit}$	23.6	3.3	-2.9	-5.0	[61BAR/BEC] <sup>d,e</sup>
cal	$\rightarrow 0$ NaClO <sub>4</sub>	25	$(3.35 \pm 0.13)$	$-(2.01 \pm 0.13)$	$-(3.97 \pm 0.13)$	[80ARE/CAL] <sup>d,e</sup>
	0.05 M		$(2.22 \pm 0.13)$	$-(3.01 \pm 0.13)$	$-(4.44 \pm 0.13)$	
	0.10		$(1.92 \pm 0.13)$	$-(3.14 \pm 0.13)$	$-(4.52 \pm 0.13)$	
	0.15		$(1.72 \pm 0.13)$	$-(3.26 \pm 0.13)$	$-(4.73 \pm 0.13)$	
$\partial pK_a / \partial T$	$\rightarrow 0$ (KNO <sub>3</sub> and Et <sub>4</sub> NBr)	37	$(3.14 \pm 0.21)$			[80DAN/RIG] <sup>d,e</sup>
$\partial pK_a / \partial T$	0.25 M $\text{K}^+/\text{Et}_4\text{N}^+$	10 - 45	$(0.5 \pm 0.8)$	$-(4.3 \pm 1.9)$	$-(4.6 \pm 3.1)$	[84DAN/OST] <sup>d,e</sup>
$\partial pK_a / \partial T$	0.1 M KNO <sub>3</sub>	10 - 45	$(3 \pm 0.7)$	$-(5 \pm 0.9)$	$-(4 \pm 1.6)$	[86CAP/ROB] <sup>d,f</sup>
cal	1 M (Na)Cl	25	$-(1.32 \pm 2)^c$	$-(4.45 \pm 2)^c$	$-(4.29 \pm 2)^c$	[86CRU/WAT] <sup>c</sup>
$\partial pK_a / \partial T$	$\rightarrow 0$ HCl	10 - 50			$-(4.23 \pm 1.2)^c$	[89YAD/GHO]
$\partial pK_a / \partial T$	$\rightarrow 0$ NaCl	10 - 50	$(1.6 \pm 0.8)^c$	$-(4.1 \pm 0.8)^c$	$-(5.4 \pm 0.8)^c$	[90DAN/ROB],
	0.16 M		$(0.4 \pm 0.8)^c$	$-(5.1 \pm 0.8)^c$	$-(5.6 \pm 0.8)^c$	[90DAN/ROB2] <sup>c</sup>
	0.36		$-(0.6 \pm 0.8)^c$	$-(6 \pm 0.8)^c$	$-(6.4 \pm 0.8)^c$	
	0.64		$-(1.2 \pm 0.8)^c$	$-(6.2 \pm 0.8)^c$	$-(6.9 \pm 0.8)^c$	
	1		$-(1.2 \pm 0.8)^c$	$-(5 \pm 0.8)^c$	$-(6.9 \pm 0.8)^c$	
$\partial pK_a / \partial T$	$\rightarrow 0$ Et <sub>4</sub> N(I)	10 - 50	$(3 \pm 0.8)^c$	$-(3.1 \pm 0.8)^c$	$-(5.0 \pm 0.8)^c$	[90ROB/STE] <sup>c</sup>
	0.16 M		$(0.5 \pm 0.8)^c$	$-(4.9 \pm 0.8)^c$	$-(6.1 \pm 0.8)^c$	
	0.36		$-(0.5 \pm 0.8)^c$	$-(5.7 \pm 0.8)^c$	$-(6.8 \pm 0.8)^c$	
	0.64		$-(1.5 \pm 0.8)^c$	$-(6.6 \pm 0.8)^c$	$-(7.7 \pm 0.8)^c$	
	1		$-(2.6 \pm 0.8)^c$	$-(7.7 \pm 0.8)^c$	$-(8.8 \pm 0.8)^c$	

(Continued on next page)

Table VII-10 (continued)

Method <sup>a</sup>	Medium <sup>b</sup>	<i>t</i> (°C)	$\Delta_r H_m$ ((VII.8),) (kJ·mol <sup>-1</sup> )		Reference
$\partial pK_a / \partial T$	$\rightarrow 0$ (Li,Na,K) <sub>3</sub> cit	5 - 35	$-(1.88 \pm 1.1)^c$	$-(3.47 \pm 1.1)^c$	[91APE/BAR]
$\partial pK_a / \partial T$	??	25 - 45 - 44.1	- 38.7	- 33.3	[91BAP] <sup>d,e</sup>
$\partial pK_a / \partial T$	$\rightarrow 0$ (H <sub>3</sub> Na) <sub>3</sub> cit	25 - 50 - 24.8	- 31.5	- 68.7	[96SAE/KHA] <sup>d,g</sup>
$\partial pK_a / \partial T$	<i>0.1 m</i> (NaCl)	5 - 150	$(1.84 \pm 1.0)^c$	$-(1.10 \pm 1.0)^c$	[97BEN/PAL] <sup>h</sup>
	<i>0.3</i>		$(1.28 \pm 1.0)^c$	$-(3.32 \pm 1.0)^c$	
	<i>0.6</i>		$-(0.64 \pm 1.0)^c$	$-(4.03 \pm 1.0)^c$	
	<i>1.0</i>		$-(1.07 \pm 1.0)^c$	$-(4.90 \pm 1.0)^c$	
cal	<i>1.03 m</i> NaCl	25	$(0.94 \pm 0.6)$	$-(3.80 \pm 0.85)$	[2001STE/FOT]
	<i>1.55</i>		$(0.00 \pm 0.6)$	$-(4.60 \pm 0.85)$	
	<i>2.08</i>		$-(0.81 \pm 0.6)$	$-(5.42 \pm 0.85)$	
	<i>3.17</i>		$-(3.00 \pm 0.6)$	$-(7.04 \pm 0.85)$	
	<i>5.41</i>		$-(4.16 \pm 0.6)$	$-(10.21 \pm 0.85)$	

a: Methods: cal = calorimetry;  $\partial pK_a / \partial T$  = temperature dependence of protonation constants.

b: Values in *italics* are reported in molal units in the original publication. Et<sub>4</sub>N<sup>+</sup> stands for tetraethylammonium.

c: Uncertainties assigned in this review.

d: Reference not included in the review procedure.

e: See comments in Appendix A.

f: The total citrate concentrations in [86CAP/ROB] were too large (up to 0.01 M) to ensure a constant ionic medium.

g: “Mixed” protonation constants, defined using concentrations for citrate species but activity for H<sup>+</sup>, were obtained in [96SAE/KHA].

h: The data from [97BEN/PAL] were recalculated in this review as described in Appendix A.

Most of the calorimetric investigations on the protonation of citrate are associated with several problems [61BAR/BEC], [80ARE/CAL], [86CRU/WAT], (*cf.* discussions in Appendix A). For example, the ionic strength was not kept constant in [61BAR/BEC], [86CRU/WAT]. Because of this, the study by [61BAR/BEC] is not considered in this review, and a large uncertainty is assigned to the values determined in [86CRU/WAT]. The study by Arena *et al.* [80ARE/CAL] is rejected because apparently the enthalpy changes were corrected for alkali cation complexation. The most extensive calorimetric study is [2001STE/FOT] and in the other extreme [84REK/GAL] contains only qualitative information on the heat of neutralisation of pH-buffers.

Reaction enthalpies were obtained in several studies by fitting the temperature variation of protonation constants to some model function. Some of these values were not included in this review because of different kinds of shortcomings:

- protonation constants mixing concentrations and activities (*i.e.*, “pH” does not refer to  $-\log_{10}H^+$ ): [96SAE/KHA],
- equilibrium constants corrected for alkali cation complexation: [80DAN/RIG],
- mixed ionic media: [84DAN/OST], [90DAN/ROB], [90DAN/ROB2].

- citrate concentration high enough to affect substantially the nature of the ionic medium: [\[86CAP/ROB\]](#),
- no details given or no original experimental data: [\[91BAP\]](#), [\[92TAN/NOM\]](#).

Most of these rejected references are discussed in Appendix A. An overview of the remaining literature values reveals that the reported enthalpy changes for the individual protonation steps:



are small:  $\Delta_r H_m$  (VII.8) values range between  $-11$  and  $+5 \text{ kJ}\cdot\text{mol}^{-1}$ , depending on the ionic media, as expected for the dissociation of carboxylic groups. The corresponding heat capacity changes,  $\Delta_r C_{p,m}$  (VII.8), are reported to be in the range  $80$  to  $260 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . For temperatures between  $0$  and  $50^\circ\text{C}$  these values correspond to quite small changes of the equilibrium constants.

Large uncertainties are expected in the determination of  $\Delta_r H_m$  from the  $T$ -variation of  $\log_{10} K$ . For the studies considered in this review that used this methodology [\[29BJE/UNM\]](#), [\[49BAT/PIN\]](#), [\[89YAD/GHO\]](#), [\[90DAN/ROB\]](#), [\[90DAN/ROB2\]](#), [\[90ROB/STE\]](#), [\[91APE/BAR\]](#), [\[97BEN/PAL\]](#) the uncertainty was estimated from the rules of error propagation and the relationship:

$$\Delta_r H_m = RT^2 \ln(10) \left( \frac{\partial \log_{10} K(T)}{\partial T} \right)_P$$

for example, for an uncertainty of  $\pm 0.02$  in the  $\log_{10} K$  values, determined over the temperature range  $5$  to  $50^\circ\text{C}$ , the total uncertainty in  $\Delta_r H_m$  was estimated to be  $\pm 1.1 \text{ kJ}\cdot\text{mol}^{-1}$ . This method was used to estimate or to increase the uncertainties in reported  $\Delta_r H_m$  data obtained from the  $T$ -variation of  $\log_{10} K$ . For this procedure the total uncertainty in the individual measurements of  $\log_{10} K$  was set to at least  $\pm 0.02 \log_{10}$ -units. For studies where both  $\Delta_r H_m$  and  $\Delta_r C_{p,m}$  were obtained from the  $T$ -variation of  $\log_{10} K$  the uncertainty assigned with the method outlined above was decreased by one third.

The selected  $\Delta_r H_m$  (VII.8) data and the corresponding uncertainties assigned by this review, listed in Table VII-10 were treated according to the SIT model (*cf.* Section V.3.6), and a multi-linear least-squares regression was performed (*cf.* Figure VII-9 to Figure VII-11). The standard enthalpy changes of reaction were found to be:

$$\begin{aligned} \Delta_r H_m^\circ ((\text{VII.8}), r=1) &= (3.3 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}, \\ \Delta_r H_m^\circ ((\text{VII.8}), r=2) &= -(2.4 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}, \\ \Delta_r H_m^\circ ((\text{VII.8}), r=3) &= -(4.5 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}. \end{aligned}$$

Figure VII-9: Enthalpy changes at 25°C for the reaction:  $\text{cit}^{3-} + \text{H}^+ \rightleftharpoons \text{Hcit}^{2-}$  plotted according to the SIT methodology.

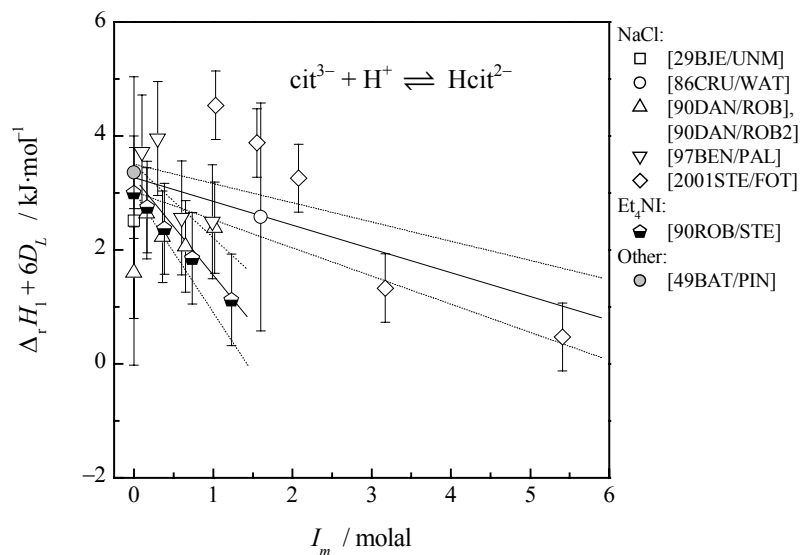


Figure VII-10: Enthalpy changes at 25°C for the reaction:  $\text{Hcit}^{2-} + \text{H}^+ \rightleftharpoons \text{H}_2\text{cit}^-$  plotted according to the SIT methodology.

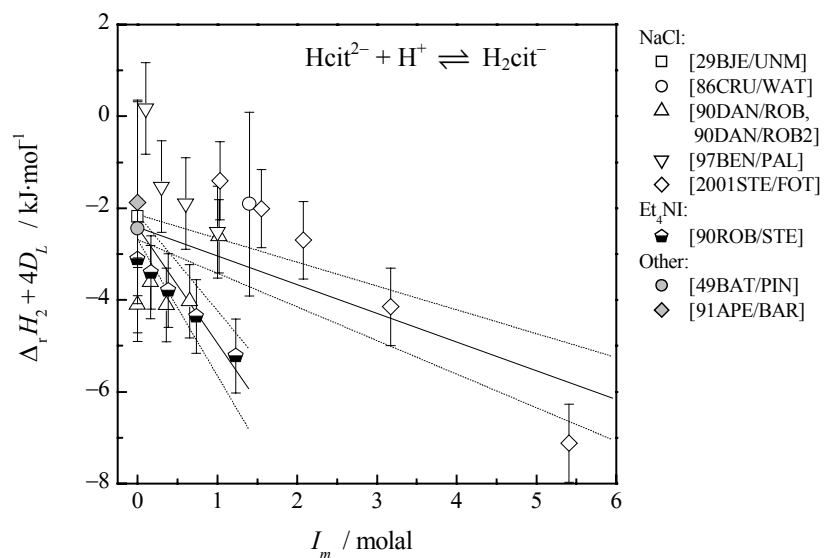
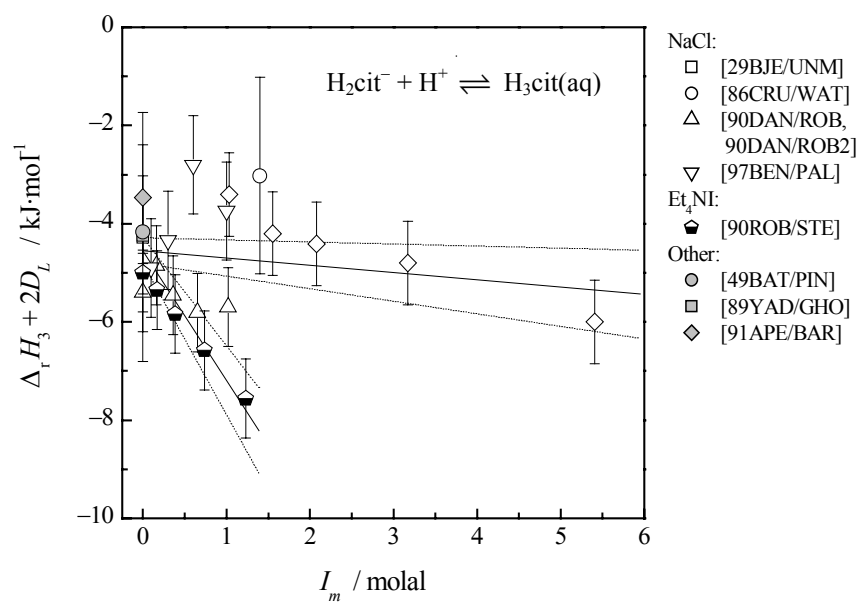


Figure VII-11: Enthalpy changes at 25°C for the reaction:  $\text{H}_2\text{cit}^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{cit}(\text{aq})$  plotted according to the SIT methodology.





From the slopes of the regressions it should be possible to obtain values for  $\Delta\epsilon_{L,r}$ . The regressions of the protonation enthalpies for citrate in NaCl solutions gave:  $\Delta\epsilon_{L,1} = (0.6 \pm 0.2) \times 10^{-3}$ ,  $\Delta\epsilon_{L,2} = (0.9 \pm 0.2) \times 10^{-3}$ , and  $\Delta\epsilon_{L,3} = (0.2 \pm 0.2) \times 10^{-3}$ ; and in Et<sub>4</sub>NI media:  $\Delta\epsilon_{L,1} = (2.5 \pm 0.8) \times 10^{-3}$ ,  $\Delta\epsilon_{L,2} = (3.4 \pm 0.8) \times 10^{-3}$ , and  $\Delta\epsilon_{L,3} = (3.6 \pm 0.8) \times 10^{-3}$  (all in units of kg·K<sup>-1</sup>·mol<sup>-1</sup>). However, because of the large uncertainties that are associated with most of the data, and because the ionic strength range studied is so limited, the  $\Delta\epsilon_L$  values are not recommended in this review.

In several cases [49BAT/PIN], [90DAN/ROB2], [90ROB/STE], [91APE/BAR], [97BEN/PAL] the constant heat capacity model was used, and the authors reported  $\Delta_r C_{p,m}$  values. Heat capacity changes have also been determined calorimetrically at a pressure of 3.5 bar and in the temperature range 5 to 120°C [2001PAT/WOO]. From the data at zero ionic strength the following weighted averages are selected:

$$\begin{aligned}\Delta_r C_{p,m}^o((\text{VII.8}), r=1) &= (222 \pm 14) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ \Delta_r C_{p,m}^o((\text{VII.8}), r=2) &= (167 \pm 8) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} \\ \Delta_r C_{p,m}^o((\text{VII.8}), r=3) &= (116 \pm 6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.\end{aligned}$$

The selections made in Section VII.3 lead to the following formation and entropy values:

$$\begin{aligned}\Delta_f G_m^o(\text{H}_2\text{cit}^-, 298.15 \text{ K}) &= -(1225.8 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f H_m^o(\text{H}_2\text{cit}^-, 298.15 \text{ K}) &= -(1519.0 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1} \\ S_m^o(\text{H}_2\text{cit}^-, 298.15 \text{ K}) &= (291.9 \pm 1.1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \\ \Delta_f G_m^o(\text{Hcit}^{2-}, 298.15 \text{ K}) &= -(1198.6 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f H_m^o(\text{Hcit}^{2-}, 298.15 \text{ K}) &= -(1516.6 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1} \\ S_m^o(\text{Hcit}^{2-}, 298.15 \text{ K}) &= (208.4 \pm 1.5) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}, \\ \Delta_f G_m^o(\text{cit}^{3-}, 298.15 \text{ K}) &= -(1162.3 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1} \\ \Delta_f H_m^o(\text{cit}^{3-}, 298.15 \text{ K}) &= -(1519.9 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1} \\ S_m^o(\text{cit}^{3-}, 298.15 \text{ K}) &= (75.6 \pm 1.9) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.\end{aligned}$$

## VII.4 Alkali metal citrate compounds and complexes

### VII.4.1 Complexes with Na<sup>+</sup> and K<sup>+</sup>

Equilibrium constants for the formation of citrate complexes with either Na<sup>+</sup> or K<sup>+</sup> are reported in several studies, *cf.* Table VII-11.

Table VII-11: Literature data on the formation of citrate complexes with alkali cations ( $M^+$  = either  $Na^+$  or  $K^+$ ). The equilibrium constants correspond to reactions:  $mM^+ + qH_rL^{(r-3)} \rightleftharpoons [M_m(H_rL)_q]^{(m+q(r-3))}$ , with  $\beta_{q,r,m} = [M_m(H_rL)_q]^{(m+q(r-3))} / [M^+]^m [H_rL^{(r-3)}]^q$ .

Method <sup>a</sup>	<i>I</i> (M)	Medium	<i>t</i> (°C)	$M^+$	$\log_{10} \beta_{1,0,1}$ $M(cit)^{2-}$	Reference
gl	0.16	Me <sub>4</sub> NCl / NaCl	25	Na <sup>+</sup>	− 0.70	[61WAL]
				K <sup>+</sup>	− 0.43	
ise	≈ 0.16	THAM <sup>b</sup> / NaCl	25	Na <sup>+</sup>	(0.70 ± 0.01)	[64REC/ZAM] <sup>b</sup>
				K <sup>+</sup>	(0.59 ± 0.01)	
gl, Δp <i>K</i> <sub>a</sub>	→ 0	Me <sub>4</sub> NCl / NaClO <sub>4</sub>	25 ?	Na <sup>+</sup>	(1.35 ± 0.05)	[80ARE/CAL] <sup>c, d</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.15 <sup>e</sup>	Et <sub>4</sub> NBr / KNO <sub>3</sub>	37	K <sup>+</sup>	(0.56 ± 0.05)	[80DAN/RIG] <sup>e, f</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.15	Et <sub>4</sub> N <sup>+</sup> / K <sup>+</sup> / Na <sup>+</sup>	37	Na <sup>+</sup>	(0.68 ± 0.05)	[81CUC/DAN] <sup>d</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.25 <sup>e</sup>	(Et <sub>4</sub> NBr / K(Cl,NO <sub>3</sub> ))	25	K <sup>+</sup>	(0.57 ± 0.03)	[84DAN/OST] <sup>c, e</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.25 <sup>e</sup>	(Et <sub>4</sub> N <sup>+</sup> / NaNO <sub>3</sub> )	25	Na <sup>+</sup>	(0.68 ± 0.05)	[85DAN/ROB] <sup>e</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.1	Et <sub>4</sub> NI / (Na,K)Cl	25	Na <sup>+</sup>	1.03	[90DAN/ROB], [90DAN/ROB2] <sup>c, f, g</sup>
	0.5				1.03	
	1				1.21	
	0.1			K <sup>+</sup>	0.90	
	0.5				0.91	
	1				1.08	
ise	→ 0	(Me <sub>4</sub> N)Cl	25	Na <sup>+</sup>	(1.43 ± 0.02)	[95ROB/GIA] <sup>f, h</sup>
	0.1				(0.93 ± 0.02)	
	0.16				(0.88 ± 0.02)	
	→ 0			K <sup>+</sup>	(1.42 ± 0.05)	
	0.1				(0.92 ± 0.05)	
	0.16				(0.87 ± 0.05)	
Method <sup>a</sup>	<i>I</i> (M)	Medium	<i>t</i> (°C)	$M^+$	$\log_{10} \beta_{1,0,2}$ $M_2(cit)^-$	Reference
gl, Δp <i>K</i> <sub>a</sub>	0.1	(Et <sub>4</sub> NI / (Na,K)Cl)	25	Na <sup>+</sup>	1.48	[90DAN/ROB], [90DAN/ROB2] <sup>c, f, g</sup>
	0.5				1.50	
	1				1.91	
	0.1			K <sup>+</sup>	1.03	
	0.5				1.05	
	1				1.35	
ise	→ 0	(Me <sub>4</sub> N)Cl	25	Na <sup>+</sup>	(2.31 ± 0.02)	[95ROB/GIA] <sup>f, h</sup>
	0.1				(1.47 ± 0.02)	
	0.16				(1.39 ± 0.02)	
	→ 0			K <sup>+</sup>	(1.95 ± 0.06)	
	0.1				(1.11 ± 0.06)	
	0.16				(1.04 ± 0.06)	

(Continued on next page)

Table VII-11: (continued)

Method <sup>a</sup>	<i>I</i> (M)	Medium	<i>t</i> (°C)	M <sup>+</sup>	log <sub>10</sub> β <sub>1,1,1</sub> M(Hcit) <sup>−</sup>	Reference
gl, Δp <i>K</i> <sub>a</sub>	→ 0	Me <sub>4</sub> NCl / NaClO <sub>4</sub>	25 ?	Na <sup>+</sup>	(0.6 ± 0.1)	[80ARE/CAL] <sup>c, d</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.15 <sup>e</sup>	Et <sub>4</sub> NBr / KNO <sub>3</sub>	37	K <sup>+</sup>	− (0.30 ± 0.02)	[80DAN/RIG] <sup>e, f</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.15	Et <sub>4</sub> N <sup>+</sup> / K <sup>+</sup> / Na <sup>+</sup>	37	Na <sup>+</sup>	(0.10 ± 0.15)	[81CUC/DAN] <sup>d</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.25 <sup>e</sup>	(Et <sub>4</sub> NBr / K(Cl,NO <sub>3</sub> ))	25	K <sup>+</sup>	(0.11 ± 0.09)	[84DAN/OST] <sup>c, e</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.25 <sup>e</sup>	(Et <sub>4</sub> N <sup>+</sup> / NaNO <sub>3</sub> )	25	Na <sup>+</sup>	(0.06 ± 0.07))	[85DAN/ROB] <sup>c</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.1	(Et <sub>4</sub> N <sup>+</sup> / (Na,K)Cl)	25	Na <sup>+</sup>	0.53	[90DAN/ROB] <sup>c, f, g</sup>
	0.5				0.54	
	1				0.68	
	0.1			K <sup>+</sup>	0.33	
	0.5				0.34	
	1				0.47	
Method <sup>a</sup>	<i>I</i> (M)	Medium	<i>t</i> (°C)	M <sup>+</sup>	log <sub>10</sub> β <sub>1,2,1</sub> M(H <sub>2</sub> cit)aq	Reference
gl, Δp <i>K</i> <sub>a</sub>	→ 0	Me <sub>4</sub> NCl / NaClO <sub>4</sub>	25 ?	Na <sup>+</sup>	(0.25 ± 0.1)	[80ARE/CAL] <sup>c, d</sup>
gl, Δp <i>K</i> <sub>a</sub>	0.25 <sup>e</sup>	(Et <sub>4</sub> NBr / K(Cl,NO <sub>3</sub> ))	25	K <sup>+</sup>	− (0.20 ± 0.15)	[84DAN/OST] <sup>c, e</sup>

- a: Methods: gl = pH-glass electrode; ise = ion selective electrode; Δp*K*<sub>a</sub> = the formation constants for alkali-metal complexation were obtained from differences in protonation constants determined in different background electrolytes (alkali electrolytes *versus* tetraalkylammonium salts).
- b: THAM = tris(hydroxymethyl)aminomethane, (HOCH<sub>2</sub>)<sub>3</sub>CNH<sub>2</sub>. The possibility of Na<sup>+</sup> complexes with THAM was not considered.
- c: Δ<sub>r</sub>*H*<sub>m</sub> and Δ<sub>r</sub>*S*<sub>m</sub> values are also reported.
- d: Combined measurements in NaClO<sub>4</sub> with previous literature data in tetraalkylammonium electrolytes, *cf.* Appendix A.
- e: A broader range of ionic strengths was studied, but only values at one ionic strength were reported.
- f: Included the formation of ion pairs in the background electrolyte (NaCl(aq), KCl(aq), or KNO<sub>3</sub>(aq)).
- g: Reported also the following equilibrium constants: log<sub>10</sub> *K* = (0.64 ± 0.03) and (0.73 ± 0.08) for: K<sub>2</sub>(cit)<sup>−</sup> + Na<sub>2</sub>(cit)<sup>−</sup> ⇌ 2 KNa(cit)<sup>−</sup> and Na<sub>2</sub>(Hcit)(aq) + K<sub>2</sub>(Hcit)(aq) ⇌ 2 KNa(Hcit)(aq), respectively.
- h: The ionic strength was not kept constant during the experiments.

Two experimental methods have been used: emf measurements with ion-selective electrodes, and comparison of protonation constants obtained in different ionic media.

The latter approach is based on the assumption that tetraalkylammonium ions do not form ion pairs with citrate anions, and that any differences in the values for the protonation constants in different media with the same ionic strength are due to the formation of alkali-metal complexes. However, a comparison between the following two values (*cf.* Table VII-2):

$$\log_{10} K_1 = (6.02 \pm 0.02)^1 \text{ in } 1.21 \text{ m Et}_4\text{NI at } 25^\circ\text{C, [90ROB/STE]}$$

$$\log_{10} K_1 = (5.67 \pm 0.01) \text{ in } 1.014 \text{ m Me}_4\text{NCl at } 25^\circ\text{C, [97FOT/GIA]}$$

reveals that specific ion interactions (activity coefficient effects) also may induce differences in protonation constants. There is therefore a large uncertainty associated with all the references that used this methodology (labelled “ $\Delta pK_a$ ” in Table VII-11). With this method the existence of protonated complexes has also been postulated ( $M(\text{Hcit})^-$  and  $M(\text{H}_2\text{cit})(\text{aq})$ ), but these complexes must be regarded with scepticism when considering the uncertainties associated with this technique.

Two studies used ion-selective electrodes to determine the stability of citrate complexes with  $\text{Na}^+$  and  $\text{K}^+$  [64REC/ZAM], [95ROB/GIA]. Both studies have an important limitation in their experimental methodology: the ionic strength was not accurately controlled. Rechnitz and Zamochnick [64REC/ZAM] “adjusted” the ionic strength with THAM (tris(hydroxymethyl)aminomethane,  $(\text{HOCH}_2)_3\text{CNH}_2$ ), a compound usually used as pH-buffer, without investigating the possibility of formation of sodium complexes with THAM (see [82SIG/SCH]). Furthermore, the concentration of  $\text{cit}^{3-}$  in these experiments (10 mM) had a large contribution to the total ionic strength, as compared with the concentrations of the “background” electrolyte (0.1 M  $(\text{HOCH}_2)_3\text{CNH}_3^+$  and 0.2 M  $(\text{HOCH}_2)_3\text{CNH}_2$ ).

De Robertis *et al.* [95ROB/GIA] also used a Na-sensitive glass electrode, and they described in their paper that “our measurements were carried out at different ionic strength values, and vary substantially during the experiments”. The equilibrium constants reported by these authors are therefore dependent on their model for activity coefficients. Furthermore, the authors also considered the formation of weak ion pairs, such as  $\text{NaCl}(\text{aq})$  and  $\text{KCl}(\text{aq})$ , in disagreement with the SIT methodology used in this review. Calculations using the equilibrium constants reported by De Robertis *et al.* [95ROB/GIA] indicate that the complexes  $\text{Na}_2(\text{cit})^-$  and  $\text{K}_2(\text{cit})^-$  were always below 8% of the total alkali metal. Therefore the existence of these complexes should not be considered as completely proven.

In conclusion, although there is some evidence suggesting the formation of citrate complexes with  $\text{Na}^+$  and  $\text{K}^+$ , there are many uncertainties concerning their stoichiometry and stability, and the complexes, if formed, are weak ( $K \lesssim 10 \text{ kg}\cdot\text{mol}^{-1}$ ). In this review the interactions between alkali-metal ions and citrate at  $25^\circ\text{C}$  are instead treated as specific ion interaction effects included in the activity coefficients, *cf.* Section VII.3.

Enthalpy changes for citrate complexation with  $\text{Na}^+$  and  $\text{K}^+$  have been reported in three studies (Table VII-11), but as in the case of the equilibrium constants, no enthalpy changes can be recommended by this review. In [84DAN/OST], [90DAN/ROB],

<sup>1</sup> The equilibrium constant and ionic strength have been converted to molal units. The original value was  $\log_{10} K_1 = (6.099 \pm 0.02)$  in 1 M  $\text{Et}_4\text{NI}$  [90ROB/STE].

[90DAN/ROB2], values of  $\Delta_r H_m^\circ$  for the formation of citrate complex,  $(M(\text{cit})^{2-})$ , were obtained from the temperature variation of formation constants, which were obtained by comparing protonation constants obtained in different ionic media. Because the temperature variations are small and the uncertainties with this methodology large, these data are not considered by this review. In [80ARE/CAL], enthalpy changes for  $\text{Na}^+$  - citrate complexation were determined calorimetrically, without specifying how this was performed, and therefore these data can not be included in this review.

## VII.5 Magnesium and calcium citrate compounds and complexes

### VII.5.1 Magnesium and calcium citrate complexes

The experimental equilibrium data found in the literature on the complex formation of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  with citrate are listed in Table VII-12.

Table VII-12: Literature data on the formation constants for citrate complexes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The uncertainties are given as reported in the references.

Method	Ionic medium	$t$ ( $^\circ\text{C}$ )	$\log_{10} \beta^a$	Reference
$\text{Mg}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Mg}(\text{cit})^-$				
(b)	0.155–0.163 M (NaCl)	22	3.22	[34HAS/MCL]
sol	0.08 M (NaCl + $\text{K}_2\text{SO}_4$ )	37	3.58	[39NOR]
pol	0.09 M	25	3.29	[59LI/LIN]
pot	0.16 M ( $(\text{CH}_3)_4\text{NCl}$ , NaCl or KCl)	25	3.55	[61WAL]
cix	0.1 M $\text{NH}_4\text{Cl}$	25	3.16	[63TOB/MIL]
sp	0.1 M Tris and Tea	25	3.63	[63WAT/TRO]
pot	0.1 M ( $\text{NaClO}_4$ )	20	3.40	[64CAM/OST]
cix	0.01–0.09 M (NaCl) $\rightarrow 0$	25	3.96	[64TOB/MIL]
pot		32.5	3.46	[65PAT/PAN]
pot	0.1 M $(\text{CH}_3)_4\text{NCl}$	25	3.73	[65TAT/GRZ]
pot	0.1 M ( $(\text{CH}_3)_4\text{NCl}$ )	25	3.85	[70GRZ/TAT]
pot	0.15 M NaCl	37	3.34	[74MEY]
pot	0.1 M $\text{KNO}_3$	25	$(3.38 \pm 0.07)$	[75FIE/COB]
pot	0.1 M $\text{KNO}_3$	25	3.63	[80PEA]
pot	0.03 M ( $\text{KNO}_3$ )	37	$(3.940 \pm 0.005)$	[82AMI/DAN]
pot	0.1 M ( $\text{KNO}_3$ )	37	$(3.451 \pm 0.005)$	[82AMI/DAN]
pot	0.3 M ( $\text{KNO}_3$ )	37	$(3.068 \pm 0.005)$	[82AMI/DAN]
(c)	$\rightarrow 0$	25	$(4.92 \pm 0.05)$	[82HIR/KIS]
pot	0.1 M (NaCl)	25	$(3.46 \pm 0.06)$	[85RIZ/ANT]
pot	0.15 M $\text{NaClO}_4$	37	$(3.33 \pm 0.01)$	[87BLA/BER]
pot	1.0 M $\text{NaClO}_4$	30 ?	3.62	[88GHA/MAN]

(Continued on next page)

Table VII-12: (continued)

Method	Ionic medium	<i>t</i> (°C)	$\log_{10} \beta^a$	Reference
$\text{Mg}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Mg}(\text{cit})^-$				
cou	0.15 M NaCl	25	3.27	[93GLA/MAJ]
cou	0.15 M NaCl	37	3.24	[93GLA/MAJ]
pot	0.5 M NaClO <sub>4</sub>	25	(2.71 ± 0.01)	[95PII/LAJ]
pot	0.3 m NaCl	25	(2.97 ± 0.01)	[2001CHO/BON]
pot	1 m NaCl	25	(2.40 ± 0.03)	[2001CHO/BON]
pot	2 m NaCl	25	(1.97 ± 0.05)	[2001CHO/BON]
pot	3 m NaCl	25	(2.02 ± 0.04)	[2001CHO/BON]
pot	4 m NaCl	25	(2.08 ± 0.02)	[2001CHO/BON]
pot	5 m NaCl	25	(2.07 ± 0.02)	[2001CHO/BON]
pot	0.1 M NaCl	25	(3.31 ± 0.02)	[2001SAR]
$\text{Mg}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Mg}(\text{Hcit})(\text{aq})$				
pol	0.09 M	25	1.60	[59LI/LIN]
pot	0.1 M (NaClO <sub>4</sub> )	20	1.84	[64CAM/OST]
pot	0.1 M (CH <sub>3</sub> ) <sub>4</sub> NCl	25	1.85	[65TAT/GRZ]
pot	0.1 M ((CH <sub>3</sub> ) <sub>4</sub> NCl)	25	1.92	[70GRZ/TAT]
pot	0.15 M NaCl	37	1.62	[74MEY]
pot	0.1 M KNO <sub>3</sub>	25	(1.96 ± 0.19)	[75FIE/COB]
pot	0.1 M KNO <sub>3</sub>	25	1.78	[80PEA]
pot	0.03 M (KNO <sub>3</sub> )	37	(1.79 ± 0.05)	[82AMI/DAN]
pot	0.1 M (KNO <sub>3</sub> )	37	(1.51 ± 0.07)	[82AMI/DAN]
pot	0.3 M (KNO <sub>3</sub> )	37	(1.60 ± 0.03)	[82AMI/DAN]
(c)	→ 0	25	(1.67 ± 1.20)	[82HIR/KIS]
pot	0.1 M (NaCl)	25	(2.13 ± 0.10)	[85RIZ/ANT]
pot	0.15 M NaClO <sub>4</sub>	37	(1.94 ± 0.02)	[87BLA/BER]
pot	0.5 M NaClO <sub>4</sub>	25	(1.23 ± 0.12)	[95PII/LAJ]
pot	0.3 m NaCl	25	(1.7 ± 0.2)	[2001CHO/BON]
pot	1 m NaCl	25	(1.1 ± 0.1)	[2001CHO/BON]
pot	2 m NaCl	25	(0.77 ± 0.01)	[2001CHO/BON]
pot	3 m NaCl	25	(0.98 ± 0.02)	[2001CHO/BON]
pot	4 m NaCl	25	(1.2 ± 0.1)	[2001CHO/BON]
pot	5 m NaCl	25	(1.2 ± 0.1)	[2001CHO/BON]
pot	0.1 M NaCl	25	(2.18 ± 0.03)	[2001SAR]
$\text{Mg}^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Mg}(\text{H}_2\text{cit})^+$				
pot	0.1 M NaClO <sub>4</sub>	20	0.84	[64CAM/OST]
pot	0.1 M KNO <sub>3</sub>	25	0.60	[80PEA]
pot	0.15 M NaClO <sub>4</sub>	37	(1.23 ± 0.06)	[87BLA/BER]
pot	0.1 M NaCl	25	(1.66 ± 0.4)	[2001SAR]

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Table VII-12: (continued)

Method	Ionic medium	<i>t</i> (°C)	$\log_{10} \beta^a$	Reference
$\text{Mg}^{2+} + 2\text{cit}^{3-} + \text{H}^+ \rightleftharpoons \text{Mg}_2\text{H}(\text{cit})_2^{3-}$				
pot	0.15 M NaClO <sub>4</sub>	37	(10.41 ± 0.07)	[87BLA/BER]
pot	0.1 M NaCl	25	(11.00 ± 0.02)	[2001SAR]
$\text{Mg}^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{Mg}(\text{cit})_2^{4-}$				
pot	0.15 M NaClO <sub>4</sub>	37	(5.13 ± 0.04)	[87BLA/BER]
pot	0.1 M NaCl	25	(5.17 ± 0.02)	[2001SAR]
$\text{Mg}^{2+} + \text{cit}^{3-} - \text{H}^+ \rightleftharpoons \text{MgH}_1(\text{cit})^{2-}$				
pot	0.1 M NaCl	25	-(8.51 ± 0.03)	[2001SAR]
$2\text{Mg}^{2+} + 2\text{cit}^{3-} - 2\text{H}^+ \rightleftharpoons \text{Mg}_2\text{H}_2(\text{cit})_2^{4-}$				
pot	0.15 M NaClO <sub>4</sub>	37	-(12.64 ± 0.03)	[87BLA/BER]
$\text{Mg}^{2+} + \text{cit}^{3-} - 2\text{H}^+ \rightleftharpoons \text{MgH}_2(\text{cit})^{3-}$				
pot	0.15 M NaClO <sub>4</sub>	37	-(18.47 ± 0.02)	[87BLA/BER]
pot	0.1 M NaCl	25	-(21.13 ± 0.07)	[2001SAR]
$\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$				
(b)	0.155–0.163 M (NaCl)	22	(3.23 ± 0.03)	[34HAS/MCL]
sol	0.155–0.163 M (NaCl + KIO <sub>3</sub> )	25	3.21	[36MUU/LEB]
sol	0.08 M (NaCl + K <sub>2</sub> SO <sub>4</sub> )	37	3.50	[39NOR]
ise–Ca <sup>2+</sup>	0.04 – 0.31 m (NaCl) → 0.15 m (NaCl)	25	3.17	[46JOS]
dialysis	0.03 M	2	3.46	[48PYN]
pot	→ 0	r. t.	(4.84 ± 0.01)	[51HEI]
cix	0.16 M NaCl	25	(3.15 ± 0.01)	[52SCH/LIN]
pot	0.15 M NaCl	28	3.12	[57LEF]
pot	?	33	3.42	[61PAT/PAN]
pot	0.16 M ((CH <sub>3</sub> ) <sub>4</sub> NCl, NaCl or KCl)	25	3.15	[61WAL]
cix	0.16 M NaCl	25	3.16	[63MAT]
pot	0.1 M NaClO <sub>4</sub>	20	3.55	[64CAM/OST]
pot	0.1 M (KNO <sub>3</sub> )	20	3.24	[69BOS/MAR]
ise–Ca <sup>2+</sup>	0.1 M NaClO <sub>4</sub>	25	3.67	[69REC/HSE]
cix	0.2 M NH <sub>4</sub> Cl	19.6	(3.15 ± 0.015)	[71RUM]
cix	0.2 M NH <sub>4</sub> Cl	28.2	(3.10 ± 0.015)	[71RUM]
cix	0.2 M NH <sub>4</sub> Cl	38	(3.04 ± 0.015)	[71RUM]
cix	0.2 M NH <sub>4</sub> Cl	51.4	(2.97 ± 0.015)	[71RUM]
cix	0.2 M NH <sub>4</sub> Cl	65.0	(2.82 ± 0.015)	[71RUM]
pot	0.15 M NaCl	37	3.27	[74MEY]
pot	0.1 M KNO <sub>3</sub>	25	(3.50 ± 0.06)	[75FIE/COB]

(Continued on next page)

Table VII-12: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$				
pot	0.1 M (NaClO <sub>4</sub> )	25	3.54	[75RAM/MAN]
?	?	?	2.95	[79BUL/SAC]
ise-Ca <sup>2+</sup>	0.1 M (NaCl)	25	(3.42 ± 0.06)	[79CRA/MOO]
pot	0.1 M KNO <sub>3</sub>	25	3.64	[80PEA]
pot	→ 0	25	4.87	[80PEA]
pot	0.03 M (KNO <sub>3</sub> )	37	(3.909 ± 0.003)	[82AMI/DAN]
pot	0.1 M (KNO <sub>3</sub> )	37	(3.485 ± 0.006)	[82AMI/DAN]
pot	0.3 M (KNO <sub>3</sub> )	37	(2.936 ± 0.007)	[82AMI/DAN]
(c)	→ 0	25	(4.85 ± 0.05)	[82HIR/KIS]
pot	0.1 M (NaCl)	25	(3.43 ± 0.04)	[85RIZ/ANT]
pot	0.15 M NaClO <sub>4</sub>	37	(3.36 ± 0.01)	[87BLA/BER]
pot	1.0 M NaClO <sub>4</sub>	30 ?	3.02	[88GHA/MAN]
ise-Ca <sup>2+</sup>	0.0198 M NaCl	37	(3.23 ± 0.02)	[91SIN/YEB]
ise-Ca <sup>2+</sup>	0.056 M NaCl	37	(3.27 ± 0.04)	[91SIN/YEB]
ise-Ca <sup>2+</sup>	0.15 M NaCl	37	(3.69 ± 0.01)	[91SIN/YEB]
ise-Ca <sup>2+</sup>	0.17 M NaCl	37	(4.08 ± 0.05)	[91SIN/YEB]
ise-Ca <sup>2+</sup>	0.15 M NaCl	18	3.27	[91SIN/YEB]
ise-Ca <sup>2+</sup>	0.15 M NaCl	25	3.26	[91SIN/YEB]
ise-Ca <sup>2+</sup>	0.15 M NaCl	37	3.27	[91SIN/YEB]
ise-Ca <sup>2+</sup>	0.15 M NaCl	45	3.25	[91SIN/YEB]
sol	0.15 M NaCl	37	3.29	[91SIN/YEB]
cou	0.1 M NaClO <sub>4</sub>	25	3.5	[92GLA/HUL]
cou	0.15 M NaCl	25	3.17	[93GLA/MAJ]
cou	0.15 M NaCl	37	3.28	[93GLA/MAJ]
pot	0.5 M NaClO <sub>4</sub>	25	(2.71 ± 0.01)	[95PII/LAJ]
cal	0.1 M (NaCl)	25	(3.42 ± 0.02)	[96MIR/PAS]
cal	0.2 M (NaCl)	25	(3.11 ± 0.02)	[96MIR/PAS]
cal	0.3 M (NaCl)	25	(2.83 ± 0.02)	[96MIR/PAS]
cal	0.4 M (NaCl)	25	(2.70 ± 0.02)	[96MIR/PAS]
cal	0.5 M (NaCl)	25	(2.38 ± 0.02)	[96MIR/PAS]
cal	→ 0	25	(4.80 ± 0.03)	[96MIR/PAS]
pot	0.1 M NaCl	25	(3.38 ± 0.1)	[2001SAR]

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Table VII-12: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{Ca}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Ca}(\text{Hcit})(\text{aq})$				
sol	0.110 M (NaCl + KIO <sub>3</sub> )	25	2.3	[36MUU/LEB]
pot	→ 0	r. t.	(3.29 ± 0.01)	[51HEI]
sol	0.03–0.06 M → 0		3.09	[53DAV/HOY]
cix	0.16 M NaCl	25	2.67	[63MAT]
pot	0.1 M (NaClO <sub>4</sub> )	20	2.10	[64CAM/OST]
pot	0.15 M NaCl	37	1.82	[74MEY]
pot	0.1 M KNO <sub>3</sub>	25	(2.32 ± 0.15)	[75FIE/COB]
pot	0.1 M KNO <sub>3</sub>	25	2.03	[80PEA]
pot	→ 0	25	3.03	[80PEA]
pot	0.03 M (KNO <sub>3</sub> )	37	(2.23 ± 0.02)	[82AMI/DAN]
pot	0.1 M (KNO <sub>3</sub> )	37	(2.09 ± 0.02)	[82AMI/DAN]
pot	0.3 M (KNO <sub>3</sub> )	37	(1.65 ± 0.05)	[82AMI/DAN]
(c)	→ 0	25	(2.79 ± 0.13)	[82HIR/KIS]
pot	0.1 M (NaCl)	25	(2.80 ± 0.20)	[85RIZ/ANT]
pot	0.15 M NaClO <sub>4</sub>	37	(2.08 ± 0.02)	[87BLA/BER]
pot	0.5 M NaClO <sub>4</sub>	25	(1.38 ± 0.09)	[95PII/LAJ]
pot	0.1 M NaCl	25	(2.07 ± 0.02)	[2001SAR]
$\text{Ca}^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Ca}(\text{H}_2\text{cit})^+$				
sol	0.03–0.06 M → 0		1.10	[53DAV/HOY], [55DAV/HOY]
pot	0.1 M (NaClO <sub>4</sub> )	20	1.05	[64CAM/OST]
pot	0.1 M KNO <sub>3</sub>	25	1.04	[80PEA]
pot	0.15 M NaClO <sub>4</sub>	37	(1.23 ± 0.03)	[87BLA/BER]
pot	0.1 M NaCl	25	(1.18 ± 0.04)	[2001SAR]
$\text{Ca}^{2+} + 2\text{cit}^{3-} + \text{H}^+ \rightleftharpoons \text{CaH}(\text{cit})_2^{3-}$				
pot	0.1 M NaCl	25	(10.60 ± 0.04)	[2001SAR]
$\text{Ca}^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})_2^{4-}$				
cix	0.2 M NH <sub>4</sub> Cl	25	(4.33 ± 0.05)	[71RUM]
pot	0.15 M NaClO <sub>4</sub>	37	(4.97 ± 0.04)	[87BLA/BER]
pot	0.1 M NaCl	25	(5.44 ± 0.02)	[2001SAR]

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Table VII-12: (continued)

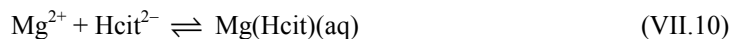
Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{Ca}^{2+} + \text{cit}^{3-} - \text{H}^+ \rightleftharpoons \text{CaH}_{-1}(\text{cit})^{2-}$				
pot	0.15 M NaClO <sub>4</sub>	37	$-(8.94 \pm 0.03)$	[87BLA/BER]
pot	0.1 M NaCl	25	$-(9.06 \pm 0.01)$	[2001SAR]
$\text{Ca}^{2+} + 2\text{cit}^{3-} - 2\text{H}^+ \rightleftharpoons \text{CaH}_{-2}(\text{cit})_2^{6-}$				
pot	0.15 M NaClO <sub>4</sub>	37	$-(16.81 \pm 0.02)$	[87BLA/BER]

a: Refers to the reactions indicated, the ionic strength and temperature given in the table. Uncertainties are those given in the references.

b: Frog heart method (see Appendix A [34HAS/MCL]).

c: Isotachophoresis.

Most of these experimental equilibrium constants were obtained by potentiometric titration. Probable reactions are:



Also the formation of a number of other species has been postulated to fit experimental data:  $\text{Mg}(\text{Hcit})(\text{cit})^{3-}$ ,  $\text{Ca}(\text{Hcit})(\text{cit})^{3-}$ ,  $\text{Mg}(\text{cit})_2^{4-}$ ,  $\text{Ca}(\text{cit})_2^{4-}$ ,  $\text{Mg}(\text{H}_{-1}\text{cit})^{2-}$ ,  $\text{Ca}(\text{H}_{-1}\text{cit})^{2-}$ ,  $\text{Ca}(\text{H}_{-1}\text{cit})_2^{6-}$ ,  $\text{Mg}_2(\text{H}_{-1}\text{cit})_2^{4-}$ ,  $\text{Mg}(\text{H}_{-2}\text{cit})^{3-}$  [71RUM], [87BLA/BER], [2001SAR]. However, the existence of these species is doubtful and the numerical results are not credited by this review (*cf.* Appendix A).

The formation of  $\text{Mg}(\text{cit})^-$ ,  $\text{Mg}(\text{Hcit})(\text{aq})$ ,  $\text{Ca}(\text{cit})^-$  and  $\text{Ca}(\text{Hcit})(\text{aq})$  is commonly accepted in the literature. Although very weak, the formation of  $\text{Mg}(\text{H}_2\text{cit})^-$  and  $\text{Ca}(\text{H}_2\text{cit})^-$  is also indicated ([64CAM/OST], [80PEA], [87BLA/BER]). To show the extent of the complex species of  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  citrates formed under ordinary conditions, the simulated titration curves of  $2 \times 10^{-3}$  M citric acid in the absence and presence of  $2 \times 10^{-3}$  M  $\text{Ca}^{2+}$  at  $I = 0.1$  M, and the distribution of the  $\text{Ca}^{2+}$ -citrates as a function of  $-\log_{10} [\text{H}^+]$  in this titration procedure are given in Figure VII-12 and Figure VII-13, respectively. For the simulation, both the values accepted in this review (at  $I = 0.1$  M) for the protonation constants and the formation constants of Ca-citrate complexes (discussed later in this section) are used. Figure VII-13 indicates that the predominant species in the course of the potentiometric titration are  $\text{Ca}(\text{cit})^-$  and  $\text{Ca}(\text{Hcit})$ . As shown by this example, the contribution of  $\text{Mg}(\text{H}_2\text{cit})^+$  or  $\text{Ca}(\text{H}_2\text{cit})^+$  is significant only at a lower pH region. Since the titration curves of citric acid in the absence and presence of the

metal ion do not differ much in this region, very careful measurements of pH (and the corresponding conversion to  $-\log_{10}[\text{H}^+]$ ) should be done for the determination of these formation constants.

Figure VII-12: Simulated titration curves of (1)  $2 \times 10^{-3}$  M citric acid, (2)  $2 \times 10^{-3}$  M citric acid and  $2 \times 10^{-3}$  M  $\text{Ca}^{2+}$  at  $I = 0.1$  M with the following assumptions:

$$\log_{10} K_1 (r=1) = 5.69, \log_{10} K_2 (r=2) = 4.36 \text{ and } \log_{10} K_3 (r=3) = 2.92$$

$$\text{for } \text{H}^+ + \text{H}_{r-1}\text{cit}^{r-4} \rightleftharpoons \text{H}_r\text{cit}^{r-3}, \text{ and } \log_{10} \beta_1 \text{ (VII.12)} = 3.48,$$

$$\log_{10} \beta_1 \text{ (VII.13)} = 2.05, \log_{10} \beta_1 \text{ (VII.14)} = 1.09$$

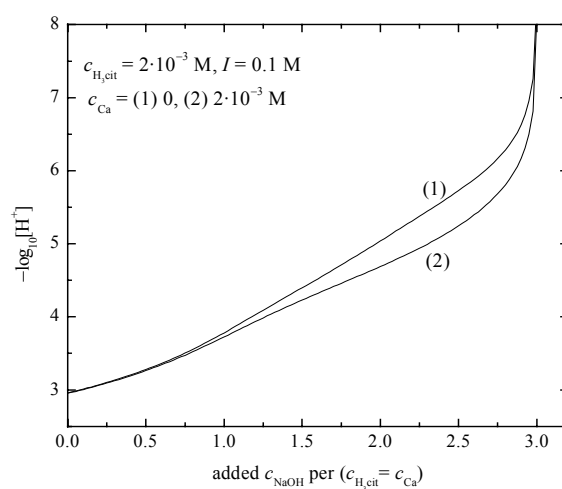
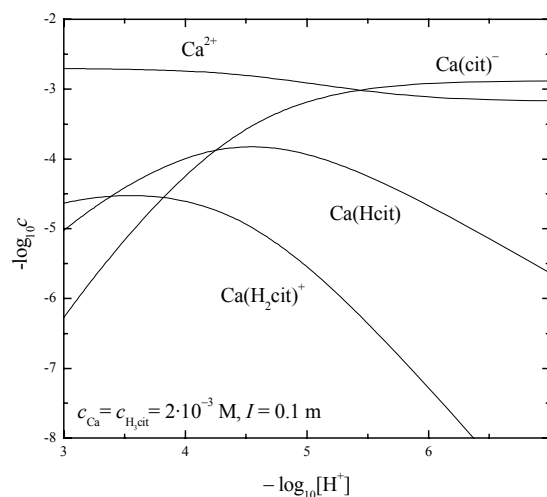


Figure VII-13: Distribution of complex species in the simulated titration of  $2 \times 10^{-3}$  M citric acid and  $2 \times 10^{-3}$  M  $\text{Ca}^{2+}$  at  $I = 0.1$  M (shown in Figure VII-12).



Because of various shortcomings in the experimental procedures or in the reporting of the results, the values of [34HAS/MCL], [36MUU/LEB], [39NOR], [48PYN], [51HEI], [53DAV/HOY], [59LI/LIN], [61PAT/PAN], [61WAL], [63MAT], [63TOB/MIL], [64TOB/MIL], [65PAT/PAN], [69BOS/MAR], [71RUM], [75RAM/MAN], [79BUL/SAC], [82HIR/KIS], [85RIZ/ANT], [88GHA/MAN], [96MIR/PAS], [2001SAR] have been rejected by this review (*cf.* Appendix A).

Based on the discussion of the remaining literature studies (see Appendix A), values listed in Table VII-13 are accepted as reliable in this review. Data at  $I \leq 0.5$  M ( $\cong 0.5$  m) are available in various ionic media. At  $I_m \leq 0.5$  m, the contribution of the term  $\Delta\epsilon I_m$  to the SIT formulation can be considered to be smaller than the experimental uncertainties, except in the cases of  $(\text{CH}_3)_4\text{NCl}$  medium where the interaction of  $(\text{CH}_3)_4\text{N}^+$  with citrate cannot be neglected.

Table VII-13: Accepted formation constants for citrate complexes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  used to derive the selected values. Uncertainties have been estimated in this review.

Ionic medium	$t$ (°C)	$\log_{10} \beta_1^a$	Reference
$\text{Mg}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Mg}(\text{cit})^-$			
0.03 M $\text{KNO}_3$	37	$(3.94 \pm 0.1)$	[82AMI/DAN]
0.1 M $\text{KNO}_3$	25	$(3.38 \pm 0.3)$	[75FIE/COB]
0.1 M $\text{KNO}_3$	25	$(3.50 \pm 0.1)$	[80PEA]
0.1 M $\text{KNO}_3$	37	$(3.45 \pm 0.1)$	[82AMI/DAN]
0.3 M $\text{KNO}_3$	37	$(3.07 \pm 0.1)$	[82AMI/DAN]
0.1 M $\text{NaClO}_4$	20	$(3.40 \pm 0.15)$	[64CAM/OST]
0.5 M $\text{NaClO}_4$	25	$(2.71 \pm 0.1)$	[95PII/LAJ]
0.1 M $(\text{CH}_3)_4\text{NCl}$	25	$(3.73 \pm 0.2)$	[65TAT/GRZ]
0.1 M $(\text{CH}_3)_4\text{NCl}$	25	$(3.85 \pm 0.2)$	[70GRZ/TAT]
0.15 M $\text{NaCl}$	25	$(3.27 \pm 0.2)$	[93GLA/MAJ]
0.15 M $\text{NaClO}_4$	37	$(3.33 \pm 0.1)$	[87BLA/BER]
0.15 M $\text{NaCl}$	37	$(3.24 \pm 0.2)$	[93GLA/MAJ]
0.15 M $\text{NaCl}$	37	$(3.34 \pm 0.5)$	[74MEY]
0.3 m $\text{NaCl}$	25	$(2.97 \pm 0.2)$	[2001CHO/BON]
1 m $\text{NaCl}$	25	$(2.40 \pm 0.2)$	[2001CHO/BON]
2 m $\text{NaCl}$	25	$(1.97 \pm 0.2)$	[2001CHO/BON]
3 m $\text{NaCl}$	25	$(2.02 \pm 0.2)$	[2001CHO/BON]
4 m $\text{NaCl}$	25	$(2.08 \pm 0.2)$	[2001CHO/BON]
5 m $\text{NaCl}$	25	$(2.07 \pm 0.2)$	[2001CHO/BON]

(Continued on next page)

Table VII-13: (continued)

Ionic medium	<i>t</i> (°C)	$\log_{10} \beta_1^a$	Reference
$\text{Mg}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Mg}(\text{Hcit})(\text{aq})$			
0.03 M KNO <sub>3</sub>	37	(1.79 ± 0.2)	[82AMI/DAN]
0.1 M KNO <sub>3</sub>	25	(1.96 ± 0.5)	[75FIE/COB]
0.1 M KNO <sub>3</sub>	25	(1.78 ± 0.2)	[80PEA]
0.1 M KNO <sub>3</sub>	37	(1.51 ± 0.2)	[82AMI/DAN]
0.3 M KNO <sub>3</sub>	37	(1.60 ± 0.2)	[82AMI/DAN]
0.1 M NaClO <sub>4</sub>	20	(1.84 ± 0.15)	[64CAM/OST]
0.5 M NaClO <sub>4</sub>	25	(1.23 ± 0.2)	[95PII/LAJ]
0.1 M (CH <sub>3</sub> ) <sub>4</sub> NCl	25	(1.85 ± 0.2)	[65TAT/GRZ]
0.1 M (CH <sub>3</sub> ) <sub>4</sub> NCl	25	(1.92 ± 0.2)	[70GRZ/TAT]
0.15 M NaClO <sub>4</sub>	37	(1.94 ± 0.2)	[87BLA/BER]
0.15 M NaCl	37	(1.62 ± 0.5)	[74MEY]
1 m NaCl	25	(1.1 ± 0.3)	[2001CHO/BON]
2 m NaCl	25	(0.77 ± 0.3)	[2001CHO/BON]
3 m NaCl	25	(0.98 ± 0.3)	[2001CHO/BON]
4 m NaCl	25	(1.2 ± 0.3)	[2001CHO/BON]
5 m NaCl	25	(1.2 ± 0.3)	[2001CHO/BON]
$\text{Mg}^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Mg}(\text{H}_2\text{cit})^+$			
0.1 M KNO <sub>3</sub>	25	(0.60 ± 0.4)	[80PEA]
0.1 M NaClO <sub>4</sub>	20	(0.84 ± 0.2)	[64CAM/OST]
0.15 M NaClO <sub>4</sub>	37	(1.23 ± 0.4)	[87BLA/BER]
$\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$			
0.03 M KNO <sub>3</sub>	37	(3.91 ± 0.1)	[82AMI/DAN]
0.1 M KNO <sub>3</sub>	25	(3.50 ± 0.3)	[75FIE/COB]
0.1 M KNO <sub>3</sub>	25	(3.50 ± 0.1)	[80PEA]
0.1 M KNO <sub>3</sub>	37	(3.49 ± 0.1)	[82AMI/DAN]
0.3 M KNO <sub>3</sub>	37	(2.94 ± 0.1)	[82AMI/DAN]
0.1 M NaClO <sub>4</sub>	20	(3.55 ± 0.15)	[64CAM/OST]
0.1 M NaClO <sub>4</sub>	25	(3.67 ± 0.2)	[69REC/HSE]
0.1 M NaClO <sub>4</sub>	25	(3.5 ± 0.2)	[92GLA/HUL]
0.5 M NaClO <sub>4</sub>	25	(2.71 ± 0.1)	[95PII/LAJ]
0.15 M NaClO <sub>4</sub>	37	(3.36 ± 0.1)	[87BLA/BER]
0.1 M NaCl	25	(3.42 ± 0.2)	[79CRA/MOO]
0.15 M NaCl	25	(3.17 ± 0.4)	[46JOS]
0.16 M NaCl	25	(3.15 ± 0.2)	[52SCH/LIN]

(Continued on next page)

Table VII-13: (continued)

Ionic medium	$t$ (°C)	$\log_{10} \beta_1^a$	Reference
$\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$			
0.15 M NaCl	25	$(3.17 \pm 0.2)$	[93GLA/MAJ]
0.15 M NaCl	37	$(3.28 \pm 0.2)$	[93GLA/MAJ]
0.15M NaCl	37	$(3.27 \pm 0.5)$	[74MEY]
0.16 M NaCl	18–45	$(3.25 \pm 0.1)$	[91SIN/YEB]
$\text{Ca}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Ca}(\text{Hcit})(\text{aq})$			
0.03 M KNO <sub>3</sub>	37	$(2.23 \pm 0.2)$	[82AMI/DAN]
0.1 M KNO <sub>3</sub>	25	$(2.32 \pm 0.5)$	[75FIE/COB]
0.1 M KNO <sub>3</sub>	25	$(2.03 \pm 0.2)$	[80PEA]
0.1 M KNO <sub>3</sub>	37	$(2.09 \pm 0.2)$	[82AMI/DAN]
0.3 M KNO <sub>3</sub>	37	$(1.65 \pm 0.2)$	[82AMI/DAN]
0.1 M NaClO <sub>4</sub>	20	$(2.10 \pm 0.15)$	[64CAM/OST]
0.5 M NaClO <sub>4</sub>	25	$(1.38 \pm 0.2)$	[95PII/LAJ]
0.15 M NaClO <sub>4</sub>	37	$(2.08 \pm 0.2)$	[87BLA/BER]
0.15M NaCl	37	$(1.82 \pm 0.5)$	[74MEY]
$\text{Ca}^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Ca}(\text{H}_2\text{cit})^+$			
0.1 M KNO <sub>3</sub>	25	$(1.04 \pm 0.4)$	[80PEA]
0.1 M NaClO <sub>4</sub>	20	$(1.05 \pm 0.2)$	[64CAM/OST]
0.15 M NaClO <sub>4</sub>	37	$(1.23 \pm 0.4)$	[87BLA/BER]

a: Refers to the reactions indicated, the ionic strength and temperature given in the table.

The values of the equilibrium constant,  $\log_{10} \beta_1$  for Reaction (VII.9), listed in Table VII-13 (except the cases of  $(\text{CH}_3)_4\text{NCl}$  medium) were fitted to the following equation:

$$\log_{10} \beta_1 = \log_{10} \beta_1^\circ + \frac{0.5091 \Delta z^2 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} - \Delta \epsilon I_m \quad (\text{VII.15})$$

where:  $\Delta \epsilon = \epsilon(\text{Na}^+, \text{Mg}(\text{cit})^-) - \epsilon(\text{Mg}^{2+}, \text{Cl}^-) - \epsilon(\text{Na}^+, \text{cit}^{3-})$

$$\epsilon(\text{Mg}^{2+}, \text{Cl}^-) = (0.19 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$$

$$\epsilon(\text{Na}^+, \text{cit}^{3-}) = -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1}.$$

The result of the fitting is shown in Figure VII-14 and Figure VII-16 with the fitted and selected values of:

$$\log_{10} \beta_1^\circ (\text{VII.9}) = (4.81 \pm 0.03) \text{ and } \epsilon(\text{Na}^+, \text{Mg}(\text{cit})^-) = (0.03 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}.$$

The value of  $\epsilon(\text{Na}^+, \text{Mg}(\text{cit})^-)$  is consistent with the generally observed values for the interaction of  $\text{Na}^+$  with complex anions of charge  $-1$ .

Figure VII-14: Fitting of the values of  $\log_{10} \beta$  of  $\text{Mg}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Mg}(\text{cit})^-$  at each ionic strength (given in Table VII-13) to the SIT equation. Solid line is drawn by using the result of the fitting equation (VII.15) with:

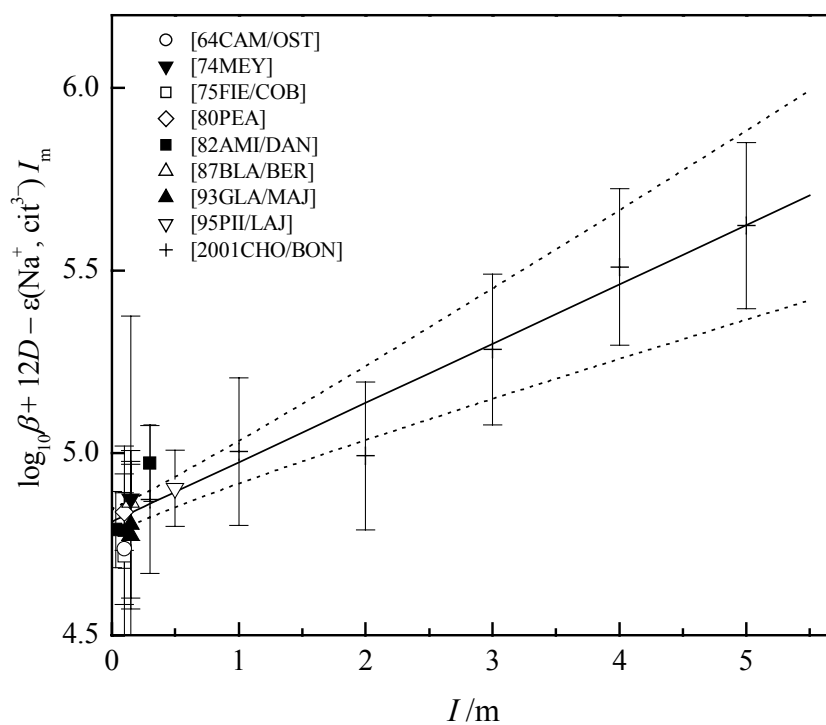
$$\log_{10} \beta_1^\circ (\text{VII.9}) = (4.81 \pm 0.03), \Delta Z^2 = -12,$$

$$\Delta \varepsilon' = \varepsilon(\text{Na}^+, \text{Mg}(\text{cit})^-) - \varepsilon(\text{Mg}^{2+}, \text{Cl}^-)$$

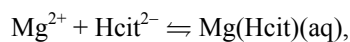
$$\varepsilon(\text{Mg}^{2+}, \text{Cl}^-) = (0.19 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(\text{Na}^+, \text{cit}^{3-}) = -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(\text{Na}^+, \text{Mg}(\text{cit})^-) = (0.03 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}.$$



For Reaction (VII.10),



the values listed in Table VII-13 were used to fit equation:

$$\log_{10} \beta_1 = \log_{10} \beta_1^\circ + \frac{0.5091 \Delta z^2 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} - \Delta \varepsilon I_m \quad (\text{VII.16})$$

where  $\log_{10} \beta_1^\circ$  and  $\Delta \varepsilon$  are treated as fitting parameters. The result of the fitting is shown in Figure VII-15 and Figure VII-16 with the values of:

$$\log_{10} \beta_1^\circ (\text{VII.10}) = (2.60 \pm 0.07) \text{ and } \Delta \varepsilon = - (0.13 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}.$$

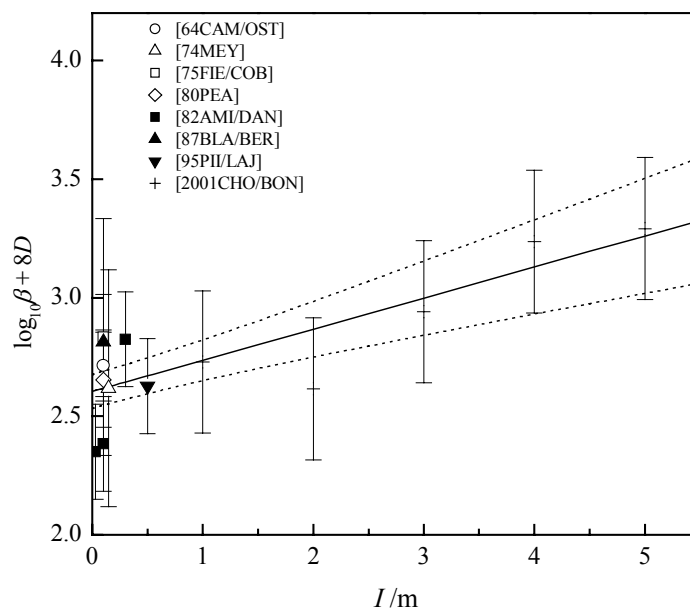
The value of  $\Delta \varepsilon$  is consistent with the selected values of  $\varepsilon$ :

$$\Delta \varepsilon = -\varepsilon(\text{Mg}^{2+}, \text{Cl}^-) - \varepsilon(\text{Na}^+, \text{Hcit}^{2-}) = - (0.19 \pm 0.02) + (0.04 \pm 0.02) = - (0.15 \pm 0.03).$$

Thus, this review selects the above value of  $\log_{10} \beta_1^\circ$  with previously selected values of  $\varepsilon$ .

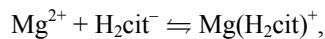
Figure VII-15: Fitting of the values of  $\log_{10} \beta_1$  (VII.10) at each ionic strength (given in Table VII-13) to the SIT equation. Solid line is drawn by using the result of the fitting equation (VII.16).

$$\log_{10} \beta_1^\circ (\text{VII.10}) = (2.60 \pm 0.07); \Delta \varepsilon = - (0.13 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}.$$





For Reaction (VII.11),



the values listed in Table VII-13 were used in the equation:

$$\log_{10} \beta = \log_{10} \beta^{\circ} + \frac{0.5091 \Delta z^2 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad (\text{VII.17})$$

where the  $\Delta \varepsilon I_m$  term is neglected since the data are limited to  $I \leq 0.5 \text{ M}$  ( $\cong 0.5 \text{ m}$ ). The result of the fitting is shown in Figure VII-16. The selected values for magnesium complexes of citrate are summarised in Table VII-14.

Figure VII-16: Fitting of the values of  $\log_{10} \beta_1$  of  $\text{Mg}^{2+}$ -citrate at each ionic strength to

$$\log_{10} \beta_1 = \log_{10} \beta_1^{\circ} + \frac{0.5091 \Delta z^2 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} - \Delta \varepsilon I_m$$

where

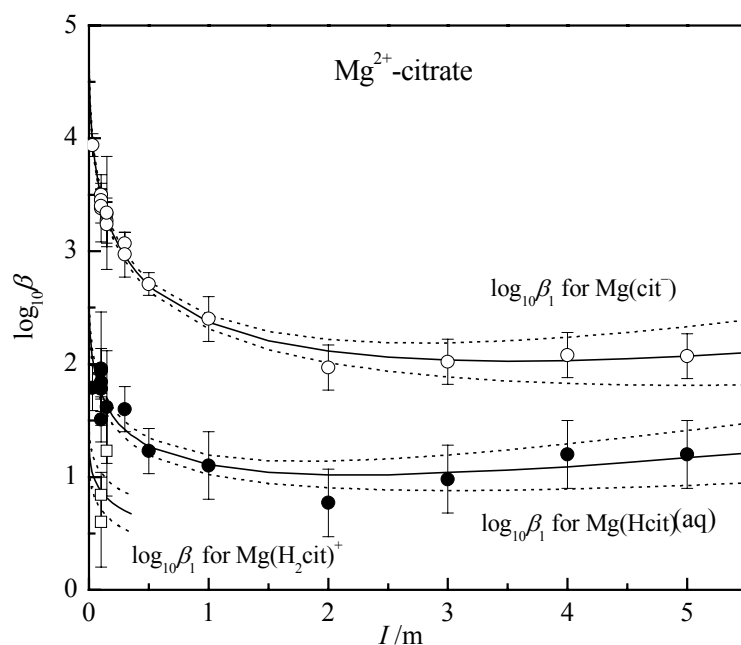
$$\log_{10} \beta_1^{\circ} (\text{VII.11}) = (1.31 \pm 0.16), \quad \Delta z^2 = -4, \quad \Delta \varepsilon I_m = 0$$

$$\log_{10} \beta_1^{\circ} (\text{VII.10}) = (2.60 \pm 0.07), \quad \Delta z^2 = -8, \quad \Delta \varepsilon = -(0.13 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$$

$$\log_{10} \beta_1^{\circ} (\text{VII.9}) = (4.81 \pm 0.03) \quad \Delta z^2 = -12, \quad \Delta \varepsilon = \Delta \varepsilon' - \varepsilon(\text{Na}^+, \text{cit}^{3-})$$

$$\Delta \varepsilon' = -(0.16 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1},$$

$$\varepsilon(\text{cit}^{3-}, \text{Na}^+) = -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m, \text{ kg} \cdot \text{mol}^{-1}$$



Selected values for the calcium complexes,  $\text{Ca}(\text{cit})^-$ ,  $\text{Ca}(\text{Hcit})(\text{aq})$  and  $\text{Ca}(\text{H}_2\text{cit})^+$  were obtained in a manner similar to that used for magnesium species, by assuming that the contribution of  $\Delta\epsilon I_m$  term is negligible. The results of the fittings are shown in Figure VII-17, and the selected values are given in Table VII-14.

Figure VII-17: Fitting of the values of  $\log_{10} \beta_1$  of  $\text{Ca}^{2+}$ -citrate at each ionic strength to

$$\log_{10} \beta_1 = \log_{10} \beta_1^\circ + \frac{0.5091 \Delta z^2 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}}$$

where

$$\begin{aligned} \log_{10} \beta_1^\circ (\text{VII.14}) &= (1.53 \pm 0.16) & \Delta z^2 &= -4 \\ \log_{10} \beta_1^\circ (\text{VII.13}) &= (2.92 \pm 0.07) & \Delta z^2 &= -8 \\ \log_{10} \beta_1^\circ (\text{VII.12}) &= (4.80 \pm 0.03) & \Delta z^2 &= -12. \end{aligned}$$

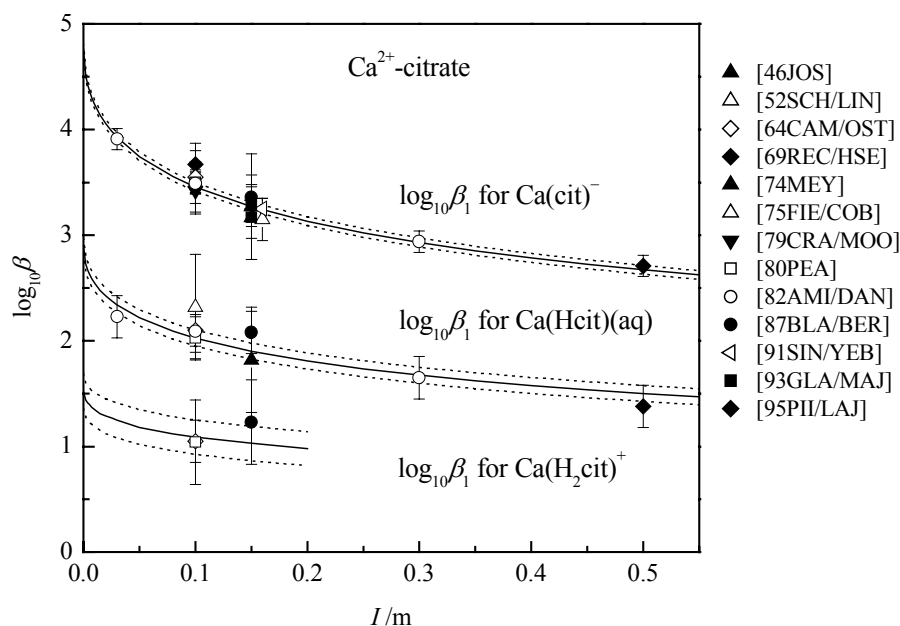


Table VII-14: Selected formation constants for the citrate complexes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  at 25°C.

Reaction	$\log_{10} \beta^\circ$
$\text{Mg}^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Mg}(\text{H}_2\text{cit})^+$	$(1.31 \pm 0.16)$
$\text{Mg}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Mg}(\text{Hcit})(\text{aq})$	$(2.60 \pm 0.07)$
$\text{Mg}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Mg}(\text{cit})^-$	$(4.81 \pm 0.03)$
$\text{Ca}^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Ca}(\text{H}_2\text{cit})^+$	$(1.53 \pm 0.16)$
$\text{Ca}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Ca}(\text{Hcit})(\text{aq})$	$(2.92 \pm 0.07)$
$\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$	$(4.80 \pm 0.03)$

Table VII-13 contains several data at 37°C. Data at 25°C and at 37°C were obtained by different authors and the differences between those at 25°C and at 37°C are within the estimated uncertainties. Singh *et al.* [91SIN/YEB] also obtained the values of  $\log_{10} \beta_1^\circ$  (VII.12) for  $\text{Ca}(\text{cit})^-$  from the measurements at 18, 25, 37, 45°C and  $I = 0.15 - 0.17$  M NaCl. The temperature dependence of  $\log_{10} \beta_1^\circ$  (VII.12) was smaller than their experimental error. From these observations, we can estimate that the variation of  $\log_{10} \beta_1^\circ$  (VII.9) and  $\log_{10} \beta_1^\circ$  (VII.12) for  $\text{Mg}(\text{cit})^-$  and  $\text{Ca}(\text{cit})^-$  are less than 0.1 for the temperature difference of 45 and 18°C. From the relations:

$$|\Delta \log_{10} \beta_1 / \Delta T| < 0.1 / (45 - 18) \text{ and } d \ln \beta_1 / dT = -\Delta H / RT^2,$$

we can roughly estimate that for  $\text{Ca}(\text{cit})^-$ ,  $\Delta_r H_m^\circ$  (VII.12) =  $(0 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$  at  $I_m = 0.1$  m. For the formation of  $\text{M}(\text{Hcit})(\text{aq})$  and  $\text{M}(\text{H}_2\text{cit})^+$  ( $M = \text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ ), the uncertainties are too large to discuss their temperature dependences. By using isothermal calorimeter, Mironov *et al.* [96MIR/PAS] directly obtained  $\log_{10} \beta_1^\circ$  (VII.12) and  $\Delta_r H_m^\circ$  (VII.12) at  $I = 0.1 - 0.5$  M NaCl, pH = 12 and 25°C. The values of  $\Delta_r H_m^\circ$  (VII.12) are  $1.2 \text{ kJ} \cdot \text{mol}^{-1}$  ( $I = 0.1$  M),  $2.1 \text{ kJ} \cdot \text{mol}^{-1}$  ( $I = 0.2$  M),  $3.0 \text{ kJ} \cdot \text{mol}^{-1}$  ( $I = 0.3$  M),  $3.4 \text{ kJ} \cdot \text{mol}^{-1}$  ( $I = 0.4$  M) and  $3.7 \text{ kJ} \cdot \text{mol}^{-1}$  ( $I = 0.5$  M) with the uncertainties of  $\pm 0.2$  to  $\pm 0.3$ . They are small and do not contradict the general observation of the temperature dependence of  $\log_{10} \beta_1^\circ$  (VII.12). However these data may contain much larger errors than given by the authors since there is a possibility of the formation of hydroxide and chloride complexes of  $\text{Ca}^{2+}$  under the condition adopted in this work (see Appendix A). In conclusion, this review selects the value of  $\Delta_r H_m^\circ$  (VII.12) with a large uncertainty as:

$$\Delta_r H_m^\circ ((\text{VII.12}), 298.15 \text{ K}) = (0 \pm 6) \text{ kJ mol}^{-1}.$$

The above selections yield the formation and molar entropy values summarised in Table VII-15:

Table VII-15: Selected Gibbs energy of formation of the citrate complexes of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  and selected molar entropy of  $\text{Ca}(\text{cit})^-$ .

Species	$\Delta_f G_m^\circ$ (kJ·mol <sup>-1</sup> )	$\Delta_f H_m^\circ$ (kJ·mol <sup>-1</sup> )	$S_m^\circ$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
$\text{Mg}(\text{H}_2\text{cit})^+$	$-(1688.7 \pm 2.6)$		
$\text{Mg}(\text{Hcit})(\text{aq})$	$-(1668.8 \pm 2.4)$		
$\text{Mg}(\text{cit})^-$	$-(1645.1 \pm 2.4)$		
$\text{Ca}(\text{H}_2\text{cit})^+$	$-(1787.4 \pm 2.4)$		
$\text{Ca}(\text{Hcit})(\text{aq})$	$-(1768.0 \pm 2.3)$		
$\text{Ca}(\text{cit})^-$	$-(1742.5 \pm 2.3)$	$-(2062.9 \pm 6.4)$	$(111 \pm 20)$

### VII.5.2 Magnesium and calcium citrate compounds

In Table VII-16, there are several papers reporting the solubility products of the solid species of  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  with citrate. All the experimental points reported in these papers are summarised in Figure VII-18.

Table VII-16: Literature data on the solubility product of the solid compounds of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  with citrate.

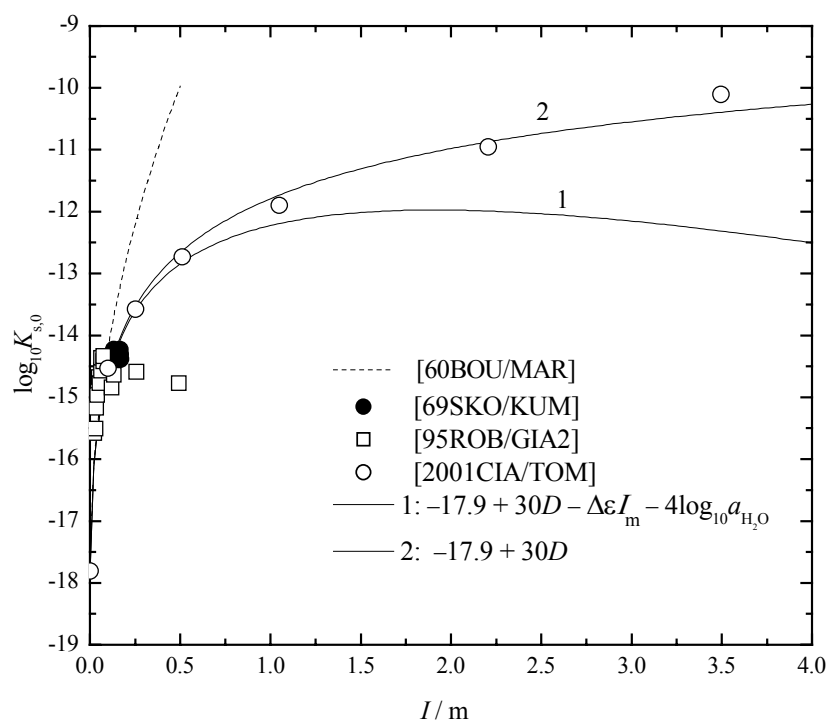
Ionic medium	$t$ (°C)	$\log_{10} K_{s,0}^a$	Reference
$\text{Mg}_3(\text{cit})_2 \cdot 15\text{H}_2\text{O}(\text{cr}) \rightleftharpoons 3\text{Mg}^{2+} + 2\text{cit}^{3-} + 15\text{H}_2\text{O}(\text{l})$			
0.17–0.22 M (H, Na)ClO <sub>4</sub> → 0.1	25	$-(11.10 \pm 0.04)$	[69SKO/KUM]
$\text{Mg}_3(\text{cit})_2 \cdot 9\text{H}_2\text{O}(\text{cr}) \rightleftharpoons 3\text{Mg}^{2+} + 2\text{cit}^{3-} + 9\text{H}_2\text{O}(\text{l})$			
not described	13 → 58	$0.0467 \rightarrow 0.0705 \text{ mol} \cdot \text{kg}^{-1} \text{ }^c$	[93APE]
$\text{Mg}_3(\text{cit})_2 \cdot 14\text{H}_2\text{O}(\text{cr}) \rightleftharpoons 3\text{Mg}^{2+} + 2\text{cit}^{3-} + 14\text{H}_2\text{O}(\text{l})$			
not described	13 → 53	$0.0295 \rightarrow 0.1077 \text{ mol kg}^{-1} \text{ }^c$	[93APE]
$\text{Ca}_3(\text{cit})_2 \cdot 4\text{H}_2\text{O}(\text{cr}) \rightleftharpoons 3\text{Ca}^{2+} + 2\text{cit}^{3-} + 4\text{H}_2\text{O}(\text{l})$			
0.004 – 0.5 M (Na,Ca)cit	21	$-(17.63 \pm 0.08) + (10.84 \pm 0.23) \sqrt{I_m}$	[60BOU/MAR]
0.12 – 0.17 M (H, Na)ClO <sub>4</sub> → 0.1	25	$-(14.68 \pm 0.09)$	[69SKO/KUM]
not described	10 → 58	$0.0017 \rightarrow 0.0014 \text{ mol kg}^{-1} \text{ }^c$	[93APE]
0.01 – 0.54 M (NaCl) or ((CH <sub>3</sub> ) <sub>4</sub> NCl) → 0	25	$-16.95 + 30g(I) - 8.52I \text{ }^b$	[95ROB/GIA2]
0.10 – 3.50 m NaClO <sub>4</sub> → 0	25	$-(17.81 \pm 0.03)$	[2001CIA/TOM]
$\text{Ca}(\text{Hcit})(\text{cr}) \rightleftharpoons \text{Ca}^{2+} + \text{H}^+ + \text{cit}^{3-}$			
0.01–0.54 M (NaCl) or ((CH <sub>3</sub> ) <sub>4</sub> NCl) → 0	25	$-11.35 + 14g(I) - 5.95I \text{ }^b$	[95ROB/GIA2]

a: Refers to the reactions indicated, the ionic strength and temperature given in the table. Uncertainties are those given in the references.

b:  $g(I) = \sqrt{I}/(2 + 3\sqrt{I}) + 0.1I^{3/2}$ .

c: Only total solubilities are reported.

Figure VII-18: The experimental solubility product data of  $\text{Ca}_3(\text{cit})_2 \cdot 4\text{H}_2\text{O}(\text{cr})$  and the fitting of the selected values using equation (VII.19), including and neglecting the  $\Delta\varepsilon$  and  $n \log_{10} a_{\text{H}_2\text{O}}$  terms.



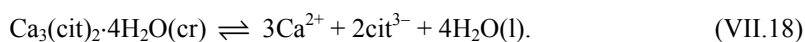
The data by [95ROB/GIA2] begin to decrease with  $I$  at a fairly low ionic strength of around 0.1 m. Since it is unlikely for the ionic interaction term to have such a large contribution, this review does not accept the values given by [95ROB/GIA2] (see Appendix A). The data by [2001CIA/TOM] were obtained by treating the data with the value of  $\varepsilon(\text{cit}^{3-}, \text{Na}^+) = -(0.08 \pm 0.03) - (0.06 \pm 0.01) m_{\text{Na}}$ . This value is different from that selected by NEA-TDB review. Based on the discussion in the Appendix A, only the data at lower ionic strength were accepted by this review. The values accepted as reliable are given in Table VII-17.

Table VII-17: Accepted literature values of the solubility product of the solid compounds of  $\text{Ca}^{2+}$  with citrate to estimate the selected values at 25°C.

Ionic medium	$\log_{10} K_{s,0}^a$	Reference
$\text{Ca}_3(\text{cit})_2 \cdot 4\text{H}_2\text{O}(\text{cr}) \rightleftharpoons 3\text{Ca}^{2+} + 2\text{cit}^{3-} + 4\text{H}_2\text{O}(\text{l})$		
0 m	$-(17.8 \pm 0.2)$	<a href="#">[2001CIA/TOM]</a>
0.10 m $\text{NaClO}_4$	$-(14.5 \pm 0.2)$	<a href="#">[2001CIA/TOM]</a>
0.25 m $\text{NaClO}_4$	$-(13.6 \pm 0.2)$	<a href="#">[2001CIA/TOM]</a>
0.51 m $\text{NaClO}_4$	$-(12.8 \pm 0.2)$	<a href="#">[2001CIA/TOM]</a>

a: Refers to the reaction indicated and the ionic strength given in the table. Uncertainties are estimated by this review.

For the  $\text{Ca}^{2+}$ -citrate system, this review considered the values for the following reaction:



According to the SIT, the equilibrium constant should be expressed by:

$$\log_{10} K_{s,0} = \log_{10} K_{s,0}^o + \Delta z^2 D - \Delta \varepsilon I_m - n \log_{10} a_{\text{H}_2\text{O}} \quad (\text{VII.19})$$

$$\text{where: } D = \frac{0.5091 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}},$$

$$\Delta \varepsilon = 3\varepsilon(\text{Ca}^{2+}, \text{ClO}_4^-) + 2\varepsilon(\text{cit}^{3-}, \text{Na}^+),$$

$$\varepsilon(\text{Ca}^{2+}, \text{ClO}_4^-) = 0.27, \quad \varepsilon(\text{cit}^{3-}, \text{Na}^+) = -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m,$$

$$\Delta z^2 = 3 \times 2^2 + 2 \times 3^2 = 30,$$

and  $n = 4$ .

Since the accepted data are limited to  $I_m \leq 0.5$  m, a SIT analysis neglecting the  $\Delta \varepsilon$  and  $n \log_{10} a_{\text{H}_2\text{O}}$  terms has been conducted in this review. This resulted in the selected constant for the solubility product of  $\text{Ca}^{2+}$  citrate at 25°C.

$$\log_{10} K_{s,0}^o (\text{VII.18}) = -(17.90 \pm 0.10)$$

Accordingly, the selected value for the Gibbs energy of formation is:

$$\Delta_f G_m^o (\text{Ca}_3(\text{cit})_2 \cdot 4\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = -(5033.7 \pm 5.1) \text{ kJ} \cdot \text{mol}^{-1}.$$

The solid lines marked (1) and (2) in Figure VII-18 are the calculated values using this value in Equation (VII.19) including and neglecting  $\Delta \varepsilon$  and  $n \log_{10} a_{\text{H}_2\text{O}}$  terms, respectively. Since the data in [\[2001CIA/TOM\]](#) were obtained by assuming a different value of  $\varepsilon(\text{cit}^{3-}, \text{Na}^+)$ , the points at higher ionic strengths do not agree with the estimation by using the value selected by this review.

## VII.6 Selenium citrate compounds and complexes

No experimental data could be found for the selenium citrate system.

## VII.7 Nickel citrate compounds and complexes

No thermodynamic data for Ni citrate compounds could be identified in this review (see also Section VII.1.1).

The experimental equilibrium data found on the complex formation of  $\text{Ni}^{2+}$  with citrate are listed in Table VII-18. Potentiometric titrations were used in most studies. Except for the species proposed by Sari [2001SAR] which are rejected by this review (see comments in Appendix A), the formation of  $\text{Ni}(\text{H}_2\text{cit})^+$ ,  $\text{Ni}(\text{Hcit})(\text{aq})$  and  $\text{Ni}(\text{cit})^-$  in the lower pH region is commonly accepted in the literature. When the ratio of citrate to nickel is higher, the formation of  $\text{Ni}(\text{cit})_2^{4-}$  can be detected [80HED/LID]. In the higher pH region where the amount of base ( $\text{OH}^-$ ) is in excess of  $3 C_{\text{H}_3\text{cit}}$ ,  $\text{Ni}(\text{cit})^-$  is reported to react with one equivalent of base in many papers ([45BOB/JOR], [57PAT/PAN2], [58HEI/FRI], [58MIG/SYC], [65PAT/PAN2], [70BES/CHA], [76DAN/OST], [80STI/WIK], [84SAL/DEV]), suggesting that the alcoholic OH of the citrate ligand in  $\text{Ni}(\text{cit})^-$  is much easier to be deprotonated as compared to that in  $\text{cit}^{3-}$ . Many papers ([45BOB/JOR], [57PAT/PAN2], [58HEI/FRI], [58MIG/SYC], [65PAT/PAN2], [70BES/CHA], [84SAL/DEV], [89ISH/ENO]) consider the formation of  $\text{Ni}(\text{H}_{-1}\text{cit})^{2-}$ . Other proposed species are  $\text{Ni}_2(\text{H}_{-1}\text{cit})_2^{4-}$  (or  $\text{Ni}_2(\text{cit})_2(\text{OH})_2^{4-}$ ) by [76DAN/OST] and  $\text{Ni}_4(\text{OH})(\text{H}_{-1}\text{cit})_3^{5-}$  by [80STI/WIK]. At the moment, there is no well-grounded argument about the speciation, that is, no examinations have been done for the speciation other than the potentiometric titration at a certain fixed concentrations of  $\text{Ni}^{2+}$  and citrate. Moreover, the experimental data are considered to be affected by the hydrolysis reactions of  $\text{Ni}^{2+}$  since the formation of the proposed species proceeds in the pH region where hydrolysis of nickel occurs. This is illustrated in Figure VII-19 which shows the simulated titration curve considering both the formation of  $\text{Ni}(\text{H}_2\text{cit})^+$ ,  $\text{Ni}(\text{Hcit})(\text{aq})$ ,  $\text{Ni}(\text{cit})^-$ ,  $\text{Ni}(\text{cit})_2^{4-}$  and the hydrolysis of  $\text{Ni}^{2+}$ , but excluding any other species. It is clear that the data should be analysed considering the simultaneous hydrolysis reactions of  $\text{Ni}^{2+}$ . This review could not judge the exact species nor its formation constant.

Table VII-18: Literature data on the formation constants for citrate complexes of  $\text{Ni}^{2+}$ .

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{Ni}^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Ni}(\text{H}_2\text{cit})^+$				(VII.20)
pot	0.1 M $\text{NaClO}_4$	20	1.75	[64CAM/OST]
dis	0.5 M $\text{NaNO}_3$	25 (?)	$(1.55 \pm 0.04)$	[72KER/CHU]
pot	1 M $\text{NaClO}_4$	25	1.45	[78KER/CHU]
pot	0.1 M $\text{KNO}_3$	25	$(1.50 \pm 0.16)$	[80HED/LID]
$\text{Ni}^{2+} + \text{H}_3\text{cit} \rightleftharpoons \text{Ni}(\text{H}_2\text{cit})^+ + \text{H}^+$				(VII.21)
zone electrophoresis	0.7 M $\text{KNO}_3$	25 (?)	- 1.4	[70BES/CHA]
$\text{Ni}^{2+} + 2\text{H}_2\text{cit}^- \rightleftharpoons \text{Ni}(\text{H}_2\text{cit})_2(\text{aq})$				(VII.22)
NMR			1.8	[84SAL/DEV]
pot	0.1 M $\text{NaCl}$	25	$(4.989 \pm 0.105)$	[2001SAR]
$\text{Ni}^{2+} + \text{H}^+ + \text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{Hcit})(\text{aq})$				(VII.23)
pot	0.1 $\text{KNO}_3$	25	$(8.75 \pm 0.01)$	[80STI/WIK]
pot	0.25 $\text{KNO}_3(?)$	25	$(8.75 \pm 0.05)$	[84DAN/OST] <sup>b</sup>
pot	0.1 $\text{KNO}_3(?)$	25	$(9.13 \pm 0.06)$	[88DAN/OST] <sup>b</sup>
$\text{Ni}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Ni}(\text{Hcit})(\text{aq})$				(VII.24)
pot	0.25 M $\text{KNO}_3$	32.5	3.37	[57PAT/PAN2]
pot	0.15 M ( $\text{Ni}^{2+}$ , $\text{NO}_3^-$ )	25	$(3.19 \pm 0.15)$	[59LI/LIN]
pot	0.1 M $\text{NaClO}_4$	20	3.30	[64CAM/OST]
dis	0.5 M $\text{NaNO}_3$	25 (?)	$(2.90 \pm 0.04)$	[72KER/CHU]
pot	0.1 M $\text{KNO}_3$	25	$(3.34 \pm 0.07)$	[75FIE/COB]
pot	0.1 M $\text{KNO}_3$	25	$(3.23 \pm 0.03)$	[76DAN/OST]
pot	1 M $\text{NaClO}_4$	25	2.90	[78KER/CHU]
pot	0.1 M $\text{KCl}$	25	$(3.35 \pm 0.06)$	[80HED/LID]
NMR			2.6	[84SAL/DEV]
$\text{Ni}(\text{OH})_2(\text{s}) + \text{Hcit}^{2-} \rightleftharpoons \text{Ni}(\text{H}_- \text{cit})^{2-} + 2 \text{H}_2\text{O}$				(VII.25)
sol		35	3.21	[65PAT/PAN2]
$\text{Ni}^{2+} + 2\text{Hcit}^{2-} \rightleftharpoons \text{Ni}(\text{Hcit})_2^{2-}$				(VII.26)
NMR			4.3	[84SAL/DEV]
pot	0.1 M $\text{NaCl}$	25	$(6.721 \pm 0.04)$	[2001SAR]
$\text{Ni}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})^-$				(VII.27)
amperometric titration		25	3.39	[45BOB/JOR]
pot	0.25 M $\text{KNO}_3$	32.5	6.12	[57PAT/PAN2]
pot, cond, sp		25 (?)	$(4.40 \pm 0.12)$ $(4.54 \pm 0.08)$	[58HEI/FRI]
pot	2 M $\text{KNO}_3$	25	4.99	[58MIG/SYC]
pot	0.15 M ( $\text{Ni}^{2+}$ , $\text{NO}_3^-$ )	25	$(5.11 \pm 0.15)$	[59LI/LIN]
pol	0.1 M $\text{NaCl}$	r. t.	4.05	[61ISH/YOK]
sp		r. t.	3.20, 3.62	

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Table VII-18: (continued)

Method	Ionic medium	<i>t</i> (°C)	$\log_{10} \beta^a$	Reference
pot	0.1 M NaClO <sub>4</sub>	20	5.40	[64CAM/OST]
dis	0.5 M NaNO <sub>3</sub>	25 (?)	(4.25 ± 0.12)	[72KER/CHU]
pot	0.1 M KNO <sub>3</sub>	25	(5.40 ± 0.04)	[75FIE/COB]
pot	0.1 M KNO <sub>3</sub>	25	(5.30 ± 0.02)	[76DAN/OST]
pot	1 M NaClO <sub>4</sub>	25	4.30	[78KER/CHU]
pot	0.1 M KNO <sub>3</sub>	25	(5.49 ± 0.04)	[80HED/LID]
pot	0.25 KNO <sub>3</sub> (?)	25	(5.09 ± 0.05)	[84DAN/OST] <sup>b</sup>
NMR			4.6	[84SAL/DEV]
pot	0.1 KNO <sub>3</sub> (?)	25	(5.35 ± 0.06)	[88DAN/OST] <sup>b</sup>
pot	0.1 M KNO <sub>3</sub>	25	(4.54 ± 0.04)	[93AZA/HAS]
dis	0.3 - 5 m NaCl → <i>I</i> = 0	20	(6.82 ± 0.10)	[2000BOR/CHO]
$\text{Ni(OH)}_2(\text{s}) + \text{H}_2\text{cit}^- \rightleftharpoons \text{Ni(cit)}^- + 2\text{H}_2\text{O}$				(VII.28)
sol		35	6.835	[65PAT/PAN2]
$\text{Ni}^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{Ni(cit)}_2^{4-}$				(VII.29)
pot	2 M KNO <sub>3</sub>	25	7.76	[58MIG/SYC]
pot	0.1 M KNO <sub>3</sub>	25	(7.82 ± 0.20)	[80HED/LID]
pot	0.25 KNO <sub>3</sub> (?)	25	(7.93 ± 0.09)	[84DAN/OST] <sup>b</sup>
NMR			8.0	[84SAL/DEV]
pot	0.1 KNO <sub>3</sub> (?)	25	(8.11 ± 0.06)	[88DAN/OST] <sup>b</sup>
pot	0.1 M NaCl	25	(7.747 ± 0.015)	[2001SAR]
$\text{Ni(cit)}^- + \text{cit}^{3-} \rightleftharpoons \text{Ni(cit)}_2^{4-}$				(VII.30)
pot, sp	0.1 M KNO <sub>3</sub>	25	(2.85 ± 0.02)	[80STI/WIK]
$\text{Ni}^{2+} + 3\text{cit}^{3-} \rightleftharpoons \text{Ni(cit)}_3^{7-}$				(VII.31)
NMR			8.8	[84SAL/DEV]
$\text{Ni}^{2+} + \text{H}_- \text{cit}^{4-} \rightleftharpoons \text{Ni(H}_- \text{cit)}^{2-}$				(VII.32)
pot, cond, sp		25 (?)	11.22	[58HEI/FRI]
pot	2 M KNO <sub>3</sub>	25	5.27	[58MIG/SYC]
$\text{Ni(cit)}^- \rightleftharpoons \text{Ni(H}_- \text{cit)}^{2-} + \text{H}^+$				(VII.33)
pot	0.25 M KNO <sub>3</sub>	32.5	- 7.87	[57PAT/PAN2]
sol		35	- 7.89	[65PAT/PAN2]
$\text{Ni(H}_2 \text{cit)}^+ \rightleftharpoons \text{Ni(H}_- \text{cit)}^{2-} + 3\text{H}^+$				(VII.34)
zone electrophoresis	0.7 M KNO <sub>3</sub>	25 (?)	- 12.9	[70BES/CHA]
$\text{Ni}^{2+} + \text{H}^+ + 2\text{cit}^{3-} \rightleftharpoons \text{NiH(cit)}_2^{3-}$				(VII.35)
pot	0.25 KNO <sub>3</sub> (?)	25	(12.94 ± 0.11)	[84DAN/OST] <sup>b</sup>
pot	0.1 KNO <sub>3</sub> (?)	25	(13.5 ± 0.2)	[88DAN/OST] <sup>b</sup>
pot	0.1 M NaCl	25	(13.549 ± 0.028)	[2001SAR]

(Continued on next page)

Table VII-18: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{Ni}^{2+} + 3\text{H}^+ + 2\text{cit}^{3-} \rightleftharpoons \text{NiH}_3(\text{cit})_2^-$				(VII.36)
pot	0.1 M NaCl	25	$(21.55 \pm 0.06)$	[2001SAR]
$\text{Ni}^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{H}_{-1}\text{cit})(\text{cit})^{5-} + \text{H}^+$				(VII.37)
pot	0.1 M NaCl	25	$-(2.34 \pm 0.01)$	[2001SAR]
$\text{Ni}^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{H}_{-1}\text{cit})_2^{6-} + 2\text{H}^+$				(VII.38)
pot	0.25 KNO <sub>3</sub> (?)	25	$-(4.76 \pm 0.09)$	[84DAN/OST] <sup>b</sup>
pot	0.1 KNO <sub>3</sub> (?)	25	$-(4.64 \pm 0.06)$	[88DAN/OST] <sup>b</sup>
pot	0.1 M NaCl	25	$-(13.55 \pm 0.02)$	[2001SAR]
$4\text{Ni}^{2+} + 3\text{cit}^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{Ni}_4(\text{OH})(\text{H}_{-1}\text{cit})_3^{5-} + 4\text{H}^+$				(VII.39)
pot, sp	0.1 M KNO <sub>3</sub>	25	$-7.1$	[80STI/WIK]
$2\text{Ni}^{2+} + \text{cit}^{3-} + \text{H}_{-1}\text{cit}^{4-} \rightleftharpoons \text{Ni}_2(\text{cit})(\text{H}_{-1}\text{cit})^{3-}$				(VII.40)
NMR			14.8	[84SAL/DEV]
$2\text{Ni}^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{Ni}_2(\text{H}_{-1}\text{cit})_2^{4-} + 2\text{H}^+$				(VII.41)
pot	0.1 M KNO <sub>3</sub>	25	$-(4.71 \pm 0.03)$	[76DAN/OST]
$2\text{Ni}^{2+} + 2\text{H}_{-1}\text{cit} \rightleftharpoons \text{Ni}_2(\text{H}_{-1}\text{cit})_2^{4-}$				(VII.42)
NMR			$(17.7 \pm 0.02)$	[84SAL/DEV]

a: Refers to the reactions indicated, the ionic strength and temperature given in the table. Uncertainties are those given in the references.

b: The values at 10, 35, 45°C and  $\Delta_r H_m$  are also reported but not listed in this table.

r.t.: room temperature

Figure VII-19 and Figure VII-20 show the simulated titration curve and the distribution of the species in the titration calculated by this review using the values of the hydrolysis constants and solubility products of  $\text{Ni}(\text{OH})_2(\text{cr})$  recommended by Plyasunova *et al.* [98PLY/ZHA]. The results indicate that the precipitation of  $\text{Ni}(\text{OH})_2(\text{cr})$  occurs immediately after the amount of base ( $C_{\text{OH}}$ ) exceeds  $3C_{\text{H}_3\text{cit}}$ . This review considers that the speciation at  $C_{\text{OH}} \geq 3C_{\text{H}_3\text{cit}}$  and the assigned stability constants for the relevant species are affected by the slowly progressing precipitation. Thus, this review does not consider these species and values.

Figure VII-19: Simulated titration curves of (1)  $5 \times 10^{-3}$  M citric acid, (2)  $5 \times 10^{-3}$  M citric acid and  $5 \times 10^{-3}$  M  $\text{Ni}^{2+}$  at  $I = 0.1$  M, with the following assumptions:

For  $\text{H}^+ + \text{H}_{r-1}\text{cit}^{r-4} \rightleftharpoons \text{H}_r\text{cit}^{r-3}$ ,

$$\log_{10} K_1 (r=1) = 5.69, \log_{10} K_2 (r=2) = 4.36, \log_{10} K_3 (r=3) = 2.92$$

For Ni-citrate ccomplexation:

$$\log_{10} \beta_1 ((\text{VII.20}), \text{Ni}(\text{H}_2\text{cit})^+) = 1.63, \log_{10} \beta_1 ((\text{VII.24}),$$

$$\text{Ni}(\text{Hcit})(\text{aq})) = 3.32, \log_{10} \beta_1 ((\text{VII.27}), \text{Ni}(\text{cit})^-) = 5.46,$$

$$\log_{10} \beta_1 ((\text{VII.29}), \text{Ni}(\text{cit})_2^{4-}) = 7.82$$

For  $m\text{Ni}^{2+} + n\text{H}_2\text{O} \rightleftharpoons \text{Ni}_m(\text{OH})_n^{2m-n} + n\text{H}^+$  [\[98PLY/ZHA\]](#)

$$\log_{10} K_{2,1} (\text{Ni}(\text{OH})_2(\text{cr})) = -10.52, \log_{10} K_{1,1} (\text{NiOH}^+) = -9.50,$$

$$\log_{10} K_{2,1} (\text{Ni}(\text{OH})_2(\text{aq})) = -18.0, \log_{10} K_{3,1} (\text{Ni}(\text{OH})_3^-) = -29.7,$$

$$\log_{10} K_{4,1} (\text{Ni}(\text{OH})_4^{2-}) = -44.96, \log_{10} K_{1,2} (\text{Ni}_2\text{OH}^{3+}) = -9.8,$$

$$\log_{10} K_{4,4} (\text{Ni}_4(\text{OH})_4^{4+}) = -27.9$$

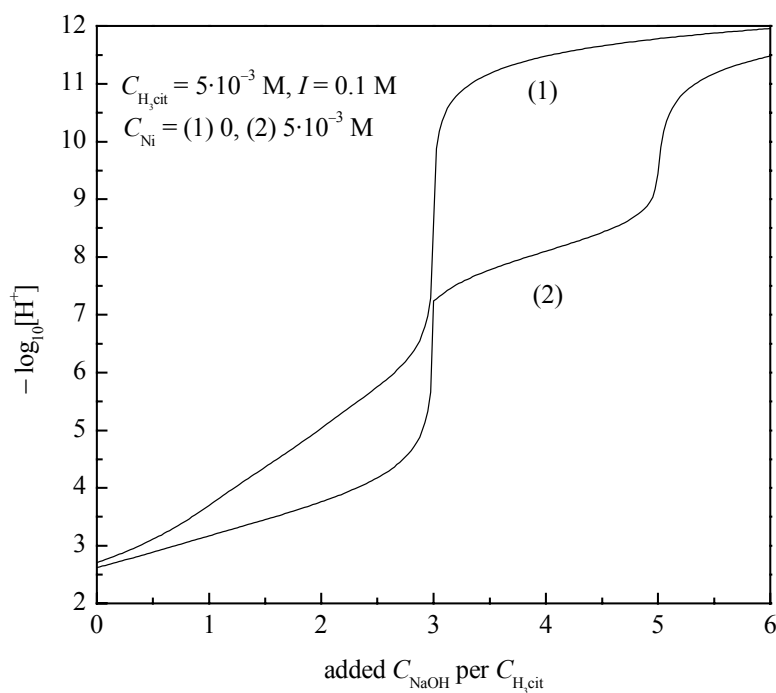
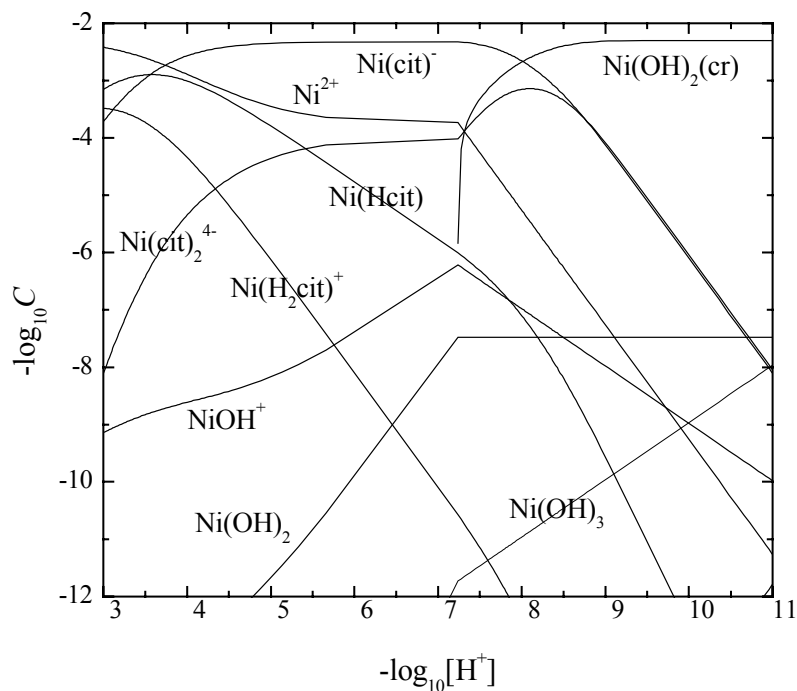


Figure VII-20: Distribution of complex species in the simulated titration of  $5 \times 10^{-3}$  M citric acid and  $5 \times 10^{-3}$  M  $\text{Ni}^{2+}$  at  $I = 0.1$  M (shown in Figure VII-19). Concentration of  $\text{Ni}(\text{OH})_2(\text{cr})$  is expressed by the amount of precipitate divided by the volume of the solution.



Because of various shortcomings in the experimental procedures or in the reporting of the results, the values of [\[45BOB/JOR\]](#), [\[57PAT/PAN2\]](#), [\[58HEI/FRI\]](#), [\[58MIG/SYC\]](#), [\[59LI/LIN\]](#), [\[61ISH/YOK\]](#), [\[65PAT/PAN2\]](#), [\[70BES/CHA\]](#), [\[72KER/CHU\]](#), [\[80STI/WIK\]](#), [\[84SAL/DEV\]](#), [\[93AZA/HAS\]](#), [\[2001SAR\]](#) have been rejected by this review (*cf.* Appendix A).

Based on the discussion of the remaining literature studies (see Appendix A) the constants listed in Table VII-19 are accepted in this review, where the data at 20°C and 25°C are found to be identical within the limit of the given uncertainties.

Table VII-19: Accepted formation constants for citrate complexes of  $\text{Ni}^{2+}$  at 25°C used to derive the selected values.

Ionic medium	$\log_{10} \beta^a$	Reference
$\text{Ni}^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Ni}(\text{H}_2\text{cit})^+$ (VII.20)		
0.1 M $\text{NaClO}_4$	$(1.75 \pm 0.30)$	[64CAM/OST]
0.1 M $\text{KNO}_3$	$(1.50 \pm 0.32)$	[80HED/LID]
1 M $\text{NaClO}_4$	$(1.45 \pm 0.40)$	[78KER/CHU]
$\text{Ni}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Ni}(\text{Hcit})(\text{aq})$ (VII.24)		
0.1 M $\text{NaClO}_4$	$(3.30 \pm 0.20)$	[64CAM/OST]
0.1 M $\text{KNO}_3$	$(3.34 \pm 0.20)$	[75FIE/COB]
0.1 M $\text{KNO}_3$	$(3.23 \pm 0.20)$	[76DAN/OST]
0.1 M $\text{KCl}$	$(3.35 \pm 0.12)$	[80HED/LID]
1 M $\text{NaClO}_4$	$(2.90 \pm 0.40)$	[78KER/CHU]
$\text{Ni}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})^-$ (VII.27)		
0.3 - 5 m $\text{NaCl} \rightarrow I = 0$	$(6.82 \pm 0.10)$	[2000BOR/CHO]
0.1 M $\text{NaClO}_4$	$(5.40 \pm 0.20)$	[64CAM/OST]
0.1 M $\text{KNO}_3$	$(5.40 \pm 0.10)$	[75FIE/COB]
0.1 M $\text{KNO}_3$	$(5.30 \pm 0.20)$	[76DAN/OST]
0.1 M $\text{KNO}_3$	$(5.49 \pm 0.08)$	[80HED/LID]
1 M $\text{NaClO}_4$	$(4.30 \pm 0.40)$	[78KER/CHU]
$\text{Ni}^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})_2^{4-}$ (VII.29)		
0.1 M $\text{KNO}_3$	$(7.82 \pm 0.40)$	[80HED/LID]

a: Refers to the reactions indicated, the ionic strength and temperature given in the table.  
Uncertainties are estimated in this review.

In Table VII-19, the estimated uncertainties of the values at  $I = 0.10$  M ( $= 0.10$  m) in  $\text{NaClO}_4$  and  $\text{KNO}_3$  media are larger than the term  $\Delta\epsilon I_m$ . Thus, SIT analyses were conducted based on the assumption that the data in Table VII-19 are identical to those in  $\text{NaClO}_4$  media. In the cases of  $\text{Ni}(\text{H}_2\text{cit})^+$  and  $\text{Ni}(\text{Hcit})(\text{aq})$ , the data were fitted to the following equation,

$$\log_{10} \beta_1 - \Delta z^2 D = \log_{10} \beta_1^0 - \Delta\epsilon I_m \quad (\text{VII.43})$$

where  $\Delta\epsilon = \epsilon(\text{Ni}(\text{H}_2\text{cit})^+, \text{ClO}_4^-) - \epsilon(\text{Ni}^{2+}, \text{ClO}_4^-) - \epsilon(\text{Na}^+, \text{H}_2\text{cit}^-)$  and  $\Delta z^2 = -4$   
and  $\Delta\epsilon = -\epsilon(\text{Ni}^{2+}, \text{ClO}_4^-) - \epsilon(\text{Hcit}^{2-}, \text{Na}^+) + \epsilon(\text{Ni}(\text{Hcit})(\text{aq}), \text{NaClO}_4)$  and  $\Delta z^2 = -8$  respectively.

In the case of  $\text{Ni}(\text{cit})^-$ , data were fitted to the following equation:

$$\log_{10} \beta_1 - \Delta z^2 D + \epsilon(\text{Na}^+, \text{cit}^{3-}) I_m = \log_{10} \beta_1^0 - \Delta\epsilon' I_m \quad (\text{VII.44})$$

where  $\Delta\epsilon' = \epsilon(\text{Na}^+, \text{Ni}(\text{cit})^-) - \epsilon(\text{Ni}^{2+}, \text{ClO}_4^-)$

$\epsilon(\text{cit}^{3-}, \text{Na}^+) = -(0.15 \pm 0.03) + (0.13 \pm 0.03)\log_{10} I_m$  ( $\text{kg}\cdot\text{mol}^{-1}$ ) and  $\Delta z^2 = -12$ .

The results of the fittings are given in Figure VII-21. For the formation of  $\text{Ni}(\text{cit})_2^{4-}$ , the value of  $\log_{10} \beta^\circ$  was obtained by simply neglecting the  $\Delta\epsilon I_m$  term at low ionic strength of 0.1 M and a larger uncertainty was given. Table VII-20 lists the equilibrium constants selected in this review for the nickel-citrate system.

Figure VII-21: Fitting of the values of  $\log_{10} \beta$  for the  $\text{Ni}^{2+}$ -citrate system at each ionic strength (given in Table VII-19) to equations (VII.43) and (VII.44). Solid lines are drawn by using the result of the fitting (given in Table VII-20).

$$\text{Solid lines : } \log_{10} \beta_1 = \log_{10} \beta_1^\circ + \Delta z^2 D - \Delta\epsilon I_m \text{ where } D = \frac{0.5091\sqrt{I_m}}{1 + 1.5\sqrt{I_m}}$$

$$\log_{10} \beta_1^\circ \text{ (VII.20)} = (2.05 \pm 0.25), \Delta z^2 = -4, \Delta\epsilon = -(0.2 \pm 0.5) \text{ kg} \cdot \text{mol}^{-1}$$

$$\log_{10} \beta_1^\circ \text{ (VII.24)} = (4.16 \pm 0.10), \Delta z^2 = -8, \Delta\epsilon = -(0.4 \pm 0.5) \text{ kg} \cdot \text{mol}^{-1}$$

$$\log_{10} \beta_1^\circ \text{ (VII.27)} = (6.76 \pm 0.08), \Delta z^2 = -12, \Delta\epsilon = \Delta\epsilon' - \epsilon(\text{cit}^{3-}, \text{Na}^+),$$

$$\Delta\epsilon' = -(0.05 \pm 0.41) \text{ kg} \cdot \text{mol}^{-1},$$

$$\epsilon(\text{cit}^{3-}, \text{Na}^+) = -(0.15 \pm 0.03) + (0.13 \pm 0.03)\log_{10} I_m \text{ kg} \cdot \text{mol}^{-1}$$

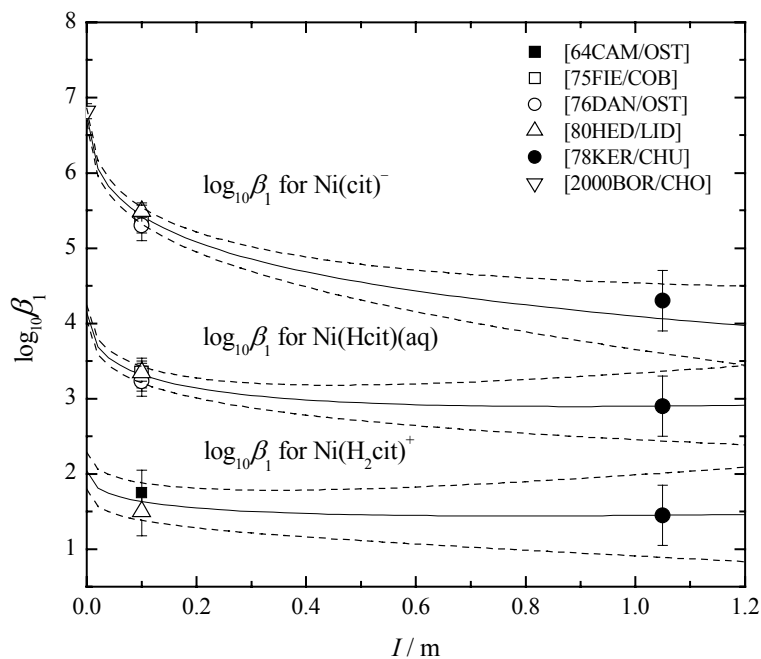


Table VII-20: Selected formation constants for the citrate complexes of  $\text{Ni}^{2+}$  at 25°C.

Reaction	$\log_{10} K^\circ$
$\text{Ni}^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Ni}(\text{H}_2\text{cit})^+$	$(2.05 \pm 0.25)$
$\text{Ni}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Ni}(\text{Hcit})(\text{aq})$	$(4.16 \pm 0.10)$
$\text{Ni}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})^-$	$(6.76 \pm 0.08)$
$\text{Ni}^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})_2^{4-}$	$(8.5 \pm 0.4)$

From the obtained values of  $\Delta\varepsilon$  and  $\Delta\varepsilon'$  given in the caption of Figure VII-21 and using the values of  $\varepsilon(\text{Ni}^{2+}, \text{ClO}_4^-) = (0.370 \pm 0.032) \text{ kg}\cdot\text{mol}^{-1}$  [2005GAM/BUG],  $\varepsilon(\text{H}_2\text{cit}^-, \text{Na}^+) = -(0.05 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{Hcit}^{2-}, \text{Na}^+) = -(0.04 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  (obtained in this review), the specific ion interaction parameters for the Ni-citrate complexes can be estimated to be  $\varepsilon(\text{Ni}(\text{H}_2\text{cit})^+, \text{ClO}_4^-) = (0.12 \pm 0.5) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{Ni}(\text{Hcit})(\text{aq}), \text{NaClO}_4) = -(0.07 \pm 0.5) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{Ni}(\text{cit})^-, \text{Na}^+) = (0.22 \pm 0.5) \text{ kg}\cdot\text{mol}^{-1}$ . It is not possible to evaluate the reliability of these values due to their large uncertainties.

The above selections yield:

$$\Delta_f G_m^\circ(\text{Ni}(\text{H}_2\text{cit})^+, 298.15 \text{ K}) = -(1283.3 \pm 2.6) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Ni}(\text{Hcit}), \text{aq}, 298.15 \text{ K}) = -(1268.1 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Ni}(\text{cit})^-, 298.15 \text{ K}) = -(1246.6 \pm 2.2) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ(\text{Ni}(\text{cit})_2^{4-}, 298.15 \text{ K}) = -(2418.8 \pm 4.7) \text{ kJ}\cdot\text{mol}^{-1}.$$

## VII.8 Technetium citrate compounds and complexes

Despite the various oxidation states of technetium, only a limited number of papers ([77MUN], [77MUN2], [77MUN/GRO], [81MUE]), all published by the same author, dealing with the complex formation of technetium(IV) with citrate could be found. Although [77MUN/GRO] suggests a very strong Tc citrate complex formation which suppresses the precipitation of technetium hydroxides similarly to other tetravalent metal ions such as Zr(IV) ([78STR/KAR]), U(IV) and Th(IV) ([60ADA/SMI], [66NEB/URB], [74SHA/KII]), the stoichiometries of the species formed are not well established (see discussion of [77MUN/GRO] in Appendix A). No thermodynamic data are reported by Münze ([77MUN], [77MUN2], [77MUN/GRO], [81MUE]).

## VII.9 Zirconium citrate compounds and complexes

No thermodynamic data for Zr citrate compounds could be identified in this review (see also Section VII.1.1).

As shown in Table VII-21, there is only a limited number of papers dealing with the complex formation of Zr(IV) with citrate. Although these papers suggest a very strong complex formation which suppresses the precipitation of zirconium hydroxides up to a fairly high pH, similarly to other tetravalent metal ions such as Tc(IV) ([77MUN/GRO]), U(IV) and Th(IV) ([60ADA/SMI], [66NEB/URB], [74SHA/KII]), even the stoichiometries of the species formed are not well established. Among the papers listed in Table VII-21, two papers ([60RYA/ERM], [75ZAI/NIK]) claim the formation of  $\text{Zr}(\text{H}_2\text{cit})^{3+}$ , one ([66KOR/SHE2]) claims the formation of  $\text{Zr}(\text{Hcit})^{2+}$ , and the other ([78STR/KAR]) claims the formation of  $\text{Zr}(\text{cit})^+$ ,  $\text{Zr}(\text{cit})_2^{2-}$  and the species complexed with  $\text{H}_1\text{cit}^{4-}$ . Due to the strong tendency of  $\text{Zr}^{4+}$  to be hydrolysed and the strong interaction with the ligand, the complex formation of Zr(IV) with citrate can be studied mainly in highly acidic solutions, where the activity coefficients of the relevant species are very difficult to be estimated. Unfortunately, the conditions studied in the papers listed in Table VII-21 are limited and their speciation cannot be relied on. So far, the present review cannot select any value for the complex formation of Zr(IV) with citrate.

Table VII-21: Literature data on the formation constants for citrate complexes of  $\text{Zr}^{4+}$ .

Method	Ionic medium	$t$ (°C)	$K$ <sup>a</sup>	Reference
$\text{Zr}^{4+} + \text{H}_3\text{cit}(\text{aq}) \rightleftharpoons \text{Zr}(\text{H}_2\text{cit})^{3+} + \text{H}^+$				
cix	2 M HClO <sub>4</sub>	?	$K/[\text{H}^+] = (1300 \pm 216)$ <sup>b</sup>	<a href="#">[60RYA/ERM]</a> , <a href="#">[64RYA/MAR]</a>
dis	2 M LiNO <sub>3</sub> , 0.1 – 2 M HNO <sub>3</sub>	25	(310 ± 20)	<a href="#">[75ZAI/NIK]</a>
	4 M LiNO <sub>3</sub> , 0.1 – 2 M HNO <sub>3</sub>		(121 ± 9)	
	6 M LiNO <sub>3</sub> , 0.1 – 2 M HNO <sub>3</sub>		(90 ± 6)	
$\text{Zr}^{4+} + \text{Hcit}^{2-} \rightleftharpoons \text{Zr}(\text{Hcit})^{2+}$				
sp	1 M HCl	18 – 20	$(6.0 \pm 0.5) \times 10^{10}$	<a href="#">[66KOR/SHE2]</a>
$\text{Zr}^{4+} + \text{cit}^{3-} \rightleftharpoons \text{Zr}(\text{cit})^+$				
(c)	not controlled	?	$1.4 \times 10^6$ (at pH 0)	<a href="#">[68KOZ]</a>
NMR	not controlled	?	$0.7 \times 10^8$ (at pH 3.0)	<a href="#">[78STR/KAR]</a>
			$1 \times 10^8$ (at pH 3.1)	
			$0.4 \times 10^8$ (at pH 3.2)	
			$1 \times 10^8$ (at pH 3.4)	
$\text{Zr}^{4+} + 2\text{cit}^{3-} \rightleftharpoons \text{Zr}(\text{cit})_2^{2-}$				
NMR	not controlled	?	$1 \times 10^{14}$ (at pH 3.0)	<a href="#">[78STR/KAR]</a>
			$6 \times 10^{14}$ (at pH 3.1)	
			$1 \times 10^{14}$ (at pH 3.2)	
			$1 \times 10^{14}$ (at pH 3.4)	

a: Refers to the reactions indicated, the ionic strength and temperature given in the table. Uncertainties are those given in the references.

b: This is a conditional constant given at 2 M  $\text{HClO}_4$ . See the discussion for [60RYA/ERM].

c: Metal indicator method [68KOZ].



## VII.10 Uranium citrate compounds and complexes

No thermodynamic data for uranium citrate compounds could be identified in this review (see also Section VII.1.1).

### VII.10.1 U(IV) citrate complexes

Concerning citrate complexes of the tetravalent uranium, there is a limited number of papers (Table VII-22). Similarly to other tetravalent metal ions such as Tc(IV) ([77MUN/GRO]) and Zr(IV) ([78STR/KAR]), the papers listed in Table VII-22 suggest a very strong complex formation of U(IV) with citrate which suppresses the precipitation of hydroxides up to a fairly high pH. However, the stoichiometries of the species formed are not well established due to the strong tendency of  $U^{4+}$  to hydrolyse and too strong complex formation with citrate. So far, the present review cannot select any value for the complex formation of U(IV) with citrate.

Table VII-22: Literature data on the formation constants for citrate complexes of  $U^{4+}$ .

Method	Ionic medium	$t$ (°C)	$\log_{10} K^a$	Reference
$U^{4+} + cit^{3-} \rightleftharpoons Ucit^+$				
sp	0.1 M (H, Na)ClO <sub>4</sub>	r.t.	9.72 (at pH 1.50) to 3.93 (at pH 4.50) <sup>b</sup>	[60ADA/SMI]
pot	0.5 M HNO <sub>3</sub>	?	11.53	[66NEB/URB]
$U^{4+} + 2cit^{3-} \rightleftharpoons U(cit)_2^{2-}$				
pot	0.5 M HNO <sub>3</sub>		19.46	[66NEB/URB]
$U^{4+} + H_3cit \rightleftharpoons U(Hcit)^{2+} + 2H^+$				
pot	4 M (H, Na)ClO <sub>4</sub>	22	$0.85 \pm 0.03$	[74SHA/KII]

a: Refers to the reactions indicated, the ionic strength and temperature given in the table. Uncertainties are those given in the references.

b: From the dependence of  $\log_{10} K$  on pH, the actual complex was considered as  $U(OH)_2cit^-$ .

r. t.: Room temperature.

### VII.10.2 U(VI) citrate complexes

With hexavalent uranium ( $UO_2^{2+}$ ),  $H_2cit^-$ ,  $Hcit^{2-}$  and  $cit^{3-}$  may form complexes. However,  $UO_2^{2+}$  has a linear dioxo structure and the ligand should coordinate in the equatorial plane perpendicular to the O–U–O axis, and this sets some constraints on the stoichiometry of the complexes due to the steric hindrance. Because of this, only two carboxylate groups may be simultaneously coordinated to the central uranium, resulting in the strong interaction of the alcoholic hydroxyl and the uranium. Thus, it is to be expected that the stability of  $UO_2cit^-$  may not be much larger than that of  $UO_2(Hcit)(aq)$ . Furthermore, the species containing  $cit^{3-}$  as ligand may form polynuclear complexes bridged by non-bonded carboxylate groups.

A summary of the experimental data available for the citrate complexes of  $UO_2^{2+}$  is presented in Table VII-23.

Table VII-23: Literature data on the formation constants for the citrate complexes of  $\text{UO}_2^{2+}$ .

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{UO}_2^{2+} + \text{cit}^{3-} \rightleftharpoons \text{UO}_2(\text{cit})^-$				
sp	not controlled	?	3.165	[54HEI/BOB]
pot	0.15 M NaCl	25	8.5	[59LI/LIN]
pot	0.1 M $\text{KNO}_3$	25	$(7.40 \pm 0.21)$	[65RAJ/MAR]
	1.0 M $\text{KNO}_3$	25	$(6.87 \pm 0.11)$	
pot	1.0 M $\text{KNO}_3$	25	5.78	[72MAR/KLO]
cix	0.1 M $\text{Na}(\text{H}_2\text{cit})$	25	7.22	[75OHY/ODA]
sp	1 M $(\text{H}_3\text{Na}, (\text{UO}_2)_{0.5})_3\text{cit}$	25	6.20	[80VAN/KUC]
		25	$(7.17 \pm 0.16)$	
sp	0.05 M $\text{NaClO}_4$	20	3.93	[89ABD/ALI]
dis	5 <i>m</i> NaCl	25	$(6.04 \pm 0.01)$	[96BOR/LIS]
dis	0.3 <i>m</i> NaCl	25	$(7.30 \pm 0.04)$	[99BRO/POK]
	1.0 <i>m</i> NaCl	25	$(7.08 \pm 0.01)$	
	2.0 <i>m</i> NaCl	25	$(7.22 \pm 0.02)$	
	3.0 <i>m</i> NaCl	25	$(7.10 \pm 0.01)$	
	4.0 <i>m</i> NaCl	25	$(7.02 \pm 0.01)$	
	5.0 <i>m</i> NaCl	25	$(7.03 \pm 0.02)$	
cix	0.1 M $\text{NaClO}_4$	21	$(6.69 \pm 0.03)$	[2000LEN/CAB]
$\text{UO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{UO}_2(\text{cit})_2^{4-}$				
dis	5 <i>m</i> NaCl	25	$(10.98 \pm 0.03)$	[96BOR/LIS]
$2 \text{UO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons (\text{UO}_2)_2(\text{cit})_2^{2-}$				
pot	0.136 M $\text{KNO}_3$	25	19.26 <sup>b</sup>	[60FEL/NOR]
pot	0.1 M $\text{KNO}_3$	25	$(18.87 \pm 0.06)$	[65RAJ/MAR]
	1.0 M $\text{KNO}_3$	25	$(17.70 \pm 0.04)$	
pot	0.15 M NaCl	25	18.90	[59LI/LIN]
pot	1.0 M $\text{KNO}_3$	25	17.57	[72MAR/KLO]
sp	1 M $(\text{H}_3\text{Na}, (\text{UO}_2)_{0.5})_3\text{cit}$	25	15.25	[80VAN/KUC]
		25	$(17.00 \pm 0.14)$	
$2 \text{UO}_2^{2+} + 3 \text{cit}^{3-} \rightleftharpoons (\text{UO}_2)_2(\text{cit})_3^{5-}$				
sp	not controlled	?	6.095	[54HEI/BOB]
$2 \text{UO}_2(\text{cit})^- \rightleftharpoons (\text{UO}_2)_2(\text{cit})_2^{2-}$				
dis	0.15 M $\text{NaNO}_3$	20	$\geq 6.0$	[70ADI/KLO]
$\text{UO}_2^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{UO}_2(\text{Hcit})(\text{aq})$				
cix	0.1 M $\text{Na}(\text{H}_2\text{cit})$	25	4.23	[75OHY/ODA], [75OHY]
sp	1 M $(\text{H}_3\text{Na}, (\text{UO}_2)_{0.5})_3\text{cit}$	25	3.82	[80VAN/KUC]
		25	$(4.56 \pm 0.26)$	

(Continued on next page)

Table VII-23 (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{UO}_2^{2+} + 2\text{Hcit}^{2-} \rightleftharpoons \text{UO}_2(\text{Hcit})_2^{2-}$				
?	?	25	$\cong 11.2$	[62STA/BAL]
$\text{UO}_2^{2+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{UO}_2(\text{H}_2\text{cit})^+$				
cix	0.1 M Na(H <sub>2</sub> cit)	25	2.79	[75OHY/ODA]
sp	1 M (H,Na, (UO <sub>2</sub> ) <sub>0.5</sub> ) <sub>3</sub> (cit)	25	1.53	[80VAN/KUC]
$2 \text{UO}_2^{2+} + 2\text{H}_2\text{cit}^- \rightleftharpoons (\text{UO}_2)_2(\text{H}_2\text{cit})_2^{2+}$				
sp	1 M (H,Na, (UO <sub>2</sub> ) <sub>0.5</sub> ) <sub>3</sub> (cit)	25	8.89	[80VAN/KUC]
$\text{UO}_2^{2+} + \text{M}^{z+} + 2\text{H}_3\text{cit}^- \rightleftharpoons \text{UO}_2\text{M}(\text{H}_3\text{cit})_2^{z-6} + 8\text{H}^+$				
pot	M = Fe(III)	25	2.45	[89MAN/APE]
	M = Al(III)	25	8.21	
	M = In(III)	25	11.30	
	M = Cu(II)	25	-1.41	

a: Refers to the reactions indicated, the ionic strength and temperature given in the table. Uncertainties are those given in the references.

b: Recalculated from the reported value. See the discussion on [60FEL/NOR].

Among the publications on the determination of equilibrium constants for  $\text{UO}_2^{2+}$  citrate system, four papers, [59LI/LIN], [60FEL/NOR], [65RAJ/MAR] and [72MAR/KLO], report potentiometric titrations of solutions containing  $\text{UO}_2^{2+}$  and  $\text{H}_3\text{cit}$ . The titration curves exhibit a first and a second inflection point at 3 and 3 + 5/3 moles of base per mole of  $\text{UO}_2^{2+}$ . Mass balance equations for these titrations are:

$$C_L = [\text{H}_3\text{L}] + [\text{H}_2\text{L}] + [\text{HL}] + [\text{L}] + [\text{ML}] + [\text{MHL}] + [\text{MH}_2\text{L}] + 2[\text{M}_2\text{L}_2],$$

$$C_M = [\text{M}] + [\text{ML}] + 2[\text{M}_2\text{L}_2] + [\text{MHL}] + [\text{MH}_2\text{L}] + \sum p[\text{M}_p(\text{OH})_q],$$

$$3C_L - C_{\text{OH}} = 3[\text{H}_3\text{L}] + 2[\text{H}_2\text{L}] + [\text{HL}] + [\text{MHL}] + 2[\text{MH}_2\text{L}] - \sum q[\text{M}_p(\text{OH})_q] + [\text{H}^+]$$

where L and M denote  $\text{cit}^{3-}$  and  $\text{UO}_2^{2+}$ , respectively, and charges are omitted for brevity.  $C_L$ ,  $C_M$  and  $C_{\text{OH}}$  are the total added concentrations of citric acid ( $\text{H}_3\text{cit}$ ),  $\text{UO}_2^{2+}$  and NaOH, respectively. The formation constants for the complexes are expressed by:

$$[\text{H}_r\text{L}] = \beta_{r(\text{H})} [\text{H}^+]^r [\text{L}],$$

$$[\text{M}_p(\text{H}_r\text{L})_q] = \beta_{q,p} [\text{M}]^p [\text{H}_r\text{L}]^q,$$

$$[\text{M}_p(\text{OH})_q] = {}^*\beta_{q(\text{OH}),p} \frac{[\text{M}]^p}{[\text{H}^+]^q}.$$

If  $C_L$ ,  $C_M$  and  $C_{\text{OH}}$  and the formation constants are known, these equations can be solved to give the equilibrium concentrations of all species.

Although Li *et al.* [59LI/LIN] reported that equimolar concentrations of  $\text{UO}_2^{2+}$

and citric acid react to form only a mononuclear chelate  $\text{UO}_2(\text{cit})^-$ , Feldman *et al.* [60FEL/NOR] showed that their data could be interpreted in terms of the formation of the dimer  $(\text{UO}_2)_2(\text{cit})_2^{2-}$ . Posterior and more elaborate studies [60FEL/NOR], [65RAJ/MAR] and [72MAR/KLO] also revealed that the predominating species should be the dimer  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  under these conditions. This is also supported by the observation [60FEL/NOR], [72MAR/KLO] of the similar formation of the dimer  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  and the mixed-metal complex  $\text{UO}_2\text{InL}_2$  where L is  $\text{cit}^{3-}$ , malate ( $\text{OOCCH}_2\text{CH}(\text{OH})\text{COO}^{2-}$ ) and tartrate ( $\text{OOCCH}(\text{OH})\text{CH}(\text{OH})\text{COO}^{2-}$ ). Assuming the formation of the monomer  $\text{UO}_2\text{cit}^-$  and the dimer  $(\text{UO}_2)_2(\text{cit})_2^{2-}$ , the above equations are simplified to:

$$C_L = [\text{H}_3\text{L}] + [\text{H}_2\text{L}] + [\text{HL}] + [\text{L}] + [\text{ML}] + 2[\text{M}_2\text{L}_2],$$

$$C_M = [\text{M}] + [\text{ML}] + 2[\text{M}_2\text{L}_2],$$

$$3C_L - C_{\text{OH}} = 3[\text{H}_3\text{L}] + 2[\text{H}_2\text{L}] + [\text{HL}] + [\text{H}^+].$$

$[\text{H}_3\text{L}]$ ,  $[\text{H}_2\text{L}]$ ,  $[\text{HL}]$  and  $[\text{L}]$  can be expressed in terms of  $C'_L$  and  $[\text{H}^+]$ :

$$[\text{H}_r\text{L}] = C'_L \alpha_r,$$

$$\text{where: } C'_L = [\text{H}_3\text{L}] + [\text{H}_2\text{L}] + [\text{HL}] + [\text{L}] \text{ and } \alpha_r = \frac{\beta_{r(\text{H})}[\text{H}^+]^r}{\sum_{r=0}^3 \beta_{r(\text{H})}[\text{H}^+]^r} \quad (\beta_{0(\text{H})} = 1)$$

Since the equation for  $3C_L - C_{\text{OH}}$  can be transformed into:

$$3C_L - C_{\text{OH}} - [\text{H}^+] = (3\alpha_3 + 2\alpha_2 + \alpha_1)C'_L,$$

$C'_L$  can be estimated from the measured pH, which in turn enables to estimate  $[\text{M}]$  and  $[\text{L}]$  by:

$$[\text{L}] = C'_L \alpha_0,$$

$$[\text{M}] = C_M - (C_L - C'_L).$$

Therefore, if the monomer ML is the predominant species in the titration process, the following  $\beta_1$  for the formation of ML is obtained as a constant.

$$\beta_1 = \frac{[\text{ML}]}{[\text{M}] \cdot [\text{L}]} = \frac{C_L - C'_L}{(C_M - C_L + C'_L)(C'_L \alpha_0)}.$$

Alternatively, if the dimer  $\text{M}_2\text{L}_2$  is the predominant species, with the following equilibrium constant,

$$\beta_{2,2} = \frac{[\text{M}_2\text{L}_2]}{[\text{M}]^2 \cdot [\text{L}]^2} = \frac{(C_L - C'_L)/2}{(C_M - C_L + C'_L)^2 (C'_L \alpha_0)^2}$$

fairly constant  $\log_{10} \beta_{2,2}$  values were obtained by Feldman *et al.* [60FEL/NOR], Rajan *et al.* [65RAJ/MAR] and Markovits *et al.* [72MAR/KLO], indicating a good reproducibility of the potentiometric titration.

From the second inflection point in the titration curves, the authors of [60FEL/NOR] and [65RAJ/MAR] inferred the formation of a trimeric species

$(\text{UO}_2)_3(\text{cit})_3(\text{OH})_5^{8-}$ . However, taking into account the possible formation of hydroxides of  $\text{UO}_2^{2+}$ , this second inflection point can be expected even without citric acid. Figure VII-22 shows the simulated titration curve which is calculated by assuming the formation of hydroxide complexes without precipitation. Although the reported observations, showing no precipitation in this pH region, suggest the formation of complex(es) with  $\text{H}_3\text{cit}^{4-}$  or of mixed hydroxide-citrate complex(es), their formation constant(s) should be estimated without neglecting the simultaneously proceeding hydrolysis reactions, since the proposed reaction(s) occurs at the similar pH as shown by Figure VII-23. At present, the trimerization of the citrate complex is not considered as proven by this review.

Figure VII-22: Simulated titration curves of 0.01 M citric acid (upper dashed line), 0.01 M citric acid and 0.01 M  $\text{UO}_2^{2+}$  (solid line), and 0.01 M strong acid (lower dashed line) at  $I = 0.1$  M. The protonation constants selected in this review have been used:

For  $\text{H}^+ + \text{H}_{r-1}\text{cit}^{r-4} \rightleftharpoons \text{H}_r\text{cit}^{r-3}$ .

$$\log_{10} K_1 (r=1) = 5.70, \log_{10} K_2 (r=2) = 4.36, \log_{10} K_3 (r=3) = 2.92.$$

For the U(VI)-citrate complexes,  $p\text{UO}_2^{2+} + q\text{H}_r\text{cit}^{r-3} \rightleftharpoons (\text{UO}_2)_p(\text{H}_r\text{cit})_q^{2p+q(r-3)}$ , the equilibrium constants used are:

$$\text{UO}_2(\text{cit})^-: 7.67, (\text{UO}_2)_2(\text{cit})_2^{2-}: 19.02, \text{UO}_2(\text{Hcit})(\text{aq}): 4.23.$$

For the hydrolysis of U(VI),  $p\text{UO}_2^{2+} + q(\text{H}_2\text{O}) \rightleftharpoons (\text{UO}_2)_p(\text{OH})_q^{2p-q} + q\text{H}^+$ , the equilibrium constants used are:

$$\text{UO}_2\text{OH}^+: -5.43, \text{UO}_2(\text{OH})_2(\text{aq}): -10.52, (\text{UO}_2)_2(\text{OH})_2^{2+}: -5.81, \\ (\text{UO}_2)_3(\text{OH})_4^{2+}: -12.30 \text{ and } (\text{UO}_2)_3(\text{OH})_5^+: -16.15.$$

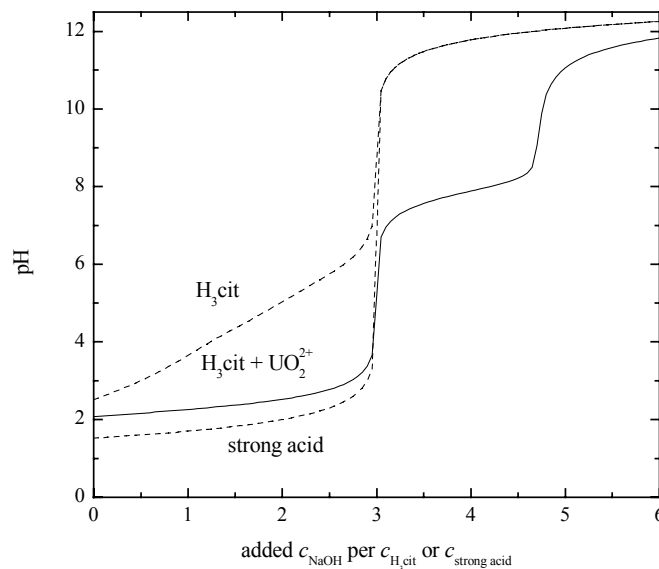
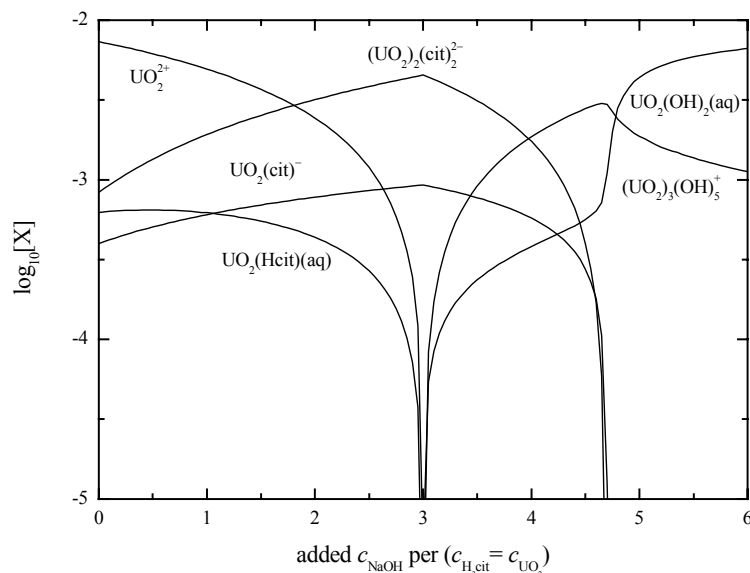


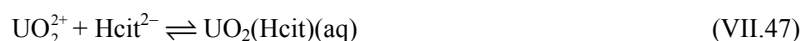
Figure VII-23: Changes in the concentrations of the relevant species in the titration of 0.01 M citric acid and 0.01 M  $\text{UO}_2^{2+}$  shown in Figure VII-22. The same equilibrium constants were used as in Figure VII-22.



As compared to the fact that potentiometry gives a relatively reliable value of  $\log_{10} \beta_{2,2}$  for  $(\text{UO}_2)_2(\text{cit})_2^{2-}$ , solvent extraction [99BRO/POK], ion exchange [75OHY], [75OHY/ODA] and spectrophotometry [80VAN/KUC] at lower  $\text{UO}_2^{2+}$  concentrations give a reliable value of  $\log_{10} \beta_1$  for  $\text{UO}_2(\text{cit})^-$ . Especially, Bronikowski *et al.* [99BRO/POK] give values of  $\log_{10} \beta_1$  for  $\text{UO}_2(\text{cit})^-$  at different ionic strengths which can be used for SIT analysis. Although the stabilities of the complexes with protonated ligands,  $\text{UO}_2(\text{Hcit})(\text{aq})$ ,  $\text{UO}_2(\text{H}_2\text{cit})^+$  and  $(\text{UO}_2)_2(\text{H}_2\text{cit})_2^{2+}$  are reported, these species would be formed in appreciable amounts only at lower pH. Among these species, only  $\text{UO}_2(\text{Hcit})(\text{aq})$  is considered to be plausible in this review.

Because of various shortcomings in the experimental procedures or in the reporting of the results, the values of [54HEI/BOB], [62STA/BAL], [70ADI/KLO], [89ABD/ALI], [89MAN/APE], [2000LEN/CAB] have been rejected by this review (*cf.* Appendix A).

Based on the discussion of the remaining literature (*cf.* Appendix A), constants listed in Table VII-24 for the following reactions:



are accepted to derive the selected values in this review.

Table VII-24: Accepted formation constants for citrate complexes of  $\text{UO}_2^{2+}$  used to derive the selected values at 25°C.

Ionic medium	$\log_{10} \beta_{\text{app}}^{\text{a}}$	$\log_{10} \beta^{\text{b}}$	Reference
$\text{UO}_2^{2+} + \text{cit}^{3-} \rightleftharpoons \text{UO}_2\text{cit}^-$			
0.10 M $\text{NaH}_2\text{cit}$	$(7.22 \pm 0.3)$	$(7.22 \pm 0.3)$	[75OHY/ODA]
0.1 M $\text{KNO}_3$	$(7.4 \pm 0.5)$	$(7.43 \pm 0.5)$	[65RAJ/MAR]
1.0 M $\text{KNO}_3$	$(6.84 \pm 0.5)$	$(7.23 \pm 0.5)$	[65RAJ/MAR]
1 M $(\text{H}_2\text{Na}_4(\text{UO}_2)_{0.5})(\text{cit})$	$(7.17 \pm 1.0)$	$(7.17 \pm 1.0)$	[80VAN/KUC]
0.3 m $\text{NaCl}$	$(7.30 \pm 0.3)$	$(7.35 \pm 0.3)$	[99BRO/POK]
1.0 m $\text{NaCl}$	$(7.07 \pm 0.3)$	$(7.20 \pm 0.3)$	
2.0 m $\text{NaCl}$	$(7.20 \pm 0.3)$	$(7.46 \pm 0.3)$	
3.0 m $\text{NaCl}$	$(7.07 \pm 0.3)$	$(7.51 \pm 0.3)$	
4.0 m $\text{NaCl}$	$(6.98 \pm 0.3)$	$(7.67 \pm 0.4)$	
5.0 m $\text{NaCl}$	$(6.98 \pm 0.3)$	$(7.98 \pm 0.5)$	
$2 \text{UO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons (\text{UO}_2)_2(\text{cit})_2^{2-}$			
0.1 M $\text{KNO}_3$	$(18.87 \pm 0.1)$	$(18.90 \pm 0.10)$	[65RAJ/MAR]
0.136 M $\text{KNO}_3$	$(19.18 \pm 0.3)$	$(19.22 \pm 0.30)$	[60FEL/NOR]
0.15 M $\text{NaCl}$	$(18.89 \pm 0.2)$	$(18.92 \pm 0.20)$	[59LI/LIN]
1.0 M $\text{KNO}_3$	$(17.62 \pm 0.1)$	$(17.79 \pm 0.19)$	[65RAJ/MAR]
1 M $(\text{H}_2\text{Na}_4(\text{UO}_2)_{0.5})(\text{cit})$	$(17.00 \pm 1.0)$	$(17.00 \pm 1.0)$	[80VAN/KUC]
2 M $\text{KNO}_3$	$(17.45 \pm 0.2)$	$(17.78 \pm 0.45)$	[72MAR/KLO]
$\text{UO}_2^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{UO}_2(\text{Hcit})(\text{aq})$			
0.10 M $\text{NaH}_2(\text{cit})$	$(4.23 \pm 0.5)$	$(4.23 \pm 0.5)$	[75OHY/ODA]
1 M $(\text{H}_2\text{Na}_4(\text{UO}_2)_{0.5})(\text{cit})$	$(4.56 \pm 1.0)$	$(4.56 \pm 1.0)$	[80VAN/KUC]

a: Values of  $\log_{10} \beta_{\text{app}}$  are converted into molality units.b: Values of  $\log_{10} \beta$  are corrected for chloride or nitrate complex formation.

In the Table VII-24, the reported values were converted into  $\log_{10} \beta_{\text{app}}$  in molality units. Then the values of  $\log_{10} \beta_{\text{app}}$  were corrected for the complex formation of  $\text{UO}_2^{2+}$  with  $\text{Cl}^-$  or  $\text{NO}_3^-$ . Grenthe *et al.* [92GRE/FUG] select the following formation constants:  $\log_{10} \beta_1^0 = (0.17 \pm 0.02)$  for  $\text{UO}_2^{2+} + \text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}^+$ ,  $\log_{10} \beta_2^0 = -(1.1 \pm 0.4)$  for  $\text{UO}_2^{2+} + 2\text{Cl}^- \rightleftharpoons \text{UO}_2\text{Cl}_2(\text{aq})$ , and  $\log_{10} \beta_1^0 = (0.3 \pm 0.15)$  for  $\text{UO}_2^{2+} + \text{NO}_3^- \rightleftharpoons \text{UO}_2(\text{NO}_3)^+$  with the assumptions  $\varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) = \varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = \varepsilon(\text{UO}_2^{2+}, \text{NO}_3^-) = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$  and  $\varepsilon(\text{UO}_2\text{Cl}^+, \text{Cl}^-) = \varepsilon(\text{UO}_2\text{Cl}^+, \text{ClO}_4^-) = \varepsilon(\text{UO}_2^{2+}, \text{NO}_3^-) = (0.33 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$  (Section B.2 in [2001LEM/FUG]). From these values, and using  $\varepsilon(\text{Na}^+, \text{Cl}^-) = \varepsilon(\text{Na}^+, \text{NO}_3^-) = (0.03 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}$  (*cf.* Appendix B), the values of  $\log_{10} \beta_1$  and  $\log_{10} \beta_2$  in [99BRO/POK] were corrected at each ionic strength by the following equation:

$$\log_{10} \beta(\text{corrected}) = \log_{10} \beta(\text{reported}) + \log_{10} (1 + \beta_{1,X}[\text{X}^-] + \beta_{2,X}[\text{X}^-]^2) \quad (\text{VII.48})$$

where  $\text{X}^-$  is  $\text{Cl}^-$  or  $\text{NO}_3^-$ .

The magnitude of the correction (*cf.* Table VII-24) is not large as compared to the estimated uncertainties of the values. For  $\log_{10} \beta_1$  (VII.45) for  $\text{UO}_2(\text{cit})^-$  since  $\varepsilon(\text{Na}^+, \text{cit}^{3-})$  is dependent on ionic strength, the analysis was conducted in the form of:

$$\log_{10} \beta - \frac{0.5091 \Delta z^2 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} - \varepsilon(\text{Na}^+, \text{cit}^{3-}) I_m = \log_{10} \beta^0 - \Delta \varepsilon' I_m \quad (\text{VII.49})$$

$$\text{where} \quad \varepsilon(\text{Na}^+, \text{cit}^{3-}) = -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m, \quad (\text{VII.50})$$

$$\text{and} \quad \Delta \varepsilon' = \varepsilon(\text{UO}_2(\text{cit})^-, \text{Na}^+) - \varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) \quad (\text{VII.51})$$

For the data obtained in  $\text{KNO}_3$  media, the calculation of the left-hand side of equation (VII.49) was carried out with using  $\varepsilon(\text{K}^+, \text{cit}^{3-}) = (0.02 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$  in place of  $\varepsilon(\text{Na}^+, \text{cit}^{3-})$ .

The result of fitting to equation (VII.49) is shown in Figure VII-24 and a plot of  $\log_{10} \beta$  against  $I_m$  is shown in Figure VII-25.

Figure VII-24: Fitting of the values of  $\log_{10} \beta$  (VII.45) at each ionic strength (given in Table VII-24) to the SIT equation. Solid line is drawn by using the result of the fitting Equation (VII.49).

$$\begin{aligned} \log_{10} \beta_1^0 \text{ (VII.45)} &= (8.96 \pm 0.17), \quad \Delta z^2 = -12, \quad \Delta \varepsilon = \Delta \varepsilon' - \varepsilon(\text{cit}^{3-}, \text{M}^+), \\ \Delta \varepsilon' &= -(0.57 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}, \\ \varepsilon(\text{cit}^{3-}, \text{M}^+) &= \varepsilon(\text{cit}^{3-}, \text{Na}^+) - (0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1} \\ \text{or} \quad &= \varepsilon(\text{cit}^{3-}, \text{K}^+) = (0.02 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}. \end{aligned}$$

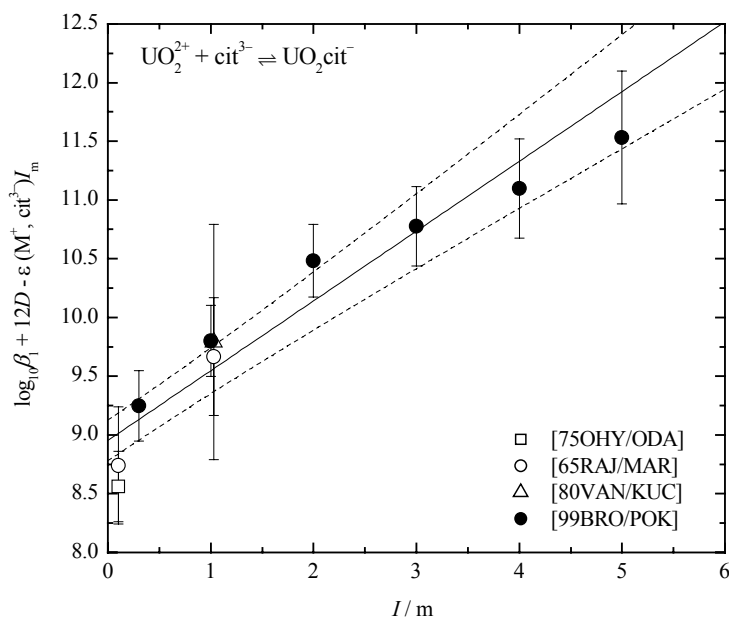
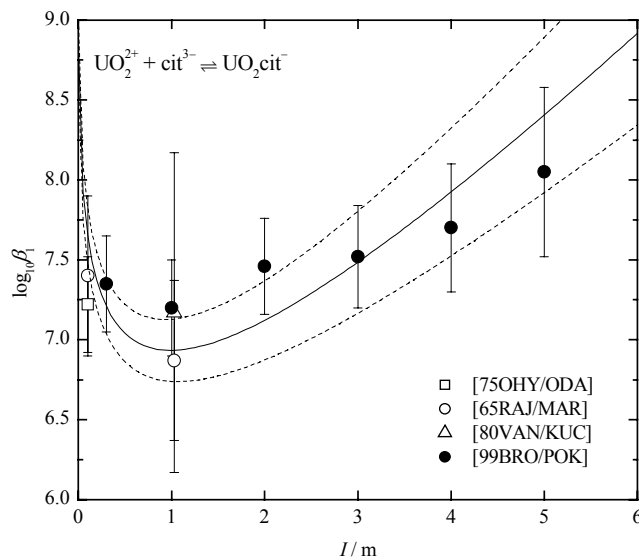




Figure VII-25: A plot  $\log_{10} \beta_1$  (VII.45) against  $I_m$ . The solid line is drawn using the SIT model with:  $\log_{10} \beta_1^\circ$  (VII.45) =  $(8.96 \pm 0.17)$ ,  $\Delta\epsilon' = -(0.57 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}$ , and  $\epsilon(\text{cit}^{3-}, \text{Na}^+) = -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1}$



The fitting results in the following values:

$$\log_{10} \beta_1^\circ \text{ (VII.45)} = (8.96 \pm 0.17) \text{ and } \Delta\epsilon' = -(0.57 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}.$$

From the obtained  $\Delta\epsilon'$  and using  $\epsilon(\text{UO}_2^{2+}, \text{Cl}^-) = (0.46 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ , it is possible to estimate that  $\epsilon(\text{UO}_2(\text{cit})^-, \text{Na}^+)$  equal to:  $-(0.11 \pm 0.09) \text{ kg} \cdot \text{mol}^{-1}$ . Due to the large uncertainty in the estimated  $\epsilon(\text{UO}_2(\text{cit})^-, \text{Na}^+)$ , we cannot judge whether this value is consistent with the other values of  $\epsilon$  for the interaction of  $\text{Na}^+$  with a complex with charge  $-1$ . Thus, this review selects only the value of  $\log_{10} \beta^\circ$  (VII.45), cf. Table VII-25:

$$\log_{10} \beta_1^\circ \text{ (VII.45)} = (8.96 \pm 0.17).$$

For the formation of  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  and  $\text{UO}_2(\text{Hcit})(\text{aq})$ , the analysis was done simply using the expression:

$$\log_{10} \beta - \frac{0.5091 \Delta z^2 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} = \log_{10} \beta^\circ - \Delta\epsilon I_m \quad (\text{VII.52})$$

since the available data are obtained at rather lower ionic strength. The result for  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  of the fitting of equation (VII.52) is shown in Figure VII-26 and in the form of the plot of  $\log_{10} \beta$  (VII.46) against  $I_m$  in Figure VII-27.

Figure VII-26: Fitting of the values of  $\log_{10} \beta$  (VII.46) at each ionic strength (*cf.* Table VII-24) to the SIT equation (VII.52). The solid line is drawn by using the result of the fitting given below.

$$\log_{10} \beta_{2,2}^0 \text{ (VII.46)} = (21.34 \pm 0.5), \Delta\epsilon = -(0.8 \pm 0.2) \text{ kg}\cdot\text{mol}^{-1}.$$

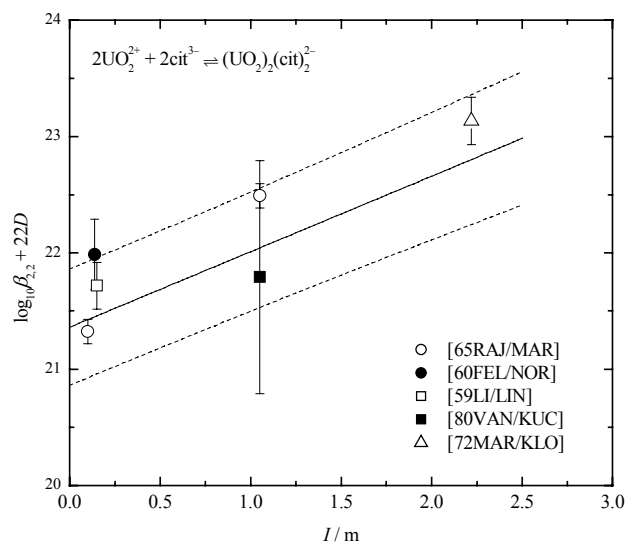
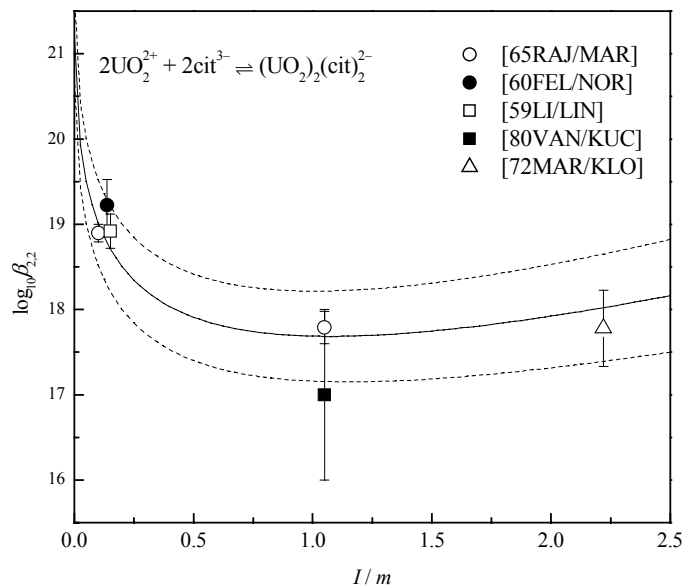


Figure VII-27: Values of  $\log_{10} \beta$  (VII.46) versus ionic strength. The solid line is drawn by using the result of the fitting given below,  $\log_{10} \beta_{2,2}^0 \text{ (VII.46)} = (21.34 \pm 0.5)$ ,  $\Delta\epsilon = -(0.8 \pm 0.2) \text{ kg}\cdot\text{mol}^{-1}$



The fitting of the accepted values for  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  results in:

$$\log_{10} \beta_{2,2}^\circ (\text{VII.46}) = (21.34 \pm 0.5) \text{ and } \Delta\epsilon = - (0.8 \pm 0.2) \text{ kg} \cdot \text{mol}^{-1},$$

and for the reaction  $\text{UO}_2^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{UO}_2(\text{Hcit})(\text{aq})$ , the two accepted literature values (Table VII-24) give:

$$\log_{10} \beta^\circ (\text{VII.47}) = (5.0 \pm 0.6) \text{ and } \Delta\epsilon = - (1 \pm 1) \text{ kg} \cdot \text{mol}^{-1}.$$

The values of  $\Delta\epsilon$  cannot be selected since the number of experimental results is very limited. Due to the scarcity of reliable data, this review assigns larger uncertainties to the values obtained from the fitting procedures. In conclusion, Table VII-25 lists the selected equilibrium constants in the uranium(VI)-citrate system.<sup>1</sup>

Table VII-25: Selected formation constants for the citrate complexes of  $\text{UO}_2^{2+}$  at 25°C.

Reaction	$\log_{10} \beta_i^\circ$
$\text{UO}_2^{2+} + \text{cit}^{3-} \rightleftharpoons \text{UO}_2(\text{cit})^-$	$(8.96 \pm 0.17)$
$2 \text{UO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons (\text{UO}_2)_2(\text{cit})_2^{2-}$	$(21.3 \pm 0.5)$
$\text{UO}_2^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{UO}_2\text{Hcit}(\text{aq})$	$(5.0 \pm 1.0)$

The selection in Table VII-25 yields:

$$\Delta_f G_m^\circ (\text{UO}_2(\text{cit})^-, 298.15 \text{ K}) = - (2166.0 \pm 2.8) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f G_m^\circ ((\text{UO}_2)_2(\text{cit})_2^{2-}, 298.15 \text{ K}) = - (4351.2 \pm 6.0) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta_f G_m^\circ (\text{UO}_2\text{Hcit}, \text{aq}, 298.15 \text{ K}) = - (2180.0 \pm 6.3) \text{ kJ} \cdot \text{mol}^{-1}.$$

## VII.11 Neptunium citrate compounds and complexes

A literature search by this review on the thermodynamics of neptunium-citrate systems revealed only information concerning the aqueous complexes of neptunium(V). Similarly to the case of  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^+$  has a linear dioxo structure and the ligand should coordinate in the equatorial plane perpendicular to the O–Np–O axis. This sets some constraints on the stoichiometry of the complexes due to the steric hindrance. Due to the smaller formal charge of  $\text{NpO}_2^+$  as compared to  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^+$  forms only one-to-one complexes with  $\text{cit}^{3-}$ , whose stability is relatively small. A summary of the equilibrium data available for the  $\text{NpO}_2^+$  citrate system is presented in Table VII-26.

<sup>1</sup> A paper by Kantar *et al.* [2005KAN/GIL], available to the reviewers only in the final stage of preparation of this book, reports ion-exchange experiments which were performed to evaluate the formation of U(VI) – citrate and U(VI) – Fe(III) – citrate complexes. The stability constant for the reaction  $\text{UO}_2^{2+} + \text{cit}^{3-} \rightleftharpoons \text{UO}_2\text{cit}^-$  ( $\log_{10} K_1^\circ = 8.7 \pm 0.6$  at  $I = 0$ ), determined by the authors from ion-exchange data, is in agreement with the value selected in this review ( $\log_{10} K_1^\circ = (8.96 \pm 0.17)$ ). For a consistent evaluation of the mixed complexes in the U(VI) – Fe(III) – citrate system NEA selected data on Fe(III) hydrolysis are needed.

Table VII-26: Literature data on the formation constants of citrate complexes of  $\text{NpO}_2^+$ .

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> β <sup>a</sup>	Reference
NpO <sub>2</sub> <sup>+</sup> + Hcit <sup>2-</sup> ⇌ NpO <sub>2</sub> (Hcit) <sup>-</sup>				
cix	0.05 M NH <sub>4</sub> ClO <sub>4</sub>	20	(2.69 ± 0.12)	<a href="#">[61MOS/MAR]</a>
dis	~ 0.05 M NH <sub>4</sub> (CH <sub>3</sub> COO)	25	2.37	<a href="#">[82INO/TOC]</a>
sp	0.05 M	?	(2.49 ± 0.05)	<a href="#">[85SEV]</a>
NpO <sub>2</sub> <sup>+</sup> + cit <sup>3-</sup> ⇌ NpO <sub>2</sub> (cit) <sup>2-</sup>				
cix	0.05 M NH <sub>4</sub> ClO <sub>4</sub>	20	(3.67 ± 0.09)	<a href="#">[61MOS/MAR]</a>
sp	1 M (NaClO <sub>4</sub> )	(25.0 ± 0.2)	(4.42 ± 0.11)	<a href="#">[72STO]</a>
dis	~ 0.05 M NH <sub>4</sub> (CH <sub>3</sub> COO)	25	3.94	<a href="#">[82INO/TOC]</a>
cix	0.1 M NaClO <sub>4</sub>	10	(4.70 ± 0.53)	<a href="#">[84REE/DAN]</a>
		22	(4.84 ± 0.72)	
		35	(4.93 ± 0.11)	
sp	0.05 M	?	(2.87 ± 0.05)	<a href="#">[85SEV]</a>
sp	2.0 M NaClO <sub>4</sub>	25	(2.49 ± 0.02)	<a href="#">[90RIZ/NEC]</a>
dis	5.0 m NaCl	25	(2.40 ± 0.06)	<a href="#">[96BOR/LIS]</a>
dis	0.10 m NaClO <sub>4</sub>	25	(3.03 ± 0.17)	<a href="#">[97POK/CHO]</a>
	0.30 m NaClO <sub>4</sub>		(2.89 ± 0.03)	
	0.50 m NaClO <sub>4</sub>		(2.73 ± 0.01)	
	1.0 m NaClO <sub>4</sub>		(2.74 ± 0.03)	
	2.0 m NaClO <sub>4</sub>		(2.81 ± 0.02)	
	3.0 m NaClO <sub>4</sub>		(2.89 ± 0.01)	
	4.0 m NaClO <sub>4</sub>		(2.95 ± 0.02)	
	5.0 m NaClO <sub>4</sub>		(3.03 ± 0.03)	
	7.0 m NaClO <sub>4</sub>		(3.20 ± 0.05)	
	9.0 m NaClO <sub>4</sub>		(3.11 ± 0.02)	
	0.1 m NaCl	25	(2.97 ± 0.01)	
	0.3 m NaCl		(2.62 ± 0.05)	
	0.5 m NaCl		(2.60 ± 0.02)	
dis	1.0 m NaCl		(2.39 ± 0.01)	<a href="#">[99BRO/POK]</a>
	2.0 m NaCl		(2.50 ± 0.07)	
	3.0 m NaCl		(2.52 ± 0.01)	
	4.0 m NaCl		(2.56 ± 0.05)	
	5.0 m NaCl		(2.56 ± 0.03)	
	NpO <sub>2</sub> <sup>+</sup> + cit <sup>3-</sup> + OH <sup>-</sup> ⇌ NpO <sub>2</sub> (cit)(OH) <sup>3-</sup>			
sp	0.05 M	?	(7.40 ± 0.05)	<a href="#">[85SEV]</a>

a: Refers to the reactions indicated, the ionic strength and temperature given in the table.  
Uncertainties are those given in the references.

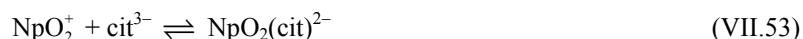
Based on the discussion of the literature studies in Appendix A, the constants listed in Table VII-27 are accepted in this review. Note that [\[92TOC/INO3\]](#) does not report thermodynamic constants.

Table VII-27: Accepted formation constants for citrate complexes of  $\text{NpO}_2^+$  used to derive the selected values at 25°C.

Ionic Medium	$\log_{10} \beta_1^a$	Reference
$\text{NpO}_2^+ + \text{cit}^{3-} \rightleftharpoons \text{NpO}_2\text{cit}^{2-}$		
2.2 m $\text{NaClO}_4$	$(2.44 \pm 0.05)$	<a href="#">[90RIZ/NEC]</a>
0.10 m $\text{NaClO}_4$	$(3.03 \pm 0.20)$	<a href="#">[97POK/CHO]</a>
0.30 m $\text{NaClO}_4$	$(2.88 \pm 0.10)$	
0.50 m $\text{NaClO}_4$	$(2.72 \pm 0.10)$	
1.0 m $\text{NaClO}_4$	$(2.74 \pm 0.10)$	
2.00 m $\text{NaClO}_4$	$(2.81 \pm 0.10)$	
3.00 m $\text{NaClO}_4$	$(2.89 \pm 0.10)$	
4.00 m $\text{NaClO}_4$	$(2.95 \pm 0.10)$	
5.00 m $\text{NaClO}_4$	$(3.03 \pm 0.10)$	
0.1 m $\text{NaCl}$	$(2.97 \pm 0.10)$	<a href="#">[99BRO/POK]</a>
0.3 m $\text{NaCl}$	$(2.62 \pm 0.10)$	
0.5 m $\text{NaCl}$	$(2.59 \pm 0.10)$	
1.0 m $\text{NaCl}$	$(2.38 \pm 0.10)$	
2.0 m $\text{NaCl}$	$(2.48 \pm 0.10)$	
3.0 m $\text{NaCl}$	$(2.49 \pm 0.10)$	
4.0 m $\text{NaCl}$	$(2.52 \pm 0.10)$	
5.0 m $\text{NaCl}$	$(2.51 \pm 0.10)$	

a: The values of  $\log_{10} \beta$  are converted into molality units.

Although the weak formation of  $\text{NpO}_2(\text{Hcit})^-$  is probable ([\[61MOS/MAR\]](#), [\[85SEV\]](#)), the values of the stability constant reported are not enough reliable to be accepted. Thus, this review only considers the reaction:



For the SIT analysis, the data obtained in  $\text{NaClO}_4$  ([\[97POK/CHO\]](#) and [\[90RIZ/NEC\]](#),  $I_m \leq 5 \text{ m}$ ) and in  $\text{NaCl}$  ([\[99BRO/POK\]](#),  $I_m \leq 5 \text{ m}$ ) are used. Since there are two series of data and  $\varepsilon(\text{cit}^{3-}, \text{Na}^+)$  is dependant on  $I_m$ , the analysis is conducted in the form of:

$$\begin{aligned} \log_{10} \beta_1 - \frac{\Delta z^2 \times 0.5091 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} - (\varepsilon(\text{NpO}_2^+, \text{X}^-) + \varepsilon(\text{Na}^+, \text{cit}^{3-})) I_m \\ = \log_{10} \beta_1^0 - \varepsilon(\text{Na}^+, \text{NpO}_2(\text{cit})^{2-}) I_m \end{aligned} \quad (\text{VII.54})$$

to obtain  $\log_{10} \beta_1^0$  (VII.53) and  $\varepsilon(\text{Na}^+, \text{NpO}_2(\text{cit})^{2-})$ . The values of  $\Delta z^2 = -6$  and  $\varepsilon(\text{NpO}_2^+, \text{ClO}_4^-) = (0.25 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$  and  $\varepsilon(\text{NpO}_2^+, \text{Cl}^-) = (0.09 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}$  [2001LEM/FUG] and  $\varepsilon(\text{Na}^+, \text{cit}^{3-}) = -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1}$  (selected by this review) were used. The result of the SIT analysis is shown in Figure VII-28. In Figure VII-29, the result is also shown as the plot of  $\log_{10} \beta$  (VII.53) against  $I_m$ . As shown in Figure VII-29,  $\varepsilon(\text{NpO}_2^+, \text{ClO}_4^-) = 0.25 \text{ kg} \cdot \text{mol}^{-1}$  and  $\varepsilon(\text{NpO}_2^+, \text{Cl}^-) = 0.09 \text{ kg} \cdot \text{mol}^{-1}$  approximately describe the difference in  $\log_{10} \beta_1^0$  (VII.53) between  $\text{NaClO}_4$  and  $\text{NaCl}$  media.

Figure VII-28: Fitting of the values of  $\log_{10} \beta$  (VII.53) at each ionic strength (Table VII-27) to the SIT equation. Solid line is drawn using the result of the fitting Eq. (VII.54), with:

$$\begin{aligned} \log_{10} \beta_1^0 (\text{VII.53}) &= (3.68 \pm 0.05), \quad \Delta z^2 = -6, \\ \varepsilon(\text{cit}^{3-}, \text{Na}^+) &= -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1}, \\ \varepsilon(\text{NpO}_2 \text{cit}^{2-}, \text{Na}^+) &= -(0.06 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1} \\ \varepsilon(\text{NpO}_2^+, \text{ClO}_4^-) &= (0.25 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1} \\ \varepsilon(\text{NpO}_2^+, \text{Cl}^-) &= (0.09 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}. \end{aligned}$$

The uncertainties in the data include those from  $\varepsilon(\text{cit}^{3-}, \text{Na}^+)$  and from  $\varepsilon(\text{NpO}_2^+, \text{X}^-)$ .

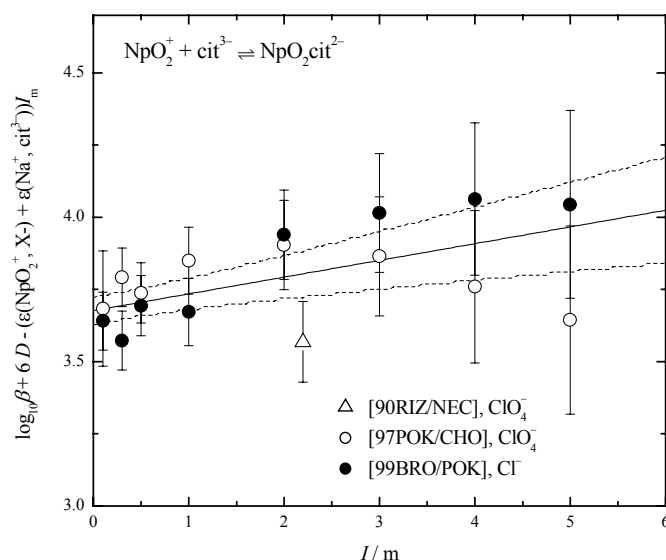
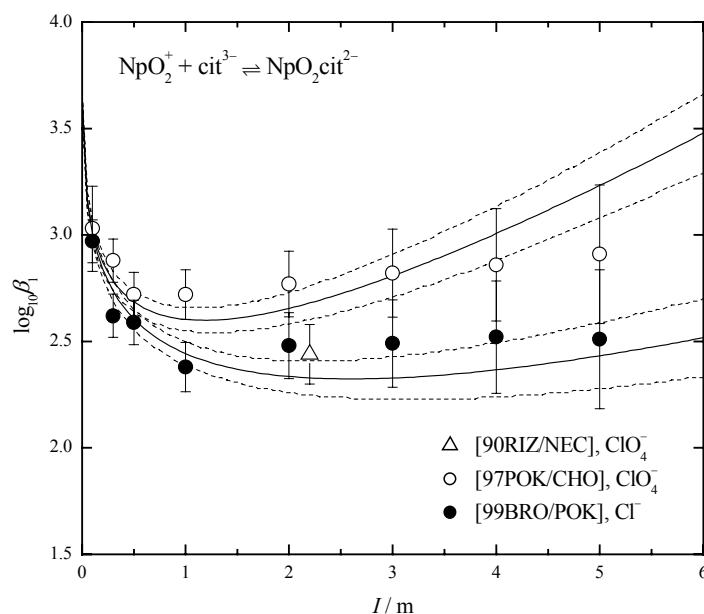


Figure VII-29: Plot of  $\log_{10} \beta_1$  (VII.53) versus ionic strength. The uncertainties in the data include those from  $\varepsilon(\text{Na}^+, \text{cit}^{3-})$  and from  $\varepsilon(\text{NpO}_2^+, \text{X}^-)$ . Solid lines:

$$\log_{10} \beta_1 = \log_{10} \beta_1^\circ + \frac{\Delta z^2 \times 0.5091 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} - \Delta \varepsilon I_m$$

$$\begin{aligned} \Delta \varepsilon &= \varepsilon(\text{NpO}_2\text{cit}^{2-}, \text{Na}^+) - \varepsilon(\text{NpO}_2^+, \text{X}^-) - \varepsilon(\text{cit}^{3-}, \text{Na}^+), \\ \varepsilon(\text{cit}^{3-}, \text{Na}^+) &= -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1} \\ \varepsilon(\text{NpO}_2\text{cit}^{2-}, \text{Na}^+) &= -(0.06 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1} \\ \varepsilon(\text{NpO}_2^+, \text{ClO}_4^-) &= (0.25 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1}, \\ \varepsilon(\text{NpO}_2^+, \text{Cl}^-) &= (0.09 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1} \end{aligned}$$



The selected formation constant for the citrate complex of  $\text{NpO}_2^+$  at 25°C is:

$$\begin{aligned} \log_{10} \beta_1^\circ \text{ (VII.53)} &= (3.68 \pm 0.05), \\ \text{with } \varepsilon(\text{Na}^+, \text{NpO}_2(\text{cit})^{2-}) &= -(0.06 \pm 0.03). \end{aligned}$$

The selection above yields:

$$\Delta_f G_m^\circ(\text{NpO}_2(\text{cit})^{2-}, 298.15 \text{ K}) = -(2091.0 \pm 6.0) \text{ kJ} \cdot \text{mol}^{-1}.$$

## VII.12 Plutonium citrate compounds and complexes

A literature search by this review on the thermodynamics of plutonium-citrate systems revealed information concerning the aqueous complexes of plutonium(III), plutonium(IV) and plutonium(VI). No thermodynamic data for Pu citrate compounds could be identified (see also Section VII.1.1).

As shown in Table VII-28 and Table VII-29, there is only one paper dealing with the complex formation of  $\text{Pu}^{3+}$  and  $\text{PuO}_2^{2+}$  with citrate, respectively. Based on the discussion of [89POC] and [75NEB/AND] in Appendix A, these values are not considered reliable enough to derive selected values.

Table VII-28: Literature data for the formation constants of citrate complexes of  $\text{Pu}^{3+}$ .

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta_1^a$	Reference
$\text{Pu}^{3+} + \text{Hcit}^{2-} \rightleftharpoons \text{Pu}(\text{Hcit})^+$				
pot	0.1 M KCl	20-22	$(4.82 \pm 0.27)$	[89POC]
$\text{Pu}^{3+} + \text{cit}^{3-} \rightleftharpoons \text{Pu}(\text{cit})(\text{aq})$				
pot	0.1 M KCl	20-22	$(6.71 \pm 0.25)$	[89POC]
$\text{Pu}^{3+} + \text{H}_2\text{Cit}^{4-} \rightleftharpoons \text{Pu}(\text{H}_2\text{Cit})^-$				
pot	0.1 M KCl	20-22	$(15.33 \pm 0.30)$	[89POC]

a: Refers to the reactions indicated, the ionic strength and temperature given in the table. Uncertainties are estimated in this review.

Table VII-29: Literature data for the formation constants of citrate complexes of  $\text{PuO}_2^{2+}$ .

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{PuO}_2^{2+} + \text{cit}^{3-} \rightleftharpoons \text{PuO}_2\text{cit}^-$				
sp	0.5 M HClO <sub>4</sub>	25	9.00	<a href="#">[75NEB/AND]</a>
		35	8.90	
$\text{PuO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{PuO}_2(\text{cit})_2^{4-}$				
pot	0.5 M HClO <sub>4</sub>	25	14.98	<a href="#">[75NEB/AND]</a>
		35	14.85	

a: Refers to the reactions indicated, the ionic strength and temperature given in the table.

The information on the complex formation of  $\text{Pu}^{4+}$  with citrate is also limited as shown in Table VII-30.



Table VII-30: Experimental equilibrium data for Pu<sup>4+</sup> citrate system at 25°C.

Method	Ionic medium	Reaction	log <sub>10</sub> K <sup>a</sup>	Reference
gl	0.5 M NaClO <sub>4</sub>	Pu <sup>4+</sup> + cit <sup>3-</sup> ⇌ Pu(cit) <sup>+</sup>	15.8	<a href="#">[66NEB2]</a>
		Pu <sup>4+</sup> + 2cit <sup>3-</sup> ⇌ Pu(cit) <sub>2</sub> <sup>2-</sup>	29.0	
sp	0.5 M NaClO <sub>4</sub>	Pu <sup>4+</sup> + cit <sup>3-</sup> ⇌ Pu(cit) <sup>+</sup>	14.72 – 15.43	<a href="#">[66NEB]</a>
		Pu <sup>4+</sup> + 2cit <sup>3-</sup> ⇌ Pu(cit) <sub>2</sub> <sup>2-</sup>	30.20 – 29.83	
redox	0.5 M NaClO <sub>4</sub>	Pu <sup>4+</sup> + cit <sup>3-</sup> ⇌ Pu(cit) <sup>+</sup>	15.5	<a href="#">[66NEB2]</a>
		Pu <sup>4+</sup> + 2cit <sup>3-</sup> ⇌ Pu(cit) <sub>2</sub> <sup>2-</sup>	30	
dis	1.0 M LiClO <sub>4</sub>	Pu <sup>4+</sup> + H <sub>3</sub> cit ⇌ Pu(H <sub>2</sub> cit) <sup>3+</sup> + H <sup>+</sup>	2.85	<a href="#">[72MET/GUI3]</a>
		Pu <sup>4+</sup> + H <sub>3</sub> cit ⇌ Pu(Hcit) <sub>2</sub> <sup>2+</sup> + 2H <sup>+</sup>	1.85	
		Pu <sup>4+</sup> + H <sub>3</sub> cit ⇌ Pu(cit) <sup>+</sup> + 3H <sup>+</sup>	0.1	
		Pu <sup>4+</sup> + H <sub>3</sub> cit + H <sub>2</sub> O ⇌ Pu(cit)(OH)(aq) + 4H <sup>+</sup>	– 5.63	
		Pu <sup>4+</sup> + H <sub>3</sub> cit + 2H <sub>2</sub> O ⇌ Pu(cit)(OH) <sub>2</sub> <sup>-</sup> + 5H <sup>+</sup>	– 9.85	
		Pu <sup>4+</sup> + 2H <sub>3</sub> cit ⇌ Pu(H <sub>3</sub> cit)(H <sub>2</sub> cit) <sup>3+</sup> + H <sup>+</sup>	4	
		Pu <sup>4+</sup> + 2H <sub>3</sub> cit ⇌ Pu(H <sub>2</sub> cit) <sub>2</sub> <sup>2+</sup> + 2H <sup>+</sup>	3.5	
		Pu <sup>4+</sup> + 2H <sub>3</sub> cit ⇌ Pu(Hcit) <sub>2</sub> (aq) + 4H <sup>+</sup>	– 1.53	
		Pu <sup>4+</sup> + 2H <sub>3</sub> cit ⇌ Pu(cit) <sub>2</sub> <sup>2-</sup> + 6H <sup>+</sup>	– 7.5	
		Pu <sup>4+</sup> + 2H <sub>3</sub> cit + 2H <sub>2</sub> O ⇌ Pu(cit) <sub>2</sub> (OH) <sub>2</sub> <sup>4-</sup> + 8H <sup>+</sup>	– 16.6	
dis	1 M LiNO <sub>3</sub>	Pu <sup>4+</sup> + H <sub>3</sub> cit ⇌ Pu(Hcit) <sub>2</sub> <sup>2+</sup> + 2H <sup>+</sup>	1.63	<a href="#">[75ZAI/NIK]</a>
	2 M LiNO <sub>3</sub>		1.04	
	4 M LiNO <sub>3</sub>		0.46	
	6 M LiNO <sub>3</sub>		– 0.07	

a: Refers to the reactions indicated, the ionic strength and temperature given in the table.

Although very strong complex formation is expected, the stoichiometry of the species formed is not well established. As the interaction is very strong, it can be studied only in highly acidic solutions (pH less than 0.5), where the activity coefficients of the relevant species are very difficult to be estimated. As a result, the values in Table VII-30 are dependent on the assumption of the complex species formed under the corresponding experimental condition. Since any study on plutonium complex formation involves the difficulties of controlling the oxidation state and of avoiding hydrolysis, Raymond *et al.* [\[87RAY/DUF\]](#) and Choppin *et al.* [\[96CHO/ERT\]](#) studied instead the complex formation of Th<sup>4+</sup> with citrate, where Pu<sup>4+</sup> and Th<sup>4+</sup> are considered to be similar in complex formation and Th<sup>4+</sup> is known not to hydrolyse up to pH around 4 (*cf.* Appendix A).

Considering the analogy between Th(IV) and Pu(IV), Pu(H<sub>2</sub>cit)<sup>3+</sup>, Pu(H<sub>2</sub>cit)<sub>2</sub><sup>2+</sup>, Pu(Hcit)<sub>2</sub><sup>2+</sup>, Pu(Hcit)<sub>2</sub>(aq), Pu(cit)<sup>+</sup> and Pu(cit)<sub>2</sub><sup>2-</sup> are deemed most possible among the various species considered. To compare the values of the formation constants obtained for these species, the data in Table VII-30 are converted into log<sub>10</sub> β using the protonation constants of citric acid selected in this review, and the resulting equilibrium con-

stants are shown in Table VII-31. Some data for  $\text{Th}^{4+}$  are also listed for comparison ( $\log_{10} K_{1(\text{H})}^{\circ} = 6.33$  obtained from the data in [96CHO/ERT] is used for this conversion). Although the data roughly agree with each other, there are not enough reliable values to select any values for  $\text{Pu}^{4+}$  citrates.

Table VII-31: Literature data on the formation constants for citrate complexes of  $\text{Pu}^{4+}$  or  $\text{Th}^{4+}$  expressed as  $\log_{10} \beta$  at 25°C.

Reaction	Ionic medium	$\log_{10} \beta$	Reference
$\text{Pu}^{4+} + \text{H}_2\text{cit}^- \rightleftharpoons \text{Pu}(\text{H}_2\text{cit})^{3+}$	1.0 M $\text{LiClO}_4$	5.61	[72MET/GUI3]
$\text{Pu}^{4+} + \text{Hcit}^{2-} \rightleftharpoons \text{Pu}(\text{Hcit})^{2+}$	1.0 M $\text{LiClO}_4$	8.71	[72MET/GUI3]
	1 M $\text{NaNO}_3$	8.44	[75ZAI/NIK]
	2 M $\text{NaNO}_3$	7.78	
	4 M $\text{NaNO}_3$	7.23	
	6 M $\text{NaNO}_3$	6.79	
$\text{Pu}^{4+} + \text{cit}^{3-} \rightleftharpoons \text{Pu}(\text{cit})^+$	0.5 M $\text{NaClO}_4$	$(15.3 \pm 1)$	[66NEB], [66NEB2]
	1.0 M $\text{LiClO}_4$	11.9	[72MET/GUI3]
$\text{Pu}^{4+} + 2\text{cit}^{3-} \rightleftharpoons \text{Pu}(\text{cit})_2^{2-}$	0.5 M $\text{NaClO}_4$	$(30 \pm 1)$	[66NEB], [66NEB2]
$\text{Th}^{4+} + \text{Hcit}^{2-} \rightleftharpoons \text{Th}(\text{Hcit})^{2+}$	1~14 m $\text{NaClO}_4 \rightarrow I = 0$	10.27	[96CHO/ERT]
$\text{Th}^{4+} + 2\text{Hcit}^{2-} \rightleftharpoons \text{Th}(\text{Hcit})_2(\text{aq})$	1~14 m $\text{NaClO}_4 \rightarrow I = 0$	19.24	
$\text{Th}^{4+} + \text{cit}^{3-} \rightleftharpoons \text{Th}(\text{cit})^+$	1~14 m $\text{NaClO}_4 \rightarrow I = 0$	13.7	

### VII.13 Americium citrate compounds and complexes

A literature search by this review on the thermodynamics of americium-citrate systems revealed only information concerning the aqueous complexes of americium(III). No thermodynamic data for Am citrate compounds could be identified (see also Section VII.1.1). The experimental equilibrium data found on the complex formation of  $\text{Am}^{3+}$  with citrate are listed in Table VII-32.

Table VII-32: Literature data on the formation constants for citrate complexes of  $\text{Am}^{3+}$ .

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{Am}^{3+} + \text{Hcit}^{2-} \rightleftharpoons \text{Am}(\text{Hcit})^+$				
dis	0.1 M $\text{LiClO}_4$	25	4.57	[84BOU/GUI]
pot	0.1 M $\text{LiClO}_4$	25	5.83	[84BOU/GUI]
cix	0.1 M $\text{NaCl}$	25	$(5.31 \pm 0.02)$	[71OHY/OHY]
sp	1.0 M $\text{NaClO}_4$	25	$(4.53 \pm 0.04)$	[72EBE/MOA]
$\text{Am}^{3+} + 2\text{Hcit}^{2-} \rightleftharpoons \text{Am}(\text{Hcit})_2^-$				
dis	0.1 M $\text{LiClO}_4$	25	8.94	[84BOU/GUI]
cix	0.1 M $\text{NaCl}$	25	$(8.23 \pm 0.02)$	[71OHY/OHY]
$\text{Am}^{3+} + \text{Hcit}^{2-} + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{Hcit})(\text{cit})^{2-}$				
dis	0.1 M $\text{LiClO}_4$	25	10.6	[71GUI/BOU]
em	0.1 M ?	25	$(10.2 \pm 0.1)$	[71STE]
dis	0.1 M $\text{LiClO}_4$	25	$(10.76 \pm 0.20)$	[74HUB/HUS], [76HUB/HUS]
dis	0.1 M $\text{LiClO}_4$	25	10.77	[84BOU/GUI]
pot	0.1 M $\text{LiClO}_4$	25	13.44	[84BOU/GUI]
$\text{Am}^{3+} + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})(\text{aq})$				
dis	0.1 M $\text{LiClO}_4$	25	7.7	[71GUI/BOU]
em	0.1 M ?	25	$(7.74 \pm 0.08)$	[71STE]
dis	0.1 M $\text{LiClO}_4$	25	8.0	[84BOU/GUI]
pot	0.1 M $\text{LiClO}_4$	25	8.69	[84BOU/GUI]
cix	0.1 M $\text{NaCl}$	25	$(6.74 \pm 0.08)$	[71OHY/OHY]
sp	1.0 M $\text{NaClO}_4$	25	$(6.96 \pm 0.06)$	[72EBE/MOA]
dis	0.3 m $\text{NaCl}$	25	$(5.9 \pm 0.1)$	[2001CHO/BON]
dis	1 m $\text{NaCl}$	25	$(5.2 \pm 0.1)$	[2001CHO/BON]
dis	2 m $\text{NaCl}$	25	$(5.0 \pm 0.1)$	[2001CHO/BON]
dis	3 m $\text{NaCl}$	25	$(4.84 \pm 0.02)$	[2001CHO/BON]
dis	4 m $\text{NaCl}$	25	$(5.38 \pm 0.06)$	[2001CHO/BON]
dis	5 m $\text{NaCl}$	25	$(5.1 \pm 0.2)$	[2001CHO/BON]
$\text{Am}^{3+} + 2\text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})_2^{3-}$				
em	0.1 M ?	25	$(10.9 \pm 0.2)$	[71STE]
dis	0.1 M $\text{LiClO}_4$	25	$(12.16 \pm 0.20)$	[74HUB/HUS]
dis	0.1 M $\text{LiClO}_4$	25	12.1	[84BOU/GUI]
pot	0.1 M $\text{LiClO}_4$	25	14.29	[84BOU/GUI]
cix	0.1 M $\text{NaCl}$	25	$(11.55 \pm 0.08)$	[71OHY/OHY]
sp	1.0 M $\text{NaClO}_4$	25	$(10.3 \pm 0.2)$	[72EBE/MOA]

(Continued on next page)

Table VII-32: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10} \beta^a$	Reference
$\text{Am}^{3+} + \text{cit}^{3-} + \text{OH}^- \rightleftharpoons \text{Am}(\text{cit})(\text{OH})^-$				
pot	0.1 M $\text{LiClO}_4$	25	10.53	[84BOU/GUI]
$\text{Am}(\text{cit})(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{Am}(\text{cit})(\text{OH})^- + \text{H}^+$				
sp	1.0 M $\text{NaClO}_4$	25	$(5.61 \pm 0.02)$	[72EBE/MOA]
$2\text{Am}^{3+} + 2\text{cit}^{3-} + 2\text{OH}^- \rightleftharpoons (\text{Am}(\text{cit})(\text{OH}))_2^{2-}$				
pot	0.1 M $\text{LiClO}_4$	25	22.80	[84BOU/GUI]

a: Refers to the reactions indicated, the ionic strength and temperature given in the table. Uncertainties are those given in the references.

Due to the fairly strong complex formation and strong dependence of the interaction on pH, agreement has not been reached among research groups as to the speciation and stability constants. Among the species proposed,  $\text{Am}(\text{Hcit})^+$ ,  $\text{Am}(\text{Hcit})_2^-$ ,  $\text{Am}(\text{cit})(\text{aq})$  and  $\text{Am}(\text{cit})_2^{3-}$  are considered most plausible by this review. Based on the discussion of the experimental studies in Appendix A, the equilibrium constants listed in Table VII-33 are accepted to derive the selected values in this review. Since [71GUI/BOU], [74HUB/HUS] and [84BOU/GUI] are the reports from the same group, only the values listed in [84BOU/GUI] are accepted. The values from [71OHY/OHY] and [2001CHO/BON] are corrected for the complex formation between  $\text{Am}^{3+}$  and  $\text{Cl}^-$ .

Table VII-33: Accepted formation constants for citrate complexes of  $\text{Am}^{3+}$  at 25°C used to derive the selected values.

Ionic medium	$\log_{10} \beta_{\text{app}}^a$	$\log_{10} \beta^b$	Reference
$\text{Am}^{3+} + \text{Hcit}^{2-} \rightleftharpoons \text{Am}(\text{Hcit})^+$			
0.1 m $\text{LiClO}_4$	$(4.57 \pm 0.5)$	$(4.57 \pm 0.5)$	[84BOU/GUI]
0.1 m $\text{NaCl}$	$(5.31 \pm 0.5)$	$(5.33 \pm 0.5)$	[71OHY/OHY]
1.05 m $\text{NaClO}_4$	$(4.51 \pm 0.5)$	$(4.51 \pm 0.5)$	[72EBE/MOA]
$\text{Am}^{3+} + 2\text{Hcit}^{2-} \rightleftharpoons \text{Am}(\text{Hcit})_2^-$			
0.1 m $\text{LiClO}_4$	$(8.93 \pm 0.5)$	$(8.93 \pm 0.5)$	[84BOU/GUI]
0.1 m $\text{NaCl}$	$(8.23 \pm 0.5)$	$(8.24 \pm 0.5)$	[71OHY/OHY]

(Continued on next page)

Table VII-33: (continued)

Ionic medium	$\log_{10}\beta_{\text{app}}$ <sup>a</sup>	$\log_{10}\beta$ <sup>b</sup>	Reference
$\text{Am}^{3+} + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})(\text{aq})$			
0.1 m LiClO <sub>4</sub>	(8.0 ± 0.5)	(8.0 ± 0.5)	[71GUI/BOU], [84BOU/GUI]
0.1 m NaCl	(6.74 ± 0.5)	(6.8 ± 0.5)	[71OHY/OHY]
1.05 m NaClO <sub>4</sub>	(6.94 ± 0.5)	(6.94 ± 0.5)	[72EBE/MOA]
0.3 m NaCl	(5.90 ± 0.2)	(5.93 ± 0.21)	[2001CHO/BON]
1 m NaCl	(5.19 ± 0.2)	(5.25 ± 0.21)	[2001CHO/BON]
2 m NaCl	(4.98 ± 0.2)	(5.09 ± 0.22)	[2001CHO/BON]
3 m NaCl	(4.81 ± 0.2)	(4.99 ± 0.24)	[2001CHO/BON]
4 m NaCl	(5.34 ± 0.2)	(5.63 ± 0.25)	[2001CHO/BON]
5 m NaCl	(5.05 ± 0.2)	(5.52 ± 0.26)	[2001CHO/BON]
$\text{Am}^{3+} + 2 \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})_2^{3-}$			
0.1 m LiClO <sub>4</sub>	(12.1 ± 0.5)	(12.1 ± 0.5)	[74HUB/HUS], [84BOU/GUI]
0.1 m NaCl	(11.57 ± 0.5)	(11.59 ± 0.5)	[71OHY/OHY]
1.0 m NaClO <sub>4</sub>	(10.3 ± 0.5)	(10.3 ± 0.5)	[72EBE/MOA]

a: The values of  $\log_{10}\beta_{\text{app}}$  are those converted into molality unit.

b: The values of  $\log_{10}\beta$  are those corrected for chloride complex formation.

The NEA-TDB reviews [95SIL/BID] and [2003GUI/FAN] select the formation constants,  $\log_{10} \beta_{\text{I}(\text{Cl})}^{\circ} = (0.24 \pm 0.03)$ , for:



and  $\log_{10} \beta_{2(\text{Cl})}^{\circ} = -(0.74 \pm 0.05)$  [2003GUI/FAN] for



with the assumptions of  $\varepsilon(\text{Am}^{3+}, \text{Cl}^{-}) = \varepsilon(\text{Am}^{3+}, \text{ClO}_4^{-}) = (0.49 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$  and  $\varepsilon(\text{AmCl}^{2+}, \text{Cl}^{-}) = \varepsilon(\text{AmCl}^{2+}, \text{ClO}_4^{-}) = (0.39 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$ , and  $\varepsilon(\text{AmCl}_2^{+}, \text{Cl}^{-}) = \varepsilon(\text{AmF}_2^{+}, \text{ClO}_4^{-}) = (0.17 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}$  [95SIL/BID]. From these values with  $\varepsilon(\text{Na}^{+}, \text{Cl}^{-}) = (0.03 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}$  (Appendix B), the values of  $\log_{10}\beta_{\text{I}(\text{Cl})}$  and  $\log_{10}\beta_{2(\text{Cl})}$  at each ionic strength were estimated and they were used to apply corrections to equilibrium constants for the formation of  $\text{Am}(\text{cit})(\text{aq})$ ,  $\text{Am}(\text{cit})_2^{3-}$  and  $\text{Am}(\text{Hcit})_2^{-}$  according to the following equation:

$$\log_{10}\beta(\text{corrected}) = \log_{10}\beta(\text{reported}) + \log_{10}(1 + \beta_{\text{I}(\text{Cl})} [\text{Cl}^{-}] + \beta_{2(\text{Cl})} [\text{Cl}^{-}]^2) \quad (\text{VII.57})$$

The corrections were less than 0.5  $\log_{10}$ -units at all ionic strengths. To conduct the SIT analyses, this review has considered that the contribution of  $\Delta\varepsilon I$  at  $I \leq 1 \text{ M}$  is within the uncertainties of the equilibrium constants, and it can be neglected. For  $\log_{10} \beta_1$  of the reaction:



the SIT analysis was conducted with the values obtained in NaCl medium and with those obtained at  $I \leq 1$  M listed in Table VII-33. Since  $\varepsilon(\text{Na}^+, \text{cit}^{3-})$  is dependent on ionic strength, the analysis was conducted using the following equation:

$$\log_{10} \beta - \varepsilon(\text{M}^+, \text{cit}^{3-}) I_m = \log_{10} \beta^0 + \frac{0.5091 \Delta z^2 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} + \varepsilon(\text{Am}^{3+}, \text{Cl}^-) I_m \quad (\text{VII.59})$$

where  $\Delta z^2 = -18$

$$\varepsilon(\text{Am}^{3+}, \text{Cl}^-) = \varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1} \quad (\text{VII.60})$$

and  $\varepsilon(\text{M}^+, \text{cit}^{3-})$  is

$$\varepsilon(\text{Na}^+, \text{cit}^{3-}) = -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1} \quad (\text{VII.61})$$

for [71OHY/OHY] and [2001CHO/BON] and

$$\varepsilon(\text{Li}^+, \text{cit}^{3-}) = -(0.55 \pm 0.11) + (0.3 \pm 0.2) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1} \quad (\text{VII.62})$$

for [71GUI/BOU].

As shown in Figure VII-30 and Figure VII-31, the data fits well the model with the estimated value of  $\log_{10} \beta_1^0$  (VII.58) =  $(8.55 \pm 0.09)$ .

When the fitting was carried out with  $\varepsilon(\text{Am}^{3+}, \text{Cl}^-)$  as a variable parameter as well as  $\log_{10} \beta^0$ , the analysis gave:

$$\log_{10} \beta_1^0 = (8.86 \pm 0.15) \text{ and } \varepsilon(\text{Am}^{3+}, \text{Cl}^-) = (0.34 \pm 0.05) \text{ kg} \cdot \text{mol}^{-1},$$

in fair agreement with the recommended values of  $\varepsilon$ .

The data of [72EBE/MOA] and [84BOU/GUI] considerably deviate from the fitted line, presumably due to the differences in their ionic media or to overlooked systematic errors in these works. Thus, this review selects the value of:

$$\log_{10} \beta_1^0 \text{ (VII.58)} = (8.55 \pm 0.09)$$

obtained from the SIT regression, but with an increased uncertainty, and the already recommended values of  $\varepsilon$ .

Figure VII-30: Fitting of the values of  $\log_{10} \beta_1$  (VII.58) at each ionic strength (Table VII-33) to the SIT equation. Solid line is drawn using the result of fitting Eq. (VII.59) with:

$$\begin{aligned}\log_{10} \beta_1^0 \text{ (VII.58)} &= (8.55 \pm 0.20), \quad \Delta z^2 = -18, \\ \varepsilon(\text{Am}^{3+}, \text{Cl}^-) &= \varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1} \\ \varepsilon(\text{Na}^+, \text{cit}^{3-}) &= -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1} \\ \varepsilon(\text{Li}^+, \text{cit}^{3-}) &= -(0.55 \pm 0.11) + (0.3 \pm 0.2) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1}.\end{aligned}$$

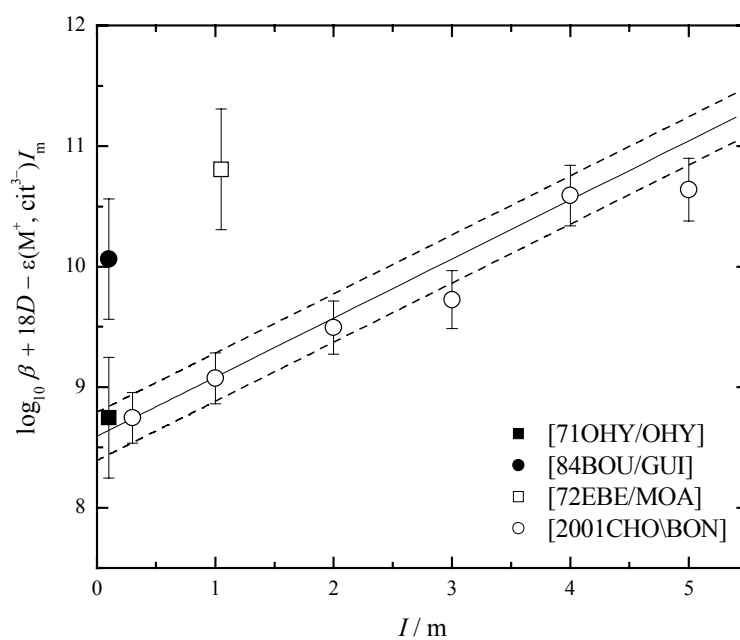


Figure VII-31: A plot of  $\log_{10} \beta$  against  $I_m$  for the reactions, (VII.58) and :

Solid lines are drawn using the result of fitting equation (VII.59).

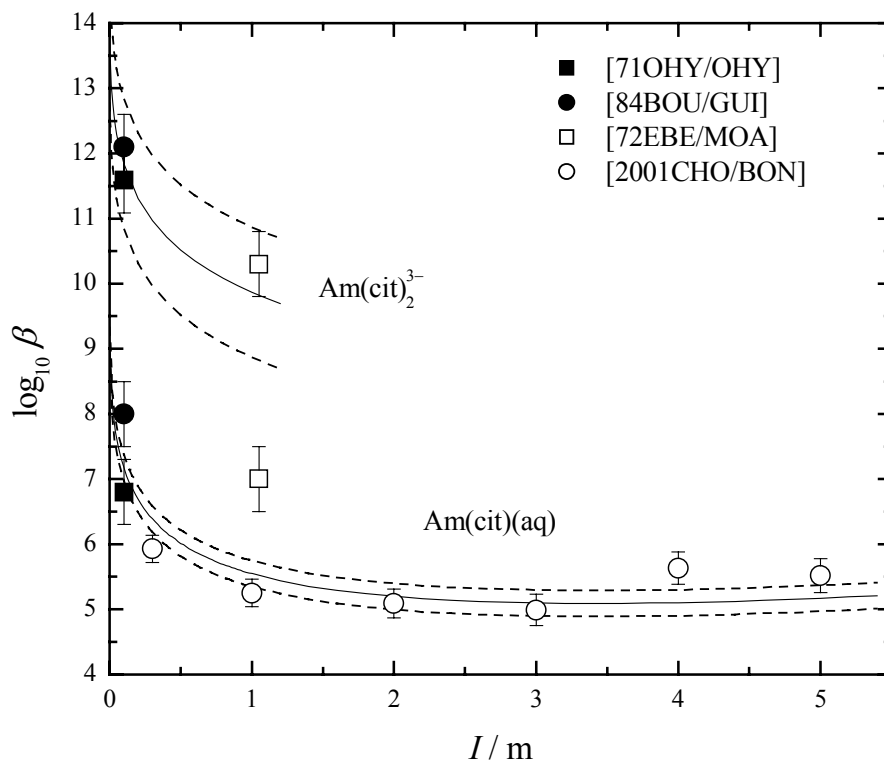
$$\log_{10} \beta_1^\circ (\text{VII.58}) = (8.55 \pm 0.20), \Delta z^2 = -18,$$

$$\Delta \varepsilon = -\varepsilon(\text{Am}^{3+}, \text{Cl}^-) - \varepsilon(\text{cit}^{3-}, \text{Na}^+),$$

$$\varepsilon(\text{Am}^{3+}, \text{Cl}^-) = (0.49 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$$

$$\varepsilon(\text{Na}^+, \text{cit}^{3-}) = -(0.115 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m \text{ kg} \cdot \text{mol}^{-1}$$

$$\log_{10} \beta_2^\circ (\text{VII.63}) = 13.9, \Delta z^2 = -18, \Delta \varepsilon I_m = 0$$





For the other reactions, the accepted literature values are quite limited. Since the uncertainties are larger than the contribution of  $\Delta\epsilon I$  at  $I_m \leq 1$  m, the SIT analyses have been carried out neglecting  $\Delta\epsilon I$  :

$$\log_{10} \beta = \log_{10} \beta^\circ + \frac{0.5091 \Delta z^2 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad (\text{VII.64})$$

The results of the fittings are shown in and Figure VII-32. The estimated values of  $\log_{10} \beta^\circ$  and their uncertainties are:

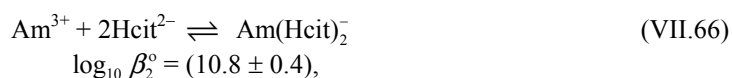
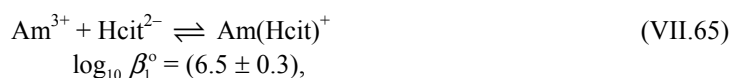
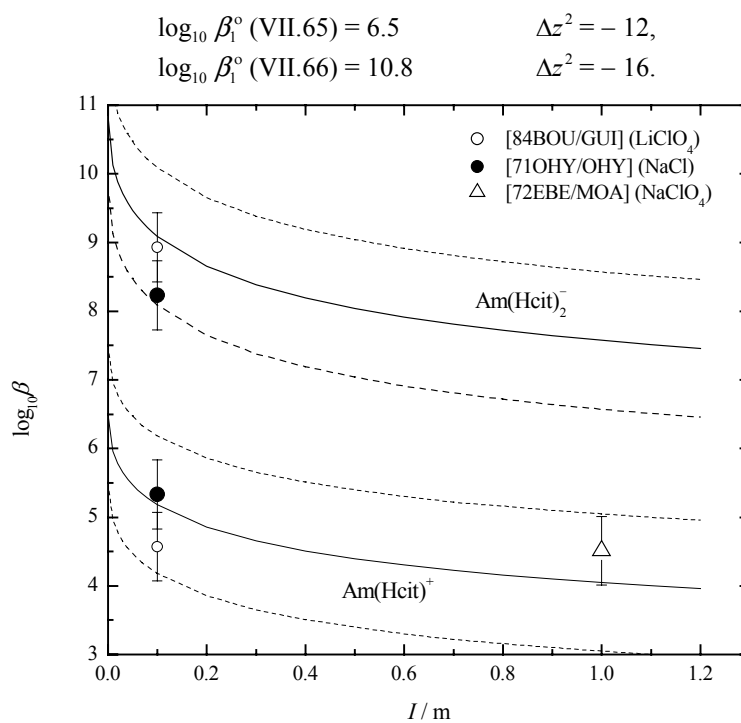


Figure VII-32: A Plot of  $\log_{10}\beta$  against  $I_m$ . Solid lines are drawn by using the results of fitting equation (VII.64).



As seen in Figure VII-31 and in Figure VII-32, the amounts of available data are quite limited and have relatively large uncertainties. The estimated value of  $\log_{10} \beta^\circ$  may contain still larger uncertainties as compared to the uncertainties in the individual experimental values, which are estimated by this review from an evaluation of the original publications. Therefore, this review selects the values of the formation constants obtained from the SIT fittings with increased uncertainties as listed in Table VII-34. To show the outline of the complex species of  $\text{Am}^{3+}$  citrates formed, the distribution of the  $\text{Am}^{3+}$  citrates as a function of  $-\log_{10}[\text{H}^+]$  is given in Figure VII-33. For the simulation, the values selected in this review (extrapolated to  $I = 0.1 \text{ M}$ ) were used for the protonation constants and formation constants as listed in the Figure caption.

Table VII-34: Selected formation constants for the citrate complexes of  $\text{Am}^{3+}$  at 25°C.

Reaction	$\log_{10} \beta^\circ$
$\text{Am}^{3+} + \text{Hcit}^{2-} \rightleftharpoons \text{Am}(\text{Hcit})^+$	$(6.5 \pm 1.0)$
$\text{Am}^{3+} + 2\text{Hcit}^{2-} \rightleftharpoons \text{Am}(\text{Hcit})_2^-$	$(10.8 \pm 1.0)$
$\text{Am}^{3+} + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})(\text{aq})$	$(8.55 \pm 0.20)$
$\text{Am}^{3+} + 2\text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})_2^{3-}$	$(13.9 \pm 1.0)$

The selections in Table VII-34 yield:

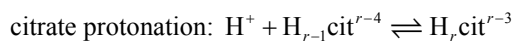
$$\Delta_f G_m^\circ (\text{Am}(\text{Hcit})^+, 298.15 \text{ K}) = - (1834.4 \pm 7.7) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ (\text{Am}(\text{Hcit})_2^-, 298.15 \text{ K}) = - (3057.5 \pm 8.4) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ (\text{Am}(\text{cit}), \text{aq}, 298.15 \text{ K}) = - (1809.8 \pm 5.3) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_f G_m^\circ (\text{Am}(\text{cit})_2^{3-}, 298.15 \text{ K}) = - (3002.6 \pm 8.5) \text{ kJ}\cdot\text{mol}^{-1}.$$

Figure VII-33: Distribution of Am(III)-citrate complex species in solutions containing  $10^{-6}$  M Am(III) and  $10^{-3}$  M citric acid as a function of  $-\log_{10}[\text{H}^+]$  at  $I = 0.1$  M. The following equilibrium constants have been used:

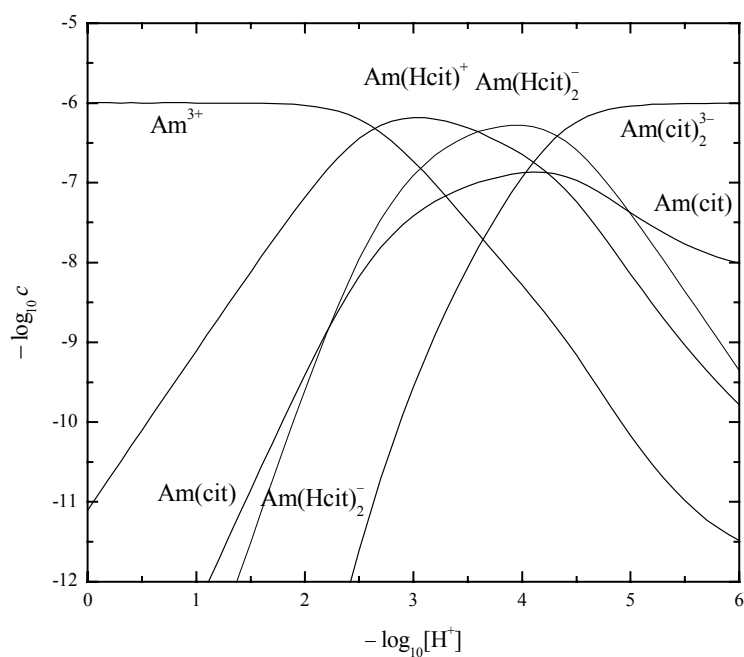


$$\log_{10} K_1 (r=1) = 5.70, \log_{10} K_2 (r=2) = 4.36 \text{ and } \log_{10} K_3 (r=3) = 2.92$$

Am(III)citrate complexes:

$$\log_{10} \beta \text{ ((VII.58), Am(cit)(aq))} = 6.92, \log_{10} \beta \text{ ((VII.63), Am(cit)}_2^{3-}) = 11.84,$$

$$\log_{10} \beta \text{ ((VII.65), Am(Hcit)}^+) = 5.18, \log_{10} \beta \text{ ((VII.66), Am(Hcit)}_2^-) = 9.09.$$





## Chapter VIII

# Discussion of data selection for ethylenediaminetetraacetate (edta) compounds and complexes

### VIII.1 Introduction

This acid has the formula  $C_{10}H_{16}N_2O_8$  (molecular weight:  $292.242\text{ g}\cdot\text{mol}^{-1}$ ; CAS Registry Number: 60-00-4), and although it is usually referred to as ethylenediaminetetraacetic acid, about 40 other names are known, for example: EDTA, Titriplex, Trilon B, Cheelox, Complexon II, *etc.*

Ethylenediaminetetraacetic acid may release up to four protons, but it may also act as a base, accepting up to two  $H^+$  ions. Following the rules by the IUPAC, in reactions and formulae the abbreviation  $H_4\text{edta}$  is used for the acid, and  $H_n\text{edta}^{(n-4)}$  for the different protonation steps. For example, the deprotonated ethylenediaminetetraacetate ligand in aqueous solutions is denoted as:  $\text{edta}^{4-}$ . In formulae where the abbreviation is preceded by a lower case it is enclosed in parenthesis, as in  $\text{Na}(\text{edta})^{3-}$ . Also protonated forms of the edta ligand is enclosed in parenthesis, as in  $\text{Ni}(\text{Hedta})^-$ . It should however be noted that what one obtains from most experiments is the global composition of the complexes, in this example  $\text{NiHedta}^-$ , and that using most techniques this complex is indistinguishable with *e.g.*  $\text{Ni}(\text{OH})(\text{H}_2\text{edta})^-$ . The ethylenediaminetetraacetate group in metal ion complexes is simply denoted as edta.

Ethylenediaminetetraacetic acid behaves like most aminoacids forming zwitterions [\[47SCH/ACK\]](#). This is reflected for example in the crystal structure of  $\text{H}_4\text{edta}\cdot\text{H}_2\text{O}(\text{cr})$ , (*cf.* Figure VIII-1).

Owing to its ability to form several chelate rings, the ethylenediaminetetraacetate ligand is a strong complexing agent. Metal-edta complexes have important practical applications in analytical and separations chemistry. The 1:1 complexes are most common, for example:  $\text{Ni}(\text{edta})^{2-}$ ,  $\text{Ni}(\text{Hedta})^-$ ,  $\text{Ni}(\text{H}_2\text{edta})(\text{aq})$ , *etc.* The structures

for two of these complexes, obtained from single-crystal X-ray investigations, are shown in Figure VIII-2. Mixed-ligand complexes are also quite common, especially for larger cations, such as lanthanides, actinides, *etc.* Two of these complexes are shown in Figure VIII-3. Polynuclear complexes with edta are also known. In some of these complexes edta behaves as a “bridge”, co-ordinated to two metal atoms. Examples of polynuclear complexes are shown in Figure VIII-4.

Figure VIII-1: The structure of  $H_4\text{edta}$  as a double zwitterion [74LAD/POV].

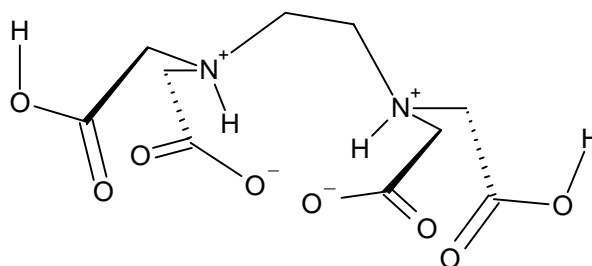


Figure VIII-2: The structure of: (a)  $\text{Ni}(\text{edta})^{2-}$  [84NES/POR2], and (b)  $\text{Ni}(\text{Hedta})(\text{H}_2\text{O})^-$  [86POL/FIL].

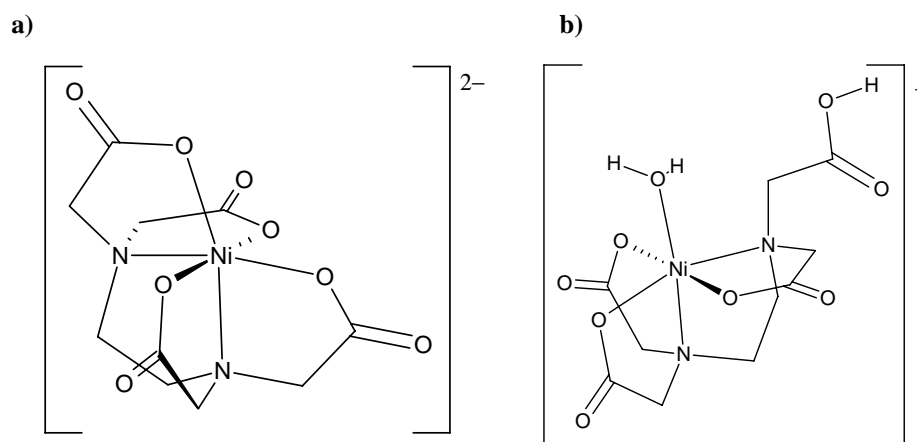


Figure VIII-3: Structures of two mixed-ligand complexes:  $\text{ZrCO}_3\text{edta}^{2-}$  [95MIS/SER] and  $\text{ThF}_3\text{edta}^{3-}$  [85MIK/LOB].

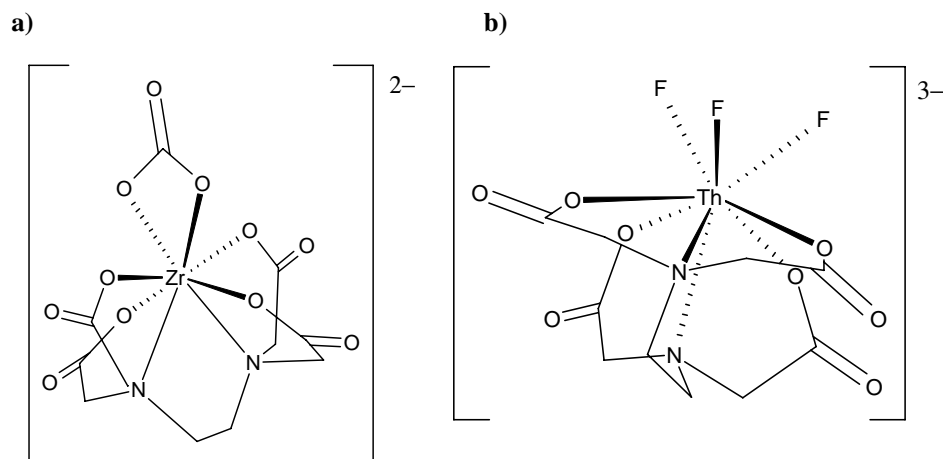
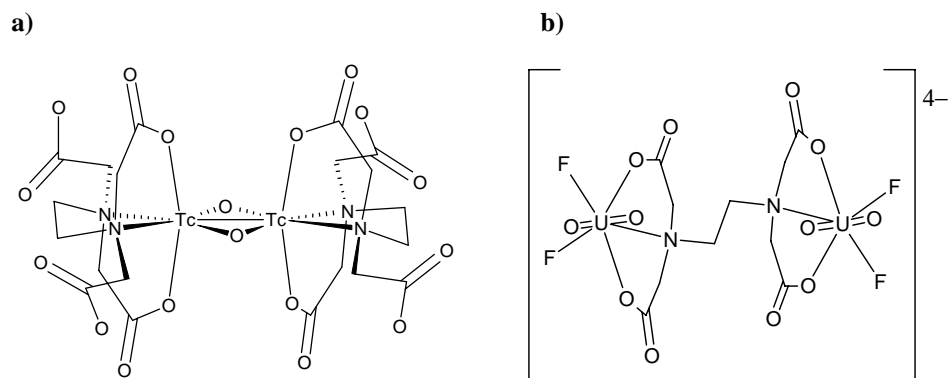


Figure VIII-4: Structures of polynuclear edta complexes:  $\text{Tc}_2\text{O}_2(\text{H}_2\text{edta})_2$  [81BUE/AND], and  $(\text{UO}_2\text{F}_2)_2\text{edta}^{4-}$  [85SHC/ORL].



## VIII.2 H<sub>4</sub>edta(cr)

Two crystalline modifications of H<sub>4</sub>edta exist:  $\alpha$  and  $\beta$  [73LAD/POV], [74LAD/POV]. The common  $\beta$ -form is anhydrous H<sub>4</sub>edta(cr), while  $\alpha$ -H<sub>4</sub>edta is a hydrate, perhaps with variable amounts of water of crystallization and unstable to exposure in air. The crystal structure of a sample of  $\alpha$ -edta with composition H<sub>4</sub>edta·0.39H<sub>2</sub>O(cr) was reported in [74LAD/POV].

All thermodynamic information available on ethylenediaminetetraacetic acid corresponds to the stable  $\beta$ -form: H<sub>4</sub>edta(cr).

### VIII.2.1 Thermodynamic properties

The heat of combustion of H<sub>4</sub>edta(cr) has been determined [67ADA/CAR], [88VAS/BOR]. From these data the enthalpy of formation is calculated to be:

$$\Delta_f H_m^\circ(\text{H}_4\text{edta, cr, 298.15 K}) = -(1759.8 \pm 1.5) \text{ kJ}\cdot\text{mol}^{-1}$$

which is selected by this review.

There is no information on the standard entropy or heat capacity of H<sub>4</sub>edta(cr).

### VIII.2.2 Solubility of H<sub>4</sub>edta(cr)

The solubility of H<sub>4</sub>edta(cr) in aqueous solutions has been determined in several studies [58MEC/SCH], [58YOS/IGU], [59BEC/GOR], [59BEC/GOR2], [59IGU/YOS], [59KLY/SMI4], [60BEC/GOR], [60PAL/UDA], [62KRO/ERM], [63TAN/TER], [67AND], [67MES/VIN], [72SMY], [74BUL], [74TER/NIK], [75LAG/LAG], [82TER/IVA], [83KRA/DEC], [89SAL/BOO], [99KAR/HAR].

From solubility data of H<sub>4</sub>edta(cr) in solutions of varying acidity, it is possible to determine the equilibrium constant for:



as well as some of the values for the protonation constants:  $K_6$ ,  $K_5$ ,  $K_4$ , etc., depending on the acidity range studied. It should be noted that “H<sub>4</sub>edta(aq)” is an equilibrium mixture of two isomeric zwitterions, as indicated in Figure VIII-6. Some of the investigations that reported the solubility of H<sub>4</sub>edta(cr) as a function of either pH or  $[\text{H}^+]_{\text{TOT}}$  were not included in this review, either because they were not performed using a constant ionic medium, [58MEC/SCH], [59BEC/GOR2], [59BEC/GOR2], [60BEC/GOR], [60PAL/UDA], [89SAL/BOO], [99KAR/HAR], or for other reasons discussed in the corresponding entries of Appendix A, [59KLY/SMI4], [63TAN/TER], [72SMY], [74BUL], [74TER/NIK].

The studies considered in this review are listed in Table VIII-1.



Table VIII-1: Literature studies considered by this review where the solubility of  $H_4\text{edta}(\text{cr})$  has been reported as a function of  $[\text{H}^+]$  (or  $[\text{H}^+]_{\text{TOT}}$ ) at constant ionic strength.

$t$ (°C)	Medium	$I$ (M)	$\log_{10} K_s$ (VIII.1)	Reference
30	(H,K)Cl	0.1	$-(3.64 \pm 0.08)^b$	<a href="#">[58YOS/IGU]</a> , <a href="#">[59IGU/YOS]</a> <sup>b</sup>
30	(H,K)Cl	0.5	$-(3.57 \pm 0.04)^b$	<a href="#">[58YOS/IGU]</a> , <a href="#">[59IGU/YOS]</a> <sup>b</sup>
25	(H,Na)NO <sub>3</sub>	2	$-(3.4 \pm 0.5)^b$	<a href="#">[62KRO/ERM]</a> <sup>b</sup>
20	(H,Na)ClO <sub>4</sub>	1	$-(3.32 \pm 0.20)^a$	<a href="#">[67AND]</a>
25	(H,K)Cl	1	$-(3.75 \pm 0.20)^a$	<a href="#">[67MES/VIN]</a>
25	(H,Na)ClO <sub>4</sub>	3	$-(2.88 \pm 0.20)^a$	<a href="#">[75LAG/LAG]</a>
20	(H,K)NO <sub>3</sub>	0.1	$-(3.95 \pm 0.20)^a$	<a href="#">[82TER/IVA]</a> <sup>b</sup>
20		2	$-(3.7 \pm 0.5)^b$	
25		0.1	$-(3.83 \pm 0.20)^a$	
21	(H,Na)ClO <sub>4</sub>	1	$-(3.45 \pm 0.20)^a$	<a href="#">[83KRA/DEC]</a>

a: uncertainty assigned in this review.

b: data recalculated in this review, *cf.* Appendix A.

In order to correlate studies performed at both 20 and 25°C, the enthalpy change for reaction (VIII.1) is needed. Two studies have reported  $\Delta_r H_m^\circ(\text{VIII.1})$  [\[58YOS/IGU\]](#), [\[59IGU/YOS\]](#) and [\[79VAS/KOC\]](#). The calorimetric study reported by Vasil'ev *et al.* in [\[79VAS/KOC\]](#) resulted in two different values of  $\Delta_r H_m^\circ(\text{VIII.1})$  in nitrate and perchlorate media as discussed in Appendix A. The data may be modelled setting a common value for  $\Delta_r H_m^\circ(\text{VIII.1})$  for all ionic media studied by Vasil'ev *et al.*, resulting in the selected value:

$$\Delta_r H_m^\circ(\text{VIII.1}) = (29 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}.$$

This selection leads to:

$$\Delta_r H_m^\circ(\text{H}_4\text{edta}, \text{aq}) = -(1730.8 \pm 3.4) \text{ kJ}\cdot\text{mol}^{-1}.$$

The equilibrium constants for reaction (VIII.1) listed in Table VIII-1 for temperatures  $\neq 25^\circ\text{C}$  were converted to 25°C values using the enthalpy change given above. This value agrees with the enthalpy change obtained by Yoshino *et al.* [\[58YOS/IGU\]](#), and Iguchi *et al.* [\[59IGU/YOS\]](#) from the temperature variation of the solubility of  $H_4\text{edta}(\text{cr})$  in “pure” water in the range 20 to 45°C, namely  $\Delta_r H_m^\circ(\text{VIII.1}) = (28 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$ , with the uncertainty assigned by this review. Although the speciation was not established in [\[58YOS/IGU\]](#), [\[59IGU/YOS\]](#), the error introduced is limited because of the small heats of protonation and dissociation of  $H_4\text{edta}(\text{aq})$ , *cf.* Section VIII.3.8.

Because of inadequacies in the original papers, the data from a few references has been reinterpreted in this review (see footnotes in Table VIII-1) as described in Appendix A. It should be pointed out that  $H_4\text{edta}(\text{aq})$  is not a dominant species. Because of this, the total uncertainties in the individual values in Table VIII-1 were set to a

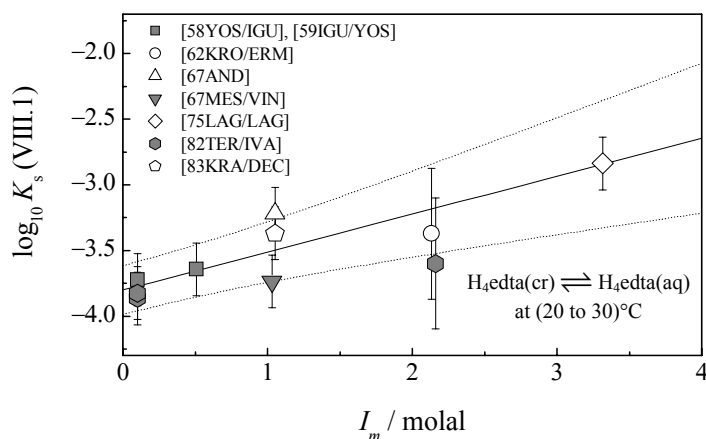
minimum value of  $\pm 0.2 \log_{10}$ -units. The data in Table VIII-1, converted to 25°C and molal units, and with increased uncertainties, is plotted in Figure VIII-5.

Reaction (VIII.1) should have a negligible ionic strength dependence, because  $\text{H}_4\text{edta}(\text{aq})$  nominally has no electric charge. Nevertheless, both anion and cation effects cannot be ruled out because  $\text{H}_4\text{edta}(\text{aq})$  is a double zwitterion. Although the ionic strength dependence for data obtained in ( $\text{H}^+$ ,  $\text{Na}^+$ ) media differs somewhat with that of the data in ( $\text{H}^+$ ,  $\text{K}^+$ ) media (Figure VIII-5), the differences are not significant. The weighted least-squares regression gives:

$$\log_{10} K_s^\circ (\text{VIII.1}) = -(3.80 \pm 0.19),$$

$$\Delta\epsilon(\text{H}_4\text{edta}) = -(0.29 \pm 0.14) \text{ kg} \cdot \text{mol}^{-1}.$$

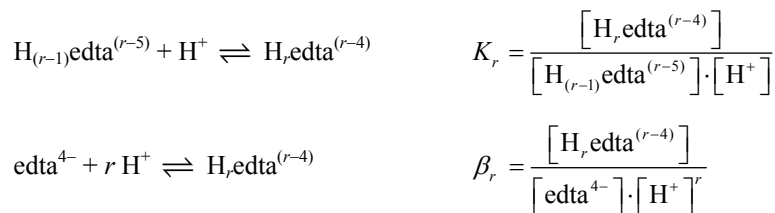
Figure VIII-5: Equilibrium constants for reaction:  $\text{H}_4\text{edta}(\text{cr}) \rightleftharpoons \text{H}_4\text{edta}(\text{aq})$ . All data converted to molal units and to 25°C when necessary. Symbols with white background correspond to ( $\text{Na}^+$ ,  $\text{H}^+$ ) media; grey background to ( $\text{K}^+$ ,  $\text{H}^+$ ) media.



### VIII.3 Acid-base equilibria of edta in aqueous solutions

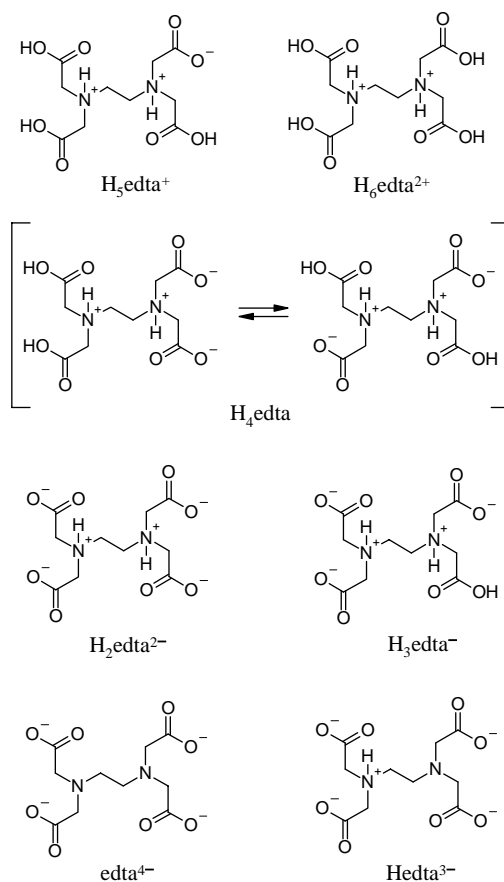
#### VIII.3.1 Introduction

When dissolved in water  $\text{H}_4\text{edta}$  forms a double zwitterion which may act both as an acid by releasing up to four protons, and as a base accepting up to two  $\text{H}^+$  ions. The schematic structures of the different edta-species are shown in Figure VIII-6. The following nomenclature is used for the protonation reactions of  $\text{edta}^{4-}$ :



where  $1 \leq r \leq 6$ . It has been reported that  $\text{edta}^{4-}$  and/or  $\text{Hedta}^{3-}$  anions may form supramolecular aggregates in alkaline solutions ( $\text{pH} \gtrsim 6$ ) with a molecular weight between 8000 and 14000 [94MUL/HAE]. The dialysis experiments suggest that aggregates are formed with a stoichiometry  $(\text{H}_p\text{edta}_x)^{(p-4x)}$ , with  $37 \leq x \leq 66$ , but the interpretation of the observed alkalimetric titration curve is wholly against the claimed polymerisation.

Figure VIII-6: Schematic structures of  $\text{H}_r\text{edta}^{(r-4)}$ .



A large number of references ( $\approx 120$ ) were found from a literature search for the acid-base equilibria of edta. The majority of these references contain studies on metal complexation, where the authors either needed values for the dissociation constants of  $\text{H}_4\text{edta}$  under the same experimental conditions as the metal-complexation study, or used the edta system to test the experimental set-up.

Most of these references contain data for relatively dilute ionic media, mostly for  $I = 0.1$  M. Only few studies have dealt with ionic media  $I \gtrsim 1$  M. With only one exception, all studies at  $I > 1.2$  M have been performed in  $\text{Na}^+$  media.

Because of the large number of references, it was advantageous to judge the quality of the experimental details quite rigorously. The following criteria were considered when discarding references during the screening process:

- Clear indication must be given that the acid-base constants were determined experimentally in the actual study, and not taken from another publication.
- The calibration method for the pH-electrodes must be indicated. They must have been calibrated in the concentration scale, and not with standard pH-buffers. That is, “pH” must refer to  $-\log_{10} [\text{H}^+]$ . References were discarded when they reported mixed acid-base constants, *i.e.* involving both proton activities and ligand concentrations:

$$K'_r = \frac{[\text{H}_r \text{edta}^{(r-4)}]}{[\text{H}_{r-1} \text{edta}^{(r-5)}] a_{\text{H}^+}}$$

It should be noted here that it is possible to correct reported mixed protonation constants with the estimated value for the single ion activity coefficient of  $\text{H}^+$ . This has not been done when reviewing the protonation constants of edta. In few cases it is reported that the glass electrodes were calibrated with standard buffers, and  $[\text{H}^+]$  calculated from pH, for example with the Davies equation. This procedure was not accepted either.

- A background electrolyte providing a constant ionic strength must be used. The ligand must not contribute significantly to the total ionic strength. Therefore in the case of  $\text{edta}^{4-}$  it must be clearly indicated that for example  $[\text{edta}]_{\text{TOT}} \leq 1$  mM if  $I = 0.1$  M.
- Temperature, ionic strength, and the nature of the background electrolyte must be given.

The acid dissociation constants of  $\text{H}_4\text{edta}$  reported in the following references were discarded from the review procedure because they did not fulfil one or more of the criteria indicated above: [\[51CAB\]](#), [\[52CAR/MAR\]](#), [\[53CAR/MAR\]](#), [\[56CAR/STA\]](#), [\[57RIN/SII\]](#), [\[59BEC/GOR\]](#), [\[59BEC/GOR2\]](#), [\[59KLY/SMI3\]](#), [\[60BEC/GOR\]](#), [\[61SIM\]](#), [\[62BAE/BEN\]](#), [\[63FUR/GIU\]](#), [\[63PAL\]](#), [\[65BOT/CHA\]](#), [\[66KUL/RAB\]](#), [\[66KUL\]](#), [\[67TIK2\]](#), [\[67TIK\]](#), [\[68KUE/SCH\]](#), [\[68NAA/POD\]](#), [\[68WAT/SCH\]](#), [\[68WIK/RIN\]](#), [\[70BAR2\]](#), [\[71ROR/MAC\]](#), [\[73CAR/SWA\]](#), [\[73CHA/RAO\]](#), [\[75LIT/NIK\]](#), [\[75VOT/BAR\]](#), [\[77CHR/BOR\]](#), [\[77HOJ/SUG\]](#), [\[77KOS/SHE\]](#), [\[77KUB/NIK\]](#), [\[80MAC/CHI\]](#), [\[80MIK/HAV\]](#), [\[81RAJ/MAI\]](#), [\[81SIR/KAL\]](#), [\[82AVD/KEA\]](#), [\[82HUA/ALF\]](#), [\[83WIL/WIL\]](#), [\[84VAS/GRE\]](#), [\[85SIN/YAD\]](#), [\[86SAL/BOO\]](#), [\[87THU/KUP\]](#), [\[88ALL/BOL\]](#), [\[88EVS/SMI\]](#), [\[89MIR\]](#), [\[89NAG/SHA\]](#), [\[89NES/HOF\]](#), [\[89SAL/BOO\]](#), [\[89SVE/DOB\]](#), [\[90AHR/DAH\]](#), [\[91DUF/MAR\]](#), [\[91SAL/BOO\]](#), [\[92TUR/SAN\]](#), [\[93MAZ/DAN\]](#), [\[94NAG\]](#), [\[95SUN/MOT\]](#), [\[96SUN/AND\]](#), [\[97DEL/FIG\]](#), [\[97VAZ/ATB\]](#), [\[97VAZ/ATB2\]](#).

[98SAL/BOO], [98SAL/BOO2]. These references are in general not discussed in Appendix A.

Data from a few other references could not be accepted for other reasons. These references have been discussed in Appendix A [59KLY/SMI4], [63TAN/TER], [77GRI/GOE], [78JAW], [80JAW], [85MAR/EVA], [86MAR/EVA], [95LIS/CHO], [96BOR/LIS], [96XUE/TRA].

The data reported in the remaining references for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and tetraalkylammonium ionic media are listed in Table VIII-2. Some of the publications listed in Table VIII-2 are further discussed in Appendix A [58YOS/IGU], [59IGU/YOS], [62KRO/ERM], [75CAR/SWA], [77OYA/MAT], [78ARE/MUS], [78MER/GAT], [82OVE/LUN], [82TER/IVA], [83DAN/RIG], [85DAN/RIG], [92GLA/HUL], [94KUM/CHA].

Only one publication [85DAN/RIG] contains results for a lithium background electrolyte, cf. Table VIII-2, and these few data were not included in the regressions to obtain selected values of protonation constants.

Table VIII-2: Literature data considered by this review on the protonation constants,  $\log_{10} K_1$ ,  $\log_{10} K_2$ ,  $\log_{10} K_3$  (Table VIII-2-a),  $\log_{10} K_4$ ,  $\log_{10} K_5$  and  $\log_{10} K_6$  (Table VIII-2-b), for  $\text{edta}^{4-}$ . Ionic strength values and equilibrium constants are expressed in  $\text{mol}\cdot\text{L}^{-1}$ . Data in *italics* are reported in molal units. If the ionic medium is shown in parenthesis, the contribution of the reacting species to the total ionic strength has been considered.

Method	<i>I</i>	Electrolyte	<i>t</i> (°C)	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$	Reference
ise-H	0.1	(KCl)	20	10.262	6.161	2.672	[47SCH/ACK]
gl	0.1	(KNO <sub>3</sub> )	20	10.23	6.16		[57SCH/AND]
ise-H	0.1	KCl	20	10.260	6.170	2.674	[58IRV/SHE]
gl	0.1	KNO <sub>3</sub>	25.3	(10.07 ± 0.01)	(6.13 ± 0.005)		[60BOH/MAR] <sup>a</sup>
gl	0.1	KCl	30	10.25	6.22	2.86	[63GRI/HUG]
gl	0.1	(KNO <sub>3</sub> )	20	10.31	6.21	2.66	[66MOE/CHU] <sup>b</sup>
			30	10.12	6.14		
gl	0.1	(Me <sub>4</sub> NCl)	20	10.44	6.16		[67AND]
gl	0.1	(KNO <sub>3</sub> )	20	10.23	6.16	2.7	
ise-H	1	(Me <sub>4</sub> NCl)	20	10.12	6.07	2.7	
ise-H	1	(KCl)	20	9.95	6.26		
gl	1	(NaClO <sub>4</sub> )	20	8.85	6.28	2.3	
gl	0.1	KCl	20	(10.23 ± 0.02)	(6.16 ± 0.01)	(2.67 ± 0.02)	[67IRV/MIL]

(Continued on next page)

Table VIII-2-a: (continued)

Method	<i>I</i>	Electrolyte	<i>t</i> (°C)	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$	Reference
sol	0.1	(K <sub>2</sub> H)Cl	25			2.54	[67MES/VIN]
gl	0.1	(K <sub>2</sub> H)Cl	25			2.57	
gl	0.1	(KNO <sub>3</sub> )	25	(10.15 ± 0.01)	(6.18 ± 0.01)	(2.69 ± 0.02)	[68SIL/SIM]
gl	0.1	(KNO <sub>3</sub> )	25	10.20	6.16		[69SIL/SIM] <sup>c</sup>
gl	0.1	(NaClO <sub>4</sub> )	20		6.16	2.7	[70AND/MAL2]
gl	3	NaClO <sub>4</sub>	25	(9.04 ± 0.05)	(7.00 ± 0.05)	(2.51 ± 0.04)	[72LAG/LAG]
gl	0.1	KNO <sub>3</sub>	25	10.27	6.19	2.79	[74BAU]
gl	0.1	(KNO <sub>3</sub> )	25	(10.25 ± 0.02)	(6.16 ± 0.02)	(2.77 ± 0.05)	[75AND/POD]
gl	1	(KCl)	25	9.78	6.18		[75BRU/KIR]
gl	0.5	(Me <sub>4</sub> NCl)	25	10.22	6.12	2.89	[75CAR/SWA]
gl	3	NaClO <sub>4</sub>	25	(9.04 ± 0.05)	(7.00 ± 0.05)	(2.51 ± 0.04)	[75LAG/LAG]
gl	1	(KBr)	20	9.95	6.26	2.3	[76AND/MAL]
gl	1	(NaBr)	20	8.85	6.21	2.36	
gl	3	(NaClO <sub>4</sub> )	25	(9.060 ± 0.005)	(7.040 ± 0.009)	(2.580 ± 0.018)	[76COR/WAL]
ise-H	1	(KCl)	25	(9.79 ± 0.01)	(6.21 ± 0.01)	(2.45 ± 0.01)	[76GAT/MER]
gl	0.1	(KCl)	25		(6.05 ± 0.03)	(2.63 ± 0.03)	[76MAK/STE]
gl	1	NaClO <sub>4</sub>	25	(8.63 ± 0.02)	(6.36 ± 0.03)	(2.64 ± 0.03)	[77OYA/MAT] <sup>d</sup>
gl	0.15	(NaClO <sub>4</sub> )	37		(6.00 ± 0.02)	(2.79 ± 0.02)	[78ARE/MUS] <sup>d</sup>
ise-H	1	(KCl)	25	(9.79 ± 0.01)	(6.21 ± 0.01)	(2.45 ± 0.01)	[78MER/GAT] <sup>d</sup>
gl	0.1	KNO <sub>3</sub>	25	10.21	6.11	2.60	[79LET/MAR]
gl	0.1	(KNO <sub>3</sub> )	35	(9.72 ± 0.02)	(6.16 ± 0.01)		[80TAQ/HUS]
gl	0.1	KNO <sub>3</sub>	25	(10.26 ± 0.02)	(6.14 ± 0.02)	(2.64 ± 0.02)	[82OVE/LUN] <sup>d</sup>
gl	0.3	Et <sub>4</sub> NI	37	(10.07 ± 0.03)	(5.94 ± 0.04)		[83DAN/RIG] <sup>d</sup>
	0.56			(10.03 ± 0.04)	(5.98 ± 0.03)		
	1			(10.10 ± 0.04)	(6.04 ± 0.02)		
sol	1	((H <sub>2</sub> Na)ClO <sub>4</sub> )	21±1			(2.50 ± 0.03)	[83KRA/DEC]
gl	0.15	NaCl	37	(9.120 ± 0.002)	(5.883 ± 0.010)		[84DUF/MAY]
gl	1	(KNO <sub>3</sub> )	25	9.93	6.23	2.58	[84GON/MOT]
gl	0.5	(NaClO <sub>4</sub> )	25	(8.90 ± 0.05)	(6.05 ± 0.04)0	(2.48 ± 0.03)	[84MED/DOM]
gl	0.1	(NaNO <sub>3</sub> )	25	(9.50 ± 0.03)	(6.18 ± 0.03)		[85DAN/RIG] <sup>d,e</sup>
	0.3			(9.08 ± 0.03)	(6.08 ± 0.03)		
	0.6			(8.83 ± 0.03)	(6.08 ± 0.03)		
	1			(8.68 ± 0.03)	(6.08 ± 0.03)		
gl	0.1	(KNO <sub>3</sub> )	25	(10.18 ± 0.03)	(6.19 ± 0.03)		
	0.3			(9.89 ± 0.03)	(6.12 ± 0.03)		
	0.6			(9.69 ± 0.03)	(6.16 ± 0.03)		
	1			(9.52 ± 0.03)	(6.23 ± 0.03)		
gl	0.1	(Me <sub>4</sub> NBr)	25	(10.35 ± 0.03)			

(Continued on next page)

Table VIII-2-a: (continued)

Method	<i>I</i>	Electrolyte	<i>t</i> (°C)	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$	Reference
	0.3			(10.21 ± 0.03)			
	0.6			(10.16 ± 0.03)			
	1			(10.11 ± 0.03)			
gl	0.1	(Et <sub>4</sub> NBr)	25	(10.37 ± 0.03)			
	0.3			(10.25 ± 0.03)			
	0.6			(10.24 ± 0.03)			
	1			(10.23 ± 0.03)			
gl	0.1	(Pr <sub>4</sub> NBr)	25	(10.39 ± 0.03)	(6.19 ± 0.03)	(2.68 ± 0.06)	
	0.3			(10.28 ± 0.03)	(6.12 ± 0.03)	(2.65 ± 0.06)	
	0.6			(10.32 ± 0.03)	(6.16 ± 0.03)	(2.69 ± 0.07)	
	1			(10.37 ± 0.03)	(6.22 ± 0.03)	(2.77 ± 0.09)	
gl	0.1	(KNO <sub>3</sub> )	25	10.19	6.13		[85SMI/MOT]
gl	0.1	(KCl)	25	10.40	6.240		[88TAQ/HUS]
gl	1	(KNO <sub>3</sub> )	25	9.80	6.17		[92AND]
gl	0.1	(NaClO <sub>4</sub> )	25		6.00		[92GLA/HUL] <sup>d</sup>
gl	0.15	Me <sub>4</sub> NCl	25	(10.35 ± 0.01)	(6.11 ± 0.01)	(2.83 ± 0.01)	[93CHE/REI]
gl	0.1	(Me <sub>4</sub> NCl)	25	(10.11 ± 0.04)	(6.19 ± 0.04)	(2.87 ± 0.04)	[94KUM/CHA] <sup>d</sup>
gl	0.5	(NaClO <sub>4</sub> )	25	(8.90 ± 0.01)	(6.05 ± 0.01)	(2.48 ± 0.02)	[95CHI/DOM]
ise-H	0.1	(NaCl)	25	(9.40 ± 0.03)			[95PAL/NGU2]
	1		25	(8.684 ± 0.004)	(5.98 ± 0.01)	(2.38 ± 0.03)	
ise-H	1	Me <sub>4</sub> N(F <sub>3</sub> CSO <sub>3</sub> )	25	(9.73 ± 0.02)	(6.07 ± 0.02)	(2.97 ± 0.05)	
gl	0.1	(NaNO <sub>3</sub> )	25	(9.498 ± 0.004)	(6.161 ± 0.006)	(2.94 ± 0.01)	[96AIZ/NAT]
gl	0.1	(Me <sub>4</sub> NNO <sub>3</sub> )	25	(10.22 ± 0.02)	(6.05 ± 0.01)	(2.71 ± 0.02)	[97DEL/QUI]
gl	0.1	(KCl)	25	9.93	6.05	2.68	[98SUN/MAR]
gl	0.3	NaCl	25	(9.18 ± 0.02)	(6.02 ± 0.02)	(2.56 ± 0.02)	[99MIZ/BON]
	1			(8.76 ± 0.02)	(6.04 ± 0.02)	(2.34 ± 0.07)	
	2			(8.68 ± 0.02)	(6.29 ± 0.02)	(2.42 ± 0.02)	
	3			(8.68 ± 0.02)	(6.51 ± 0.02)	(2.55 ± 0.02)	
	4			(8.82 ± 0.02)	(6.76 ± 0.01)	(2.50 ± 0.01)	
	5			(8.96 ± 0.02)	(7.01 ± 0.02)	(2.625 ± 0.009)	
gl	0.1	NaCl	25	(9.11 ± 0.01)	(5.99 ± 0.03)	(2.62 ± 0.04)	[2001CHO/BON] <sup>d</sup>
	0.3			(9.21 ± 0.04)	(6.08 ± 0.01)	(2.44 ± 0.2)	
	0.5			(8.83 ± 0.06)	(5.89 ± 0.01)	(2.38 ± 0.22)	
	1			(8.69 ± 0.01)	(5.99 ± 0.01)	(2.27 ± 0.03)	
	2			(8.62 ± 0.01)	(6.19 ± 0.01)	(2.34 ± 0.03)	
	3			(8.60 ± 0.01)	(6.41 ± 0.01)	(2.23 ± 0.04)	
	5			(9.01 ± 0.03)	(6.95 ± 0.01)	(2.46 ± 0.01)	

(Continued on next page)

Table VIII-2-b: (Continued)

Method	<i>I</i>	Electrolyte	<i>t</i> (°C)	$\log_{10} K_4$	$\log_{10} K_5$	$\log_{10} K_6$	Reference
ise-H	0.1	(KCl)	20	1.996			[47SCH/ACK]
ise-H	0.1	KCl	20	1.994			[58IRV/SHE]
ise-H	0.1	(K)Cl	20		(1.55 ± 0.13)		[58TIL/STA]
sol	0.1	(K,H)Cl	30	(2.0 ± 0.1) <sup>(f)</sup>	(1.3 ± 0.1) <sup>(f)</sup>		[58YOS/IGU] <sup>d,f</sup>
	0.5			(1.82 ± 0.05) <sup>(f)</sup>	(1.27 ± 0.04) <sup>(f)</sup>		[59IGU/YOS] <sup>d,f</sup>
gl	2	(KCl)	25	2.70			[60OLS/MAR]
sp	2	(Na,H)Cl	25		0.96	0.26	
sol	1	(Na,H)NO <sub>3</sub>	25			− (0.14 ± 0.08) <sup>(f)</sup>	[62KRO/ERM] <sup>d,f</sup>
	2				(1.4 ± 0.5) <sup>(f)</sup>	(0.21 ± 0.14) <sup>(f)</sup>	
	3					(0.26 ± 0.18) <sup>(f)</sup>	
gl	0.1	KCl	30	2.4			[63GRI/HUG]
gl	0.1	(KNO <sub>3</sub> )	20	2.02			[66MOE/CHU] <sup>b</sup>
sol	1	(Na,H)ClO <sub>4</sub>	20	2.2	1.4	− 0.12	[67AND]
gl	0.1	(KNO <sub>3</sub> )	20	2.0			
ise-H	1	(Me <sub>4</sub> NCl)	20	2.2			
gl	0.1	KCl	20	(1.9 ± 0.1)			[67IRV/MIL]
sol	0.1	(K,H)Cl	25	2.14	1.34		[67MES/VIN]
gl	0.1	(K,H)Cl	25	2.11			
gl	0.1	(KNO <sub>3</sub> )	25	(2.0 ± 0.1)			[68SIL/SIM]
gl	0.1	(NaClO <sub>4</sub> )	20	2			[70AND/MAL2]
gl	3	NaClO <sub>4</sub>	25	(2.13 ± 0.03)	(1.70 ± 0.03)		[72LAG/LAG]
sp	3	NaClO <sub>4</sub>	25			(0.43 ± 0.05)	
gl	0.1	KNO <sub>3</sub>	25	1.99			[74BAU]
gl	0.1	(KNO <sub>3</sub> )	25	(2.2 ± 0.1)			[75AND/POD]
gl	0.5	(Me <sub>4</sub> NCl)	25	1.8			[75CAR/SWA]
gl	3	NaClO <sub>4</sub>	25	(2.13 ± 0.03)	(1.70 ± 0.03)		[75LAG/LAG]
sp	3	NaClO <sub>4</sub>	25		(1.2 ± 0.7)	(0.43 ± 0.15)	
sol	3	NaClO <sub>4</sub>	25		(1.75 ± 0.03)	(0.15 ± 0.15)	
gl	1	(KBr)	20	2.2			[76AND/MAL]
gl	1	(NaBr)	20	2.04			
gl	3	(NaClO <sub>4</sub> )	25	(2.215 ± 0.022)			[76COR/WAL]
ise-H	1	(KCl)	25	(1.95 ± 0.01)	(1.50 ± 0.02)		[76GAT/MER]
gl	0.1	(KCl)	25	(1.88 ± 0.04)			[76MAK/STE]
gl	0.15	(NaClO <sub>4</sub> )	37	(2.10 ± 0.04)	(1.55 ± 0.15)		[78ARE/MUS] <sup>d</sup>
ise-H	1	(KCl)	25				[78MER/GAT] <sup>d</sup>
gl	0.1	KNO <sub>3</sub>	25	2.00			[79LET/MAR]

(Continued on next page)



Table VIII-2-b: (continued)

Method	<i>I</i>	Electrolyte	<i>t</i> (°C)	$\log_{10} K_4$	$\log_{10} K_5$	$\log_{10} K_6$	Reference
sol	2	(K,H)NO <sub>3</sub>	20		$(1.7 \pm 0.5)^{(f)}$	$(0.1 \pm 0.2)^{(f)}$	[82TER/IVA] <sup>d,f</sup>
sol	1	(H <sub>2</sub> Na)ClO <sub>4</sub>	(21±1)	$(1.95 \pm 0.02)$	$(1.45 \pm 0.02)$	$(0.10 \pm 0.05)$	[83KRA/DEC]
gl	1	(KNO <sub>3</sub> )	25	2.01			[84GON/MOT]
gl	0.5	(NaClO <sub>4</sub> )	25	$(1.68 \pm 0.02)$			[84MED/DOM]
gl	0.1	(Pr <sub>4</sub> NBr)	25	$(1.96 \pm 0.10)$			[85DAN/RIG] <sup>d,e</sup>
	0.3			$(1.97 \pm 0.09)$			
	0.6			$(2.02 \pm 0.11)$			
	1			$(2.09 \pm 0.13)$			
gl	0.15	Me <sub>4</sub> NCl	25	$(2.08 \pm 0.02)$			[93CHE/REI]
gl	0.1	(Me <sub>4</sub> NCl)	25	$(2.26 \pm 0.04)$			[94KUM/CHA] <sup>d</sup>
gl	0.5	(NaClO <sub>4</sub> )	25	$(1.68 \pm 0.01)$			[95CHI/DOM]
gl	0.1	(NaNO <sub>3</sub> )	25	$(1.8 \pm 0.2)$			[96AIZ/NAT]
gl	0.1	(Me <sub>4</sub> NNO <sub>3</sub> )	25	$(2.0 \pm 0.1)$			[97DEL/QUI]
gl	0.1	(KCl)	25	2.07			[98SUN/MAR]
gl	0.3	NaCl	25	$(2.14 \pm 0.05)$			[99MIZ/BON]
	1			$(2.1 \pm 0.1)$			
	2			$(1.9 \pm 0.1)$			
	3			$(2.036 \pm 0.00)$			
	4			$(2.1 \pm 0.1)$			
	5			$(2.26 \pm 0.06)$			
gl	0.1	NaCl	25	$(2.18 \pm 0.13)$			[2001CHO/BON] <sup>d</sup>
	0.3			$(2.00 \pm 0.04)$			
	0.5			$(2.03 \pm 0.05)$			
	1			$(1.92 \pm 0.01)$			
	2			$(1.95 \pm 0.04)$			
	3			$(1.87 \pm 0.08)$			
	5			$(1.97 \pm 0.01)$			

a: Data reported also at 0.1, 13.4 and 42.4°C.

b: Data reported also at 40°C.

c: Data also reported at 20, 30, 35 and 40°C.

d: See comments in Appendix A.

e: Data in LiNO<sub>3</sub> were also reported.

f: Original experimental data recalculated in this review.

Experimental difficulties to consider in the case of edta arise from the fact that the range of acidities that has to be studied is quite wide, ranging from pH  $\approx$  11 to 1. These are some of the major problems:

- if glass electrodes are used, they must be specially suited for alkaline measurements to avoid alkaline-metal effects;
- junction potentials may affect the measurements in the extremes of the pH scale (particularly if  $I \leq 0.1$  M);
- the ionic strength must be constant. For studies where  $I \leq 0.1$  M this is not easy to achieve. For example, pH values below 2 cannot be reached at  $I \leq 0.1$  M. Furthermore, in the case of  $\text{edta}^{4-}$ , it must be clearly indicated that  $[\text{edta}]_{\text{TOT}} \leq 1$  mM if  $I = 0.1$  M.

Based on the last two items, no equilibrium constant was considered if  $I < 0.1$  M. Furthermore, the uncertainty in reported equilibrium constants was increased during least-squares regressions within the review process in order to reflect these varying experimental difficulties. Otherwise the uncertainties reported in the original publications were multiplied by a factor (1.96) to obtain error limits closer to a 95% total uncertainty level, *i.e.*, including random and possible systematic deviations. The assignment of uncertainties is further discussed in each of the corresponding Sections below.

When applying the SIT model described in Appendix B to the activity coefficients of tetraalkylammonium halides, it may be shown that the specific ion-interaction coefficient,  $\varepsilon(\text{R}_4\text{N}^+, \text{X}^-)$ , depends on the ionic strength (*cf.* Section V.3.2). A proper representation of the data is achieved by setting:  $\varepsilon(\text{R}_4\text{N}^+, \text{X}^-) = \varepsilon_1(\text{R}_4\text{N}^+, \text{X}^-) + \varepsilon_2(\text{R}_4\text{N}^+, \text{X}^-) \cdot \log_{10} [\text{R}_4\text{N}^+]$ . Because of this, the ionic strength dependence of the protonation constants of  $\text{edta}^{4-}$  in tetraalkylammonium salts was in general modelled using the SIT model setting:  $\varepsilon(\text{R}_4\text{N}^+, \text{H}_n\text{edta}^{(n-4)}) = \varepsilon_1(\text{R}_4\text{N}^+, \text{H}_n\text{edta}^{(n-4)}) + \varepsilon_2(\text{R}_4\text{N}^+, \text{H}_n\text{edta}^{(n-4)}) \cdot \log_{10} [\text{R}_4\text{N}^+]$ .

A large number of references report data only at 20°C, and in a few cases only at 30, 35 or 37°C, and these  $\log_{10} K_n$  values were extrapolated to 25°C. The corrections were obtained from reaction enthalpies selected in Section VIII.3.8. The only available information for  $\text{H}_5\text{edta}^+$  and  $\text{H}_6\text{edta}^{2+}$  was  $\Delta_r H_m^\circ(\text{H}_5\text{edta}^+) + \Delta_r H_m^\circ(\text{H}_6\text{edta}^{2+}) = -(2.7 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1}$ . For the small temperature corrections performed in this review it was assumed that the enthalpy change could be divided according to  $\Delta_r H_m^\circ(\text{H}_5\text{edta}^+) = -(0.2 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r H_m^\circ(\text{H}_6\text{edta}^{2+}) = -(2.5 \pm 2.5) \text{ kJ}\cdot\text{mol}^{-1}$ . The exact partitioning between these two enthalpies has however only a minor effect on the calculated corrections.

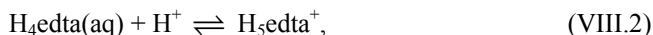
Ionic media corrections to the reaction enthalpies consist of two parts (*cf.* Section V.3.6): a Debye-Hückel expression, and a specific ion interaction ( $\Delta\varepsilon_L$ ) term. In cases where no data was available for  $\Delta\varepsilon_L$  it was set equal to  $(0 \pm 5) \cdot 10^{-3} \text{ kg}\cdot\text{mol}^{-1}$ . The resulting reaction enthalpies are all relatively small, and because of the limited temperature interval involved (from 20 to 37°C), the calculated corrections for  $\log_{10} K_n$  were always  $\leq \pm 0.17 \log_{10}$ -units. The uncertainties in the extrapolated protonation constants were also increased following the error-propagation rules described in Appendix C for the additional uncertainty in the value of  $\Delta_r H_m^\circ$ .

### VIII.3.2 Analysis of $K_5$ and $K_6$

The protonation reactions of  $\text{H}_4\text{edta}(\text{aq})$  are conveniently studied by measuring the solubility of  $\text{H}_4\text{edta}(\text{cr})$  at different acidities. The literature references are discussed in Section VIII.2.2, and the selected data are listed in Table VIII-1 and Table VIII-2. A few spectrophotometric and potentiometric determinations of the protonation of  $\text{H}_4\text{edta}(\text{aq})$  have also been reported, *cf.* Table VIII-2. Potentiometric measurements are in this case difficult because they require low ligand concentrations imposed by the solubility of  $\text{H}_4\text{edta}(\text{cr})$  ( $< 10^{-3}$  M) and relatively high acidities ( $3 \times 10^{-3}$  to 1 M). Some of the potentiometric investigations [77OYA/MAT], [78MER/GAT] were performed under conditions where precipitation could have taken place, and these references were not considered in this review (see also Appendix A).

Because of the inherent experimental difficulties in these systems, the uncertainties for the 95% confidence level were assigned as follows: when no uncertainty value was reported in the individual publication, a value of  $\pm 0.3 \log_{10}$ -units was used; all reported uncertainties below  $\pm 0.14 \log_{10}$ -units were increased to that level.

For the first protonation constant of  $\text{H}_4\text{edta}(\text{aq})$ ,



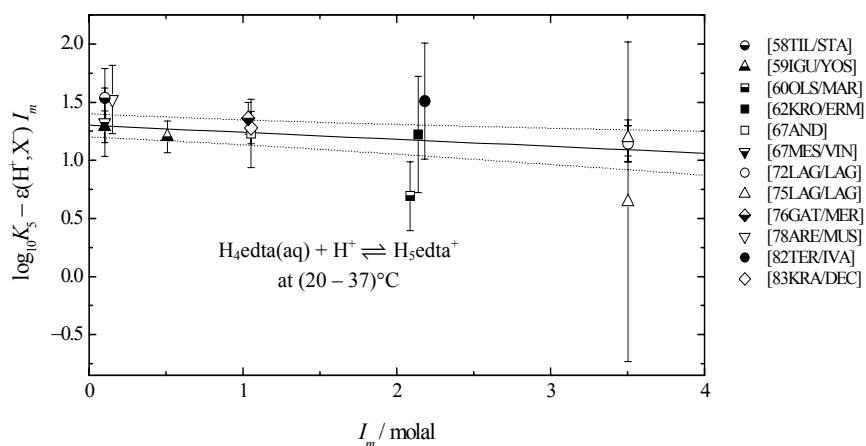
the SIT equations may be re-written as follows (*cf.* Section V.3.2):

$$\log_{10} K_5 - \Delta z^2 D - \varepsilon(\text{H}^+, \text{X}^-) I_m = \log_{10} K_5^\circ - \Delta \varepsilon_5^* I_m$$

where  $\Delta z^2 = 0$  and  $\Delta \varepsilon_5^* = \varepsilon(\text{H}_5\text{edta}^+, \text{X}^-) - \varepsilon(\text{H}_4\text{edta}(\text{aq}), \text{MX})$ , and  $\text{X}^-$  is the anion of the background electrolyte. The data were treated using a weighted least squares regression procedure. The regression plot is shown in Figure VIII-7. There appears to be no significant differences between data in the different media, mainly perchlorates and chlorides. The results of the linear regression were:

$$\log_{10} K_5^\circ (\text{VIII.2}) = (1.3 \pm 0.1) \text{ and } \Delta \varepsilon_5^* = (0.06 \pm 0.04) \text{ kg} \cdot \text{mol}^{-1}.$$

Figure VIII-7: Linear least squares SIT-regression plot for the Reaction (VIII.2). Data from Table VIII-2 have been converted to molal units in the plot, and extrapolated to 25°C when necessary.



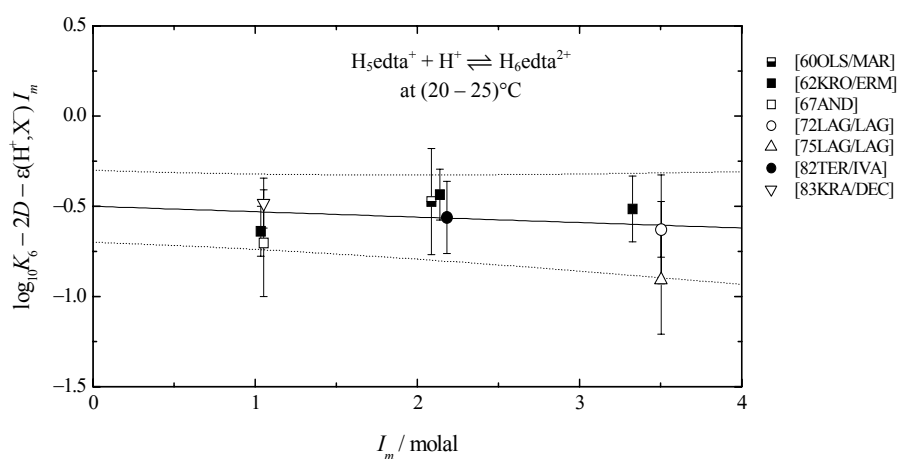
For the protonation of  $\text{H}_5\text{edta}^+$ :



$\Delta z^2 = 2$  and  $\Delta \epsilon_6^* = \epsilon(\text{H}_6\text{edta}^{2+}, \text{X}^-) - \epsilon(\text{H}_5\text{edta}^+, \text{X}^-)$ , where  $\text{X}^-$  is the anion of the background electrolyte. The data was again treated with a weighted least squares regression procedure. The regression plot is shown in Figure VIII-8. Again there appears to be no significant differences between data in the different media, mainly perchlorates and nitrates. The results of the linear regression were:

$$\log_{10} K_6^0 \text{ (VIII.3)} = -(0.5 \pm 0.2), \text{ and } \Delta \epsilon_6^* = (0.03 \pm 0.06) \text{ kg} \cdot \text{mol}^{-1}.$$

Figure VIII-8: Linear least squares SIT-regression plot for Reaction (VIII.3). Data from Table VIII-2 have been converted to molal units in the plot, and extrapolated to 25°C when necessary.



### VIII.3.3 Analysis of $K_4$

For the protonation constant of  $\text{H}_3\text{edta}^-$ ,



the SIT equation may be expressed as follows (*cf.* Section V.3.2):

$$\log_{10} K_4 - \Delta z^2 D - \varepsilon(\text{H}^+, \text{X}^-) I_{\text{m}} = \log_{10} K_4^{\circ} - \Delta \varepsilon_4^* I_{\text{m}}$$

with  $\Delta z^2 = -2$  and  $\Delta \varepsilon_4^* = \varepsilon(\text{H}_4\text{edta}(\text{aq}), \text{MX}) - \varepsilon(\text{M}^+, \text{H}_3\text{edta}^-)$ , where  $\text{M}^+$  is the cation of the background electrolyte. This reaction has been investigated in several studies by measuring the solubility of  $\text{H}_4\text{edta}(\text{cr})$  at varying acidities, and the corresponding literature references are listed in Table VIII-1. All data considered in the review procedure, including potentiometric determinations, are listed in Table VIII-2.

There are two major difficulties in determining this equilibrium constant: *i*) relatively high acidities are needed ( $[\text{H}^+] \geq 0.01 \text{ M}$ ), and this might introduce systematic errors as junction potentials; and *ii*) several protonated species coexist in the studied solutions, introducing difficulties in the interpretation of the data. In the majority of the studies the presence of  $\text{H}_5\text{edta}^+$  was neglected. These different effects are reflected in a somewhat large spread of the data, as evidenced in Figure VIII-9. Therefore, the uncertainties in the data had to be increased to a 95% confidence level as follows: in cases where no uncertainty limits were reported, a value of  $\pm 0.3 \log_{10}$ -units was used in the weighted least-squares procedure; reported uncertainties below  $\pm 0.1$  in  $\log_{10} K_4$  in the original papers were increased to  $\pm 0.2 \log_{10}$ -units in the regression analysis ( $\approx \pm 0.1 \times 1.96$ ).

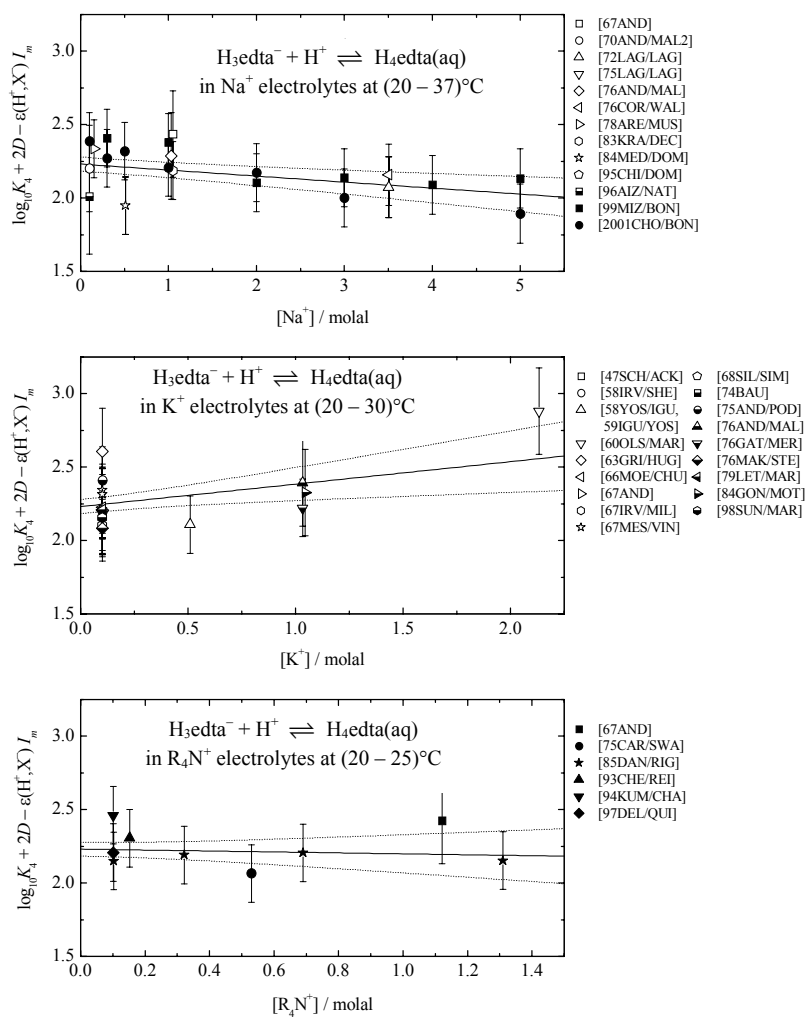
The data was treated with a weighted multi-linear least-squares regression procedure. This procedure assumes that a common value of  $\log_{10} K_4^{\circ}$  should fit all the data. For this reaction it was found that it could be assumed that  $\Delta \varepsilon_4^*$  was independent on ionic strength for all electrolytes, including tetraalkylammonium salts. The regression plots are shown in Figure VIII-9 and the selected values are listed in Table VIII-3.

Table VIII-3: Selected values of  $\log_{10} K_4^{\circ}$  (VIII.4) and  $\Delta \varepsilon_4^*$  (VIII.4).

$\log_{10} K_4^{\circ}$ (VIII.4) = $(2.23 \pm 0.05)$	
Medium <sup>a</sup>	$\Delta \varepsilon_4^*$ ( $\text{kg} \cdot \text{mol}^{-1}$ )
$\text{Na}^+$	$(0.04 \pm 0.02)$
$\text{K}^+$	$-(0.15 \pm 0.10)$
$\text{R}_4\text{N}^+$	$-(0.03 \pm 0.12)$

a:  $\text{R}_4\text{N}^+$  represents tetraalkylammonium.

Figure VIII-9: Multi-linear least squares SIT-regression plots for the reaction:  $\text{H}_3\text{edta}^- + \text{H}^+ \rightleftharpoons \text{H}_4\text{edta}(\text{aq})$ . Data from Table VIII-2 have been converted to molal units in the plots, and extrapolated to 25°C when necessary.



### VIII.3.4 Analysis of $K_3$

For the protonation constant of  $\text{H}_2\text{edta}^{2-}$ ,



$\Delta\epsilon_3^* = \epsilon(\text{M}^+, \text{H}_3\text{edta}^-) - \epsilon(\text{M}^+, \text{H}_2\text{edta}^{2-})$ , where  $\text{M}^+$  is the cation of the background electrolyte, and  $\Delta z^2 = -4$ . The data was treated with a weighted multi-linear least-squares regression procedure. This procedure assumes that a common value of  $\log_{10} K_3^0$  should fit all the data. The uncertainties were increased to obtain a consistent set of data and to correspond to a 95% confidence level. In cases where no uncertainty was given in the original publication, a value of  $\pm 0.15 \log_{10}$ -units was used in the weighted least-squares procedure. Reported uncertainties below  $\pm 0.03$  in  $\log_{10} K_3^0$  in the original papers were increased to  $\pm 0.06 \log_{10}$ -units in the regression analysis ( $\approx \pm 0.03 \times 1.96$ ).

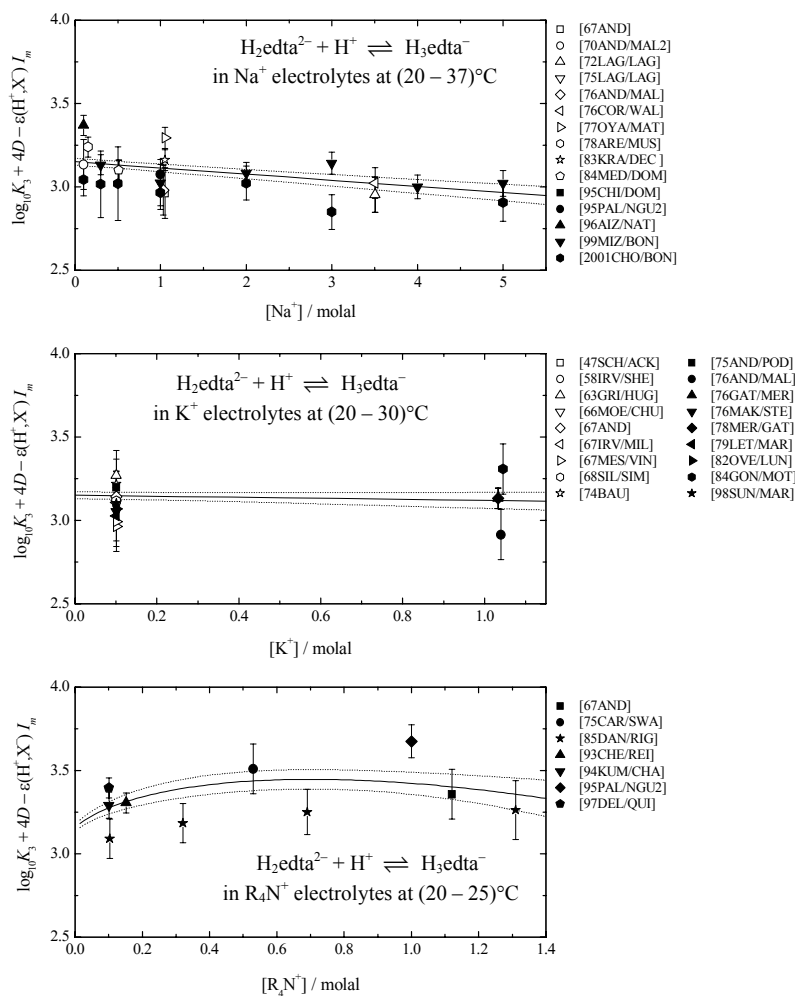
Specific ion interaction parameters between edta-anions and either  $\text{Na}^+$  or  $\text{K}^+$  were assumed to be independent of ionic strength. In the case of tetraalkylammonium it was assumed that the  $\Delta\epsilon$ -values were dependent on ionic strength according to the relation:  $\Delta\epsilon^* = \Delta\epsilon_1^* + \Delta\epsilon_2^* \log_{10} I_m$ . There is no significant difference between the data in tetramethylammonium and tetrapropylammonium and they were fitted to the same  $\Delta\epsilon^*$ . The regression plots are shown in Figure VIII-10 and the selected values are listed in Table VIII-4.

Table VIII-4: Selected values of  $\log_{10} K_3^0$  (VIII.5) and  $\Delta\epsilon_3^*$  (VIII.5).

$\log_{10} K_3^0$ (VIII.5) = $(3.15 \pm 0.02)$	
Medium <sup>a</sup>	$\Delta\epsilon_3^*$ ( $\text{kg}\cdot\text{mol}^{-1}$ )
$\text{Na}^+$	$(0.04 \pm 0.01)$
$\text{K}^+$	$(0.03 \pm 0.04)$
$\text{R}_4\text{N}^+$	$-(0.27 \pm 0.06) + (1.0 \pm 0.3) \log_{10} I_m$

a:  $\text{R}_4\text{N}^+$  represents tetramethylammonium and tetrapropylammonium.

Figure VIII-10: Multi-linear least squares SIT-regression plots for the reaction:  $\text{H}_2\text{edta}^{2-} + \text{H}^+ \rightleftharpoons \text{H}_3\text{edta}^-$ , assuming  $\Delta\epsilon_3^*$  to be independent of ionic strength for sodium and potassium electrolytes, and  $\Delta\epsilon_3^* = f(I_m)$  for tetraalkylammonium media, see text for details. Data at 25°C from Table VIII-2 have been converted to molal units in the plots, and extrapolated to 25°C when necessary.





### VIII.3.5 Analysis of $K_2$

For the protonation constant of  $\text{Hedta}^{3-}$ ,



$\Delta\epsilon_2^* = \epsilon(\text{H}_2\text{edta}^{2-}, \text{M}^+) - \epsilon(\text{Hedta}^{3-}, \text{M}^+)$ , where  $\text{M}^+$  is the cation of the background electrolyte, and  $\Delta z^2 = -6$ . The data was treated using weighted multi-linear least-squares regression. This procedure assumes that a common value of  $\log_{10} K_2^\circ$  should fit all the data. The uncertainties were increased to obtain a consistent set of data and to correspond to a 95% confidence level. In cases where no uncertainty was given in the original publication, a value of  $\pm 0.15 \log_{10}$ -units was used in the weighted least-squares procedure. Reported uncertainties below  $\pm 0.05$  in  $\log_{10} K_2^\circ$  in the original papers were increased to  $\pm 0.10 \log_{10}$ -units in the regression analysis ( $\approx \pm 0.05 \times 1.96$ ).

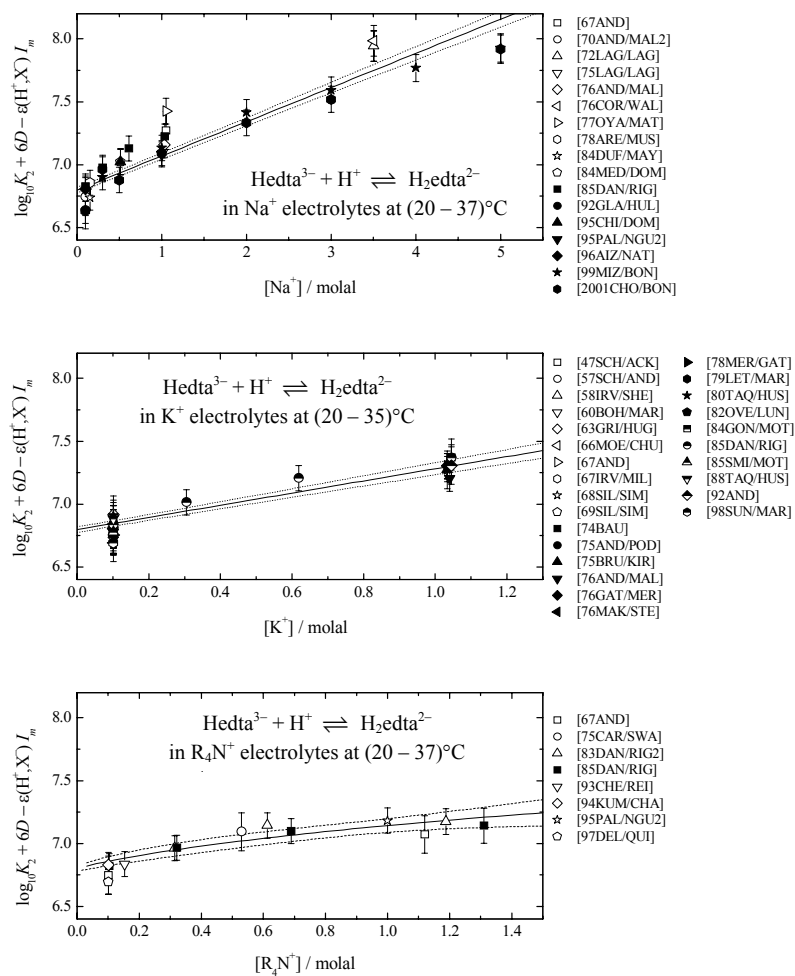
Specific ion interaction parameters between edta-anions and either  $\text{Na}^+$  or  $\text{K}^+$  were assumed to be independent on ionic strength. In the case of tetraalkylammonium it was assumed that the  $\Delta\epsilon$ -values were dependent on ionic strength according to the relation:  $\Delta\epsilon^* I_m = \Delta\epsilon_1^* + \Delta\epsilon_2^* \cdot \log_{10} I_m$ . There is no significant difference between the data in tetramethylammonium,  $\text{Me}_4\text{N}^+$ , and tetrapropylammonium,  $\text{Pr}_4\text{N}^+$ , and they were fitted to the same  $\Delta\epsilon^*$ . The regression plots are shown in Figure VIII-11 and the selected values are listed in Table VIII-5.

Table VIII-5: Selected values of  $\log_{10} K_2^\circ$  (VIII.6) and  $\Delta\epsilon_2^*$  (VIII.6).

$\log_{10} K_2^\circ$ (VIII.6) = $(6.80 \pm 0.02)$	
Medium <sup>a</sup>	$\Delta\epsilon_2^*$ ( $\text{kg} \cdot \text{mol}^{-1}$ )
$\text{Na}^+$	$-(0.27 \pm 0.01)$
$\text{K}^+$	$-(0.48 \pm 0.04)$
$\text{R}_4\text{N}^+$	$-(0.35 \pm 0.05) + (0.3 \pm 0.3) \log_{10} (I_m)$

a:  $\text{R}_4\text{N}^+$  represents tetramethyl- and tetrapropyl-ammonium.

Figure VIII-11: Multi-linear least squares SIT-regression plots for the reaction:  $\text{Hedta}^{3-} + \text{H}^+ \rightleftharpoons \text{H}_2\text{edta}^{2-}$ , assuming  $\Delta\epsilon_2^*$  to be independent of ionic strength for sodium and potassium electrolytes, and  $\Delta\epsilon_2^* = f(I_m)$  for tetraalkyl ammonium media, see text for details. Data at  $(25 \pm 5)^\circ\text{C}$  from Table VIII-2 have been converted to molal units in the plots, and extrapolated to  $25^\circ\text{C}$  when necessary.



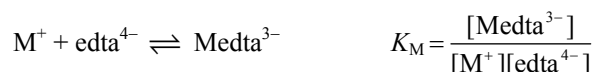
### VIII.3.6 Analysis of $K_1$

For the first protonation constant of  $\text{edta}^{4-}$ ,



$\Delta z^2 = -8$  and  $\Delta \epsilon_1^* = \epsilon(\text{M}^+, \text{Hedta}^{3-}) - \epsilon(\text{M}^+, \text{edta}^{4-})$ , where  $\text{M}^+$  is the cation of the background electrolyte. Different values of  $\log_{10} K_1^\circ$  were obtained from SIT-regressions of the data obtained in background electrolytes with the different cations:  $\text{Na}^+$ ,  $\text{K}^+$ , and tetraalkylammonium. This would be expected if alkali metal complexes are formed with  $\text{edta}^{4-}$  (see also Sections VIII.4 and V.3.3). Therefore an additional uncertainty exists in the determination of the value of  $K_1$  as compared with the other protonation constants of ethylenediaminetetraacetate.

Several stoichiometries have been postulated for the complexes between  $\text{Na}^+ / \text{K}^+$  and  $\text{edta}^{4-}$ , for example:  $\text{Na}(\text{edta})^{3-}$ ,  $\text{Na}(\text{Hedta})^{2-}$ ,  $\text{Na}_2\text{edta}^{2-}$  as sodium complexes (see Section VIII.4.1). The most commonly accepted stoichiometry is however the formation of complexes with ratio 1:1, that is:



with  $\text{M}^+ = \text{Na}^+$  or  $\text{K}^+$ . The following constants are selected by this review in Section VIII.4.1:

$$\log_{10} K_{\text{Na}}^\circ = \log_{10} \beta_1^\circ (\text{Na}(\text{edta})^{3-}, 298.15 \text{ K}) = (2.8 \pm 0.2),$$

$$\log_{10} K_{\text{K}}^\circ = \log_{10} \beta_1^\circ (\text{Kedta}^{3-}, 298.15 \text{ K}) = (1.8 \pm 0.3).$$

When evaluating the ionic-strength dependence of data for the first protonation constant of  $\text{edta}^{4-}$  in presence of a background cation that forms complexes, the following equations are applicable (*cf.* Section V.3.3):

$$\log_{10} K_1^\dagger - \Delta z^2 D - \epsilon(\text{H}^+, \text{X}^-) I_m = \log_{10} K_1^\circ - \Delta \epsilon_1^* I_m - \log_{10} (1 + K_M [\text{M}^+])$$

$$\log_{10} K_M = \log_{10} K_M^\circ + \Delta z^2 D - \Delta \epsilon_M^* I_m + \epsilon(\text{M}^+, \text{X}^-) I_m$$

where  $K_1^\dagger$  is the protonation constant determined without taking into account the formation of alkali-metal complexes,  $\Delta \epsilon_1^* = \epsilon(\text{M}^+, \text{Hedta}^{3-}) - \epsilon(\text{M}^+, \text{edta}^{4-})$ ,  $\Delta \epsilon_M^* = \epsilon(\text{M}^+, \text{Medta}^{3-}) - \epsilon(\text{M}^+, \text{edta}^{4-})$ , and  $\Delta z^2 = -8$  for both reactions (protonation and complex formation with alkali-metals).

The data was treated using weighted least-squares regression procedures. In all cases it was assumed that a common value of  $\log_{10} K_1^\circ$  should fit all the data. The uncertainties were increased to obtain a consistent set of data and to correspond to a 95% confidence level. In cases where no uncertainty was given in the original publication, a value of  $\pm 0.15 \log_{10}$ -units was used in the weighted least-squares procedure. Reported uncertainties below  $\pm 0.05$  in  $\log_{10} K_1^\circ$  in the original papers were increased to  $\pm 0.10 \log_{10}$ -units in the regression analysis ( $\approx \pm 0.05 \times 1.96$ ). Specific ion interaction parameters between  $\text{Na}^+$  and  $\text{K}^+$  and either  $\text{edta}^{4-}$  or  $\text{Hedta}^{3-}$  were assumed to be independent

on ionic strength. In the case of tetraalkylammonium media it was assumed that the individual  $\varepsilon$ -values depended on ionic strength:  $\Delta\varepsilon^* = \Delta\varepsilon_1^* + \Delta\varepsilon_2^* \cdot \log_{10} I_m$ . There is no significant difference between the data in tetramethylammonium,  $\text{Me}_4\text{N}^+$ , tetraethylammonium,  $\text{Et}_4\text{N}^+$  and tetrapropylammonium,  $\text{Pr}_4\text{N}^+$ , and they were fitted to the same  $\Delta\varepsilon^*$ .

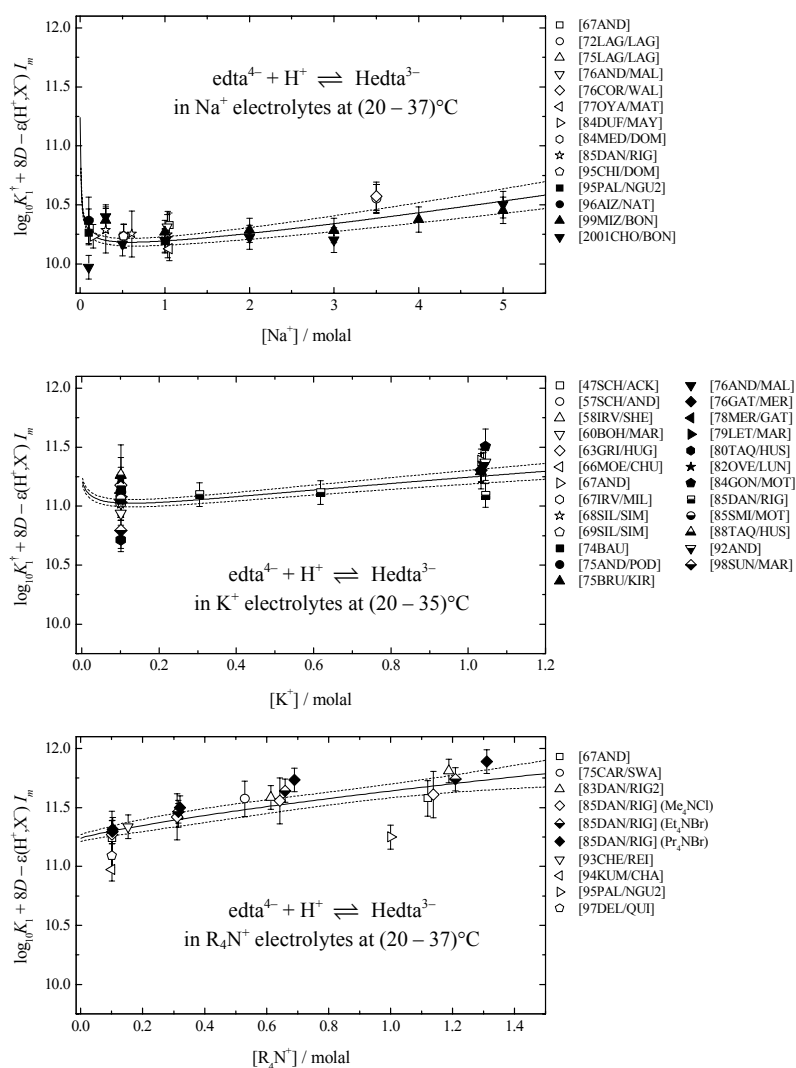
During the regression, the values of  $K^\circ(\text{Na(edta)}^{3-})$  and  $K^\circ(\text{K(edta)}^{3-})$  were set to those recommended in Section VIII.4.1. Because the values of  $\Delta\varepsilon_1^*$  and  $\Delta\varepsilon_M^*$  are highly correlated (*cf.* discussion in Section V.3.3), it was necessary to fix the values of  $\Delta\varepsilon_M^*$  to those obtained in tetraalkylammonium media (*cf.* Section VIII.4.1), namely:  $\Delta\varepsilon_{\text{Na}}^* = -(0.24 \pm 0.47) \text{ kg}\cdot\text{mol}^{-1}$  and  $\Delta\varepsilon_K^* = -(0.50 \pm 0.64) \text{ kg}\cdot\text{mol}^{-1}$ . The results from the fitting of the remaining five parameters are given in Table VIII-6. The agreement between the experimental data and this model is shown in Figure VIII-12.

Table VIII-6: Results of non-linear weighed least-squares fitting of literature data for the first protonation of  $\text{edta}^{4-}$  at  $(25 \pm 5)^\circ\text{C}$ . Five parameters were adjusted in the regression, keeping constant the following:  $\log_{10} K_{\text{Na}}^\circ = 2.8$ ,  $\Delta\varepsilon_{\text{Na}}^* = -0.24 \text{ kg}\cdot\text{mol}^{-1}$ ,  $\log_{10} K_K^\circ = 1.8$ ,  $\Delta\varepsilon_K^* = -0.50 \text{ kg}\cdot\text{mol}^{-1}$ .

$\log_{10} K_1^\circ \text{ (VIII.7)} = (11.24 \pm 0.03)$	
Medium <sup>a</sup>	$\Delta\varepsilon_1^* \text{ (kg}\cdot\text{mol}^{-1})$
$\text{Na}^+$	$-(0.42 \pm 0.02)$
$\text{K}^+$	$-(0.76 \pm 0.05)$
$\text{R}_4\text{N}^+$	$-(0.40 \pm 0.05) + (0.2 \pm 0.3) \log_{10} I_m$

a:  $\text{R}_4\text{N}^+$  represents tetramethylammonium, tetraethylammonium and tetrapropylammonium.

Figure VIII-12: Weighted least squares SIT-regression plots for the reaction:  $\text{edta}^{4-} + \text{H}^+ \rightleftharpoons \text{Hedta}^{3-}$ , assuming: *a)* the formation of  $\text{Na}(\text{edta})^{3-}$  and  $\text{Kedta}^{3-}$ ; *b)* that the values of  $\Delta\epsilon_1^*$  are independent of ionic strength for sodium and potassium electrolytes, and *c)* that  $\Delta\epsilon_1^* = f(I_m)$  for tetraalkylammonium media (see text for details). Data from Table VIII-2 have been converted to molal units in the plots, and extrapolated to 25°C when necessary.



### VIII.3.7 Selected protonation constants for edta<sup>4-</sup>

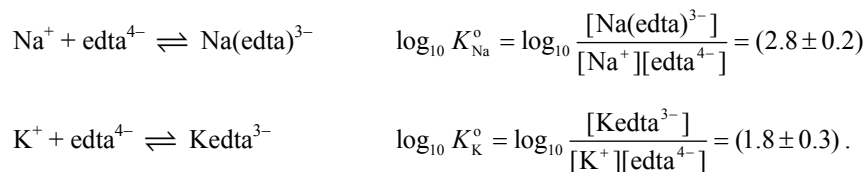
From the discussions in previous Sections, it follows that the selected values for the protonation of edta<sup>4-</sup>,



obtained in this review are:

$$\begin{aligned} \log_{10} K_1^\circ ((\text{VIII.8}), r=1, 298.15 \text{ K}) &= (11.24 \pm 0.03) & \log_{10} \beta_1^\circ &= (11.24 \pm 0.03) \\ \log_{10} K_2^\circ ((\text{VIII.8}), r=2, 298.15 \text{ K}) &= (6.80 \pm 0.02) & \log_{10} \beta_2^\circ &= (18.04 \pm 0.04) \\ \log_{10} K_3^\circ ((\text{VIII.8}), r=3, 298.15 \text{ K}) &= (3.15 \pm 0.02) & \log_{10} \beta_3^\circ &= (21.19 \pm 0.04) \\ \log_{10} K_4^\circ ((\text{VIII.8}), r=4, 298.15 \text{ K}) &= (2.23 \pm 0.05) & \log_{10} \beta_4^\circ &= (23.42 \pm 0.07) \\ \log_{10} K_5^\circ ((\text{VIII.8}), r=5, 298.15 \text{ K}) &= (1.3 \pm 0.1) & \log_{10} \beta_5^\circ &= (24.72 \pm 0.12) \\ \log_{10} K_6^\circ ((\text{VIII.8}), r=6, 298.15 \text{ K}) &= -(0.5 \pm 0.2) & \log_{10} \beta_6^\circ &= (24.22 \pm 0.23). \end{aligned}$$

It must be recalled that these constants should be used together with the formation constants for alkali metal complexation:



The selected specific ion interaction coefficients are listed in Table VIII-7. They were obtained using the  $\Delta \varepsilon_n^*$  values listed in previous subsections and  $\varepsilon(\text{H}_4\text{edta}, \text{MX}) = -(0.29 \pm 0.14) \text{ kg} \cdot \text{mol}^{-1}$ , obtained in Section VIII.2.2.

Table VIII-7: Specific ion interaction coefficients ( $\text{kg} \cdot \text{mol}^{-1}$ ) for edta<sup>4-</sup> and its protonated species.  $\text{R}_4\text{N}^+$  represents tetraalkylammonium.

$\text{M}^+ =$	$\text{Na}^+$	$\text{K}^+$	$\text{R}_4\text{N}^+$	$\text{X}^- = \text{Cl}^-, \text{ClO}_4^- \text{ or } \text{NO}_3^-$
$\varepsilon(\text{M}^+, \text{edta}^{4-})$	$(0.32 \pm 0.14)$	$(1.07 \pm 0.19)$	$(0.76 \pm 0.21) - (1.5 \pm 0.5) \log_{10} (I_m)$	
$\varepsilon(\text{M}^+, \text{Hedta}^{3-})$	$-(0.10 \pm 0.14)$	$(0.31 \pm 0.18)$	$(0.36 \pm 0.20) - (1.3 \pm 0.4) \log_{10} (I_m)$	
$\varepsilon(\text{M}^+, \text{H}_2\text{edta}^{2-})$	$-(0.37 \pm 0.14)$	$-(0.17 \pm 0.18)$	$(0.01 \pm 0.19) - (1.0 \pm 0.43) \log_{10} (I_m)$	
$\varepsilon(\text{M}^+, \text{H}_3\text{edta}^-)$	$-(0.33 \pm 0.14)$	$-(0.14 \pm 0.17)$	$-(0.26 \pm 0.18)$	
$\varepsilon(\text{H}_4\text{edta}, \text{MX})$	$-(0.29 \pm 0.14)$	$-(0.29 \pm 0.14)$	$-(0.29 \pm 0.14)$	$-(0.29 \pm 0.14)$
$\varepsilon(\text{H}_5\text{edta}^+, \text{X}^-)$				$-(0.23 \pm 0.15)$
$\varepsilon(\text{H}_6\text{edta}^{2+}, \text{X}^-)$				$-(0.20 \pm 0.16)$

Table VIII-8-a reports the values for the protonation constants and for the sodium or potassium formation constants for some ionic media commonly used in chemical equilibrium studies. Values for the “apparent” first protonation constant are given in Table VIII-8-b for the same set of background electrolytes. The calculated distribution of the different protonated forms of ethylenediaminetetraacetate as a function of pH in 1 M NaCl is shown in Figure VIII-13.

Figure VIII-13: Calculated distribution of dissolved ethylenediaminetetraacetate species as a function of pH in 1 M NaCl at 25°C.

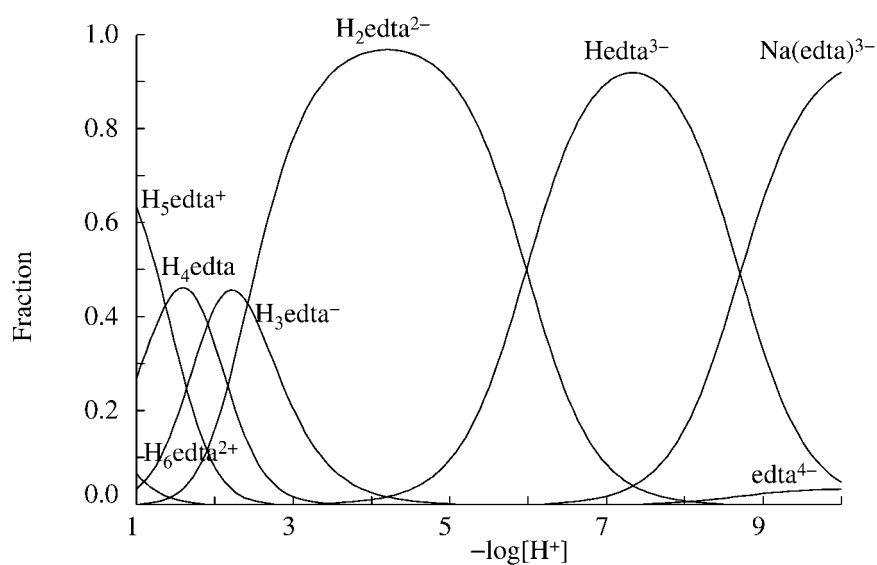


Table VIII-8-a Calculated values for the protonation constants of  $\text{edta}^{4-}$  and for alkali-metal complex formation in *Molar units* in some  $\text{Na}^+ / \text{K}^+$  electrolytes at 25 and 20°C. The SIT model for activity coefficients has been used with the  $\Delta\epsilon$  values obtained in this review. Care should be exercised when using these values: (a) data in sodium media at the highest ionic strengths are confirmed by few experimental data only, as indicated in the figures of Sections VIII.3.2 to VIII.3.6; (b) there is no experimental support for the values in potassium media at ionic strengths above 1 molal; and (c) values of  $K_5$  and  $K_6$  have only been measured at  $I \leq 3.5$  molal.

NaClO <sub>4</sub> at 25°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>Na</sub>	log <sub>10</sub> <i>K</i> <sub>1</sub>	log <sub>10</sub> <i>K</i> <sub>2</sub>	log <sub>10</sub> <i>K</i> <sub>3</sub>
0	0.000	(2.80 ± 0.20)	(11.24 ± 0.03)	(6.80 ± 0.02)	(3.15 ± 0.02)
0.1	0.101	(1.95 ± 0.21)	(10.42 ± 0.03)	(6.19 ± 0.02)	(2.73 ± 0.02)
0.25	0.254	(1.70 ± 0.23)	(10.22 ± 0.03)	(6.03 ± 0.02)	(2.60 ± 0.02)
0.5	0.513	(1.53 ± 0.31)	(10.13 ± 0.03)	(5.97 ± 0.02)	(2.51 ± 0.02)
0.75	0.779	(1.46 ± 0.42)	(10.15 ± 0.04)	(5.98 ± 0.03)	(2.47 ± 0.03)
1	1.05	(1.44 ± 0.53)	(10.21 ± 0.04)	(6.02 ± 0.03)	(2.45 ± 0.03)
2	2.21	(1.5 ± 1.1)	(10.65 ± 0.07)	(6.34 ± 0.05)	(2.48 ± 0.05)
3	3.50	(1.7 ± 1.7)	(11.27 ± 0.10)	(6.80 ± 0.08)	(2.57 ± 0.08)
4	4.95	(2.0 ± 2.3)	(12.02 ± 0.14)	(7.36 ± 0.11)	(2.69 ± 0.11)
5	6.58	(2.4 ± 3.1)	(12.89 ± 0.19)	(8.00 ± 0.15)	(2.85 ± 0.15)
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>4</sub>	log <sub>10</sub> <i>K</i> <sub>5</sub>	log <sub>10</sub> <i>K</i> <sub>6</sub>	
0	0.000	(2.23 ± 0.05)	(1.30 ± 0.10)	-(0.50 ± 0.20)	
0.1	0.101	(2.02 ± 0.05)	(1.31 ± 0.10)	-(0.27 ± 0.20)	
0.25	0.254	(1.97 ± 0.05)	(1.33 ± 0.10)	-(0.17 ± 0.20)	
0.5	0.513	(1.94 ± 0.05)	(1.35 ± 0.10)	-(0.08 ± 0.20)	
0.75	0.779	(1.94 ± 0.05)	(1.38 ± 0.11)	-(0.01 ± 0.21)	
1	1.05	(1.95 ± 0.06)	(1.41 ± 0.11)	(0.05 ± 0.21)	
2	2.21	(2.03 ± 0.08)	(1.52 ± 0.14)	(0.26 ± 0.24)	
3	3.50	(2.15 ± 0.11)	(1.65 ± 0.19)	(0.45 ± 0.30)	
4	4.95	(2.30 ± 0.15)	(1.79 ± 0.24)	(0.66 ± 0.37)	
5	6.58	(2.47 ± 0.19)	(1.95 ± 0.31)	(0.88 ± 0.46)	

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Table VIII-8-a: (continued)

NaNO <sub>3</sub> at 25°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>Na</sub>	log <sub>10</sub> <i>K</i> <sub>1</sub>	log <sub>10</sub> <i>K</i> <sub>2</sub>	log <sub>10</sub> <i>K</i> <sub>3</sub>
0	0.000	(2.80 ± 0.20)	(11.24 ± 0.03)	(6.80 ± 0.02)	(3.15 ± 0.02)
0.1	0.101	(1.95 ± 0.21)	(10.42 ± 0.03)	(6.18 ± 0.02)	(2.72 ± 0.02)
0.25	0.253	(1.69 ± 0.23)	(10.20 ± 0.03)	(6.02 ± 0.02)	(2.58 ± 0.02)
0.5	0.509	(1.51 ± 0.31)	(10.09 ± 0.03)	(5.93 ± 0.02)	(2.47 ± 0.02)
0.75	0.769	(1.42 ± 0.41)	(10.09 ± 0.03)	(5.92 ± 0.02)	(2.41 ± 0.02)
1	1.03	(1.38 ± 0.53)	(10.12 ± 0.04)	(5.94 ± 0.02)	(2.38 ± 0.02)
2	2.14	(1.4 ± 1.0)	(10.45 ± 0.06)	(6.16 ± 0.04)	(2.31 ± 0.04)
3	3.33	(1.5 ± 1.6)	(10.93 ± 0.08)	(6.48 ± 0.05)	(2.30 ± 0.05)
4	4.61	(1.7 ± 2.2)	(11.49 ± 0.11)	(6.88 ± 0.07)	(2.31 ± 0.07)
5	6.02	(1.9 ± 2.8)	(12.13 ± 0.14)	(7.32 ± 0.09)	(2.34 ± 0.09)

NaNO <sub>3</sub> at 25°C				
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>4</sub>	log <sub>10</sub> <i>K</i> <sub>5</sub>	log <sub>10</sub> <i>K</i> <sub>6</sub>
0	0.000	(2.23 ± 0.05)	(1.30 ± 0.10)	−(0.50 ± 0.20)
0.1	0.101	(2.02 ± 0.05)	(1.30 ± 0.10)	−(0.27 ± 0.20)
0.25	0.253	(1.95 ± 0.05)	(1.31 ± 0.10)	−(0.19 ± 0.20)
0.5	0.509	(1.90 ± 0.05)	(1.31 ± 0.10)	−(0.12 ± 0.20)
0.75	0.769	(1.88 ± 0.05)	(1.32 ± 0.10)	−(0.07 ± 0.21)
1	1.03	(1.87 ± 0.06)	(1.32 ± 0.11)	−(0.03 ± 0.21)
2	2.14	(1.86 ± 0.07)	(1.35 ± 0.13)	(0.08 ± 0.24)
3	3.33	(1.88 ± 0.09)	(1.38 ± 0.17)	(0.18 ± 0.28)
4	4.61	(1.91 ± 0.11)	(1.41 ± 0.21)	(0.26 ± 0.34)
5	6.02	(1.96 ± 0.14)	(1.44 ± 0.27)	(0.35 ± 0.42)

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Table VIII-8-a: (continued)

NaCl at 25°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	$\log_{10} K_{\text{Na}}$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$
0	0.000	(2.80 ± 0.20)	(11.24 ± 0.03)	(6.80 ± 0.02)	(3.15 ± 0.02)
0.1	0.100	(1.95 ± 0.21)	(10.42 ± 0.03)	(6.18 ± 0.02)	(2.72 ± 0.02)
0.25	0.252	(1.71 ± 0.23)	(10.21 ± 0.03)	(6.03 ± 0.02)	(2.59 ± 0.02)
0.5	0.506	(1.54 ± 0.31)	(10.12 ± 0.03)	(5.95 ± 0.02)	(2.49 ± 0.02)
0.75	0.762	(1.47 ± 0.41)	(10.12 ± 0.03)	(5.95 ± 0.02)	(2.45 ± 0.02)
1	1.02	(1.45 ± 0.52)	(10.16 ± 0.04)	(5.98 ± 0.02)	(2.42 ± 0.02)
2	2.09	(1.5 ± 1.0)	(10.53 ± 0.06)	(6.24 ± 0.04)	(2.41 ± 0.04)
3	3.20	(1.7 ± 1.5)	(11.02 ± 0.08)	(6.59 ± 0.05)	(2.45 ± 0.05)
4	4.37	(2.0 ± 2.1)	(11.58 ± 0.10)	(7.00 ± 0.06)	(2.51 ± 0.06)
5	5.61	(2.2 ± 2.6)	(12.20 ± 0.13)	(7.45 ± 0.08)	(2.59 ± 0.08)
<i>I</i> M	<i>I<sub>m</sub></i> molal	$\log_{10} K_4$	$\log_{10} K_5$	$\log_{10} K_6$	
0	0.000	(2.23 ± 0.05)	(1.30 ± 0.10)	-(0.50 ± 0.20)	
0.1	0.100	(2.02 ± 0.05)	(1.31 ± 0.10)	-(0.27 ± 0.20)	
0.25	0.252	(1.96 ± 0.05)	(1.32 ± 0.10)	-(0.18 ± 0.20)	
0.5	0.506	(1.93 ± 0.05)	(1.34 ± 0.10)	-(0.10 ± 0.20)	
0.75	0.762	(1.91 ± 0.05)	(1.35 ± 0.10)	-(0.04 ± 0.21)	
1	1.02	(1.91 ± 0.05)	(1.37 ± 0.11)	(0.01 ± 0.21)	
2	2.09	(1.95 ± 0.07)	(1.44 ± 0.13)	(0.17 ± 0.24)	
3	3.20	(2.02 ± 0.09)	(1.52 ± 0.17)	(0.31 ± 0.28)	
4	4.37	(2.10 ± 0.11)	(1.60 ± 0.21)	(0.45 ± 0.33)	
5	5.61	(2.20 ± 0.14)	(1.69 ± 0.25)	(0.58 ± 0.40)	
KCl at 25°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	$\log_{10} K_{\text{K}}$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$
0	0.000	(1.80 ± 0.30)	(11.24 ± 0.03)	(6.80 ± 0.02)	(3.15 ± 0.02)
0.1	0.101	(0.98 ± 0.31)	(10.46 ± 0.03)	(6.21 ± 0.02)	(2.72 ± 0.02)
0.25	0.252	(0.76 ± 0.34)	(10.30 ± 0.03)	(6.08 ± 0.02)	(2.59 ± 0.02)
0.5	0.509	(0.66 ± 0.44)	(10.29 ± 0.04)	(6.06 ± 0.03)	(2.50 ± 0.03)
0.75	0.769	(0.65 ± 0.58)	(10.38 ± 0.05)	(6.12 ± 0.04)	(2.46 ± 0.04)
1	1.03	(0.69 ± 0.73)	(10.52 ± 0.06)	(6.20 ± 0.05)	(2.44 ± 0.05)
2	2.13	(1.0 ± 1.4)	(11.28 ± 0.11)	(6.71 ± 0.09)	(2.44 ± 0.09)
3	3.31	(1.5 ± 2.1)	(12.21 ± 0.17)	(7.34 ± 0.14)	(2.50 ± 0.14)
4	4.58	(2.1 ± 2.9)	(13.26 ± 0.24)	(8.05 ± 0.19)	(2.59 ± 0.19)

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Table VIII-8-a: (continued)

KCl at 25°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	$\log_{10} K_4$	$\log_{10} K_5$	$\log_{10} K_6$	
0	0.000	(2.23 ± 0.05)	(1.30 ± 0.10)	-(0.50 ± 0.20)	
0.1	0.101	(2.04 ± 0.05)	(1.31 ± 0.10)	-(0.27 ± 0.20)	
0.25	0.252	(2.01 ± 0.06)	(1.32 ± 0.10)	-(0.18 ± 0.20)	
0.5	0.509	(2.02 ± 0.07)	(1.34 ± 0.10)	-(0.10 ± 0.20)	
0.75	0.769	(2.06 ± 0.09)	(1.36 ± 0.10)	-(0.03 ± 0.21)	
1	1.03	(2.11 ± 0.12)	(1.38 ± 0.11)	(0.02 ± 0.21)	
2	2.13	(2.37 ± 0.22)	(1.46 ± 0.13)	(0.19 ± 0.24)	
3	3.31	(2.67 ± 0.34)	(1.54 ± 0.17)	(0.34 ± 0.28)	
4	4.58	(3.01 ± 0.46)	(1.63 ± 0.21)	(0.49 ± 0.34)	
KNO <sub>3</sub> at 25°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	$\log_{10} K_K$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$
0	0.000	(1.80 ± 0.30)	(11.24 ± 0.03)	(6.80 ± 0.02)	(3.15 ± 0.02)
0.1	0.101	(0.97 ± 0.31)	(10.45 ± 0.03)	(6.20 ± 0.02)	(2.72 ± 0.02)
0.25	0.253	(0.74 ± 0.34)	(10.29 ± 0.03)	(6.07 ± 0.02)	(2.58 ± 0.02)
0.5	0.512	(0.60 ± 0.44)	(10.27 ± 0.04)	(6.04 ± 0.03)	(2.48 ± 0.03)
0.75	0.776	(0.57 ± 0.58)	(10.35 ± 0.05)	(6.08 ± 0.04)	(2.42 ± 0.04)
1	1.05	(0.58 ± 0.73)	(10.48 ± 0.06)	(6.16 ± 0.05)	(2.39 ± 0.05)
2	2.19	(0.8 ± 1.4)	(11.22 ± 0.12)	(6.64 ± 0.09)	(2.34 ± 0.09)
5	3.44	(1.2 ± 2.2)	(12.16 ± 0.18)	(7.25 ± 0.14)	(2.35 ± 0.14)
<i>I</i> M	<i>I<sub>m</sub></i> molal	$\log_{10} K_4$	$\log_{10} K_5$	$\log_{10} K_6$	
0	0.000	(2.23 ± 0.05)	(1.30 ± 0.10)	-(0.50 ± 0.20)	
0.1	0.101	(2.04 ± 0.05)	(1.30 ± 0.10)	-(0.27 ± 0.20)	
0.25	0.253	(2.00 ± 0.06)	(1.31 ± 0.10)	-(0.19 ± 0.20)	
0.5	0.512	(2.00 ± 0.07)	(1.32 ± 0.10)	-(0.12 ± 0.20)	
0.75	0.776	(2.03 ± 0.09)	(1.32 ± 0.10)	-(0.07 ± 0.21)	
1	1.05	(2.07 ± 0.12)	(1.33 ± 0.11)	-(0.03 ± 0.21)	
2	2.19	(2.28 ± 0.23)	(1.36 ± 0.13)	(0.09 ± 0.24)	
3	3.44	(2.55 ± 0.35)	(1.39 ± 0.17)	(0.20 ± 0.29)	

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Table VIII-8-a: (continued)

NaClO <sub>4</sub> at 20°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K<sub>Na</sub></i>	log <sub>10</sub> <i>K<sub>1</sub></i>	log <sub>10</sub> <i>K<sub>2</sub></i>	log <sub>10</sub> <i>K<sub>3</sub></i>
0	0.000	(2.79 ± 0.20)	(11.18 ± 0.03)	(6.75 ± 0.02)	(3.17 ± 0.02)
0.1	0.101	(1.94 ± 0.21)	(10.36 ± 0.03)	(6.14 ± 0.02)	(2.75 ± 0.02)
0.25	0.253	(1.69 ± 0.23)	(10.16 ± 0.03)	(5.99 ± 0.02)	(2.62 ± 0.02)
0.5	0.512	(1.52 ± 0.31)	(10.07 ± 0.04)	(5.92 ± 0.03)	(2.53 ± 0.03)
0.75	0.778	(1.45 ± 0.42)	(10.09 ± 0.04)	(5.93 ± 0.04)	(2.49 ± 0.04)
1	1.05	(1.43 ± 0.53)	(10.14 ± 0.05)	(5.97 ± 0.04)	(2.47 ± 0.04)
2	2.21	(1.5 ± 1.1)	(10.58 ± 0.10)	(6.30 ± 0.08)	(2.50 ± 0.08)
3	3.49	(1.7 ± 1.7)	(11.20 ± 0.15)	(6.75 ± 0.13)	(2.59 ± 0.13)
4	4.93	(2.0 ± 2.3)	(11.94 ± 0.21)	(7.30 ± 0.19)	(2.71 ± 0.19)
5	6.55	(2.4 ± 3.1)	(12.81 ± 0.27)	(7.94 ± 0.25)	(2.87 ± 0.25)
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K<sub>4</sub></i>	log <sub>10</sub> <i>K<sub>5</sub></i>	log <sub>10</sub> <i>K<sub>6</sub></i>	
0	0.000	(2.24 ± 0.05)	(1.30 ± 0.10)	−(0.51 ± 0.20)	
0.1	0.101	(2.03 ± 0.05)	(1.31 ± 0.10)	−(0.27 ± 0.20)	
0.25	0.253	(1.97 ± 0.05)	(1.33 ± 0.10)	−(0.18 ± 0.20)	
0.5	0.512	(1.95 ± 0.05)	(1.35 ± 0.10)	−(0.09 ± 0.20)	
0.75	0.778	(1.94 ± 0.06)	(1.38 ± 0.11)	−(0.02 ± 0.21)	
1	1.05	(1.95 ± 0.07)	(1.40 ± 0.12)	(0.04 ± 0.21)	
2	2.21	(2.03 ± 0.10)	(1.52 ± 0.16)	(0.25 ± 0.25)	
3	3.49	(2.15 ± 0.15)	(1.64 ± 0.21)	(0.44 ± 0.32)	
4	4.93	(2.30 ± 0.21)	(1.78 ± 0.28)	(0.65 ± 0.40)	
5	6.55	(2.47 ± 0.27)	(1.94 ± 0.37)	(0.87 ± 0.50)	
NaNO <sub>3</sub> at 20°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K<sub>Na</sub></i>	log <sub>10</sub> <i>K<sub>1</sub></i>	log <sub>10</sub> <i>K<sub>2</sub></i>	log <sub>10</sub> <i>K<sub>3</sub></i>
0	0.000	(2.79 ± 0.20)	(11.18 ± 0.03)	(6.75 ± 0.02)	(3.17 ± 0.02)
0.1	0.100	(1.94 ± 0.21)	(10.36 ± 0.03)	(6.13 ± 0.02)	(2.74 ± 0.02)
0.25	0.252	(1.68 ± 0.23)	(10.14 ± 0.03)	(5.97 ± 0.02)	(2.60 ± 0.02)
0.5	0.508	(1.49 ± 0.31)	(10.03 ± 0.03)	(5.88 ± 0.02)	(2.49 ± 0.02)
0.75	0.768	(1.41 ± 0.41)	(10.03 ± 0.04)	(5.87 ± 0.03)	(2.43 ± 0.03)
1	1.03	(1.37 ± 0.53)	(10.06 ± 0.04)	(5.89 ± 0.03)	(2.40 ± 0.03)
2	2.13	(1.4 ± 1.0)	(10.39 ± 0.07)	(6.11 ± 0.05)	(2.33 ± 0.05)
3	3.32	(1.5 ± 1.6)	(10.86 ± 0.10)	(6.44 ± 0.08)	(2.32 ± 0.08)
4	4.60	(1.7 ± 2.2)	(11.42 ± 0.13)	(6.83 ± 0.10)	(2.33 ± 0.10)
5	6.00	(1.9 ± 2.8)	(12.06 ± 0.17)	(7.27 ± 0.14)	(2.36 ± 0.14)

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Table VIII-8-a: (continued)

NaNO <sub>3</sub> at 20°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>4</sub>	log <sub>10</sub> <i>K</i> <sub>5</sub>	log <sub>10</sub> <i>K</i> <sub>6</sub>	
0	0.000	(2.24 ± 0.05)	(1.30 ± 0.10)	−(0.51 ± 0.20)	
0.1	0.100	(2.02 ± 0.05)	(1.30 ± 0.10)	−(0.28 ± 0.20)	
0.25	0.252	(1.96 ± 0.05)	(1.31 ± 0.10)	−(0.20 ± 0.20)	
0.5	0.508	(1.91 ± 0.05)	(1.31 ± 0.10)	−(0.13 ± 0.20)	
0.75	0.768	(1.88 ± 0.05)	(1.32 ± 0.11)	−(0.08 ± 0.21)	
1	1.03	(1.87 ± 0.06)	(1.32 ± 0.11)	−(0.04 ± 0.21)	
2	2.13	(1.86 ± 0.08)	(1.35 ± 0.14)	(0.07 ± 0.24)	
3	3.32	(1.88 ± 0.11)	(1.38 ± 0.18)	(0.17 ± 0.29)	
4	4.60	(1.92 ± 0.14)	(1.41 ± 0.23)	(0.25 ± 0.35)	
5	6.00	(1.96 ± 0.18)	(1.44 ± 0.29)	(0.34 ± 0.43)	
NaCl at 20°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>Na</sub>	log <sub>10</sub> <i>K</i> <sub>1</sub>	log <sub>10</sub> <i>K</i> <sub>2</sub>	log <sub>10</sub> <i>K</i> <sub>3</sub>
0	0.000	(2.79 ± 0.20)	(11.18 ± 0.03)	(6.75 ± 0.02)	(3.17 ± 0.02)
0.1	0.100	(1.94 ± 0.21)	(10.36 ± 0.03)	(6.14 ± 0.02)	(2.74 ± 0.02)
0.25	0.251	(1.69 ± 0.23)	(10.15 ± 0.03)	(5.98 ± 0.02)	(2.61 ± 0.02)
0.5	0.505	(1.53 ± 0.31)	(10.06 ± 0.03)	(5.91 ± 0.02)	(2.52 ± 0.02)
0.75	0.761	(1.46 ± 0.41)	(10.06 ± 0.04)	(5.90 ± 0.03)	(2.47 ± 0.03)
1	1.02	(1.44 ± 0.52)	(10.10 ± 0.04)	(5.93 ± 0.03)	(2.44 ± 0.03)
2	2.08	(1.5 ± 1.0)	(10.47 ± 0.07)	(6.19 ± 0.05)	(2.43 ± 0.05)
3	3.19	(1.7 ± 1.5)	(10.96 ± 0.10)	(6.54 ± 0.07)	(2.47 ± 0.07)
4	4.36	(1.9 ± 2.1)	(11.52 ± 0.13)	(6.95 ± 0.10)	(2.53 ± 0.10)
5	5.59	(2.2 ± 2.6)	(12.13 ± 0.16)	(7.40 ± 0.13)	(2.61 ± 0.13)
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>4</sub>	log <sub>10</sub> <i>K</i> <sub>5</sub>	log <sub>10</sub> <i>K</i> <sub>6</sub>	
0	0.000	(2.24 ± 0.05)	(1.30 ± 0.10)	−(0.51 ± 0.20)	
0.1	0.100	(2.03 ± 0.05)	(1.31 ± 0.10)	−(0.28 ± 0.20)	
0.25	0.251	(1.97 ± 0.05)	(1.32 ± 0.10)	−(0.19 ± 0.20)	
0.5	0.505	(1.93 ± 0.05)	(1.33 ± 0.10)	−(0.11 ± 0.20)	
0.75	0.761	(1.92 ± 0.05)	(1.35 ± 0.11)	−(0.05 ± 0.21)	
1	1.02	(1.92 ± 0.06)	(1.37 ± 0.11)	(0.00 ± 0.21)	
2	2.08	(1.96 ± 0.08)	(1.44 ± 0.14)	(0.16 ± 0.24)	
3	3.19	(2.02 ± 0.10)	(1.52 ± 0.17)	(0.30 ± 0.28)	
4	4.36	(2.11 ± 0.13)	(1.60 ± 0.22)	(0.44 ± 0.34)	
5	5.59	(2.20 ± 0.17)	(1.68 ± 0.27)	(0.57 ± 0.41)	

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Table VIII-8-a: (continued)

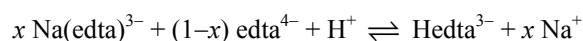
KCl at 20°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	$\log_{10} K_K$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$
0	0.000	(1.79 ± 0.30)	(11.18 ± 0.03)	(6.75 ± 0.02)	(3.17 ± 0.02)
0.1	0.100	(0.97 ± 0.31)	(10.40 ± 0.03)	(6.16 ± 0.02)	(2.74 ± 0.02)
0.25	0.252	(0.75 ± 0.34)	(10.24 ± 0.03)	(6.03 ± 0.02)	(2.61 ± 0.02)
0.5	0.508	(0.65 ± 0.44)	(10.23 ± 0.04)	(6.01 ± 0.03)	(2.52 ± 0.03)
0.75	0.768	(0.64 ± 0.58)	(10.32 ± 0.05)	(6.07 ± 0.04)	(2.48 ± 0.04)
1	1.03	(0.68 ± 0.73)	(10.46 ± 0.06)	(6.16 ± 0.05)	(2.46 ± 0.05)
2	2.13	(1.0 ± 1.4)	(11.22 ± 0.12)	(6.66 ± 0.10)	(2.46 ± 0.10)
3	3.30	(1.5 ± 2.1)	(12.14 ± 0.18)	(7.29 ± 0.15)	(2.52 ± 0.15)
4	4.57	(2.1 ± 2.9)	(13.19 ± 0.25)	(8.00 ± 0.21)	(2.61 ± 0.21)
KCl at 20°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	$\log_{10} K_4$	$\log_{10} K_5$	$\log_{10} K_6$	
0	0.000	(2.24 ± 0.05)	(1.30 ± 0.10)	-(0.51 ± 0.20)	
0.1	0.100	(2.05 ± 0.05)	(1.31 ± 0.10)	-(0.28 ± 0.20)	
0.25	0.252	(2.02 ± 0.06)	(1.32 ± 0.10)	-(0.19 ± 0.20)	
0.5	0.508	(2.03 ± 0.07)	(1.34 ± 0.10)	-(0.10 ± 0.20)	
0.75	0.768	(2.07 ± 0.09)	(1.36 ± 0.11)	-(0.04 ± 0.21)	
1	1.03	(2.12 ± 0.12)	(1.37 ± 0.11)	(0.01 ± 0.21)	
2	2.13	(2.37 ± 0.22)	(1.45 ± 0.14)	(0.18 ± 0.24)	
3	3.30	(2.67 ± 0.34)	(1.54 ± 0.18)	(0.33 ± 0.29)	
4	4.57	(3.01 ± 0.47)	(1.63 ± 0.23)	(0.48 ± 0.35)	
KNO <sub>3</sub> at 20°C					
<i>I</i> M	<i>I<sub>m</sub></i> molal	$\log_{10} K_K$	$\log_{10} K_1$	$\log_{10} K_2$	$\log_{10} K_3$
0	0.000	(1.79 ± 0.30)	(11.18 ± 0.03)	(6.75 ± 0.02)	(3.17 ± 0.02)
0.1	0.101	(0.95 ± 0.31)	(10.39 ± 0.03)	(6.16 ± 0.02)	(2.74 ± 0.02)
0.25	0.253	(0.72 ± 0.34)	(10.23 ± 0.03)	(6.02 ± 0.02)	(2.60 ± 0.02)
0.5	0.511	(0.59 ± 0.44)	(10.21 ± 0.04)	(5.99 ± 0.03)	(2.50 ± 0.03)
0.75	0.775	(0.56 ± 0.58)	(10.29 ± 0.05)	(6.04 ± 0.04)	(2.44 ± 0.04)
1	1.04	(0.57 ± 0.73)	(10.42 ± 0.06)	(6.11 ± 0.05)	(2.41 ± 0.05)
2	2.18	(0.8 ± 1.4)	(11.16 ± 0.12)	(6.59 ± 0.10)	(2.36 ± 0.10)
5	3.43	(1.2 ± 2.2)	(12.09 ± 0.19)	(7.20 ± 0.15)	(2.37 ± 0.15)

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Table VIII-8-a: (continued)

KNO <sub>3</sub> at 20°C				
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>4</sub>	log <sub>10</sub> <i>K</i> <sub>5</sub>	log <sub>10</sub> <i>K</i> <sub>6</sub>
0	0.000	(2.24 ± 0.05)	(1.30 ± 0.10)	−(0.51 ± 0.20)
0.1	0.101	(2.04 ± 0.05)	(1.30 ± 0.10)	−(0.28 ± 0.20)
0.25	0.253	(2.00 ± 0.06)	(1.31 ± 0.10)	−(0.20 ± 0.20)
0.5	0.511	(2.01 ± 0.07)	(1.31 ± 0.10)	−(0.13 ± 0.20)
0.75	0.775	(2.03 ± 0.09)	(1.32 ± 0.11)	−(0.08 ± 0.21)
1	1.04	(2.07 ± 0.12)	(1.33 ± 0.11)	−(0.04 ± 0.21)
2	2.18	(2.29 ± 0.23)	(1.36 ± 0.14)	(0.09 ± 0.24)
3	3.43	(2.55 ± 0.35)	(1.39 ± 0.18)	(0.19 ± 0.30)

Table VIII-8-b. Calculated values for the apparent first protonation constant of edta<sup>4−</sup> in Molar units in some Na<sup>+</sup> / K<sup>+</sup> background electrolytes at 25 and 20°C. The SIT model for activity coefficients has been used with the Δε values obtained in this review. The constant *K*<sub>1</sub><sup>†</sup> includes the formation of alkali-metal complexes. For example, in sodium electrolytes it corresponds to reaction:



where *x* is an undetermined fraction of alkali metal complex. Care should be exercised when using values at the highest ionic strengths in sodium media, because they are confirmed by few experimental data only, as indicated in the figures of Sections VIII.3.2 to VIII.3.6. Also note that there is no experimental support for the values in potassium media at ionic strengths above 1 molal.

25°C						
NaClO <sub>4</sub>			NaNO <sub>3</sub>		NaCl	
<i>I</i> M	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>	<i>I<sub>m</sub></i> molal	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>
0	0.000	(11.24 ± 0.03)	0.000	(11.24 ± 0.03)	0.000	(11.24 ± 0.03)
0.1	0.101	(9.43 ± 0.19)	0.101	(9.42 ± 0.19)	0.100	(9.42 ± 0.19)
0.25	0.254	(9.09 ± 0.22)	0.253	(9.08 ± 0.22)	0.252	(9.08 ± 0.22)
0.5	0.513	(8.88 ± 0.30)	0.509	(8.86 ± 0.30)	0.506	(8.85 ± 0.30)
0.75	0.779	(8.79 ± 0.40)	0.769	(8.77 ± 0.40)	0.762	(8.75 ± 0.39)
1	1.05	(8.75 ± 0.52)	1.03	(8.72 ± 0.51)	1.02	(8.70 ± 0.50)
2	2.21	(8.8 ± 1.0)	2.14	(8.8 ± 1.0)	2.09	(8.7 ± 1.0)
3	3.50	(9.0 ± 1.7)	3.33	(8.9 ± 1.6)	3.20	(8.8 ± 1.5)
4	4.95	(9.4 ± 2.3)	4.61	(9.2 ± 2.2)	4.37	(9.0 ± 2.1)
5	6.58	(9.8 ± 3.1)	6.02	(9.5 ± 2.8)	5.61	(9.3 ± 2.6)

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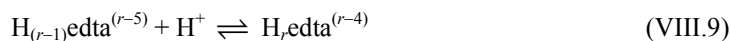
Table VIII-8 -b: (continued)

25°C						
KCl			KNO <sub>3</sub>			
<i>I</i>	<i>I<sub>m</sub></i>	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>	<i>I<sub>m</sub></i>	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>		
M	molal		molal			
0	0.000	(11.24 ± 0.03)	0.000	(11.24 ± 0.03)		
0.1	0.101	(10.17 ± 0.15)	0.101	(10.17 ± 0.15)		
0.25	0.252	(9.91 ± 0.21)	0.253	(9.91 ± 0.20)		
0.5	0.509	(9.78 ± 0.31)	0.512	(9.79 ± 0.30)		
0.75	0.769	(9.74 ± 0.45)	0.776	(9.77 ± 0.43)		
1	1.03	(9.75 ± 0.61)	1.05	(9.80 ± 0.59)		
2	2.13	(9.9 ± 1.3)	2.19	(10.1 ± 1.3)		
3	3.31	(10.2 ± 2.1)	3.44	(10.5 ± 2.2)		
4	4.58	(10.6 ± 3.0)				
20°C						
NaClO <sub>4</sub>			NaNO <sub>3</sub>		NaCl	
<i>I</i>	<i>I<sub>m</sub></i>	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>	<i>I<sub>m</sub></i>	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>	<i>I<sub>m</sub></i>	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>
M	molal		molal		molal	
0	0.000	(11.18 ± 0.03)	0.000	(11.18 ± 0.03)	0.000	(11.18 ± 0.03)
0.1	0.101	(9.38 ± 0.19)	0.100	(9.37 ± 0.19)	0.100	(9.37 ± 0.19)
0.25	0.253	(9.04 ± 0.22)	0.252	(9.03 ± 0.22)	0.251	(9.03 ± 0.22)
0.5	0.512	(8.83 ± 0.30)	0.508	(8.81 ± 0.30)	0.505	(8.81 ± 0.30)
0.75	0.778	(8.74 ± 0.40)	0.768	(8.72 ± 0.40)	0.761	(8.70 ± 0.39)
1	1.05	(8.70 ± 0.52)	1.03	(8.67 ± 0.51)	1.02	(8.65 ± 0.50)
2	2.21	(8.8 ± 1.0)	2.13	(8.7 ± 1.0)	2.08	(8.65 ± 0.99)
3	3.49	(9.0 ± 1.7)	3.32	(8.9 ± 1.6)	3.19	(8.8 ± 1.5)
4	4.93	(9.3 ± 2.3)	4.60	(9.1 ± 2.2)	4.36	(9.0 ± 2.1)
5	6.55	(9.7 ± 3.1)	6.00	(9.4 ± 2.8)	5.59	(9.2 ± 2.6)
KCl			KNO <sub>3</sub>			
<i>I</i>	<i>I<sub>m</sub></i>	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>	<i>I<sub>m</sub></i>	log <sub>10</sub> <i>K</i> <sub>1</sub> <sup>†</sup>		
M	molal		molal			
0	0.000	(11.18 ± 0.03)	0.000	(11.18 ± 0.03)		
0.1	0.100	(10.11 ± 0.15)	0.101	(10.11 ± 0.15)		
0.25	0.252	(9.86 ± 0.20)	0.253	(9.86 ± 0.20)		
0.5	0.508	(9.72 ± 0.31)	0.511	(9.74 ± 0.30)		
0.75	0.768	(9.69 ± 0.45)	0.775	(9.72 ± 0.43)		
1	1.03	(9.70 ± 0.60)	1.04	(9.75 ± 0.58)		
2	2.13	(9.9 ± 1.3)	2.18	(10.0 ± 1.3)		
3	3.30	(10.2 ± 2.1)	3.43	(10.4 ± 2.2)		
4	4.57	(10.5 ± 2.9)				



### VIII.3.8 Temperature effects

Enthalpy changes for the protonation of  $\text{edta}^{4-}$



have been determined mostly by calorimetric methods, although in a few references enthalpies were obtained from the temperature variation of protonation constants. A few of these studies have not been considered [77CHO/GOE], [82TER/IVA], [85MAR/EVA], [86MAR/EVA], [98KOC/VAS]. These references are discussed in Appendix A. In the case of [82TER/IVA] the reported enthalpy changes correspond to the differences in the literature protonation constants adopted by the authors at 20 and 25°C. As they were not the result of original measurements in [82TER/IVA] these data are not considered here. In [98KOC/VAS] the enthalpies are reported in a graph but partly corrected for ionic strength effects with an unknown function, and the data cannot be included here.

The  $\Delta_r H_m$  (VIII.9) values reported in [66MOE/CHU] and [69SIL/SIM] were not considered because they are associated with a large uncertainty: they were obtained from few values of  $\log_{10}K$  over a narrow temperature interval (20 to 40)°C.

Most of the remaining investigations have been performed in  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{R}_4\text{N}^+$  (tetraalkylammonium) salts.

Only few studies report data in  $\text{LiNO}_3$ . Daniele *et al.* [85DAN/RIG] report data for  $\Delta_r H_m$  (VIII.9),  $r = 1$ ), and only [73VAS/KOC] and [76VAS/KOC] give values of  $\Delta_r H_m$  (VIII.9),  $r = 3$  and 4). For the second protonation step, there is data both in [85DAN/RIG] and in [74VAS/KOC], but the two data sets are strongly discrepant. For example, at 1 M  $\text{LiNO}_3$  and 25°C  $\Delta_r H_m$  (VIII.9),  $r = 2$ ), is reported to be  $-(22.1 \pm 0.2)$  kJ·mol<sup>-1</sup> [74VAS/KOC], while the  $\log_{10}K(T)$ , (VIII.9),  $r = 2$ ) data in [85DAN/RIG] indicate instead  $-(9 \pm 4)$  kJ·mol<sup>-1</sup>. As described in the discussions in Appendix A for these two references, systematic errors in the  $\text{LiNO}_3$  data are suspected, especially in [74VAS/KOC]. There are however no additional literature studies in lithium media to support the data in [85DAN/RIG]. Because the amount of experiments in sodium, potassium and  $\text{R}_4\text{N}^+$  salts is sufficient to make a selection of values for  $\Delta_r H_m$  (VIII.9),  $r = 1$  and 2), enthalpy data for the first and second protonation of  $\text{edta}^{4-}$  obtained in  $\text{LiNO}_3$  were excluded in the evaluation described in this Section.

Literature data in  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{R}_4\text{N}^+$  media are listed in Table VIII-9 and Table VIII-10. Some of these studies are also discussed in Appendix A, as indicated in the corresponding table. The reported enthalpy changes for the first two individual protonation steps, corresponding to the protonation of the amine groups ( $r = 1$  and 2 in equation (VIII.9)), range between  $-33$  and  $-12$  kJ·mol<sup>-1</sup>, depending on ionic media and temperature. As expected, the reported enthalpy changes for the protonation of carboxylic groups (with  $r = 3$  to 5) are small:  $\Delta_r H_m$  (VIII.9) values range between  $+0.6$  and  $+8$  kJ·mol<sup>-1</sup>, depending on ionic media and temperature.

Table VIII-9: Literature data on the enthalpy changes for ethylenediaminetetraacetate step-wise protonation reactions in sodium, potassium or tetraalkylammonium media. Units are: mol·L<sup>-1</sup> for ionic strength (*I*), °C for temperature and kJ·mol<sup>-1</sup> for  $\Delta_r H_m$ . Enthalpy changes for other protonation reactions are listed in Table VIII-10.

Method <sup>a</sup> / Electrolyte <i>t</i>	$\Delta_r H_m$ (VIII.9)					References
	<i>r</i> =1 <sup>†</sup>	<i>r</i> =2	<i>r</i> =3	<i>r</i> =4	<i>r</i> =5	
* →0 KCl 0-30	-(22.6±1.6)	-(15.2±1.6)				<a href="#">[53CAR/MAR]<sup>b</sup></a>
cal 0.1 KCl 20	-23.8	-18.4	5.98	0.75	2.05	
cal 0.1 KNO <sub>3</sub> 20	-23.7	-18.2				<a href="#">[63AND]</a> , <a href="#">[64AND]</a>
* 0.1 KNO <sub>3</sub> 25	-(20±2)	-(33±8)				
cal 0.03 ClO <sub>4</sub> <sup>-</sup> 25	-(18.20±0.21)	-(15.10±0.54)				<a href="#">[66MOE/CHU]<sup>e</sup></a> <a href="#">[69CHR/IZA]</a>
-0.17						
* 0.1 KNO <sub>3</sub> 25	-18.4	-20.5				<a href="#">[69SIL/SIM]<sup>e</sup></a> <a href="#">[70KUG/CAR]</a>
cal 0.1 KNO <sub>3</sub> 25	-23.4	-18.2				
cal 0.2 NaClO <sub>4</sub> 25			(5.48±0.04)	(1.26±0.04)		<a href="#">[73VAS/KOC]<sup>c,d</sup></a>
0.5			(5.86±0.08)	(1.51±0.04)		
0.75			(5.86±0.13)	(1.63±0.04)		<a href="#">[74VAS/KOC]<sup>c,d</sup></a>
cal 0.2 NaNO <sub>3</sub>			(5.36±0.13)	(1.13±0.08)		
0.5			(5.23±0.04)	(0.96±0.08)		<a href="#">[76AND]</a>
0.75			(4.81±0.13)	(0.92±0.08)		
cal 0.2 KNO <sub>3</sub>			(5.36±0.04)			<a href="#">[76AND]</a>
0.5			(5.40±0.04)	(1.21±0.04)		
0.75			(5.52±0.04)	(1.21±0.10)		<a href="#">[74VAS/KOC]<sup>c,d</sup></a>
cal 0.2 KNO <sub>3</sub> 25	-(23.44±0.21)	-(19.87±0.17)				
0.5	-(24.58±0.21)	-(22.22±0.13)				<a href="#">[76AND]</a>
1	-(26.47±0.21)	-(24.10±0.13)				
cal 0.2 NaNO <sub>3</sub>		-(19.25±0.21)				<a href="#">[76AND]</a>
0.5		-(21.21±0.25)				
1		-(23.97±0.17)				<a href="#">[76AND]</a>
cal 0.2 NaCl		-(18.37±0.13)				
0.5		-(20.63±0.13)				<a href="#">[76AND]</a>
1		-(23.51±0.21)				
cal 0.2 NaClO <sub>4</sub>		-(18.66±0.08)				<a href="#">[76AND]</a>
0.5		-(21.17±0.25)				
1		-(24.14±0.17)				<a href="#">[76AND]</a>
cal 1 Me <sub>4</sub> NCl 20	-27.95	-21.55				
0.1	-24.48	-15.94				<a href="#">[76AND]</a>
1 KNO <sub>3</sub> 20	-28.20	-23.47				
0.1	-25.10	-17.57				

(Continued on next page)

Table VIII-9: (continued)

Method <sup>a</sup> /	Electrolyte	<i>t</i>	$\Delta_r H_m^\circ$ (VIII.9)					References
			<i>r</i> =1 <sup>†</sup>	<i>r</i> =2	<i>r</i> =3	<i>r</i> =4	<i>r</i> =5	
cal	0.2	KNO <sub>3</sub>	15		(3.85±0.21)			<a href="#">[76VAS/KOC]</a> <sup>c,d</sup>
	0.5				(3.68±0.04)			
	0.75				(3.85±0.08)			
cal	0.2	KNO <sub>3</sub>	35		(7.30±0.27)			
	0.5				(7.32±0.13)			
	0.75				(7.09±0.06)			
cal	0.2	NaClO <sub>4</sub>	15		(3.35±0.08)			
	0.5				(3.70±0.08)			
	0.75				(4.10±0.04)			
cal	0.2	NaClO <sub>4</sub>	35		(7.45±0.04)			
	0.75				(7.95±0.21)			
cal	0.5	KNO <sub>3</sub>	25	-(29.1±0.2)	-(22.7±0.2)			<a href="#">[77CHO/GOE]</a> <sup>c, e</sup>
cal	0.2	KNO <sub>3</sub>	15		-(20.17±0.21)			<a href="#">[78VAS/KOC]</a> <sup>c</sup>
	0.3		-(25.52±0.21)					
	0.5		-(26.38±0.17)	-(22.13±0.17)				
	1		-(27.20±0.21)	-(24.31±0.25)				
cal	0.2	KNO <sub>3</sub>	25		-(18.87±0.13)			
	0.3		-(24.87±0.21)					
	0.5		-(25.75±0.17)	-(20.84±0.21)				
	1		-(26.57±0.21)	-(22.93±0.21)				
cal	0.2	KNO <sub>3</sub>	35		-(16.95±0.25)			
	0.3		-(24.00±0.21)					
	0.5		-(24.64±0.21)	-(19.79±0.21)				
	1		-(26.07±0.25)	-(22.01±0.17)				
cal	0.2	NaClO <sub>4</sub>	15		-(20.50±0.17)			
	0.5			-(22.38±0.17)				
	1			-(25.52±0.25)				
cal	0.2	NaClO <sub>4</sub>	25		-(18.95±0.21)			
	0.5			-(20.92±0.21)				
	1			-(23.85±0.25)				
cal	0.2	NaClO <sub>4</sub>	35		-(17.74±0.21)			
	0.5			-(19.66±0.21)				
	1			-(23.05±0.21)				
*	0.1	NaNO <sub>3</sub>	10-45	-(17.6±2.0)	-(17.9±3.4)			<a href="#">[85DAN/RIG]</a> <sup>b,c,d</sup>
	0.3		-(16.8±2.0)	-(20.7±3.4)				
	0.6		-(14.9±2.0)	-(23.1±3.4)				

(Continued on next page)

Table VIII-9: (continued)

Method <sup>a</sup> /	Electrolyte	<i>t</i>	$\Delta_r H_m^\circ$ (VIII.9)					References
			<i>r</i> =1 <sup>†</sup>	<i>r</i> =2	<i>r</i> =3	<i>r</i> =4	<i>r</i> =5	
			–(12.5±3.4)	–(24.8±4.9)				
*	0.1 KNO <sub>3</sub>	10-45	–(22.3±2.0)	–(17.0±3.4)				
			–(22.3±2.0)	–(18.2±3.4)				
			–(23.9±2.0)	–(19.5±3.4)				
			–(22.3±3.4)	–(18.2±4.9)				
*	0.1 Me <sub>4</sub> NBr	10-45	–(20.1±2.0)					
			–(22.2±2.0)					
			–(23.4±2.0)					
			–(22.0±3.4)					
*	0.1 Et <sub>4</sub> N <sup>+</sup>	10-45	–(20.1±2.0)					
			–(22.2±2.0)					
			–(23.3±2.0)					
			–(22.3±3.4)					
*	0.1 Pr <sub>4</sub> NBr	10-45	–(19.5±2.0)	–(17.0±3.5)	(6.9±5.3)	(2.5±8.0)		
			–(22.3±1.5)	–(18.0±3.1)	(5.8±4.7)	(1.1±7.5)		
			–(23.9±2.0)	–(10.5±3.8)	(5.5±5.9)	(0.8±8.2)		
			–(22.3±3.0)	–(18.1±5.2)	(5.8±7.1)	(1.6±6.9)		
cal	0.2 KCl	25	–22.3	–17.2	0.84	2.51		<a href="#">[85MAR/EVA]</a> , <a href="#">[86MAR/EVA]</a> <sup>c,e</sup>
*	0.1 NaCl	0-150	–(18±2)					<a href="#">[95PAL/NGU2]</a>

<sup>†</sup>: The enthalpy change for the first protonation step of ethylenediaminetetraacetate does not take into account the complex formation with alkali metals, and therefore it refers to apparent equilibria such as:  
 $(1-x) \text{edta}^{4-} + x \text{Na(edta)}^{3-} + \text{H}^+ \rightleftharpoons \text{Hedta}^{3-} + x \text{Na}^+$ .

- a: Methods: cal = calorimetry; \*:  $\partial \text{p}K_a / \partial T$  = temperature dependence of protonation constants.  
b: Original  $\log_{10}K(T)$  data recalculated in this review using the constant heat capacity model.  
c: See comments in Appendix A.  
d: Data also reported in LiNO<sub>3</sub> ionic medium.  
e: Values not considered in the review procedure.

Table VIII-10: Literature data considered by this review on the enthalpy changes for ethylenediaminetetraacetate protonation, excluding step-wise reactions. Units are:  $\text{mol}\cdot\text{L}^{-1}$  for ionic strength ( $I$ ),  $^{\circ}\text{C}$  for temperature and  $\text{kJ}\cdot\text{mol}^{-1}$  for  $\Delta_r H_m^{\dagger}$ . Enthalpies for step-wise protonation reactions are listed in Table VIII-9.

Method <sup>a</sup>	$I$	Electrolyte	$t$ ( $^{\circ}\text{C}$ )	$\Delta_r H_m^{\dagger}$	References
$\text{edta}^{4-} + 2 \text{H}^+ \rightleftharpoons \text{H}_2\text{edta}^{2-}$					
cal	1	NaOH	25	$-(41.8 \pm 0.8)$	[58YAT/KAR] <sup>b</sup>
$\text{edta}^{4-} + 6 \text{H}^+ \rightleftharpoons \text{H}_6\text{edta}^{2+}$					
cal	$\rightarrow 0$	$\text{HClO}_4, \text{HCl}, \text{HNO}_3$	25	$-(32.0 \pm 0.6)$	[77LYM/VAS] <sup>b</sup>
cal	2	HCl	25	$-(58.0 \pm 0.4)$	[77VAS/LYM] <sup>b,c</sup>
	3			$-(68.5 \pm 0.5)$	
	4			$-(79.7 \pm 0.8)$	
	2	$\text{HNO}_3$		$-(60.5 \pm 0.4)$	
	3			$-(72.3 \pm 0.5)$	
	4			$-(83.8 \pm 0.8)$	
cal	2	HCl	15	$-(61.0 \pm 0.4)$	[77VAS/LYM2] <sup>b,c</sup>
	3			$-(71.1 \pm 0.5)$	
	4			$-(81.6 \pm 0.8)$	
	2		35	$-(54.7 \pm 0.4)$	
	3			$-(65.7 \pm 0.5)$	
	4			$-(76.9 \pm 0.8)$	
$\text{H}_4\text{edta}(\text{aq}) + 2 \text{H}^+ \rightleftharpoons \text{H}_6\text{edta}^{2+}$					
cal	1	$(\text{Li}, \text{Na}, \text{K})\text{NO}_3$	25	$-(0.29 \pm 0.21)$	[79VAS/KOC] <sup>b</sup>
	1.5			$(1.42 \pm 0.33)$	
	2			$(2.64 \pm 0.29)$	
	3			$(4.94 \pm 0.29)$	
	1	$\text{NaClO}_4$	25	$-(2.55 \pm 0.25)$	
	2			$-(5.15 \pm 0.29)$	
	3			$-(7.36 \pm 0.50)$	

<sup>†</sup>: Enthalpy changes for protonation reactions involving  $\text{edta}^{4-}$  do not take into account the complex formation with alkali metals, and therefore they refer to apparent equilibria such as:  $(1-x) \text{edta}^{4-} + x \text{Na}(\text{edta})^{3-} + n \text{H}^+ \rightleftharpoons \text{H}_n\text{edta}^{(n-4)} + x \text{Na}^+$ .

a: Methods: cal = calorimetry.

b: See comments in Appendix A.

c: From mixing  $\text{K}_4\text{edta}$  solutions with the acid indicated, and therefore, in the presence of small amounts of  $\text{K}^+$  ions.

Calorimetric measurements have been performed at temperatures ranging from 15 to 35°C, *cf.* Table VIII-9 and Table VIII-10. In a few studies the enthalpies of protonation have been determined calorimetrically only at 20°C [58TIL/STA], [63AND], [64AND], [76AND]. These were extrapolated in this review to 25°C by taking into account the temperature dependence of enthalpies of reaction, which is given by the corresponding heat capacity changes:

$$\Delta_r C_{p,m} = \left( \frac{\partial \Delta_r H_m}{\partial T} \right)_p$$

Heat capacity changes have been determined both calorimetrically and from the temperature dependence of protonation constants. The calorimetric data by Hovey, Hepler and Tremaine are most precise [85HOV/TRE], [86HOV/HEP], [88HOV/HEP2]:

$$C_{p,m}^{\circ}(\text{edta}^{4-}, 298.15 \text{ K}) = -(310 \pm 20) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}^{\circ}(\text{Hedta}^{3-}, 298.15 \text{ K}) = -(82 \pm 2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

$$C_{p,m}^{\circ}(\text{H}_2\text{edta}^{2-}, 298.15 \text{ K}) = (81 \pm 1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

These data result in  $\Delta_r C_{p,m}^{\circ}(\text{VIII.9}) = (228 \pm 20)$  and  $(163 \pm 2) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $r = 1$  and 2, respectively, which may be compared with:

- $\Delta_r C_{p,m}^{\circ}(\text{VIII.9}), r = 1) = (98 \pm 30) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  in 0.1 M NaCl obtained from the variation of protonation constants with temperature [95PAL/NGU2], and
- values obtained from the calorimetric measurements of  $(\partial \Delta_r H_m / \partial T)_p$ , *cf.* Table VIII-11.

Another literature value of  $\Delta_r C_{p,m}^{\circ}$  obtained from calorimetric measurements of  $(\partial \Delta_r H_m / \partial T)_p$  is [77VAS/LYM2]:



Literature values at 20°C for the first, second and third protonation enthalpies were extrapolated to 25°C by using appropriate values of  $\Delta_r C_{p,m}^{\circ}(\text{VIII.9})$ , if available (*cf.* Table VIII-11), or by setting  $\Delta_r C_{p,m}^{\circ}(\text{VIII.9}) = 150 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  otherwise. The values at 20°C for the fourth and fifth protonation enthalpies [58TIL/STA] were not included in the review. The uncertainty of such extrapolated values was increased by  $\pm 0.5 \text{ kJ}\cdot\text{mol}^{-1}$ .

Table VIII-9 contains some enthalpy changes derived from temperature variations of protonation constants [53CAR/MAR], [85DAN/RIG], [95PAL/NGU2]. The primary  $\log_{10}K(T)$  data was interpreted using the constant heat capacity model, either in the original paper [95PAL/NGU2] or by this review [53CAR/MAR], [85DAN/RIG].

Table VIII-11: Heat capacity changes at 25°C for the stepwise protonation reactions of edta<sup>4-</sup>. Values evaluated in this review from the temperature dependence of the corresponding enthalpy changes determined by calorimetric methods as listed in Table VIII-9.

Medium	$I$ (M)	$\Delta_r C_{p,m}$ (VIII.9) (J·K <sup>-1</sup> ·mol <sup>-1</sup> )	Reference
$r = 1$			
KNO <sub>3</sub>	0.2	(110 ± 20)	<a href="#">[78VAS/KOC]</a>
	0.3	(76 ± 20)	
	0.5	(82 ± 20)	
	1	(48 ± 20)	
$r = 2$			
KNO <sub>3</sub>	0.2	(155 ± 20)	<a href="#">[78VAS/KOC]</a>
	0.5	(123 ± 20)	
	1	(121 ± 20)	
NaClO <sub>4</sub>	0.2	(113 ± 20)	
	0.5	(138 ± 20)	
	1	(130 ± 20)	
$r = 3$			
KNO <sub>3</sub>	0.2	(173 ± 70)	<a href="#">[76VAS/KOC]</a>
	0.5	(182 ± 70)	
	0.75	(162 ± 70)	
NaClO <sub>4</sub>	0.2	(205 ± 70)	
	0.5	(212 ± 70)	
	0.75	(192 ± 70)	

For calorimetric studies, the interpretation of the data depends on the assumed speciation of the initial and final solutions in the experiments. For the first and second protonation reactions, *r* = 1 or 2 in equation (VIII.9), the species edta<sup>4-</sup>, Hedta<sup>3-</sup> and H<sub>2</sub>edta<sup>2-</sup> have a relative large pH-range of predominance, but for the other protonated forms of edta there are no intervals of pH at which they predominate. Therefore the calorimetric determination of  $\Delta_r H_m$  (VIII.9) is less prone to systematic errors for *r* = 1 or 2 than for *r* ≥ 3. During the evaluation of the data, the 95% uncertainty for calorimetric values was set to: ± 1 kJ·mol<sup>-1</sup> for *r* = 1 or 2; ± 1.5 kJ·mol<sup>-1</sup> for *r* = 3; and ± 2 kJ·mol<sup>-1</sup> for *r* = 4; unless the reported uncertainty in the original publication was larger.

The  $\Delta_r H_m$  (VIII.9) data in Table VIII-9 were treated according to the SIT equations (*cf.* Section V.3.6). Only data at 20 and 25°C were considered. Values at 20°C for the first, second and third protonation enthalpies were extrapolated to 25°C using appropriate values of  $\Delta_r C_{p,m}$  (VIII.9) as described above.

Initially, the  $\Delta_r H_m$  (VIII.9) data for each background electrolyte were treated according to the SIT equations (*cf.* Section V.3.6), using multi-linear weighted least-

squares fits to obtain values of  $\Delta_r H_m^\circ$  and  $\Delta \varepsilon_L(r, \text{MX})$ , where MX is the background electrolyte, and  $r$  is the number of  $\text{H}^+$  in reaction (VIII.9). This preliminary regression analysis revealed that the results obtained for chloride, nitrate or perchlorate media cannot be distinguished from a statistical point of view. Furthermore, for some protonation steps there was no difference between the results obtained in sodium and potassium media. Hence, all the data have been fitted subsequently with the minimum number of  $\Delta \varepsilon_L(\text{M}^+)$  parameters needed (where  $\text{M}^+$  is either  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{R}_4\text{N}^+$ ).

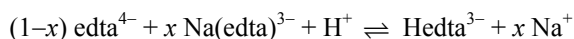
The data treated according to the SIT equations, with the uncertainties assigned in this review are shown in Figure VIII-14. The enthalpy changes and  $\Delta \varepsilon_L(r, \text{M}^+)$  values obtained from the multi-linear weighted least-squares fits are listed in Table VIII-12.

Table VIII-12. Selected enthalpy changes,  $\Delta_r H_m$  (VIII.9) and corresponding  $\Delta \varepsilon_L(\text{M}^+)$  values at 25°C.

	$r = 1$ †	$r = 2$	$r = 3$	$r = 4$
$\Delta_r H_m^\circ$ (kJ·mol <sup>-1</sup> )	$-(19.8 \pm 0.5)$	$-(15.2 \pm 0.4)$	$(7.1 \pm 0.4)$	$(1.9 \pm 1.5)$
$\Delta \varepsilon_L$ (10 <sup>-3</sup> kg·K <sup>-1</sup> ·mol <sup>-1</sup> )				
Cation				
$\text{Li}^+$			$(3.4 \pm 3.0)$	
$\text{Na}^+$	$-(24 \pm 3)$			
$\text{K}^+$	$(3.4 \pm 0.9)$			
$\text{R}_4\text{N}^+$	$(0.2 \pm 1.0)$	$(1.8 \pm 1.2)$		
$\text{Na}^+; \text{K}^+$		$(6.5 \pm 0.8)$		
$\text{Na}^+; \text{K}^+; \text{Pr}_4\text{N}^+$			$-(1.0 \pm 2.3)$	
all electrolytes				$-(0.7 \pm 3.4)$

†: Enthalpy changes for protonation reactions involving  $\text{edta}^{4-}$  do not take into account the complex formation with alkali metals, and therefore they refer to apparent equilibria such as:  
 $(1-x) \text{edta}^{4-} + x \text{Na}(\text{edta})^{3-} + n \text{H}^+ \rightleftharpoons \text{H}_n \text{edta}^{(n-4)} + x \text{Na}^+$ .

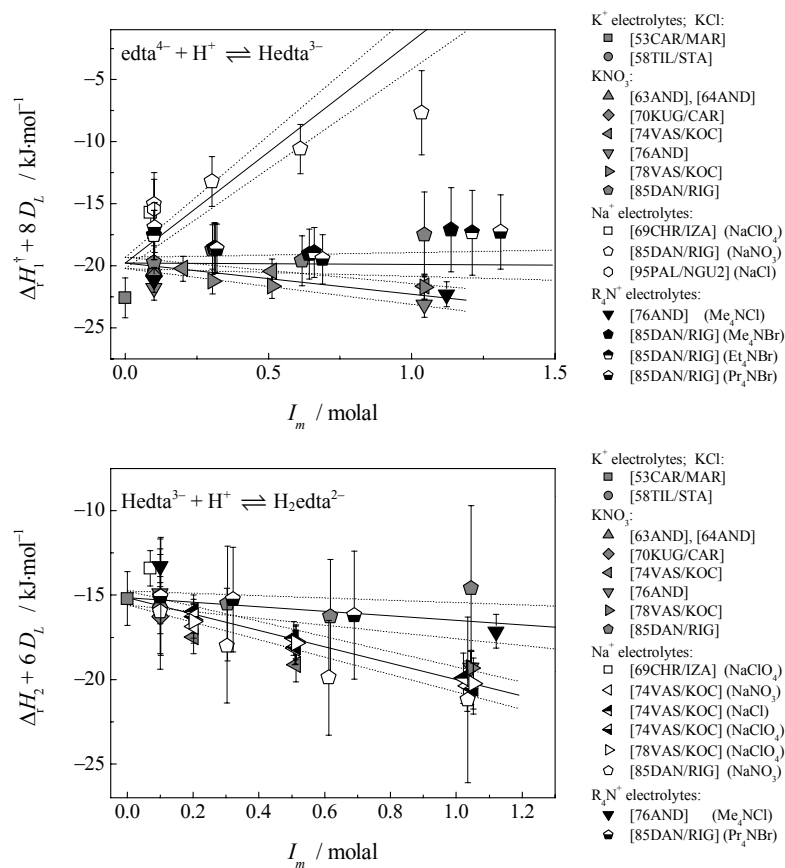
Because of alkali-metal complex formation, the data for the first protonation of  $\text{edta}^{4-}$  refers to an apparent equilibrium, *e.g.*, in the case of sodium background electrolytes:



This is indicated with a superscript “†” on equilibrium constants, enthalpy changes, *etc.* Only two references, however, report a value of  $\Delta_r H_m^\dagger$  (VIII.9),  $r = 1$  in  $\text{Na}^+$  media [85DAN/RIG], [95PAL/NGU2]. All other values of  $\Delta_r H_m^\dagger$  (VIII.9),  $r = 1$  were obtained in  $\text{K}^+$  or tetraalkylammonium ( $\text{R}_4\text{N}^+$ ) electrolytes, *cf.* Table VIII-9. The differences between the values of  $\Delta_r H_m^{\circ\dagger}$  (VIII.9),  $r = 1$  obtained in either  $\text{K}^+$  or  $\text{R}_4\text{N}^+$  media are not large as compared with the values in  $\text{NaNO}_3$ , *cf.* Table VIII-9 and Figure VIII-14. This could be expected if the values of  $x$  in the reaction above are small for  $\text{K}^+$  complex formation, or if the enthalpy of  $\text{K}^+$  coordination is small.

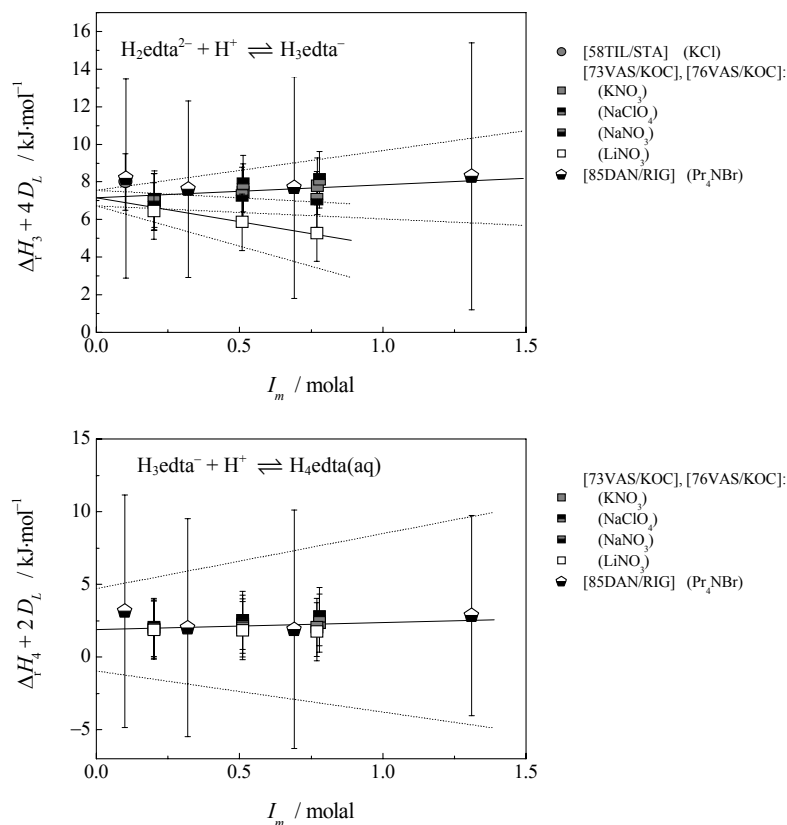


Figure VIII-14: Enthalpy changes for reactions:  $H_{(r-1)}\text{edta}^{(r-5)} + H^+ \rightleftharpoons H_r\text{edta}^{(r-4)}$  plotted according to the SIT methodology. The data for the first protonation reaction in alkali-metal media, where complexes with the medium cations may take place, corresponds instead to reaction:  $(1-x)\text{edta}^{4-} + x\text{Medta}^{3-} + H^+ \rightleftharpoons \text{Hedta}^{3-} + x\text{M}^+$ .



(Continued on next page)

Figure VIII-14: (continued)



The values in Table VIII-10 from [77LYM/VAS], [77VAS/LYM], [77VAS/LYM2], [79VAS/KOC] correspond to the following reactions:



In all these calorimetric studies the authors assumed that their final solutions only contained  $\text{H}_6\text{edta}^{2+}$ . However, calculations using the protonation constants selected by this review show that under the conditions studied the amount of  $\text{H}_5\text{edta}^+$  was not negligible (from  $\approx 30\%$  in 2 M acid, to  $\approx 15\%$  in 4 M acid). Because of this, the uncertainties in the experimental values were increased to  $\pm 2 \text{ kJ}\cdot\text{mol}^{-1}$ . The data were then treated using the SIT methodology as discussed in Section V.3.6. The weighted multi-linear least-squares fits gave  $\Delta_r H_m^\circ(\text{VIII.10}) = -(30.7 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r H_m^\circ(\text{VIII.11}) = -(2.6 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$ . The values of  $\Delta_r H_m^\circ(\text{VIII.10})$  and  $\Delta_r H_m^\circ(\text{VIII.11})$  may be combined to obtain:



which agrees with the value calculated adding the four step-wise protonation enthalpies, namely:  $-(26.0 \pm 1.7) \text{ kJ}\cdot\text{mol}^{-1}$ .

In addition,  $\Delta_r H_m^\circ(\text{VIII.11}) = \Delta_r H_m^\circ((\text{VIII.9}), r=5) + \Delta_r H_m^{\circ\dagger}((\text{VIII.9}), r=6)$ . Only one determination of  $\Delta_r H_m^\circ((\text{VIII.9}), r=5)$  has been reported, *cf.* Table VIII-9, but this value is highly dependent on the calculated ratio between  $\text{H}_5\text{edta}^+$  and  $\text{H}_4\text{edta}(\text{aq})$ , in the original publication. More data are needed to select individual values for  $\Delta_r H_m^\circ(\text{VIII.9})$  with  $r=5$  and 6.

The data from [\[58YAT/KAR\]](#), listed in Table VIII-10, cannot be compared with other results, because in these experiments substantial  $\text{Na}^+$  complex formation took place.

From the selected reaction data, the following enthalpies of formation are selected:

$$\Delta_r H_m^\circ(\text{edta}^{4-}, 298.15 \text{ K}) = -(1704.8 \pm 3.8) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m^\circ(\text{Hedta}^{3-}, 298.15 \text{ K}) = -(1724.6 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m^\circ(\text{H}_2\text{edta}^{2-}, 298.15 \text{ K}) = -(1739.8 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta_r H_m^\circ(\text{H}_3\text{edta}^-, 298.15 \text{ K}) = -(1732.7 \pm 3.7) \text{ kJ}\cdot\text{mol}^{-1}.$$

## VIII.4 Alkali metal edta compounds and complexes

### VIII.4.1 Complexes with $\text{Na}^+$ and $\text{K}^+$

It was found early that the protonation constants of  $\text{edta}^{4-}$  depend on the nature of the background electrolyte. Especially, the first protonation constant was found to be substantially lower in  $\text{Na}^+$  solutions as compared with  $\text{K}^+$  media. This was ascribed to the formation of sodium complexes, and Schwarzenbach and Ackermann [\[47SCH/ACK\]](#) determined the stability of the  $\text{Na}^+$  and  $\text{Li}^+$  complexes with  $\text{edta}^{4-}$  in 0.1 M KCl media. Since then several studies have reported equilibrium constants for the formation of ethylenediaminetetraacetate complexes with  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , *etc.* Some of these references are discussed in Appendix A [\[65PRI/SEB\]](#), [\[83ARE/MUS\]](#), [\[85DAN/RIG\]](#), [\[87BER/VAS\]](#). The references considered in this review are listed in Table VIII-13. The coordination of  $\text{Na}^+$  in  $\text{Na}_4\text{edta}\cdot 5\text{H}_2\text{O}(\text{cr})$  and  $\text{Na}_2\text{H}_2\text{edta}\cdot 2\text{H}_2\text{O}(\text{cr})$  has also been determined [\[93FON/SOL\]](#).

Table VIII-13: Literature data on the formation of  $\text{edta}^{4-}$  complexes with  $\text{Na}^+$  and  $\text{K}^+$  considered in this review. The equilibrium constants are expressed in units of  $\text{mol}\cdot\text{L}^{-1}$ , and correspond to reactions:



Method <sup>a</sup> <i>I</i>	Electrolyte <sup>b</sup>	<i>t</i>	<i>M</i> <sup>+</sup>	$\log_{10}\beta_{1,0,1}$	$\log_{10}\beta_{1,0,2}$	$\log_{10}\beta_{1,1,1}$	$\log_{10}\beta_{1,2,1}$	Reference
ise-H	0.1 KCl	20	$\text{Na}^+$	1.66				[47SCH/ACK]
ise	0.11 $\text{Na}^+/\text{Me}_4\text{N}^+$	?	$\text{Na}^+$	1.91		0.36		[63PAL] <sup>c</sup>
$\Delta pK_a$	0.32 $\text{CsCl}/\text{NaCl}$	25	$\text{Na}^+$	1.79	2.47	0.49		[65BOT/CHA] <sup>d</sup>
	$\text{CsCl}/\text{KCl}$		$\text{K}^+$	0.96		-0.31		
$\Delta pK_a$	0.1 $\text{Me}_4\text{NCl}/\text{KNO}_3$	20	$\text{K}^+$	0.8				[67AND]
$\Delta pK_a$	1 $\text{Me}_4\text{NCl}/\text{NaClO}_4$	20	$\text{Na}^+$	1.27				[67AND],[77AND]
gl	0.1 $\text{Me}_4\text{NCl}$	25	$\text{Na}^+$	$(1.82 \pm 0.01)$				[68WAT/SCH] <sup>e</sup>
	0.1		$\text{K}^+$	$(0.55 \pm 0.06)$				
	1	25	$\text{K}^+$	$(0.69 \pm 0.06)$				
$\Delta pK_a$	0.1 $\text{Et}_4\text{NClO}_4/\text{NaClO}_4$	25	$\text{Na}^+$	1.88				[71ROR/MAC] <sup>e</sup>
	$\text{Et}_4\text{NClO}_4/\text{KNO}_3$		$\text{K}^+$	0.70				
$\Delta pK_{a,\text{sp}}$	0.5 $\text{Me}_4\text{NCl}/\text{NaCl}$	25	$\text{Na}^+$	1.45				[73CAR/SWA] <sup>e</sup>
gl	1 $\text{Me}_4\text{NCl}$	20	$\text{Na}^+$	$(1.69 \pm 0.05)$				[76AND]
$\Delta pK_a$	0.1 $\text{NaCl}$		$\text{Na}^+$	$(1.85 \pm 0.05)$				
gl	0.1 $\text{Me}_4\text{NClO}_4$	25	$\text{Na}^+$	$(2.1 \pm 0.15)$		$(0.8 \pm 0.2)$		[91SAL/BOO] <sup>e</sup>
$\Delta pK_a$	$\text{Me}_4\text{NClO}_4/\text{KNO}_3$		$\text{K}^+$	$(1.6 \pm 0.3)$		$(1.08 \pm 0.16)$		
gl	0.15 $\text{Me}_4\text{NCl}$	25	$\text{Na}^+$	$(2.35 \pm 0.01)$		$(2.09 \pm 0.02)$		[93CHE/REI]
			$\text{K}^+$	$(1.60 \pm 0.02)$		$(1.57 \pm 0.03)$		$(1.51 \pm 0.04)$

a: Methods: ise-H = potentiometry with hydrogen electrode; gl = potentiometry with pH-glass electrode; ise = ion selective electrode; sp = spectrophotometry;  $\Delta pK_a$  = the formation constants for alkali-metal complexation were obtained from differences in protonation constants (alkali electrolytes *versus* tetraalkylammonium salts).

b:  $\text{Me}_4\text{N}^+$ ,  $\text{Et}_4\text{N}^+$ , and  $\text{Pr}_4\text{N}^+$ : tetramethylammonium, tetraethylammonium, and tetrapropylammonium, respectively

c: A constant ionic medium was not used. The temperature is not given in the paper. The anionic components of the solutions are not given.

d: Ionic strength not constant when determining the stability of  $\text{Na}_2\text{edta}^{2-}$ .

e: Determined the stability of metal complexes from glass electrode measurements in the activity scale (pH-buffer calibration).

Several experimental methods have been used in these studies: emf measurements with pH- and  $\text{Na}^+$ -electrodes, spectrophotometry, calorimetry, and comparison of protonation constants obtained in different ionic media. The latter approach is based on the assumption that tetraalkylammonium ions do not form ion pairs with  $\text{edta}^{4-}$ , and that any differences in the values for the protonation constants in different media with the same ionic strength are due exclusively to the formation of alkali-metal complexes. However, specific ion interactions (activity coefficient effects) also do induce differences in protonation constants, especially at  $I > 0.1$  M. This is probably the reason behind the postulated  $\text{Me}_4\text{N}^+$  and  $\text{Et}_4\text{N}^+$  complexes in [85DAN/RIG]. There is therefore a

larger uncertainty associated with all the references that used this methodology (labelled “ $\Delta pK_a$ ” in Table VIII-13).

As equilibrium constants are reported both for 20 and 25°C, it is necessary to consider first the available data on thermal effects. Enthalpy changes for the formation of  $\text{Na(edta)}^{3-}$  and  $\text{Kedta}^{3-}$  are reported in several studies [54CHA2], [65PRI/SEB], [76AND], [76VAS/BEL], [77VAS/LYM], [85DAN/RIG], [87BER/VAS]. The data from [65PRI/SEB], [85DAN/RIG], [87BER/VAS] are not included in this review, as discussed in Appendix A. Data from the remaining references are tabulated in Table VIII-14.

Table VIII-14: Literature data on the enthalpy changes for the complex formation between  $\text{edta}^{4-}$  and  $\text{Na}^+$ . The data correspond to reaction:  $\text{Na}^+ + \text{edta}^{4-} \rightleftharpoons \text{Na(edta)}^{3-}$ .

Method <sup>a</sup>	<i>I</i> (M)	Medium <sup>b</sup>	<i>t</i> (°C)	$\Delta_r H_m$ (kJ·mol <sup>-1</sup> )	References
cal	0.55	$\text{Me}_4\text{N}^+ / \text{Cl}^-$	25	– 5.9	[54CHA2] <sup>c</sup>
cal	1	$\text{Me}_4\text{NCl}$	20	– (10.8 ± 0.5)	[76AND]
	0.1	$\text{NaCl}$		– (5.4 ± 0.5)	
cal	0.3	$\text{Me}_4\text{NNO}_3$	25	– (9.71 ± 0.29)	[76VAS/BEL] <sup>d</sup>
	0.5			– (9.37 ± 0.33)	
	1			– (8.54 ± 0.13)	
	0.3	$\text{KNO}_3$	15	– (10.04 ± 0.21)	
	0.5			– (8.58 ± 0.13)	
	1			– (7.11 ± 0.21)	
	0.3		25	– (9.46 ± 0.17)	
	0.5			– (8.58 ± 0.21)	
	1			– (6.90 ± 0.25)	
	0.3		35	– (9.08 ± 0.29)	
	0.5			– (8.45 ± 0.17)	
	1			– (6.49 ± 0.29)	
cal	→ 0		25	– (7.6 ± 1.2)	[77VAS/LYM]

a: cal = calorimetry.

b:  $\text{Me}_4\text{N}^+$ : tetramethylammonium.

c: Titrated  $(\text{Me}_4\text{N})_4\text{edta}$  with 1 M  $\text{NaCl}$ . Enthalpy change is based on  $\log_{10} K(\text{Na(edta)}^{3-})$  from [47SCH/ACK] and protonation enthalpies from [53CAR/MAR].

d: Enthalpy change is based on  $\log_{10} K(\text{Na(edta)}^{3-})$  from [47SCH/ACK] extrapolated to different temperatures and ionic strengths.

The values have been treated with the SIT methodology (*cf.* Section V.3.6), and are plotted in Figure VIII-15.

The data in Figure VIII-15 show a large spread, which cannot be explained only by the differences in the ionic media, and there is no indication of an ionic strength dependence of these scattered data. Hence, this review selects a weighted average of the quantities,  $\Delta_r H_m + 8 D_L$  in Figure VIII-15 to derive the selected enthalpy value at zero ionic strength:

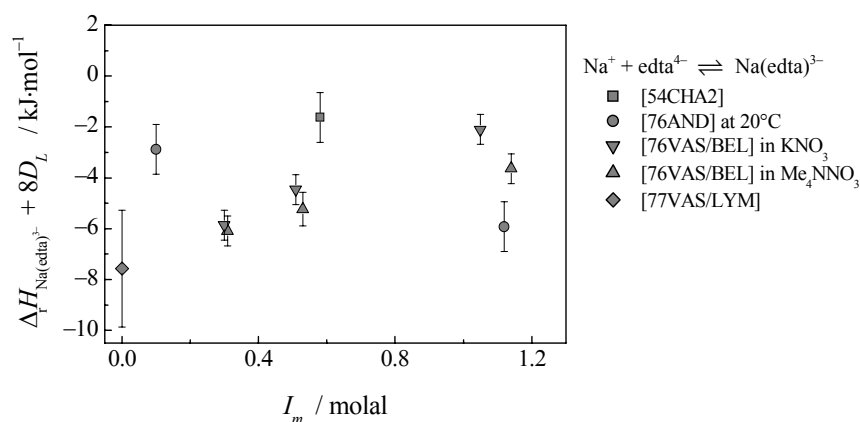


$$\Delta_r H_m^\circ (\text{VIII.12}) = -(4 \pm 3) \text{ kJ} \cdot \text{mol}^{-1}$$

This selection yields:

$$\Delta_r H_m^\circ (\text{Na}(\text{edta})^{3-}, 298.15 \text{ K}) = -(1949.1 \pm 4.8) \text{ kJ} \cdot \text{mol}^{-1}.$$

Figure VIII-15: Enthalpy data for the formation of  $\text{Na}(\text{edta})^{3-}$  plotted according to the SIT model. The term  $8 D_L$  is the Debye-Hückel term for ionic strength effects of enthalpy data for the reaction  $\text{Na}^+ + \text{edta}^{4-} \rightleftharpoons \text{Na}(\text{edta})^{3-}$  (*cf.* Section V.3.6)



The heat capacity change at 25°C may be calculated from results of the calorimetric measurements in [88HOV/HEP2]:

$$\Delta_r C_{p,m}^\circ (\text{VIII.12}) = (243 \pm 25) \text{ kJ} \cdot \text{mol}^{-1}$$

From these results it may be calculated that the equilibrium constant for the corresponding reaction will increase by  $(0.012 \pm 0.009) \log_{10}$ -units when the temperature is decreased to 20°C. This was taken into account when reviewing the literature on this equilibrium constant.

The equilibrium constants for the formation of  $\text{Na}(\text{edta})^{3-}$  and  $\text{Kedta}^{3-}$  (Table VIII-13) were converted to molal units and extrapolated to 25°C when necessary. The standard deviations for the individual data were increased to  $\pm 0.15 \log_{10}$ -units if the reported uncertainty was missing or if it was below this value. When treated according to the SIT model (*cf.* Appendix B), the data for each cation in the background electrolyte should follow a different linear dependence on  $I_m$ . In this case most of the data has been obtained in tetramethylammonium media (Table VIII-13). The plots in Figure VIII-16 show that the few values obtained in media not containing tetraalkylammonium ions appear close to the data obtained in  $\text{Me}_4\text{N}^+$  solutions.

The weighted linear least-squares regressions gave the following equilibrium constants:

$$\log_{10} K_{\text{Na}}^{\circ} = \log_{10} \beta_1^{\circ} (\text{Na}(\text{edta})^{3-}, 298.15 \text{ K}) = (2.8 \pm 0.2),$$

$$\log_{10} K_{\text{K}}^{\circ} = \log_{10} \beta_1^{\circ} (\text{Kedta}^{3-}, 298.15 \text{ K}) = (1.8 \pm 0.3),$$

which are selected by this review. The slope of the SIT regressions corresponds to:

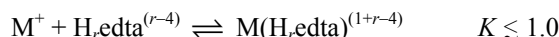
$$\begin{aligned} \varepsilon(\text{Me}_4\text{N}^+, \text{Na}(\text{edta})^{3-}) - \varepsilon(\text{Me}_4\text{N}^+, \text{edta}^{4-}) &= -(0.24 \pm 0.47) \text{ kg}\cdot\text{mol}^{-1}, \\ \varepsilon(\text{Me}_4\text{N}^+, \text{Kedta}^{3-}) - \varepsilon(\text{Me}_4\text{N}^+, \text{edta}^{4-}) &= -(0.50 \pm 0.64) \text{ kg}\cdot\text{mol}^{-1}. \end{aligned}$$

The uncertainties in these values are too large to allow any recommendations.

If the literature values obtained from comparison of protonation constants in different ionic media (labelled “ $\Delta pK_a$ ” in Table VIII-13) are not included in the regression, then the results are instead:  $\log_{10} \beta_1^{\circ} (\text{Na}(\text{edta})^{3-}) = (2.8 \pm 0.3)$  and  $\log_{10} \beta_1^{\circ} (\text{Kedta}^{3-}) = (2.0 \pm 0.5)$ , which agree with the selected values.

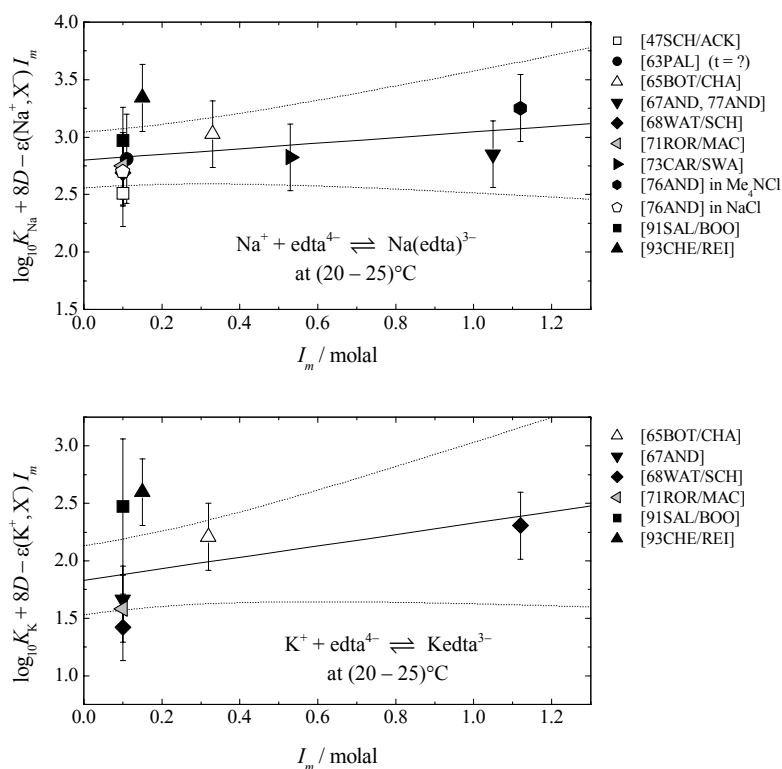
Additional complexes with stoichiometries different than  $\text{Medta}^{3-}$  are probably formed in solutions where the alkali cation concentration is perhaps 1000 times higher than that of edta. The formation of  $\text{Na}_2\text{edta}^{2-}$  was proposed in [65BOT/CHA] by comparing titration curves obtained at diverse ionic strengths. Under such conditions the activity coefficients were not controlled. No value can be recommended for this complex at present.

Equilibrium constants have been published for protonated  $\text{Na}^+$  and  $\text{K}^+$  complexes:  $\text{M}(\text{Hedta})^{2-}$  and  $\text{M}(\text{H}_2\text{edta})^-$ , cf. Table VIII-13. The reported stability of these complexes is, with one exception, quite weak:



The original studies were performed in such a way that it is not possible to ignore the possibility of variations in activity factors. In [93CHE/REI] the reported stability of these complexes is substantial for a wide pH range: the complexes account for  $\gtrsim 20\%$  of the ethylenediaminetetraacetate in solutions  $\approx 10 \text{ mM}$  in  $\text{Na}^+$  or  $\text{K}^+$  at  $\text{pH} \geq 3$ . These results are in disagreement with previous studies that indicate that it is only the first protonation constant that is substantially affected by the medium cation. The reason for this discrepancy has not been elucidated. Due to these issues, equilibrium constants for these protonated complexes cannot be recommended in this review.

Figure VIII-16: Equilibrium constants for the formation of  $\text{Na(edta)}^{3-}$  and  $\text{Kedta}^{3-}$  plotted according to the SIT methodology. Symbols with black background correspond to tetramethylammonium media, those with grey background correspond to other tetraalkylammonium media, and symbols with white background indicate other ionic media. Equilibrium constants have been converted to molal units, and extrapolated to 25°C when necessary.





## VIII.5 Magnesium and calcium edta compounds and complexes

### VIII.5.1 Magnesium and calcium edta compounds

Many edta compounds containing magnesium and calcium have been reported in the literature. The stoichiometry of the 16 compounds listed in Table VIII-15 has been confirmed by elemental analysis. Solubility measurements in H<sub>2</sub>O have been reported for several of these compounds.

Table VIII-15: Magnesium and calcium edta compounds. References reporting solubility data are marked with (sol.).

Compound	Solubility in H <sub>2</sub> O	Reference
Mg <sub>2</sub> edta·9H <sub>2</sub> O	0.098 mol·dm <sup>-3</sup>	[59VOR], [74MYA/LOG] (sol.), [76MYA/LOG] (sol.)
Mg(H <sub>2</sub> edta)·6H <sub>2</sub> O	0.0014 mol·dm <sup>-3</sup> 0.0010 mol·kg <sup>-1</sup>	[57BRI/PAR] (sol.), [59VOR], [74DUD/SHT] (sol.), [74DUD/SHT2] (sol.), [76DUD] (sol.)
Ca <sub>2</sub> edta·2H <sub>2</sub> O	0.04 mol·dm <sup>-3</sup>	[57BER/MUL] (sol.)
Ca <sub>2</sub> edta·7H <sub>2</sub> O	0.036 mol·dm <sup>-3</sup>	[74MYA/LOG] (sol.)
Ca(H <sub>2</sub> edta)·2H <sub>2</sub> O	0.014 mol·kg <sup>-1</sup>	[67BHA/KRI], [73RYK/SHT] (sol.)
CaMg(edta)·8H <sub>2</sub> O		[49PFE/SCH]
CaMg(edta)·9H <sub>2</sub> O	0.060 mol·dm <sup>-3</sup>	[74MYA/LOG] (sol.)
Na <sub>2</sub> Mg(edta)		[47SCH/ACK]
Na <sub>2</sub> Mg(edta)·4H <sub>2</sub> O	2.3 mol·kg <sup>-1</sup>	[58SAW/PAU], [73DUD/SHT] (sol.)
K <sub>2</sub> Mg(edta)·5H <sub>2</sub> O		[42PFE/OFF]
Na <sub>2</sub> Ca(edta)		[43PFE/SIM], [47SCH/ACK]
Na <sub>2</sub> Ca(edta)·2H <sub>2</sub> O	2.0 mol·kg <sup>-1</sup>	[70VOR/RKY] (sol.)
Na <sub>2</sub> Ca(edta)·3.5H <sub>2</sub> O		[58SAW/PAU]
Na <sub>2</sub> Ca(edta)·6H <sub>2</sub> O		[43PFE/SIM], [49PFE/SCH]
K <sub>2</sub> Ca(edta)·4H <sub>2</sub> O		[42PFE/OFF], [43PFE/SIM]
[Cu(NH <sub>3</sub> ) <sub>4</sub> ]Ca(edta)·8H <sub>2</sub> O		[49PFE/SCH]

Bersin *et al.* [57BER/MUL] state that the solubility of Ca<sub>2</sub>edta·2H<sub>2</sub>O is 1.6% ( $\approx 0.04$  mol·dm<sup>-3</sup>) at room temperature leading to solutions of pH 4 to 5. Myachina *et al.* [74MYA/LOG] give solubility values of 0.036 mol·dm<sup>-3</sup> for Ca<sub>2</sub>edta·7H<sub>2</sub>O, 0.060 mol·dm<sup>-3</sup> for CaMg(edta)·9H<sub>2</sub>O and 0.098 mol·dm<sup>-3</sup> for Mg<sub>2</sub>edta·9H<sub>2</sub>O. All solubilities were measured at (25.0  $\pm$  0.1)°C, but the pH of the resulting solutions is not given. Myachina *et al.* [76MYA/LOG] dissolved 3.3 weight-% Mg<sub>2</sub>edta in water, which corresponds to 0.098 mol·dm<sup>-3</sup> Mg<sub>2</sub>edta·9H<sub>2</sub>O.

Bricker and Parker, [57BRI/PAR], measured a solubility of 0.6 mg Mg(H<sub>2</sub>edta)·6H<sub>2</sub>O per ml of water ( $\approx 0.0014$  mol·dm<sup>-3</sup>) at room temperature. The pH of the resulting solution is not reported. Dudakov and Shternina [74DUD/SHT],

[74DUD/SHT2] and [76DUD] report  $0.0010 \text{ mol}\cdot\text{kg}^{-1} \text{ Mg}(\text{H}_2\text{edta})\cdot 6\text{H}_2\text{O}$  at  $25^\circ\text{C}$  leading to solutions of pH 4.2. Rykova and Shternina [73RYK/SHT] report a solubility of  $0.014 \text{ mol}\cdot\text{kg}^{-1} \text{ Ca}(\text{H}_2\text{edta})\cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$  and pH 3.8.

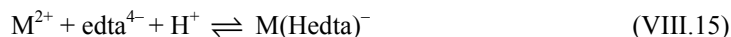
Vorob'ev *et al.* [70VOR/RVK] measured a solubility of  $2.0 \text{ mol}\cdot\text{kg}^{-1}$  at  $25^\circ\text{C}$  and pH 8.2 for  $\text{Na}_2\text{Ca}(\text{edta})\cdot 2\text{H}_2\text{O}$ . In close agreement with this value, Dudakov and Shternina [73DUD/SHT] give a solubility of  $2.3 \text{ mol}\cdot\text{kg}^{-1}$  for  $\text{Na}_2\text{Mg}(\text{edta})\cdot 4\text{H}_2\text{O}$  at  $25^\circ\text{C}$  and pH 8.0.

In qualitative terms, an overall consistent picture emerges from these solubility data. However, it is outside the scope of this review to develop a quantitative thermodynamic model for these rather soluble Mg and Ca edta compounds.

### VIII.5.2 Stability of magnesium and calcium edta complexes

Complex formation in Mg and Ca edta systems have been studied by several investigators. The equilibrium data found in the literature are summarised in Table VIII-16. From these experimental investigations we infer that the divalent alkaline earth cations form the following complexes with edta:  $\text{M}(\text{Hedta})^-$ ,  $\text{Medta}^{2-}$  and  $\text{M}_2\text{edta}(\text{aq})$ , where M stands for Mg or Ca.

The equilibrium constants in Mg and Ca edta systems usually refer to these reactions:



The coordination number, CN, of Mg and Ca can be larger than six, *i.e.* in  $[\text{Mg}(\text{H}_2\text{O})\text{edta}]^{2-}$ , CN = 7 has been found [77PAS/WHI] and in  $[\text{Ca}(\text{H}_2\text{O})_2\text{edta}]^{2-}$ , CN = 8 has been reported [79BAR/UCH]. In addition, some edta donor atoms are not bound in the 1:1 complex. Hence,  $\text{Medta}^{2-}$  can bind a second ligand X forming ternary complexes  $\text{MedtaX}$ , but their stability constants are small and difficult to be detected exactly. For  $\text{Ni}^{2+}$  (see Table VIII-22 in Section VIII.7.2) such ternary species have been studied, mainly using spectrophotometric measurements. This method does not work in the case of Mg and Ca as these cations give colorless solutions.

Table VIII-16: Experimental equilibrium data for the Mg and Ca edta systems. The uncertainties are given as reported in the references. If the ionic medium is shown in parenthesis, the contribution of the reacting species to the total ionic strength has been considered.

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Mg}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Mg}(\text{edta})^{2-}$				
ise-H	0.1 M KCl	20	8.69	[47SCH/ACK]
ise-H	<i>I</i> → 0	25	9.09	[54CAR/MAR]
ise-Hg	0.1 M NaClO <sub>4</sub>	25	8.9	[56SCH/REI]
gl	0.1 M KNO <sub>3</sub>	0.5	(8.49 ± 0.02)	[60BOH/MAR]
		13.4	(8.57 ± 0.02)	
		25.3	(8.64 ± 0.02)	
		42.4	(8.73 ± 0.01)	
ise-Hg	0.1 M (KNO <sub>3</sub> )	30	9.06	[64YEN/LIU]
dis	0.1 M KNO <sub>3</sub>	20	11	[65JOK/MAJ]
gl	0.18 M (Me <sub>4</sub> NCl)	10	8.86	[83ARE/MUS]
	0.20	20	8.82	
	0.17	25	8.93	
	0.34		8.70	
	0.53		8.67	
	0.76		8.64	
	0.17	37	8.96	
	0.35		8.86	
	0.18	45	9.15	
gl	0.15 M NaCl	37	(7.750 ± 0.006)	[84DUF/MAY]
pot	0.3 m NaCl	25	7.45	[2001CHO/BON]
	1 m NaCl	25	(6.7 ± 0.1)	
	2	25	(6.44 ± 0.03)	
	3	25	6.338	
	4	25	(6.41 ± 0.03)	
	5	25	6.52	
$\text{Mg}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Mg}(\text{Hedta})^-$				
ise-H	0.1 M KCl	20	3.85	[47SCH/ACK]
gl	0.1 M (Me <sub>4</sub> NCl)	25	(4.0 ± 0.1)	[83ARE/MUS]
$\text{Mg}^{2+} + \text{H}^+ + \text{edta}^{4-} \rightleftharpoons \text{Mg}(\text{Hedta})^-$				
pot	0.3 m NaCl	25	11.59	[2001CHO/BON]
	1 m NaCl	25	(11.0 ± 0.3)	
	2	25	(10.0 ± 0.5)	
	3	25	10.3	
	4	25	(10.7 ± 0.2)	
	5	25	10.0	

(Continued on next page)

Table VIII-16: (continued)

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Ca}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ca}(\text{edta})^{2-}$				
ise-H	0.1 M KCl	20	10.59	[47SCH/ACK]
ise-H	<i>I</i> → 0	25	10.98	[54CAR/MAR]
gl	0.1 M (KNO <sub>3</sub> )	20	(10.70 ± 0.05)	[54SCH/GUT]
pol	0.1 M (KCl)		(10.96 ± 0.40)	
ise-Hg	0.1 M NaClO <sub>4</sub>	25	10.7	[56SCH/REI]
ise-Hg	0.1 M (NaNO <sub>3</sub> )	21.7	(10.81 ± 0.10)	[57SCH/AND]
gl	0.1 M (KNO <sub>3</sub> )	20	(10.69 ± 0.05)	
gl	0.1 M KNO <sub>3</sub>	0.5	(10.94 ± 0.03)	[60BOH/MAR]
		13.4	(10.62 ± 0.03)	
		25.3	(10.42 ± 0.02)	
		42.4	(10.11 ± 0.01)	
cix	0.3 M NH <sub>4</sub> ?	?	10.45	[60MAT/SAF]
gl	0.1 M KCl	30	(10.59 ± 0.05)	[63GRI/HUG]
ise-Hg	0.1 M (KNO <sub>3</sub> )	30	10.92	[64YEN/LIU]
dis	0.1 M KNO <sub>3</sub>	20	11	[65JOK/MAJ]
gl	1.6 M KNO <sub>3</sub>	25	(9.4 ± 0.1)	[66KUL/REE]
gl	1.0 M (KNO <sub>3</sub> )	25	(9.68 ± 0.01)	[68KUE/SCH]
ise-Ca	0.01 M Et <sub>4</sub> Nac <sup>a</sup>	25	4.07 <sup>a</sup>	[68REC/LIN]
gl	0.1 M (NaClO <sub>4</sub> )	20	(10.85 ± 0.05)	[70AND/MAL]
ise-Cu	0.1 M (KNO <sub>3</sub> )	25	(10.78 ± 0.02)	[73HAN/RUZ]
gl	0.1 M (KNO <sub>3</sub> )	25	(10.73 ± 0.04)	[75AND/POD]
gl	0.5 M (Me <sub>4</sub> NCl)	25	10.28	[75CAR/SWA]
cix	?	rt	11.0	[77MOY/FRI]
ise-Ca	0.1 M (NaCl)	25	10.93	[79CRA/MOO]
gl	0.18 M (Me <sub>4</sub> NCl)	10	11.03	[83ARE/MUS]
	0.20	20	10.77	
	0.17	25	10.75	
	0.34	25	10.61	
	0.53	25	10.47	
	0.76	25	10.46	
	0.17	37	10.59	
	0.35	37	10.49	
	0.18	45	10.49	
gl	0.15 M NaCl	37	(9.360 ± 0.003)	[84DUF/MAY]
pot	0.1 M KCl	20 – 22	(10.73 ± 0.10)	[89POC]
gl	0.1 M (NaClO <sub>4</sub> )	25	10.75	[92GLA/HUL]
cal	?	25	10.7	[99GRI]

(Continued on next page)

Table VIII-16: (continued)

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Ca}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Ca}(\text{Hedta})^-$				
ise-H	0.1 M KCl	20	3.18	[47SCH/ACK]
gl	1.6 M KNO <sub>3</sub>	25	(2.8 ± 0.2)	[66KUL/REE]
gl	0.1 M (KNO <sub>3</sub> )	25	(2.94 ± 0.04)	[75AND/POD]
gl	0.5 M (Me <sub>4</sub> NCl)	25	3.47	[75CAR/SWA]
gl	0.1 M (Me <sub>4</sub> NCl)	25	(3.1 ± 0.1)	[83ARE/MUS]
cal	0.2 M KCl	25	4.23	[85MAR/EVA] [86MAR/EVA]
$\text{Ca}(\text{edta})^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{Ca}_2\text{edta}(\text{aq})$				
ise-H	0.1 M KCl	20	< 0.7	[48SCH/ACK]
cix	0.3 M NH <sub>4</sub> ?	?	2.07	[60MAT/SAF]
nmr	?	29	(1.1 ± 0.1)	[68LEY/WHI]

a: The stability constant refers to  $[\text{Ca}(\text{edta})^{2-}]/([\text{Ca}^{2+}] \cdot [\text{edta}]_{\text{total}})$  where  $[\text{edta}]_{\text{total}}$  is the total ligand species concentration at equilibrium. The ionic medium is tetraethylammonium acetate

The stabilities of the Mg and Ca edta 1:1 complexes  $K_1$  are of an order of magnitude that allows the direct investigation of their equilibria (VIII.13) in the pH range 3 to 10. A convenient method for determining the equilibrium constants of these magnesium and calcium edta complexes is the alkalimetric titration of mixtures containing the neutral protonated ligand H<sub>4</sub>edta and a salt of the investigated metal ion, preferably with a non-complexing anion, *e.g.*, NO<sub>3</sub><sup>-</sup> or ClO<sub>4</sub><sup>-</sup>. Both, the ligand and the metal salt should be present at negligible total concentrations with respect to the concentration of the background electrolyte in order to keep the activity coefficients of all species constant during the experiment. Starting with H<sub>4</sub>edta(cr), this is not difficult to realise, because in water only millimolar solutions of this acid are attained due to its low solubility (see Section VIII.2.2). From the graphic representation of the titration curves the composition of the formed species can be inferred (Figure VIII-17). Using solutions in the millimolar concentration range the metal ion complex formation occurs after the deprotonation of H<sub>4</sub>edta and H<sub>3</sub>edta<sup>-</sup> above pH 3 with simultaneous formation of M(Hedta)<sup>-</sup> and Medta<sup>2-</sup> from H<sub>2</sub>edta<sup>2-</sup> (Figure VIII-17 and Figure VIII-18). The main features shown in Figure VIII-17 are caused by the formation of Medta<sup>2-</sup>. After addition of 4 equivalents of strong base per mol edta a large pH change is observed at  $a = 4$ , which increases with increasing stability of the formed Medta<sup>2-</sup> complex (Figure VIII-17). At  $a > 4$  the titration curve represents the excess base in the solution. M(Hedta)<sup>-</sup> always remains a minor species detectable in the titration curve only at  $a \approx 2$  at pH < 5 (Figure VIII-18). In order to obtain larger concentrations of M(Hedta)<sup>-</sup> an excess of metal is needed, allowing its formation at low pH values as done in [47SCH/ACK] and [48SCH/ACK], but also under such conditions less than 10% of the metal is bound to protonated complexes.

Figure VIII-17: Simulated titration curves of  $1 \times 10^{-3}$  molal  $\text{H}_4\text{edta}(\text{aq})$  in 1 molal  $\text{NaCl}$  (upper curve) and  $1 \times 10^{-3}$  m  $\text{H}_4\text{edta}(\text{aq})$  and  $1 \times 10^{-3}$  molal  $\text{MgCl}_2$  in 1 molal  $\text{NaCl}$  (lower curve). The symbol  $a$  denotes the moles of base added per moles of ligand present in solution. Stability constants selected in this review have been used to calculate the titration curves.

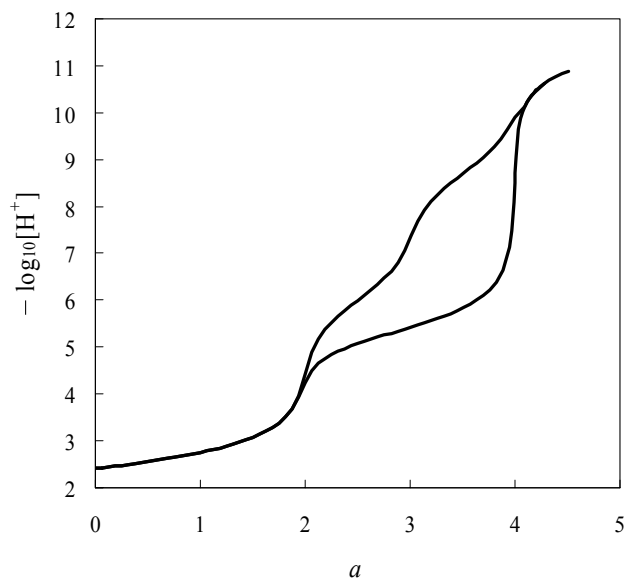
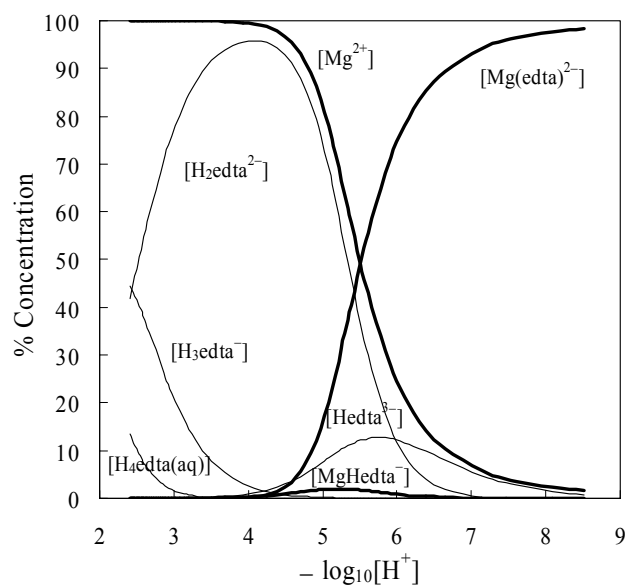


Figure VIII-18: Distribution of complex species in the simulated titration of the Mg edta system (Figure VIII-17) in 1 m  $\text{NaCl}$ .



The literature data collected in Table VIII-16 have been scrutinised in order to select reliable studies, summarised in Table VIII-17 on which the evaluation of recommended values is based.

In agreement with the rules given in [\[57BJE/SCH\]](#), [\[64SIL/MAR\]](#), [\[71SIL/MAR\]](#), the ionic medium in Table VIII-16 is given in parentheses, if the given numerical value corresponds *effectively* to the total *I*-value, corrected for the sometimes significant contribution of the reacting species, with concomitant reduction of the added amount of inert salt. Note that this rule was not respected by several authors and thus, a check of the original reference is always necessary.

The largest part of the entries in Table VIII-16 refers to measurements of the concentration of hydrogen or a metal ion with a glass electrode (gl) or an ion specific electrode (ise). From these measurements the concentrations of all species in solution forming during the alkalimetric titrations can be calculated. Note that by using an ion specific electrode also pH measurements are needed in order to obtain the concentration of the free ligand, although this is not explicitly specified in the column for the method in Table VIII-16.

Because of various shortcomings in the experimental procedures or the reporting of the results (*i.e.* electrodes used, pH calibration, ionic strength, composition of the solutions), the values of [\[54CAR/MAR\]](#), [\[60BOH/MAR\]](#), [\[60MAT/SAF\]](#), [\[65JOK/MAJ\]](#), [\[66KUL/REE\]](#), [\[68KUE/SCH\]](#), [\[75CAR/SWA\]](#), [\[77MOY/FRI\]](#), [\[85MAR/EVA\]](#), [\[86MAR/EVA\]](#), [\[89POC\]](#), [\[92GLA/HUL\]](#), [\[99GRI\]](#) have been discarded (*cf.* Appendix A). The stability constants for Mg and Ca edta reported in [\[78NOV/LUC\]](#) most probably have been taken from [\[47SCH/ACK\]](#) and [\[54SCH/GUT\]](#), although this is not explicitly stated in [\[78NOV/LUC\]](#). However, no experimental work with edta is described by [\[78NOV/LUC\]](#) and hence, their Mg and Ca edta values are not included in Table VIII-16.

In the case of [\[47SCH/ACK\]](#) only the equilibrium data for the protonated species have been considered in this review (*cf.* Appendix A).

The conditional stability constant of [\[68REC/LIN\]](#) is the only measurement in tetraethylammonium acetate. The values reported by Duffield *et al.* [\[84DUF/MAY\]](#) represent the only determination of  $\text{Ca(edta)}^{2-}$  and  $\text{Mg(edta)}^{2-}$  stability at 37°C and 0.15 M NaCl. The data of both papers have not been included in the final data evaluation.

The studies [\[56SCH/REI\]](#), [\[57SCH/AND\]](#), [\[70AND/MAL\]](#) in Na media need some comments. In the case of [\[56SCH/REI\]](#), [\[57SCH/AND\]](#) the cation exchange equilibrium  $\text{Hg(edta)}^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{Ca(edta)}^{2-} + \text{Hg}^{2+}$  has been studied by means of a Hg sensitive electrode. The Hg-edta complexation has been determined in the same medium ( $\text{NaClO}_4$  and  $\text{NaNO}_3$ , respectively), but the edta protonation constants used to calculate the stability constant of  $\text{Hg(edta)}^{2-}$  refer to potassium media. [\[56SCH/REI\]](#) used the protonation constants of [\[47SCH/ACK\]](#) determined in 0.1 M KCl, and

[57SCH/AND] determined the edta protonation constants in the same study in 0.1 M KNO<sub>3</sub>. [70AND/MAL] studied the edta complexation of Sb(III) and the cation exchange equilibrium  $\text{Sb}(\text{edta})^- + \text{Ca}^{2+} + 3 \text{OH}^- \rightleftharpoons \text{Ca}(\text{edta})^{2-} + \text{Sb}(\text{OH})_3(\text{aq})$  in 0.1 M NaClO<sub>4</sub>. Again, edta protonation constants determined in 0.1 M KNO<sub>3</sub> [67AND] have been used in the data evaluation. Hence, in all three cases the accepted values reported in Table VIII-17 have been corrected for  $\text{Kedta}^{3-}$  complexation, and *not* for  $\text{Na}(\text{edta})^{3-}$  complexation, as one would infer by just looking at the column “ionic medium”.

In the cases of [54SCH/GUT], [57SCH/AND], [63GRI/HUG], [70AND/MAL], [83ARE/MUS] the uncertainties of Table VIII-16 have been multiplied by a factor (1.96) to obtain error limits closer to a 95% total uncertainty levels, *i.e.*, including random and possible systematic errors. If this procedure resulted in uncertainty estimates < 0.1, a value of  $\pm 0.10$  is used [73HAN/RUZ], [75AND/POD]. For the review of [47SCH/ACK], [64YEN/LIU], [83ARE/MUS], [2001CHO/BON], the uncertainty estimates are detailed in Appendix A. In the case of [56SCH/REI] an uncertainty of  $\pm 0.2$  has been estimated considering the additional ambiguity arising from the use of the protonation constants of [47SCH/ACK].

Table VIII-17: Accepted formation constants for the Mg and Ca edta systems to derive the selected values. Uncertainties have been estimated in this review.

Ionic medium	<i>t</i> (°C)	$\log_{10}K$	<i>t</i> (°C)	$\log_{10}K$	$\log_{10}K^a$	Reference
$\text{Mg}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Mg}(\text{edta})^{2-}$						
0.1 M NaClO <sub>4</sub>	30	$(9.06 \pm 0.30)$	25	$(8.9 \pm 0.2)$	$(9.2 \pm 0.2)^{(c)}$	<a href="#">[56SCH/REI]</a>
0.1 M (KNO <sub>3</sub> )			25	$(9.0 \pm 0.3)^{(b)}$	$(9.3 \pm 0.3)^{(c)}$	<a href="#">[64YEN/LIU]</a>
0.17 M (Me <sub>4</sub> NCl)			25		$(8.93 \pm 0.15)$	<a href="#">[83ARE/MUS]</a>
0.34			25		$(8.70 \pm 0.15)$	
0.53			25		$(8.67 \pm 0.15)$	
0.76			25		$(8.64 \pm 0.15)$	
0.3 m NaCl			25	$(7.45 \pm 0.10)$	$(8.61 \pm 0.20)^d$	<a href="#">[2001CHO/BON]</a>
1			25	$(6.70 \pm 0.10)$	$(8.16 \pm 0.20)^d$	
2			25	$(6.44 \pm 0.10)$	$(8.24 \pm 0.20)^d$	
3	25	$(6.34 \pm 0.10)$	$(8.47 \pm 0.20)^d$			
4	25	$(6.41 \pm 0.10)$	$(8.86 \pm 0.20)^d$			
5	25	$(6.52 \pm 0.10)$	$(9.28 \pm 0.20)^d$			
$\text{Mg}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Mg}(\text{Hedta})^-$						
0.1 M KCl			20		$(3.9 \pm 0.2)$	<a href="#">[47SCH/ACK]</a>
0.1 M (Me <sub>4</sub> NCl)			25		$(4.0 \pm 0.2)$	<a href="#">[83ARE/MUS]</a>
0.3 m NaCl			25		$(4.1 \pm 0.5)$	<a href="#">[2001CHO/BON]</a>
1			25		$(4.3 \pm 0.5)$	
2			25		$(3.5 \pm 0.5)$	
3			25		$(4.0 \pm 0.5)$	
4			25		$(4.3 \pm 0.5)$	
5			25		$(3.5 \pm 0.5)$	

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Table VIII-17: (continued)

Ionic medium	<i>t</i> (°C)	$\log_{10}K$	<i>t</i> (°C)	$\log_{10}K$	$\log_{10}K^a$	Reference
$\text{Ca}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ca}(\text{edta})^{2-}$						
0.1 M (KNO <sub>3</sub> )	20	(10.70 ± 0.10)	25	(10.62 ± 0.10) <sup>b</sup>	(10.90 ± 0.10) <sup>c</sup>	[54SCH/GUT]
0.1 M NaClO <sub>4</sub>			25	(10.7 ± 0.2)	(10.99 ± 0.20) <sup>c</sup>	[56SCH/REI]
0.1 M (NaNO <sub>3</sub> )	21.7	(10.81 ± 0.20)	25	(10.76 ± 0.20) <sup>b</sup>	(11.05 ± 0.20) <sup>c</sup>	[57SCH/AND]
0.1 M (KNO <sub>3</sub> )	20	(10.69 ± 0.10)	25	(10.61 ± 0.10) <sup>b</sup>	(10.89 ± 0.10) <sup>c</sup>	
0.1 M KCl	30	(10.59 ± 0.10)	25	(10.67 ± 0.10) <sup>b</sup>	(10.96 ± 0.10) <sup>c</sup>	[63GRI/HUG]
0.1 M (KNO <sub>3</sub> )	30	(10.92 ± 0.30)	25	(11.0 ± 0.30) <sup>b</sup>	(11.3 ± 0.30) <sup>c</sup>	[64YEN/LIU]
0.1 M (NaClO <sub>4</sub> )	20	(10.85 ± 0.10)	25	(10.77 ± 0.10) <sup>b</sup>	(11.05 ± 0.10) <sup>c</sup>	[70AND/MAL]
0.1 M (KNO <sub>3</sub> )			25	(10.78 ± 0.10)	(11.07 ± 0.10) <sup>c</sup>	[73HAN/RUZ]
0.1 M (KNO <sub>3</sub> )			25	(10.73 ± 0.10)	(11.02 ± 0.10) <sup>c</sup>	[75AND/POD]
0.1 M (NaCl)					(10.96 ± 0.10) <sup>e</sup>	[79CRA/MOO]
					(10.99 ± 0.04)	mean
$\text{Ca}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ca}(\text{edta})^{2-}$						
0.17 M (Me <sub>4</sub> NCl)			25		(10.75 ± 0.15)	[83ARE/MUS]
0.34			25		(10.61 ± 0.15)	
0.53			25		(10.47 ± 0.15)	
0.76			25		(10.46 ± 0.15)	
$\text{Ca}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Ca}(\text{Hedta})^-$						
0.1 M KCl			20		(3.2 ± 0.2)	[47SCH/ACK]
0.1 M (KNO <sub>3</sub> )			25		(2.94 ± 0.10)	[75AND/POD]
0.1 M (Me <sub>4</sub> NCl)			25		(3.1 ± 0.2)	[83ARE/MUS]

a: Stability constant used in the final evaluation of selected values.

b: Temperature correction to 25°C using enthalpy values evaluated in this review (see Section VIII.5.3). At  $I = 0.1$  M the temperature correction for Ca from 20 to 25°C is  $\Delta\log_{10}K_1 = -(0.081 \pm 0.001)$ .

c: Corrected for  $\text{Kedta}^{3-}$  complexation using values evaluated in this review (see Table VIII-8-a and Table VIII-8-b). At  $I = 0.1$  M and 25°C the correction is  $\Delta\log_{10}K_1 = (0.285 \pm 0.015)$ .

d: Corrected for  $\text{Na}(\text{edta})^{3-}$  complexation using values evaluated in this review (see Table VIII-8-a). At 25°C the correction range is  $1.1 < \Delta\log_{10}K_1 < 2.8$  depending on  $I$ .

e: Evaluated in this review (*cf.* Appendix A).

For the reaction  $\text{Mg}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Mg}(\text{edta})^{2-}$  the data of [2001CHO/BON], [64YEN/LIU] and [56SCH/REI] have been considered as one data set in the regression analysis. Together with the data of [83ARE/MUS] this resulted in a multi-linear least-squares regression analysis (). The selected values are:

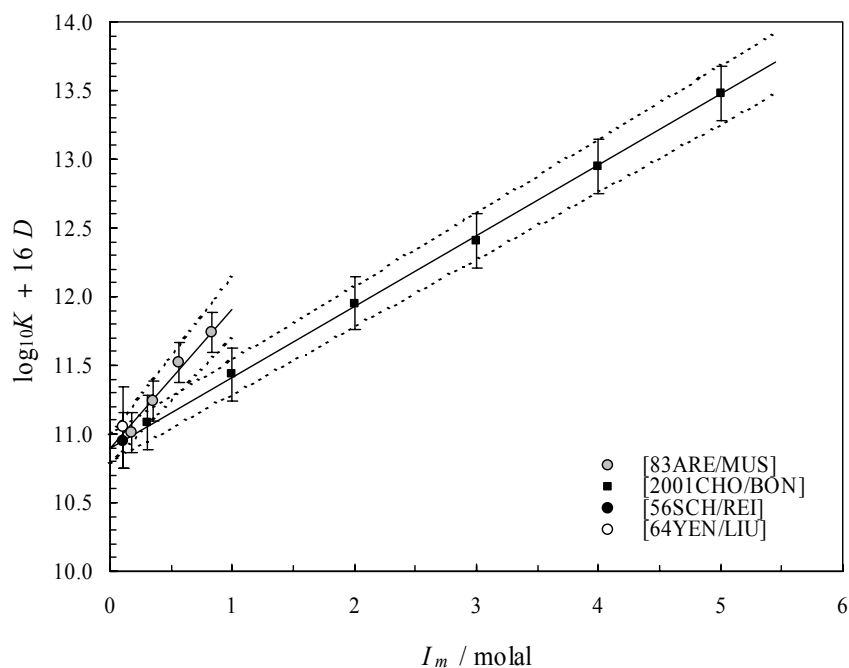
$$\log_{10} K_1^o = (10.90 \pm 0.10),$$

$$\Delta\epsilon(\text{Me}_4\text{NCl}) = -(1.02 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1},$$

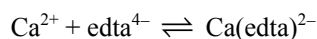
$$\Delta\epsilon(\text{NaCl}) = -(0.52 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}.$$

The SIT interaction coefficient  $\Delta\epsilon(\text{NaCl})$  allows an estimate of  $\epsilon(\text{Mg}(\text{edta})^{2-}, \text{Na}^+) = \Delta\epsilon(\text{NaCl}) + \epsilon(\text{edta}^{4-}, \text{Na}^+) + \epsilon(\text{Mg}^{2+}, \text{Cl}^-) = -(0.52 \pm 0.04) + (0.32 \pm 0.14) + (0.19 \pm 0.02) = -(0.01 \pm 0.15) \text{ kg}\cdot\text{mol}^{-1}$ .

Figure VIII-19: Multi-linear least-squares SIT regression plot for the reaction  $\text{Mg}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Mg}(\text{edta})^{2-}$ . The data of [56SCH/REI], [64YEN/LIU] and [2001CHO/BON] have been considered as one data set in the regression analysis. The results are  $\log_{10} K_1^o = (10.90 \pm 0.10)$ ,  $\Delta\epsilon(\text{Me}_4\text{NCl}) = -(1.02 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\Delta\epsilon(\text{NaCl}) = -(0.52 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$ .



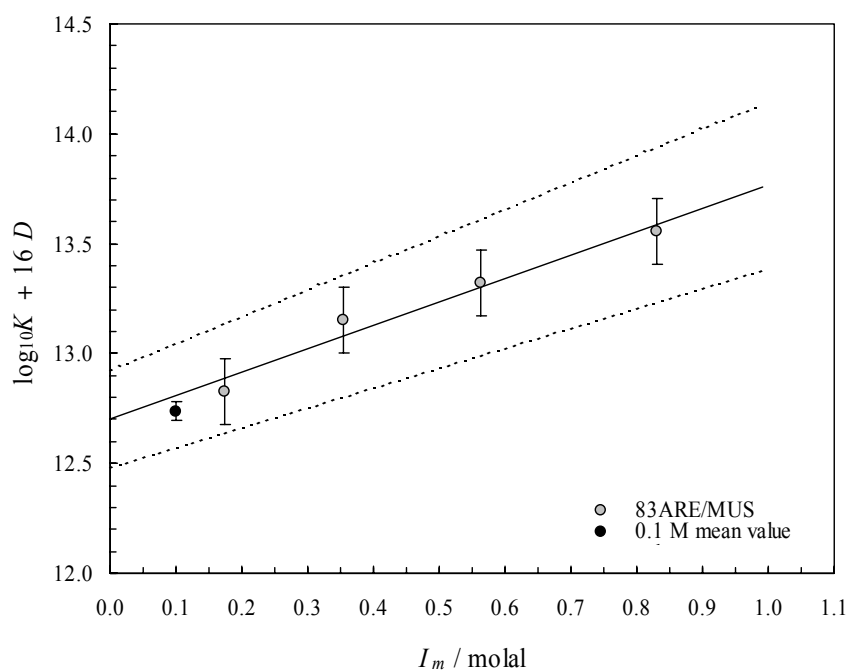
For the reaction:



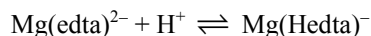
a weighted mean of  $\log_{10} K_1 = (10.99 \pm 0.04)$  was calculated from all accepted data at  $I = 0.1$  M (Table VIII-16). Extrapolation of this value to zero ionic strength assuming  $\Delta\epsilon = -(0.5 \pm 0.5) \text{ kg}\cdot\text{mol}^{-1}$  (in analogy with the results obtained for Mg in NaCl but with an increased uncertainty) results in  $\log_{10} K_1^\circ = (12.69 \pm 0.06)$ . The constant obtained from SIT extrapolation (Figure VIII-20) of data reported by [83ARE/MUS],  $\log_{10} K_1^\circ = (12.70 \pm 0.22)$ , fits well with the above results. The weighted mean of both values is selected in this review:

$$\log_{10} K_1^\circ = (12.69 \pm 0.06).$$

Figure VIII-20: Extrapolation to infinite dilution of  $\log_{10} K_1$  for the formation of  $\text{Ca}(\text{edta})^{2-}$  in tetramethylammonium chloride solution at 25°C [83ARE/MUS]. The results are  $\log_{10} K_1^\circ = (12.70 \pm 0.22)$  and  $\Delta\epsilon(\text{Me}_4\text{NCl}) = -(1.06 \pm 0.31) \text{ kg}\cdot\text{mol}^{-1}$ . The mean value derived from data at  $I = 0.1$  M (Table VIII-16) is shown for comparison.



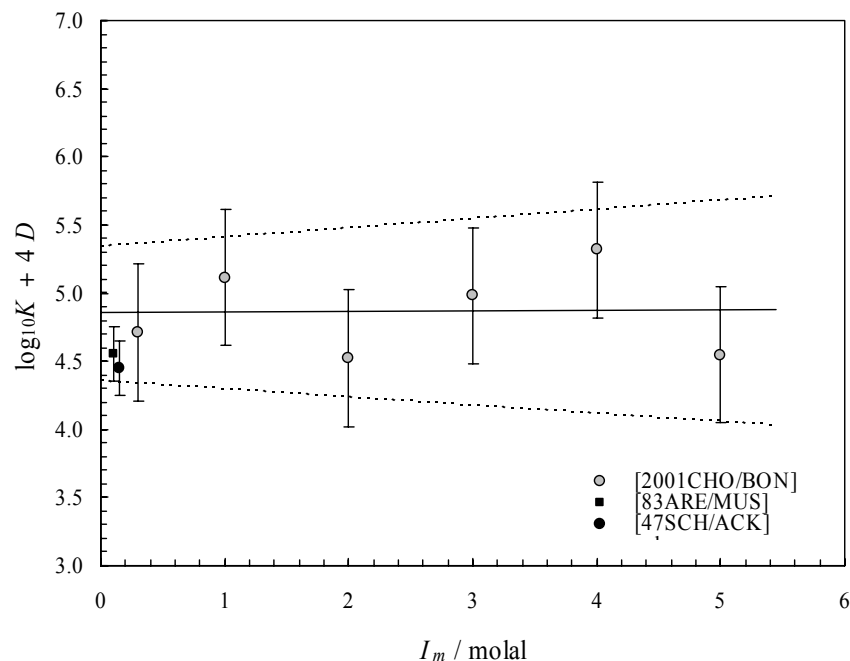
For the reaction,



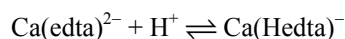
the data of [2001CHO/BON] have been extrapolated to zero ionic strength. The results are  $\log_{10} K^\circ = (4.85 \pm 0.49)$  and  $\Delta\varepsilon(\text{NaCl}) = (0.00 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}$ . The SIT interaction coefficient  $\Delta\varepsilon(\text{NaCl})$  allows an estimate of  $\varepsilon(\text{Mg}(\text{Hedta})^-, \text{Na}^+) = \Delta\varepsilon(\text{NaCl}) + \varepsilon(\text{H}^+, \text{Cl}^-) + \varepsilon(\text{Mg}(\text{edta})^{2-}, \text{Na}^+) = (0.00 \pm 0.13) + (0.12 \pm 0.01) - (0.01 \pm 0.15) = (0.11 \pm 0.20) \text{ kg}\cdot\text{mol}^{-1}$  (Figure VIII-21). Extrapolation of the values of [47SCH/ACK] and [83ARE/MUS] to zero ionic strength assuming  $\Delta\varepsilon = (0.0 \pm 0.5)$  results in  $\log_{10} K^\circ = (4.42 \pm 0.21)$  [47SCH/ACK] and  $(4.50 \pm 0.21)$  [83ARE/MUS]. The weighted mean of all three values is selected:

$$\log_{10} K^\circ = (4.5 \pm 0.2).$$

Figure VIII-21: Extrapolation to infinite dilution of  $\log_{10} K$  for the reaction  $\text{Mg}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Mg}(\text{Hedta})^-$  in NaCl at 25°C [2001CHO/BON]. The results are  $\log_{10} K^\circ(\text{VIII.14}) = (4.85 \pm 0.49)$  and  $\Delta\varepsilon(\text{NaCl}) = (0.00 \pm 0.13) \text{ kg}\cdot\text{mol}^{-1}$ . The values of [47SCH/ACK] and [83ARE/MUS] are shown for comparison.



For the reaction:



the data of [47SCH/ACK], [75AND/POD], [83ARE/MUS] were extrapolated to zero ionic strength assuming  $\Delta\epsilon = (0.0 \pm 0.5)$  (in analogy with  $\text{Mg(Hedta)}^-$ ) resulting in  $\log_{10} K^\circ = (3.75 \pm 0.21)$  [47SCH/ACK],  $\log_{10} K^\circ = (3.45 \pm 0.11)$  [75AND/POD] and  $(3.66 \pm 0.21)$  [83ARE/MUS]. The weighted mean of all three values is selected:

$$\log_{10} K^\circ = (3.54 \pm 0.09).$$

For the reaction  $\text{Ca(edta)}^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{Ca}_2\text{edta(aq)}$  no reliable data are available.

### VIII.5.3 Enthalpy of complex formation

Enthalpy data for the Mg and Ca edta systems extracted from the literature are collected in Table VIII-18. These data have been scrutinised in order to obtain the accepted data (Table VIII-19) subsequently used for evaluating the values selected in this review.

Table VIII-18: Experimental enthalpy data for the Mg and Ca edta systems. The uncertainties are given as reported in the references. If the ionic medium is shown in parenthesis, the contribution of the reacting species to the total ionic strength has been considered.

Method	Ionic medium	$t$ (°C)	$\Delta_r H_m$ (kJ·mol <sup>-1</sup> )	Reference
$\text{Mg}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Mg(edta)}^{2-}$				
$\partial \text{p}K_a / \partial T$	$I \rightarrow 0$	0 – 25	– 12	[54CAR/MAR]
cal	? M NaNO <sub>3</sub>	25	13.0 <sup>c</sup>	[54CHA2]
			13.0 <sup>d</sup>	
cal	0.1 M KNO <sub>3</sub> <sup>a</sup>	20	(13.1 ± 0.6)	[56CAR/STA]
(e)	? M Na <sup>+</sup> /?	25	23.0	[57JOR/ALL]
$\partial \text{p}K_a / \partial T$	0.1 M KNO <sub>3</sub>	0 – 42	(8 ± 4)	[60BOH/MAR]
cal	0.1 M (KNO <sub>3</sub> )	20	14.60	[63AND]
(f)	?	20 – 25	20.1	[65PRI/SEB]
cal	0.3 M (KNO <sub>3</sub> )	15	(10.92 ± 0.21)	[76VAS/BEL2]
	0.5		(10.59 ± 0.25)	
	1.0		(9.62 ± 0.17)	
	0.3	25	(12.64 ± 0.17)	
	0.5		(11.97 ± 0.17)	
	1.0		(10.50 ± 0.17)	
	0.3	35	(14.90 ± 0.17)	
	0.5		(13.68 ± 0.17)	
	1.0		(11.80 ± 0.17)	
$\partial \text{p}K_a / \partial T$	0.16 M (Me <sub>4</sub> NCl)	10 – 45	(12.1 ± 1.3)	[83ARE/MUS]

(Continued on next page)

Table VIII-18: (continued)

Method	Ionic medium	$t$ (°C)	$\Delta_r H_m$ (kJ·mol <sup>-1</sup> )	Reference
$\text{Ca}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ca}(\text{edta})^{2-}$				
$\partial \text{pK}_a / \partial T$	$I \rightarrow 0$	0 – 25	– 11	[54CAR/MAR]
cal	? M NaNO <sub>3</sub>	25	– 24.3 <sup>c</sup> – 27.2 <sup>d</sup>	[54CHA2]
cal	0.1 M KNO <sub>3</sub> <sup>(b)</sup>	20	– (27.0 ± 0.6)	[56CAR/STA]
(e)	? M Na <sup>+</sup> /?	25	– 23.8	[57JOR/ALL]
cal	0.54 – 0.86 M	25	– (19.7 ± 0.4)	[58YAT/KAR]
cal	0.6 – 1.58	25	– 24.02 – 23.10	[59YAT/KAR]
$\partial \text{pK}_a / \partial T$	0.1 M KNO <sub>3</sub>	0 – 42	– (33 ± 4)	[60BOH/MAR]
cal	0.1 M (KNO <sub>3</sub> )	20	– 27.41	[63AND]
(f)	?	20 – 25	– 23.4	[65PRI/SEB]
cal	0.3 M (KNO <sub>3</sub> )	15	– (30.46 ± 0.21)	[76VAS/BEL2]
	0.5		– (30.84 ± 0.33)	
	1.0		– (30.92 ± 0.17)	
	0.3	25	– (29.00 ± 0.29)	
	0.5		– (29.46 ± 0.25)	
	1.0		– (30.00 ± 0.17)	
	0.3	35	– (27.41 ± 0.17)	
	0.5		– (28.12 ± 0.17)	
	1.0		– (28.53 ± 0.21)	
$\partial \text{pK}_a / \partial T$	0.16 M (Me <sub>4</sub> NCl)	10 – 45	– (25.1 ± 1.3)	[83ARE/MUS]
cal	?	25	– 22.9	[99GRI]
$\text{Ca}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Ca}(\text{Hedta})^-$				
cal	0.2 M KCl	25	8.24	[85MAR/EVA][86MAR/EVA]

a: Actual ionic strength:  $0.173 < I < 0.177$  M.

b: Actual ionic strength:  $I = 0.165$  M.

c: 1 equivalent edta in solution.

d: 2 equivalents edta in solution.

e: Thermometric titration.

f: Continuous-flow enthalpimetry.

In order to obtain the heat involved in Reaction (VIII.13),



it is very important to avoid the use of solutions in which other processes, accompanied by heat evolution, occur, especially if the corresponding evolved heat is not exactly known. This can be the case if the anion of the metal salt or the cation of the ligand edta

are bound to the counterion in the separate solutions before their mixing. Then, in the subsequent complex formation, the heat consuming dissociation of the species present in the two initial solutions has to be taken into account. Such processes are investigated in solutions containing an inert salt, whose cation forms weak edta complexes. In general  $\text{KNO}_3$  was chosen as inert salt. In this case the best way to carry out calorimetric measurements is using  $\text{K}_4\text{edta}$  and metal nitrates as reagents, and to maintain the ionic strength near to that for which the equilibrium constant is known. This procedure was not always followed in calorimetric studies, causing widely varying results. For that reason the results of [54CHA2], [57JOR/ALL], [65WRI/HOL] are not accepted in this review.

Enthalpy data obtained from the temperature variation of stability constants [54CAR/MAR], [60BOH/MAR], [83ARE/MUS] have also not been accepted in this review (*cf.* Appendix A).

The rejection of the results of [58YAT/KAR], [59YAT/KAR], [65PRI/SEB], [85MAR/EVA], [86MAR/EVA], [99GRI] are discussed in Appendix A.

Note that only the Ca data of [56CAR/STA] have been included in the final data evaluation because the authors used  $\text{CaCl}_2$  in the case of  $\text{Ca}^{2+}$ , but  $\text{MgSO}_4$  in the case of  $\text{Mg}^{2+}$ . The latter unfortunate choice causes additional ambiguities in the Mg results and hence, the Mg data of [56CAR/STA] have been discarded.

The enthalpy data for Mg edta reported in [75VAS/BEL] have later been re-interpreted by [76VAS/BEL2]. Only the corrected data set according to [76VAS/BEL2] is included in Table VIII-18.

Weighted least squares SIT-regression plots (Figure VIII-22 and Figure VIII-23) using the data accepted in this review (Table VIII-19) result in the following selected values:

$$\Delta_r H_m^\circ((\text{VIII.13}), \text{M} = \text{Mg}, 298.15 \text{ K}) = (19.8 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta \varepsilon_L = -(0.5 \pm 0.7) \cdot 10^{-3} \text{ kg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta_r H_m^\circ((\text{VIII.13}), \text{M} = \text{Ca}, 298.15 \text{ K}) = -(22.2 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta \varepsilon_L = -(2.4 \pm 0.6) \cdot 10^{-3} \text{ kg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

For temperature corrections at  $I = 0.1 \text{ M}$   $\text{KNO}_3$ ,  $\text{NaNO}_3$  and  $\text{KCl}$  (*cf.* Table VIII-17) this review calculates  $\Delta_r H_m^\circ((\text{VIII.13}), 298.15 \text{ K}, I = 0.1 \text{ M}) = -(27.2 \pm 0.4)$  for  $\text{Ca}(\text{edta})^{2-}$ . This leads to  $\Delta \log_{10} K_1 = -(0.081 \pm 0.001)$  and  $\Delta \log_{10} K_1 = (0.079 \pm 0.001)$  using the van't Hoff equation for a temperature correction from 20 to 25°C and from 30 to 25°C, respectively. Likewise, for temperature corrections at  $I = 0.1 \text{ M}$   $\text{KNO}_3$  (*cf.* Table VIII-17) this review calculates  $\Delta_r H_m^\circ((\text{VIII.13}), 298.15 \text{ K}, I = 0.1 \text{ M}) = (14.7 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{Mg}(\text{edta})^{2-}$ . This leads to  $\Delta \log_{10} K_1 = -(0.042 \pm 0.001)$  using the van't Hoff equation for a temperature correction from 30 to 25°C.

Table VIII-19: Accepted enthalpy data for the Mg and Ca edta systems to derive the selected values. Uncertainties have been estimated in this review for [63AND] or have been multiplied by a factor (1.96) for [56CAR/STA], [76VAS/BEL2] to obtain error limits closer to a 95% total uncertainty level.

Method	Ionic medium	$t$ (°C)	$\Delta_r H_m$ (kJ·mol <sup>-1</sup> )	Reference
$\text{Mg}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Mg}(\text{edta})^{2-}$				
cal	0.1 M (KNO <sub>3</sub> )	20	(14.60 ± 0.40)	[63AND]
cal	0.3 M (KNO <sub>3</sub> )	25	(12.64 ± 0.33)	[76VAS/BEL2]
	0.5		(11.97 ± 0.33)	
	1.0		(10.50 ± 0.33)	
$\text{Ca}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ca}(\text{edta})^{2-}$				
cal	0.165 M	20	– (27.0 ± 1.2)	[56CAR/STA]
cal	0.1 M (KNO <sub>3</sub> )	20	– (27.41 ± 0.40)	[63AND]
cal	0.3 M (KNO <sub>3</sub> )	25	– (29.00 ± 0.57)	[76VAS/BEL2]
	0.5		– (29.46 ± 0.49)	
	1.0		– (30.00 ± 0.33)	

Figure VIII-22: Weighted least squares SIT-regression plot of enthalpy data from [63AND], [76VAS/BEL2] for the formation of  $\text{Mg}(\text{edta})^{2-}$ . The results are  $\Delta_r H_m^o = (19.8 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta \epsilon_L = -(0.5 \pm 0.7) \cdot 10^{-3} \text{ kg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

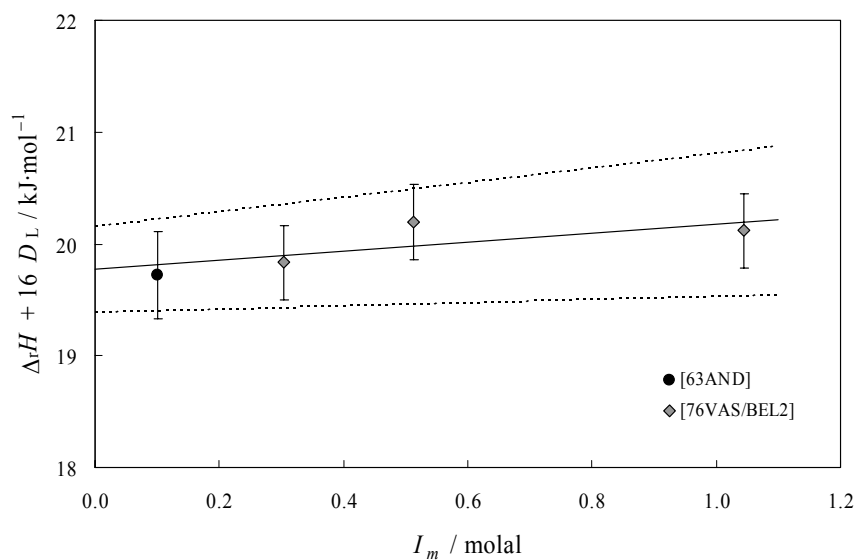
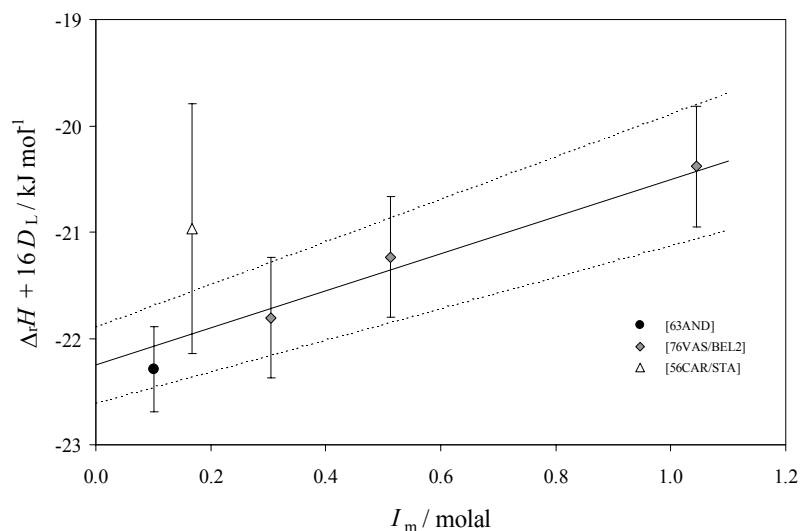




Figure VIII-23: Weighted least squares SIT-regression plot of enthalpy data from [56CAR/STA], [63AND], [76VAS/BEL2] for the formation of  $\text{Ca}(\text{edta})^{2-}$ . The results are  $\Delta_r H_m^\circ = -(22.2 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta \epsilon_L = -(2.4 \pm 0.6) \cdot 10^{-3} \text{ kg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .



## VIII.6 Selenium edta compounds and complexes

No information about thermodynamic properties of Se edta compounds and complexes could be found in the literature.

## VIII.7 Nickel edta compounds and complexes

### VIII.7.1 Nickel edta compounds

A considerable number of nickel containing edta compounds have been reported in the literature (Table VIII-20). Crystalline, but also amorphous edta complex compounds have received particular attention because of their magnetic properties.

Solubility measurements in  $\text{H}_2\text{O}$  have been reported for a few of these compounds. Astakhov and Verenikin [53AST/VER] report for  $\text{Ni}_2\text{edta} \cdot 5\text{H}_2\text{O}$  a solubility of 33 g per 100 g  $\text{H}_2\text{O}$  ( $\approx 0.7 \text{ mol} \cdot \text{kg}^{-1}$ ) and for  $\text{Na}_2\text{Ni}(\text{edta}) \cdot 2\text{H}_2\text{O}$  34.4 g per 100 g  $\text{H}_2\text{O}$  ( $\approx 0.8 \text{ mol} \cdot \text{kg}^{-1}$ ). Both values were measured at  $17^\circ\text{C}$ , the pH of the resulting solutions is not reported. Myachina *et al.* [74MYA/LOG] give solubility values of  $0.129 \text{ mol} \cdot \text{dm}^{-3}$  for  $\text{Ni}_2\text{edta} \cdot 6\text{H}_2\text{O}$ , and  $0.130 \text{ mol} \cdot \text{dm}^{-3}$  for  $\text{MgNi}(\text{edta}) \cdot 6\text{H}_2\text{O}$ , both measured at  $(25.0 \pm 0.1)^\circ\text{C}$ . The pH of the resulting solutions is not given. It is outside the scope

of this review to develop a quantitative thermodynamic model for these highly soluble Ni–edta compounds.

Table VIII-20: Nickel edta compounds. References reporting solubility data are marked with (sol.). References reporting X-ray single crystal structures are marked with (str.), (am.) refer to LAXS (Large-Angle X-ray Scattering) analyses of amorphous solids; (en) stands for ethylenediamine ( $C_2H_8N_2$ ) and (big) represents biguanide ( $C_2H_7N_5$ ).

Compound	Solubility in $H_2O$	Reference
$Ni_2edta \cdot 5H_2O$	$0.7 \text{ mol} \cdot \text{kg}^{-1}$	[53AST/VER] (sol.)
$Ni_2edta \cdot 6H_2O$	$0.129 \text{ mol} \cdot \text{dm}^{-3}$	[74MYA/LOG] (sol.), [81BEL/DRI], [82BEL/ESC], [84ESC/FUE], [84MOS/GAL] (am.), [85LEC/MOS] (am.), [86ESC/FUE], [86COR/DRI] (str.), [88CAM/MUN] (am.), [93ATZ/FIL], [95BOR/COR]
$Ni(H_2edta)$		[42BRI/HES], [42KLE/RAD], [62AXT/HAN]
$Ni(H_2edta) \cdot H_2O$		[59SMI/HOA] (str.), [67BHA/KRI]
$Ni(H_2edta) \cdot 2.5H_2O$		[93SPI/RIB]
$LiNi(Hedta)$		[86POL/FIL] (str.)
$Na_2Ni(edta) \cdot 2H_2O$	$0.8 \text{ mol} \cdot \text{kg}^{-1}$	[53AST/VER] (sol.)
$Na_2Ni(edta) \cdot 4H_2O$		[59SAW/PAU]
$Na_2Ni(edta) \cdot 6H_2O$		[49PFE/SCH]
$K_2Ni(edta)$		[90KOZ/VAS]
$MgNi(edta) \cdot 6H_2O$	$0.130 \text{ mol} \cdot \text{dm}^{-3}$	[74MYA/LOG] (sol.), [84ESC/FUE], [86ESC/FUE]
$CaNi(edta) \cdot 2H_2O$		[49PFE/SCH]
$CaNi(edta) \cdot 4H_2O$		[84NES/POR2] (str.)
$MnNi(edta) \cdot 6H_2O$		[86DRI/COR], [84ESC/FUE], [86ESC/FUE], [88TOG/KOJ], [89COR/DRI]
$Co_{0.7}Ni_{1.3}edta \cdot 2H_2O$		[86GOM/JAM]
$CoNi(edta) \cdot 2H_2O$		[86GOM/JAM]
$Co_{1.5}Ni_{0.5}edta \cdot 2H_2O$		[86GOM/JAM]
$CoNi(edta) \cdot 6H_2O$		[81BEL/DRI], [82BEL/ESC], [84ESC/FUE], [84MOS/GAL] (am.), [86ESC/FUE]
$Co_2[Ni(edta)]_2 \cdot 4H_2O$		[92SAP/COR]
$Ni[Cu(Hedta)]_2 \cdot H_2O$		[49PFE/SCH]
$Ni(en)[Ni(edta)] \cdot 4H_2O$		[81SYS/AGR] (str.)
$Ni(en)_3[Ni(edta)] \cdot 4H_2O$		[86SYS/AGR] (str.)
$Ni(big)_2[Ni(edta)] \cdot 7H_2O$		[56DUT/RAY]
$Cu(en)_2[Ni(edta)] \cdot 2H_2O$		[80AGR/SYS] (str.), [90KOZ/VAS]
$Cu(en)_2[Ni(edta)] \cdot 4H_2O$		[85LAN/KRA],
$Cu(big)_2[Ni(edta)] \cdot 7H_2O$		[56DUT/RAY]
$Zn[Ni(edta)] \cdot 6H_2O$		[84ESC/FUE], [86ESC/FUE], [87LEO/FRI] (str.)
$Pb[Ni(Hedta)(H_2O)]Cl$		[91LI/ZHA]
$N_2H_5[Ni(Hedta)] \cdot H_2O$		[94SAR/SIV]
$Li_2Ni(edta) \cdot 4Al(OH)_3 \cdot 4H_2O$		[95ISU/TAR]

### VIII.7.2 Stability of nickel edta complexes

Complex formation in Ni(II) edta systems has been studied by several investigators. The experimental equilibrium data are summarised in Table VIII-21 and Table VIII-22. In qualitative terms these data reveal that in aqueous solution edta may form the following complexes with  $\text{Ni}^{2+}$ :  $\text{Ni}(\text{H}_2\text{edta})(\text{aq})$ ,  $\text{Ni}(\text{Hedta})^-$ ,  $\text{Ni}(\text{edta})^{2-}$ ,  $\text{Ni}(\text{edta})\text{OH}^{3-}$  and other ternary complexes  $\text{Ni}(\text{edta})\text{X}$ , where X is a second ligand.

The equilibrium constants of these species usually refer to the following reactions:

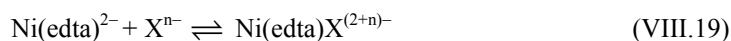
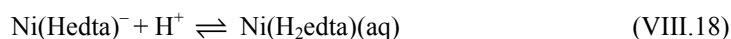


Table VIII-21: Experimental equilibrium data for the Ni edta system. The uncertainties are given as reported in the references. If the ionic medium is shown in parenthesis, the contribution of the reacting species to the total ionic strength has been considered.

Method	Ionic medium	$t$ ( $^{\circ}\text{C}$ )	$\log_{10}K$	Reference
$\text{Ni}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ni}(\text{edta})^{2-}$				
$^{63}\text{Ni}$	0.1 M ( $\text{H}_2\text{K}$ )Cl	20	19	<a href="#">[51COO/LON]</a>
gl	0.1 M (KCl)	20	$(18.56 \pm 0.07)$	<a href="#">[51SCH/FRE]</a>
sp	$\approx 0.1$ M ?	?	17.6	<a href="#">[52MAR/PLU]</a>
sp	0.1 M $\text{KNO}_3$	30	17.5	<a href="#">[53HUG/MAR]</a>
pol	0.1 M ( $\text{KNO}_3$ )	20	$(18.62 \pm 0.06)$	<a href="#">[54SCH/GUT]</a>
dis	0.1 M $\text{KClO}_4$	20	$(18.36 \pm 0.06)$	<a href="#">[63STA]</a>
dis	0.1 M $\text{KNO}_3$	20	19	<a href="#">[65JOK/MAJ]</a>
pol	0.2 M $\text{KNO}_3$	25	18.12	<a href="#">[65OGI]</a>
sol	0.10 - 0.12 M	$(22 \pm 1)$	18.79	<a href="#">[74TER/NIK2]</a>
gl	0.1 M ( $\text{KNO}_3$ )	25	$(18.52 \pm 0.05)$	<a href="#">[75AND/POD]</a>
sp	$\approx 0.1$ M (KCl)	$(20 \pm 2)$	17.83	<a href="#">[78KOR/VAL]</a>

(Continued on next page)

Table VIII-21: (continued)

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Ni}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Ni}(\text{Hedta})^-$				
pot	0.1 M KCl	25	3	<a href="#">[51COO/LON]</a>
pol	0.1 M (KNO <sub>3</sub> )	20	(3.2 ± 0.1)	<a href="#">[54SCH/GUT]</a>
pot	1.25 M NaClO <sub>4</sub>	25	2.9	<a href="#">[58COO/LON]</a>
sp	1 M NaClO <sub>4</sub>	25	2.73	<a href="#">[63BHA/KRI]</a>
			3.12	
gl	0.1 M (KNO <sub>3</sub> )	25	(3.23 ± 0.07)	<a href="#">[69BRU/NAN]</a>
sol	0.01 - 0.15 M	22	3.4	<a href="#">[74TER/NIK2]</a>
gl	1 M KNO <sub>3</sub>	25	2.96	<a href="#">[79JAN/PFE]</a>
gl	0.2 – 0.3 M	?	3.27	<a href="#">[88EVS/SMI]</a>
$\text{Ni}(\text{Hedta})^- + \text{H}^+ \rightleftharpoons \text{Ni}(\text{H}_2\text{edta})(\text{aq})$				
sol	0.02 - 0.06 M	22	1.4	<a href="#">[74TER/NIK2]</a>
gl	1 M KNO <sub>3</sub>	25	0.99	<a href="#">[79JAN/PFE]</a>
gl	0.2 – 0.3 M	?	1.46	<a href="#">[88EVS/SMI]</a>
$\text{Ni}(\text{edta})^{2-} + \text{edta}^{4-} \rightleftharpoons \text{Ni}(\text{edta})_2^{6-}$				
gl	0.2 – 0.3 M	?	1.95	<a href="#">[88EVS/SMI]</a>
$\text{Ni}(\text{Hedta})^- + \text{Hedta}^{3-} \rightleftharpoons \text{Ni}(\text{Hedta})_2^{4-}$				
gl	0.2 – 0.3 M	?	4.73	<a href="#">[88EVS/SMI]</a>
$\text{Ni}(\text{H}_2\text{edta})(\text{aq}) + \text{H}_2\text{edta}^{2-} \rightleftharpoons \text{Ni}(\text{H}_2\text{edta})_2^{2-}$				
gl	0.2 – 0.3 M	?	6.90	<a href="#">[88EVS/SMI]</a>

Table VIII-22: Experimental equilibrium data for the Ni edta X system where the ligand X forms a ternary complex Ni(edta)X. The uncertainties are given as reported in the references. If the ionic medium is shown in parenthesis, the contribution of the reacting species to the total ionic strength has been considered.

X	Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Δ <sub>r</sub> <i>H</i> <sub>m</sub> kJ·mol <sup>-1</sup>	Reference
$\text{Ni}(\text{edta})^{2-} + \text{X}^{n-} \rightleftharpoons \text{Ni}(\text{edta})\text{X}^{(2+n)-}$						
OH <sup>-</sup>	cal	0.1 M KNO <sub>3</sub>	20	(1.8 ± 0.3)	≈13	[56CAR/STA]
	sp	1 M NaClO <sub>4</sub>	25	0.41		[63BHA/KRI]
				0.55		
	cal	1.5 M (KNO <sub>3</sub> )	25	(0.93 ± 0.05)	-(9.92 ± 0.05)	[85VAS/KOZ]
ox <sup>2-</sup>	sp	1.5 M NH <sub>4</sub> NO <sub>3</sub>	25	1.43		[73BAR/FRI]
	sp	1.0 M (KNO <sub>3</sub> )	?	(0.48 ± 0.08)		[82VAS/VAS]
		1.5 M (KNO <sub>3</sub> )		(0.54 ± 0.08)		
		2.0 M (KNO <sub>3</sub> )		(0.63 ± 0.13)		
cit <sup>3-</sup>	pot	?	25	8.01 <sup>a</sup>		[91BAP]
			35	8.19 <sup>a</sup>		
			45	8.36 <sup>a</sup>		
CN <sup>-</sup>	kin	0.1 M NaClO <sub>4</sub>	25	3.76		[70COO/MAR]
NH <sub>3</sub>	sp	1 M NaClO <sub>4</sub>	25	2.26		[63BHA/KRI]
				2.56		
	sp	0.5 M KCl	25	(1.35 ± 0.05)		[67JAC/MAR]
		1 M NaClO <sub>4</sub>	25	(1.39 ± 0.01)		
	sp	1.5 M NH <sub>4</sub> NO <sub>3</sub>	25	1.30		[69FRI/DYA]
	sp	1.0 M (KNO <sub>3</sub> )	?	(1.24 ± 0.07)		[82VAS/VAS]
		1.5 M (KNO <sub>3</sub> )		(1.21 ± 0.05)		
		2.0 M (KNO <sub>3</sub> )		(1.95 ± 0.02)		
NH <sub>2</sub> OH	sp	1 M NaClO <sub>4</sub>	25	(1.52 ± 0.06)		[65BHA/RAD]
NH <sub>2</sub> NH <sub>2</sub>	sp	1 M NaClO <sub>4</sub>	25	(1.65 ± 0.06)		[65BHA/RAD]
P <sub>2</sub> O <sub>7</sub> <sup>4-</sup>	sp	1.25 M (KNO <sub>3</sub> )	?	(0.82 ± 0.08)		[82VAS/VAS]
		1.5 M (KNO <sub>3</sub> )		(0.88 ± 0.06)		
		2.0 M (KNO <sub>3</sub> )		(0.95 ± 0.12)		
pyridine	sp	1 M NaClO <sub>4</sub>	25	(1.68 ± 0.03)		[65BHA/RAD]
	sp	1.5 M NH <sub>4</sub> NO <sub>3</sub>	25	0.33		[69FRI/DYA]
ethylene-diamine	sp	1 M NaClO <sub>4</sub>	25	(2.25 ± 0.05)		[65BHA/RAD]
	cal	1.5 M (KNO <sub>3</sub> )	25	(2.36 ± 0.02)	-(46.0 ± 0.9)	[81VAS/VAS]
			35	(2.13 ± 0.04)	-(46.0 ± 1.3)	
	sp	≈ 0.05 M	25	(2.74 ± 0.35)		[83KOR/PRO]
propylenediamine	sp	1 M NaClO <sub>4</sub>	25	(2.3 ± 0.1)		[65BHA/RAD]

(Continued on next page)

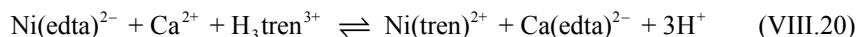
Table VIII-22: (continued)

X	Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Δ <sub>r</sub> <i>H</i> <sub>m</sub> kJ·mol <sup>-1</sup>	Reference
$\text{Ni}(\text{edta})^{2-} + \text{X}^{n-} \rightleftharpoons \text{Ni}(\text{edta})\text{X}^{(2+n)-}$						
glycine	sp	1.5 M NH <sub>4</sub> NO <sub>3</sub>	25	3.04		[73BAR/FRI]
	cal	1.5 M (KNO <sub>3</sub> )	25	(1.16 ± 0.05)	– (21.8 ± 0.8)	[82VAS/BEL]
	cal	1.5 M (KNO <sub>3</sub> )	25	(1.0 ± 0.2)	– (22.2 ± 1.3)	[86VAS/KOZ]
ida	cal	1.5 M (KNO <sub>3</sub> )	25	(0.8 ± 0.1)	– (4.0 ± 0.7)	[87VAS/KOZ]

a: The meaning of log<sub>10</sub>*K* in [91BAP] is not clear, see Appendix A.

We can infer from the data collected in Table VIII-21 and Table VIII-22 that the species Ni(H<sub>2</sub>edta)(aq) predominates in solutions at pH < 2, and the species Ni(Hedta)<sup>–</sup> predominates from pH 2 to 4. Ni(edta)<sup>2–</sup> has a very large pH range of predominance from pH 4 to 13. At pH 13 the species Ni(edta)OH<sup>3–</sup> is already present and its concentration increases with increasing pH.

The entries [51SCH/FRE], [69BRU/NAN], [75AND/POD], [79JAN/PFE] in Table VIII-21 referring to the method “gl” (glass electrode) need some comments. In all these studies solutions with equimolar amounts of Ni<sup>2+</sup> and H<sub>4</sub>edta have been used. In such solutions the 1:1 complexes Ni(H<sub>2</sub>edta)(aq), Ni(Hedta)<sup>–</sup>, Ni(edta)<sup>2–</sup> and Ni(edta)OH<sup>3–</sup> are present, depending on the pH of the solutions. Simple base titrations of such solutions yield log<sub>10</sub>*K*(VIII.18) and log<sub>10</sub>*K*(VIII.17) values of the two protonated species Ni(H<sub>2</sub>edta)(aq) and Ni(Hedta)<sup>–</sup>, respectively, if the initial pH is very low [79JAN/PFE]. If the initial pH is higher only log<sub>10</sub>*K*(VIII.17) of Ni(Hedta)<sup>–</sup> is obtained [69BRU/NAN]. At pH > 4, Ni(edta)<sup>2–</sup> is the only Ni-edta complex present in equimolar solutions and simple base titrations yield no further information. However, if a suitable protonated polyamine (H<sub>3</sub>tren<sup>3+</sup>, tren = tris(2-aminoethyl)amine) and Ca<sup>2+</sup> are present in such solutions at pH > 4, the Ni(edta)<sup>2–</sup> complex forms stepwise Ni(tren)<sup>2+</sup> and Ca(edta)<sup>2–</sup> by base titration. From the involved exchange equilibrium:

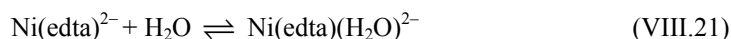


the equilibrium constant of Ni(edta)<sup>2–</sup> is obtained if the protonation constants of the two ligands edta and tren, and the formation constant of Ni(tren)<sup>2+</sup> and Ca(edta)<sup>2–</sup> are known [51SCH/FRE], [75AND/POD].

Ni(II) has a coordination number of six, and edta is an ideal candidate for a perfect octahedral coordination with Ni<sup>2+</sup> in aqueous solution. This poses the question why any ternary complexes Ni(edta)X have been observed at all (Table VIII-22). The study of ternary Ni(edta)X species in 1 M NaClO<sub>4</sub> and 25°C by Higginson and Samuel [70HIG/SAM] reveals that edta acts in Ni(edta)<sup>2–</sup> as hexadentate ligand only for 75% of the complex species, the remaining part being aquo-pentadentate. In the latter case, the exchange of the bound H<sub>2</sub>O molecule with X could explain the formation of ternary

species Ni(edta)X. Whereas for most ligands weak to moderately stable ternary Ni(edta)X complexes have been reported ( $\log_{10} K$  (VIII.19)  $< 3$ ), the most stable complexes seem to be formed with  $\text{CN}^-$  ( $\log_{10} K$  (VIII.19)  $> 3$ ). Also dinuclear ternary complexes could be formed [72BAR/FRI], [73BAR/DYA], [73BAR/FRI].

Although the two species  $\text{Ni(edta)}^{2-}$  and  $\text{Ni(edta)(H}_2\text{O)}^{2-}$  can be distinguished by different colours in aqueous solution [70HIG/SAM], no equilibrium data are available for the reaction:



Usually equilibrium constants refer to equilibria with unambiguous stoichiometry. This is not the case for equilibrium (VIII.16) where the product actually represents the sum of the concentrations of  $\text{Ni(edta)}^{2-}$  and  $\text{Ni(edta)(H}_2\text{O)}^{2-}$ . However, due to the lack of an equilibrium constant for reaction (VIII.21) this sum cannot be de-convoluted.

The experimental results collected in Table VIII-21 and Table VIII-22 have been scrutinised in order to select reliable studies, summarised in Table VIII-23, on which the evaluation of selected values is based.

Table VIII-23: Accepted formation constants for the Ni edta systems to derive the selected values. Uncertainties have been estimated in this review.

Ionic medium	$\log_{10} K$ at 20°C	$\log_{10} K$ at 25°C	$\log_{10} K^a$	Reference
$\text{Ni}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ni(edta)}^{2-}$ (VIII.16)				
0.1 M (KCl)	$(18.56 \pm 0.14)$	$(18.47 \pm 0.14)^b$	$(18.75 \pm 0.14)^c$	[51SCH/FRE]
0.1 M ( $\text{KNO}_3$ )	$(18.62 \pm 0.20)$	$(18.53 \pm 0.20)^b$	$(18.81 \pm 0.20)^c$	[54SCH/GUT]
0.1 M ( $\text{KNO}_3$ )		$(18.52 \pm 0.10)$	$(18.81 \pm 0.10)^c$	[75AND/POD]
			$(18.79 \pm 0.08)$	weighted mean
$\text{Ni(edta)}^{2-} + \text{H}^+ \rightleftharpoons \text{Ni(Hedta)}^-$ (VIII.17)				
0.1 M ( $\text{KNO}_3$ )	$(3.2 \pm 0.3)$		$(3.18 \pm 0.30)^d$	[54SCH/GUT]
0.1 M ( $\text{KNO}_3$ )			$(3.23 \pm 0.14)$	[69BRU/NAN]
			$(3.22 \pm 0.13)$	weighted mean

a: Stability constant used in the final evaluation of selected values.

b: Temperature correction to 25°C using enthalpy values evaluated in this review (see Section VIII.7.3). At  $I = 0.1$  M the temperature correction from 20 to 25°C is  $\Delta \log_{10} K = -(0.093 \pm 0.001)$ .

c: Corrected for  $\text{Kedta}^{3-}$  complexation using values evaluated in this review (see Table VIII-8-a). At  $I = 0.1$  M and 25°C the correction is  $\Delta \log_{10} K = (0.285 \pm 0.015)$ .

d: Temperature correction to 25°C using enthalpy value of [69BRU/NAN] (see Table VIII-24). At  $I = 0.1$  M the temperature correction from 20 to 25°C is  $\Delta \log_{10} K = -(0.022 \pm 0.004)$ .

The constants reported in [51COO/LON] would need corrections for the protonation of  $\text{H}_4\text{edta}$  to  $\text{H}_5\text{edta}^+$  and of  $\text{Ni(Hedta)}^-$  to  $\text{Ni(H}_2\text{edta)(aq)}$  because the pH range in this study extended to very low values. However, the equilibrium data needed for such corrections at  $I = 0.1$  M (H, K)Cl are not available and thus, the equilibrium con-

stants reported by [51COO/LON] are rejected in this review.

The study of [51SCH/FRE] is reliable. However, the  $\log_{10} K_1$  (VIII.16) value originally reported in [51SCH/FRE] has been corrected in [54SCH/GUT] considering revised equilibrium constants for  $\text{Cu}(\text{tren})^{2+}$  and  $\text{Ca}(\text{edta})^{2-}$ . This corrected value is included in Table VIII-21; its uncertainty has been increased by a factor of two in order to account for systematic errors (Table VIII-23).

In the study of [53HUG/MAR] the dissociation of the complex  $\text{Ni}(\text{edta})^{2-}$  was investigated by increasing  $[\text{H}^+]$  but without considering the formation of  $\text{Ni}(\text{Hedta})^-$  in the data analysis (*cf.* Appendix A). Thus, their reported value is not considered in this review.

For the polarographic measurements of [54SCH/GUT] an acetic acid/sodium acetate buffer was used and nickel had been added as  $\text{NiSO}_4$  salt. The effects of sodium acetate and sulphate on the nickel-edta equilibrium are difficult to assess. Nevertheless, the values reported by [54SCH/GUT] are considered in this review but with increased uncertainties (Table VIII-23).

The high edta concentration ( $1 \times 10^{-2}$  M) used by [63STA] causes a significant increase of the ionic strength from  $I = 0.1$  to  $0.2$  M during the experiments (*cf.* Appendix A). This increase is outside the limits where constant ionic activity coefficients can be assumed. Thus, the  $\log_{10} K$  (VIII.16) value reported in [63STA] is not considered in this review.

The  $\log_{10} K$  (VIII.17) value of [69BRU/NAN] is reliable; its uncertainty has been increased by a factor of two in order to account for systematic errors (Table VIII-23).

The  $\log_{10} K$  (VIII.16) value of [75AND/POD] is reliable, its uncertainty has been increased by a factor of two in order to account for systematic errors (Table VIII-23).

The values reported in [79JAN/PFE] are rejected in this review because the authors used the activity scale for their pH measurements.

The results reported in [56MAR], [63BHA/KRI], [65JOK/MAJ], [65OGI], [74TER/NIK2], [78KOR/VAL] and [88EVS/SMI] are not considered in this review (*cf.* Appendix A).

Ternary complexes (Table VIII-22) are evaluated in this review if the second ligand X refers to hydroxide, oxalate or citrate. All other data in Table VIII-22 (below the dotted line) are given for illustrative purposes only.

The species  $\text{Ni}(\text{edta})\text{OH}^{3-}$  is present in solutions of  $\text{pH} > 12$  and only a few papers report quantitative data concerning its stability [56CAR/STA], [63BHA/KRI], [85VAS/KOZ]. However, as discussed in Appendix A, all these studies suffer from various shortcomings, and no value for  $\log_{10} K^\circ$  (VIII.19) with  $\text{X} = \text{OH}$  can be recommended.



The stability of the species  $\text{Ni}(\text{edta})(\text{ox})^{4-}$  has been investigated by two groups [73BAR/FRI], [82VAS/VAS]. The results obtained at similar ionic strength differ by one order of magnitude (Table VIII-22). The results of [82VAS/VAS] have been rejected by this review (*cf.* Appendix A), and based on a single determination at 1.5 M  $\text{NH}_4\text{NO}_3$  [73BAR/FRI], which is not unreasonable but needs confirmation, no value for  $\log_{10} K^\circ$  (VIII.19) with  $X = \text{ox}$  can be recommended.

There is only one study of ternary Ni-edta-citrate complexes [91BAP]. Because of various shortcomings the paper of [91BAP] is rejected by this review (*cf.* Appendix A).

Summarising, for the evaluation of  $\log_{10} K$  (VIII.16) remain only the values from [51SCH/FRE], [54SCH/GUT] at 20°C and [75AND/POD] at 25°C (Table VIII-23). The values at 20°C are corrected to 25°C by  $\Delta \log_{10} K = -(0.093 \pm 0.001)$ , obtained with the van't Hoff equation using  $\Delta_r H_m = -(31.0 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$  evaluated in this review (see Section VIII.7.3). In addition, all  $\log_{10} K$  values at 25°C are corrected by  $\Delta \log_{10} K = (0.285 \pm 0.015)$  in order to account for  $\text{K}^+$  complexation with  $\text{Kedta}^{3-}$  equilibrium constants recommended for 0.1 M KCl and 0.1 M  $\text{KNO}_3$  in this review (Table VIII-8-a, Section VIII.3.7). A weighted mean of  $\log_{10} K$  (VIII.16) =  $(18.79 \pm 0.08)$  is obtained at  $I = 0.1$  and 25°C. Because only data for  $I = 0.1$  M are considered the SIT extrapolation can be done neglecting  $\Delta \epsilon$ , *i.e.*,  $\log_{10} K^\circ$  (VIII.16) =  $18.79 - \Delta z^2 \times D = 18.79 + 16 \times 0.1095 = (20.54 \pm 0.08)$ . Assuming  $|\Delta \epsilon| \leq 1$ , extrapolating from  $I = 0.1$  M to zero ionic strength results in an additional uncertainty of  $\pm 0.1$  at maximum.

Hence, the selected value is:

$$\log_{10} K^\circ \text{ (VIII.16)} = (20.54 \pm 0.13).$$

For the evaluation of  $\log_{10} K$  (VIII.17) remain only the values from [54SCH/GUT] at 20°C and [69BRU/NAN] at 25°C (Table VIII-23). The value at 20°C is corrected to 25°C by  $\Delta \log_{10} K = -(0.022 \pm 0.004)$ , obtained with the van't Hoff equation using  $\Delta_r H_m = -(7.5 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$ , the enthalpy of protonation of  $\text{Ni}(\text{edta})^{2-}$  measured at 0.1 M  $\text{KNO}_3$  [69BRU/NAN]. A weighted mean of  $\log_{10} K$  (VIII.17) =  $(3.22 \pm 0.13)$  is obtained at  $I = 0.1$  and 25°C. Because only data for  $I = 0.1$  M are considered the SIT-extrapolation can be done neglecting  $\Delta \epsilon$ , *i.e.*,  $\log_{10} K^\circ$  (VIII.17) =  $3.22 - \Delta z^2 \times D = 3.22 + 4 \times 0.1095 = (3.66 \pm 0.13)$ . Assuming  $|\Delta \epsilon| \leq 1$ , extrapolating from  $I = 0.1$  M to zero ionic strength results in an additional uncertainty of  $\pm 0.1$  at maximum.

Hence, the selected value is:

$$\log_{10} K^\circ \text{ (VIII.17)} = (3.66 \pm 0.16).$$

No equilibrium constants can be selected for  $\text{Ni}(\text{H}_2\text{edta})(\text{aq})$ ,  $\text{Ni}(\text{edta})\text{OH}^{3-}$ ,  $\text{Ni}(\text{edta})(\text{ox})^{4-}$ , and  $\text{Ni}(\text{edta})(\text{cit})^{5-}$ .

### VIII.7.3 Enthalpy of nickel edta complex formation

Enthalpy data for the Ni-edta systems extracted from the literature are collected in Table VIII-24. These data have been scrutinised in order to obtain the accepted data subsequently used for evaluating the values selected in this review.

Table VIII-24: Experimental enthalpy data for the Ni edta system. The uncertainties are given as reported in the references. If the ionic medium is shown in parenthesis, the contribution of the reacting species to the total ionic strength has been considered.

Method	Ionic medium	<i>t</i> (°C)	$\Delta_r H_m$ kJ·mol <sup>-1</sup>	Reference
$\text{Ni}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ni}(\text{edta})^{2-}$				
cal	? M NaNO <sub>3</sub>	25	– 31.8 <sup>b</sup> – 32.6 <sup>c</sup>	[54CHA2]
cal	0.1 M KNO <sub>3</sub> <sup>a</sup>	20	– (34.94 ± 0.63)	[56CAR/STA]
(d)	? M Na <sup>+</sup> /?	25	– 31.0	[57JOR/ALL]
cal	0.22 – 1.58 M	25	– 28.79 – 31.30	[59YAT/KAR]
cal	0.1 M (KNO <sub>3</sub> )	20	– 31.59	[63AND]
(e)	?	20 - 25	– 30.1	[65PRI/SEB]
cal	0.1 M KNO <sub>3</sub>	25	– 35.6	[65WRI/HOL]
cal	0.3 M (KNO <sub>3</sub> )	15	– (33.76 ± 0.17)	[76VAS/BEL3]
	0.5		– (34.43 ± 0.21)	
	1.0		– (35.56 ± 0.21)	
	0.3	25	– (32.47 ± 0.17)	
	0.5		– (33.10 ± 0.13)	
	1.0		– (34.64 ± 0.21)	
	0.3	35	– (31.63 ± 0.17)	
	0.5		– (32.01 ± 0.08)	
	1.0		– (33.35 ± 0.23)	
$\text{Ni}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Ni}(\text{Hedta})^-$				
cal	0.1 M (KNO <sub>3</sub> )	25	– (7.5 ± 1.3)	[69BRU/NAN]
$\text{Ni}(\text{edta})^{2-} + \text{OH}^- \rightleftharpoons \text{Ni}(\text{edta})\text{OH}^{3-}$				
cal	0.1 M KNO <sub>3</sub>	20	≈ 13	[56CAR/STA]
cal	1.5 M (KNO <sub>3</sub> )	25	– (9.92 ± 0.05)	[85VAS/KOZ]

a: Actual ionic strength: 0.173 < *I* < 0.177 M.

b: 1 equivalent edta in solution.

c: 2 equivalents edta in solution.

d: Thermometric titration.

e: Continuous-flow enthalpimetry.

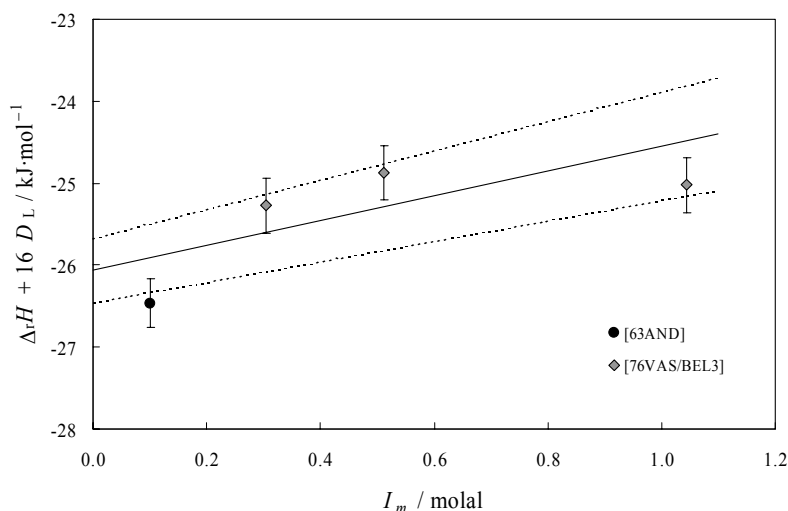
In order to obtain the heat involved in (VIII.16), in general  $\text{KNO}_3$  was chosen as inert salt. In this case the best way to carry out calorimetric measurements is using  $\text{K}_4\text{edta}$  and metal nitrates as reagents, and to maintain the ionic strength near to that for which the equilibrium constant is known. This procedure was not always followed in calorimetric studies, causing widely varying results. For example, [56CAR/STA] used  $\text{NiSO}_4$  in  $\text{KNO}_3$  solutions. For that reason the results of [54CHA2], [56CAR/STA], [57JOR/ALL] are not accepted in this review (*cf.* Appendix A).

The results of [59YAT/KAR], [65PRI/SEB], [65WRI/HOL], [85VAS/KOZ] are also rejected (see the discussions in Appendix A).

For the final evaluation of enthalpy data for reaction (VIII.16) remain the values of [63AND] (with an uncertainty of  $\pm 0.3$  estimated in this review) and the data of [76VAS/BEL3] at  $25^\circ\text{C}$ . In the latter case the uncertainties given in Table VIII-24 have been multiplied by a factor (1.96) to obtain error limits closer to a 95% total uncertainty levels, *i.e.*, including random and possible systematic errors.

A weighted linear regression using the enthalpy data of [63AND] and the  $25^\circ\text{C}$  data of [76VAS/BEL3] gives  $\Delta_r H_m^\circ((\text{VIII.16}), 298.15\text{K}) = -(26.1 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$  with  $\Delta\epsilon_L = -(2.1 \pm 0.7) \times 10^{-3} \text{ kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (Figure VIII-24). However, in evident contrast with the results obtained for  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  where the two data sets of [63AND] and [76VAS/BEL2] reveal a good overall linear correlation (Figure VIII-22 and Figure VIII-23), a strong deviation from the expected linearity is seen in the case of  $\text{Ni}^{2+}$  (Figure VIII-24).

Figure VIII-24: Weighted least squares SIT-regression plot of enthalpy data from [63AND], [76VAS/BEL3] for the formation of  $\text{Ni}(\text{edta})^{2-}$ . The results are  $\Delta_r H_m^\circ(\text{VIII.16}) = -(26.1 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta\epsilon_L = -(2.1 \pm 0.7) \times 10^{-3} \text{ kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .



A possible explanation is that for the values at low ionic strength in Figure VIII-24 the complex  $\text{Ni}(\text{edta})(\text{H}_2\text{O})^{2-}$  predominates, whereas at the larger  $I$  values  $\text{Ni}(\text{edta})^{2-}$  becomes the predominating complex (see discussion in Section VIII.7.2 of the results of Higginson and Samuel [70HIG/SAM] in terms of reaction (VIII.21)). The values of the enthalpy of complex formation  $\Delta_r H_m^\circ$  of the two complexes are expected to be different. The same statement in principle is true for  $K$  (VIII.16). Enthalpy data perhaps reveal much better a change in the structure of the formed complex than the formation constants. This can be explained with the large compensation of the terms for  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$  in reaction (VIII.21). The values of the conventional stability constants of similar complexes involving other ligands are very near [71AND/WEN], but for edta such data have not been reported.

Excluding the value for  $I = 1 \text{ M}$  ( $\text{KNO}_3$ ) in the regression analysis, an approximate value for  $\text{Ni}(\text{edta})(\text{H}_2\text{O})^{2-}$  can be derived, *i.e.*  $\Delta_r H_m^\circ(\text{Ni}(\text{edta})(\text{H}_2\text{O})^{2-}, 298.15 \text{ K}) = -(26.7 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta \varepsilon_L = -(5.1 \pm 1.3) \times 10^{-3} \text{ kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . However, this question can only be solved by more extended measurements, and this review selects the values derived from all experimental data in Figure VIII-24, *i.e.*,

$$\Delta_r H_m^\circ(\text{VIII.16}) = -(26.1 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta \varepsilon_L = -(2.1 \pm 0.7) \times 10^{-3} \text{ kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_r H_m^\circ(\text{Ni}(\text{edta})^{2-}, 298.15 \text{ K}) = -(1785.9 \pm 3.9) \text{ kJ}\cdot\text{mol}^{-1}.$$

For temperature corrections at  $I = 0.1 \text{ M}$   $\text{KNO}_3$  and  $\text{KCl}$  (*cf.* Table VIII-23) this review calculates  $\Delta_r H_m^\circ((\text{VIII.16}), 298.15 \text{ K}, I = 0.1 \text{ M}) = -(31.0 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ . This leads to  $\Delta \log_{10} K = -(0.093 \pm 0.001)$  using the van't Hoff equation for a temperature correction from 20 to 25°C.

Only one study concerns the heat involved in reaction (VIII.17) [69BRU/NAN]. The result seems to be reasonable and it has been used for temperature corrections in this review (Table VIII-23). However, based on a single determination only, which is not unreasonable but needs confirmation, no value for  $\Delta_r H_m^\circ((\text{VIII.17}), 298.15 \text{ K})$  can be recommended.

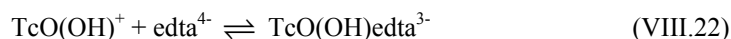
## VIII.8 Technetium edta compounds and complexes

### VIII.8.1 Technetium edta compounds

The structure of a Tc(IV) complex salt of edta,  $\text{H}_4(\text{TcO})_2(\text{edta})_2 \cdot 5\text{H}_2\text{O}$ , has been determined [81BUE/AND]. However, no chemical thermodynamic data are available for this compound.

### VIII.8.2 Technetium edta complexes

Only three studies report data on the complex formation between Tc and edta. Gorski and Koch [69GOR/KOC], [70GOR/KOC] dissolved freshly prepared hydrous oxide of Tc(IV) in HClO<sub>4</sub> and obtained an aqueous solution containing an unknown trace concentration of technetium(IV). In the pH range 1 to 2.5 they investigated the ionic mobility by electrophoresis, and they studied the formation of complexes in the presence of complexing ligands by cation exchange and by electrophoresis. The results were interpreted by assuming the presence of TcO<sup>2+</sup> at pH 1, reacting to TcO(OH)<sup>+</sup> and TcO(OH)<sub>2</sub>(aq) at higher pH, and the concomitant formation of TcO(OH)nta<sup>2-</sup>, TcO(OH)(nta)<sub>2</sub><sup>5-</sup> and TcO(OH)edta<sup>3-</sup>. The unexpectedly high value of log<sub>10</sub> K<sub>1</sub> = 19.1 for the reaction:



differs considerably from the value evaluated in this review for NpO<sub>2</sub><sup>+</sup> (log<sub>10</sub> K<sub>1</sub> = (9.23 ± 0.13) cf. Section VIII.11.2.3).

Recent measurements show that Tc(IV) is only stable in reducing solutions. Consequently, experimental studies of Tc(IV) demand an exact control of the redox state and the composition of the species present in solution. However, Gorski and Koch [69GOR/KOC], [70GOR/KOC] do not mention any measures to control the redox state of Tc in their experiments.

The crystal structure determination of H<sub>4</sub>(TcO)<sub>2</sub>(edta)<sub>2</sub> [81BUE/AND] shows that the two Tc metal ions form two equal μ-O bridges with the two oxygen atoms, leaving four Tc coordination sites for the organic ligand (see Figure VIII-4-a in Section VIII.1). In accordance with these observations, the data obtained by Gorski and Koch [69GOR/KOC], [70GOR/KOC] for the diprotonic acid TcO<sup>2+</sup> strongly indicate the presence of polymeric Tc species.

Finally, reaching aqueous equilibrium in a system containing Tc(IV) needs normally days [83AND/GAS] but no hint about reaction times is given in [69GOR/KOC], [70GOR/KOC].

For these reasons all the equilibrium data reported in [69GOR/KOC], [70GOR/KOC] need confirmation, and no equilibrium constants have been selected in this review.

From [Tc(thiourea)<sub>6</sub>]<sup>3+</sup> [96REY/TER] and Na<sub>2</sub>H<sub>2</sub>edta, a brown solid Tc(III)-edta was obtained [98GON/KRE]. By a combination of different techniques (UV-Vis, IR and <sup>1</sup>H-NMR spectroscopy, <sup>99</sup>Tc elemental analyses and cerimetric titrations, it was concluded that the 1:1 complex is formed (Na[Tc(edta)]·2H<sub>2</sub>O). The complex is much more stable than [Tc(thiourea)<sub>6</sub>]<sup>3+</sup>. Solutions of Tc(III)-edta at pH values between 2 and 6 were not altered after storing for 5 days.

## VIII.9 Zirconium edta compounds and complexes

### VIII.9.1 Zirconium edta compounds

The first paper [57BOB/RAF] reporting zirconium edta compounds proposes a variety of “insoluble compounds” with zirconium to edta ratios 3:2, 2:1, 3:1, 4:1 and 6:1. These compounds have been inferred from titrations of zirconium nitrate with edta, but no quantitative data are given and the proposed compounds have not been confirmed by any other study.

Zirconyl chloride reacts with edta or its disodium salt in an acidic medium to yield the  $[\text{Zr}(\text{edta})]\cdot 4\text{H}_2\text{O}$  chelate [98MAR/SHL].

Two papers reporting structures of Zr edta compounds were found:  $\text{Zr}(\text{edta})(\text{H}_2\text{O})_2$  [74POZ/POR] and  $(\text{CN}_3\text{H}_6)_2[\text{Zr}(\text{edta})\text{CO}_3]$  (see Figure VIII-3-a in Section VIII.1) [95MIS/SER]. These structure data reveal a coordination number of 8 for Zr complex salts, and we infer the same coordination number for  $\text{Zr}^{4+}$  in aqueous solution. This means that two edta molecules can be bound by  $\text{Zr}^{4+}$ , forming not only 1:1 but also 1:2 Zr edta complexes, as proposed by [77KOS/SHE].

No thermodynamic data are available for these Zr edta compounds.

### VIII.9.2 Stability of zirconium edta complexes

$\text{Zr}^{4+}$  forms a very stable 1:1 edta complex, which hydrolyses at pH 5 – 6 with dimerisation [64INT/MAR], [67BOT/AND]. The equilibria in alkaline solution are complicated by the precipitation of hydrolytic products. Under such conditions, also the formation of  $\text{Zr}(\text{edta})_2^{4-}$  was postulated [77KOS/SHE].

A more recent study [96YUC/HOK] reports the formation of mixed Zr–edta–F complexes. The maximum coordination number of 8 for Zr, as inferred from crystal structure analyses (see above), is reached with the complex  $\text{Zr}(\text{edta})\text{F}_2^{2-}$ .

In Table VIII-25 experimental equilibrium data found in the literature are presented. Data obtained from measurements under strong acidic conditions, *i.e.* measurements in 1 and 2 M  $\text{HClO}_4$ , are generally more important for deriving Zr edta stability constants than other data, because under such conditions the effects of zirconium hydrolysis are minimised. However, in all cases difficult corrections have to be applied to the experimental data in order to derive Zr edta stability constants.

As discussed in detail in Appendix A, several papers [56MOR/JUS], [63KYR/CAL], [64INT/MAR], [64PAN/VLA], [66ERM/MAR], [66LAP/PAN], [67BUD/HAA], [67TIK2], [68KOZ], [75TER/SHE], [77KOS/SHE], [87JOA/BIG] are not accepted in this review for evaluation of Zr edta stability constants.

Recently, Vasil'ev *et al.* [99VAS/KAT] determined  $K_1$  spectrophotometrically at room temperature in 1 M  $\text{HClO}_4$  by ligand competition. Their result,  $\log_{10}K_1 =$

( $29.93 \pm 0.10$ ), belongs to the more convincing ones because of the very low total metal ion concentration ( $3 \times 10^{-5}$  M) used in their experiments in order to avoid polymerization of zirconium. Considering the edta protonation constants they used in their data analysis, the uncertainty of  $K_1$  has to be increased. Furthermore, [99VAS/KAT] took Zr hydrolysis data from Nazarenko *et al.* [78NAZ/ANT], which are considered too high to be consistent *e.g.*, with the evaluation of [76BAE/MES].

Table VIII-25: Experimental equilibrium data for the Zr edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	[H <sup>+</sup> ]	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Zr}^{4+} + \text{edta}^{4-} \rightleftharpoons \text{Zr}(\text{edta})(\text{aq})$					
sp	0.1 M NaClO <sub>4</sub>	0.01 M	25	19.4	[56MOR/JUS]
sorption	0.1 M	0.1 M	20	( $29.5 \pm 0.5$ )	[63KYR/CAL]
	1 M HNO <sub>3</sub>	1 M		( $28.5 \pm 0.3$ )	
	5 M HNO <sub>3</sub>	5 M		( $30.6 \pm 0.2$ )	
sorption	3.0 M (H,Na)NO <sub>3</sub>	1.0 M	?	29.70	[64CAL/KYR]
		1.2 M		30.10	
		1.4 M		29.65	
		1.6 M		30.42	
		1.8 M		30.53	
		2.0 M		30.61	
		2.2 M		30.73	
		2.4 M		30.86	
		2.6 M		30.86	
		2.8 M		30.77	
	1.0 M HNO <sub>3</sub>	1.0 M		28.46	
	2.0 M HNO <sub>3</sub>	2.0 M		30.58	
	3.0 M HNO <sub>3</sub>	3.0 M		31.11	
	4.0 M HNO <sub>3</sub>	4.0 M		30.92	
	5.0 M HNO <sub>3</sub>	5.0 M		30.63	
sp	0.1 M (KCl)	0.01 M	25	( $29.0 \pm 0.9$ )	[64INT/MAR]
ix	0.23 M HClO <sub>4</sub>	0.23 M	?	29.0	[66ERM/MAR]
	1 M HClO <sub>4</sub>	1 M	?	28.0	
red	1 M (H,Na)ClO <sub>4</sub>	1 M	20	27.7	[67BOT/AND]
sp	0.8 N HCl	?	25	( $31.9 \pm 0.2$ )	[67BUD/HAA]
cix	1.2 M HCl	1.2 M	20	( $28.96 \pm 0.04$ )	[67TIK2]
pol	3.6 M HNO <sub>3</sub>	1.78 M	?	28.4	[69SOC/VOL]
ix	2 M HClO <sub>4</sub>	2.0 M	20	27.91	[70PRA/HAV]
sp	1 M HClO <sub>4</sub>	1 M	r. t.	( $29.93 \pm 0.10$ )	[99VAS/KAT]

(Continued on next page)

Table VIII-25: (continued)

Method	Ionic medium	[H <sup>+</sup> ]	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Zr(OH)}_2^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Zr(edta)(aq)} + 2 \text{OH}^-$					
dis	1 M NH <sub>4</sub> NO <sub>3</sub>	pH 9.9	?	(21.86 ± 0.05)	<a href="#">[87JOA/BIG]</a>
	2.5 M NH <sub>4</sub> NO <sub>3</sub>	pH 9.9		(21.50 ± 0.02)	
$\text{ZrL}_{II} + \text{edta}^{4-} \rightleftharpoons \text{Zr(edta)}_2^{4-} \text{ }^a$					
nmr	1 M	pH > 6	?	(1.8 ± 0.2)	<a href="#">[77KOS/SHE]</a>
$\text{Zr}^{4+} + 2 \text{edta}^{4-} \rightleftharpoons \text{Zr(edta)}_2^{4-}$					
sp	0.01 M HClO <sub>4</sub>	0.01 M	?	(7.9 ± 0.1)	<a href="#">[66LAP/PAN]</a>
$\text{Zr(edta)(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{Zr(edta)OH}^- + \text{H}^+$					
pot	0.1 M (KCl)	0.01 M	25	− 6.2	<a href="#">[64INT/MAR]</a>
red	1 M (H,Na)ClO <sub>4</sub>	1 M	20	− 6.1	<a href="#">[67BOT/AND]</a>
$2 \text{Zr(edta)OH}^- \rightleftharpoons (\text{Zr(edta)OH})_2^{2-}$					
pot	0.1 M (KCl)	0.01 M	25	3.5	<a href="#">[64INT/MAR]</a>
$\text{Zr(edta)(aq)} + \text{F}^- \rightleftharpoons \text{Zr(edta)F}^-$					
ise-F	0.1 M KNO <sub>3</sub>		25	4.62	<a href="#">[96YUC/HOK]</a>
$\text{Zr(edta)F}^- + \text{F}^- \rightleftharpoons \text{Zr(edta)F}_2^{2-}$					
ise-F	0.1 M KNO <sub>3</sub>		25	2.8	<a href="#">[96YUC/HOK]</a>

a: See discussion of [\[77KOS/SHE\]](#) in Appendix A.

r. t.: room temperature

However, unlike the other metal ions considered in this review, no NEA selected values for Zr hydrolysis were available at the time of the preparation of this chapter. Thus, a final consistent evaluation of Zr edta complexation has to be postponed until selected Zr hydrolysis data are available.

For the time being our review only results in a list of promising papers for a later re-evaluation: [\[64CAL/KYR\]](#), [\[67BOT/AND\]](#), [\[69SOC/VOL\]](#), [\[70PRA/HAV\]](#), [\[96YUC/HOK\]](#), [\[99VAS/KAT\]](#). However, all data reported in these studies need difficult corrections, and there is no guarantee that a re-evaluation using consistent auxiliary data will lead to selected values for Zr edta complexes.

A final remark concerning Zr edta complexation might be in place: an investigation of Zr edta complexation avoiding hydrolytic equilibria was never realised, in contrast to several other metal ions. For instance, in the case of Pd(II), also exhibiting an intricate, difficult and not well known hydrolysis behavior, the complexation with Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup> and SCN<sup>−</sup> is well known. This allowed not only the determination of the involved equilibrium constants, but subsequently also the derivation of formation constants with other polydentate ligands, for instance by use of potentiometric and spectrophotometric methods.



### VIII.9.3 Enthalpy of zirconium edta complex formation

The thermal effects of the reaction of zirconium with edta have been determined in a calorimeter with an isothermal jacket at 25°C in 2, 3, 3.7 and 4 M HClO<sub>4</sub> [78VAS/LYM], and at 15 and 35°C in 2, 3 and 3.7 M HClO<sub>4</sub> [78VAS/LYM2]. The authors assumed that their solutions only contained H<sub>6</sub>edta<sup>2+</sup>. However, as discussed in Section VIII.3.8, the amount of H<sub>5</sub>edta<sup>+</sup> was not negligible under the experimental conditions of [78VAS/LYM], [78VAS/LYM2] (from ≈ 30% in 2 M acid, to ≈ 15% in 4 M acid). Because of this, the uncertainties in the experimental values should be increased to ± 2 kJ·mol<sup>-1</sup> in any further evaluation. However, a final consistent evaluation of the enthalpy of Zr edta complexation has to be postponed until selected Zr hydrolysis data are available.

Table VIII-26: Experimental enthalpy data for the Zr edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	<i>t</i> (°C)	$\Delta_r H_m$ (kJ mol <sup>-1</sup> )	Reference
$Zr^{4+} + H_6edta^{2+} \rightleftharpoons Zr(edta)(aq) + 6 H^+$				
cal	2 M HClO <sub>4</sub>	25	(24.5 ± 0.6)	[78VAS/LYM]
	3 M HClO <sub>4</sub>		(23.9 ± 0.8)	
	3 M HClO <sub>4</sub>		(24.0 ± 0.8)	
	4 M HClO <sub>4</sub>		(23.7 ± 0.7)	
	2 M HClO <sub>4</sub>		(24.5 ± 0.1)	
	3 M HClO <sub>4</sub>		(25.0 ± 0.3)	
	3.7 M HClO <sub>4</sub>		(23.9 ± 0.2)	
cal	2 M HClO <sub>4</sub>	15	(27.5 ± 0.3)	[78VAS/LYM2]
	3 M HClO <sub>4</sub>		(28.2 ± 0.3)	
	3.7 M HClO <sub>4</sub>		(28.2 ± 0.3)	
	2 M HClO <sub>4</sub>	35	(23.0 ± 0.2)	
	3 M HClO <sub>4</sub>		(22.6 ± 0.2)	
	3.7 M HClO <sub>4</sub>		(22.5 ± 0.2)	

## VIII.10 Uranium edta compounds and complexes

### VIII.10.1 Uranium edta compounds

#### VIII.10.1.1 U(IV) edta compounds

Some solid complex salts containing U(IV) have been isolated. The stoichiometry of the 14 compounds listed in Table VIII-27 has been confirmed by elemental analysis. [63ERM/KRO] report that the compound Uedta·*n*H<sub>2</sub>O, where *n* can vary between 2.5 and 3.5, “is stable in air for a long time and its solubility in water at 25°C is 6.45·10<sup>-3</sup>

M". The same authors state that the K and NH<sub>4</sub> compounds "have a low solubility in water", whereas the Ca, Sr and Ba compounds "are almost insoluble in water", but no quantitative data are given by [\[63ERM/KRO\]](#).

Table VIII-27: U(IV) edta compounds. A reference reporting solubility data is marked with (sol.). C(NH<sub>2</sub>)<sub>3</sub><sup>+</sup> = guanidinium cation.

Compound	Reference
Uedta·2H <sub>2</sub> O	<a href="#">[43BRI/THI]</a>
Uedta·2.5–3.5H <sub>2</sub> O	<a href="#">[63ERM/KRO]</a> (sol.)
U <sub>2</sub> edta(OH) <sub>4</sub> · <i>n</i> H <sub>2</sub> O	<a href="#">[63ERM/KRO]</a>
K <sub>2</sub> H <sub>2</sub> U <sub>2</sub> (edta) <sub>3</sub> ·9H <sub>2</sub> O	<a href="#">[63ERM/KRO]</a>
K <sub>2</sub> H <sub>2</sub> U <sub>2</sub> (edta) <sub>3</sub> ·18H <sub>2</sub> O	<a href="#">[63ERM/KRO]</a>
(NH <sub>4</sub> ) <sub>2</sub> H <sub>2</sub> U <sub>2</sub> (edta) <sub>3</sub> ·8H <sub>2</sub> O	<a href="#">[63ERM/KRO]</a>
(NH <sub>4</sub> ) <sub>2</sub> H <sub>2</sub> U <sub>2</sub> (edta) <sub>3</sub> ·16H <sub>2</sub> O	<a href="#">[63ERM/KRO]</a>
Ca <sub>2</sub> U <sub>2</sub> (edta) <sub>3</sub> ·12H <sub>2</sub> O	<a href="#">[63ERM/KRO]</a>
Sr <sub>2</sub> U <sub>2</sub> (edta) <sub>3</sub> ·18H <sub>2</sub> O	<a href="#">[63ERM/KRO]</a>
Ba <sub>2</sub> U <sub>2</sub> (edta) <sub>3</sub> ·18H <sub>2</sub> O	<a href="#">[63ERM/KRO]</a>
(C(NH <sub>2</sub> ) <sub>3</sub> ) <sub>2</sub> [UedtaCl <sub>2</sub> ]·4H <sub>2</sub> O	<a href="#">[83SHC/MIK]</a>
(C(NH <sub>2</sub> ) <sub>3</sub> ) <sub>3</sub> [UedtaF <sub>3</sub> ]	<a href="#">[83SHC/MIK]</a>
(C(NH <sub>2</sub> ) <sub>3</sub> ) <sub>4</sub> [Uedta(CO <sub>3</sub> ) <sub>2</sub> ]	<a href="#">[83SHC/MIK]</a>
(C(NH <sub>2</sub> ) <sub>3</sub> ) <sub>4</sub> [Uedta(ox) <sub>2</sub> ]·3H <sub>2</sub> O	<a href="#">[83SHC/MIK]</a>

#### VIII.10.1.2 U(VI) edta compounds

A number of solid complex salts containing U(VI) has been isolated and described in the literature. The stoichiometry of the 14 compounds listed in Table VIII-28 has been confirmed by elemental analysis. X-ray crystal structure data are reported for only one compound, (C(NH<sub>2</sub>)<sub>3</sub>)<sub>4</sub>[(UO<sub>2</sub>F<sub>2</sub>)<sub>2</sub>edta], in [\[85SHC/ORL\]](#). The solubility of UO<sub>2</sub>(H<sub>2</sub>edta)·H<sub>2</sub>O has been investigated by [\[59KLY/SMI3\]](#). At a pH below 3 the solid phase contains H<sub>4</sub>edta(cr) and UO<sub>2</sub>(H<sub>2</sub>edta)·H<sub>2</sub>O, and at a pH above 5 the solubility increases sharply because of complex formation. In the pH range 3.0 – 4.5 [\[59KLY/SMI3\]](#) measured total uranium concentrations of about 2·10<sup>-4</sup> M and total edta concentrations of about 0.02 M and calculated a solubility product. However, the results of [\[59KLY/SMI3\]](#) are not accepted in this review (*cf.* Appendix A).

Table VIII-28: U(VI) edta compounds. A reference reporting solubility data is marked with (sol.), and a reference reporting an X-ray single crystal structure is marked with (str.), see also Figure VIII-4b in Section VIII.1.  $\text{C}(\text{NH}_2)_3^+$  = guanidinium cation and ac = acetate anion.

Compound	Reference
$\text{UO}_2(\text{H}_2\text{edta})\cdot\text{H}_2\text{O}$	[42BRI/HES], [59KLY/SMI3] (sol.), [64BHA/KRI], [85SHC/ORL]
$(\text{UO}_2)_2\text{edta}\cdot\text{H}_2\text{O}$	[85SHC/ORL]
$(\text{UO}_2)_2(\text{H}_2\text{O})_2\text{edta}$	[85SHC/ORL]
$(\text{UO}_2)_2\text{edta}\cdot 4\text{H}_2\text{O}$	[64BHA/KRI], [83SHC/MIK], [85SHC/ORL]
$(\text{C}(\text{NH}_2)_3)_4[(\text{UO}_2\text{F}_2)_2\text{edta}]$	[83SHC/MIK], [85SHC/ORL] (str.)
$(\text{C}(\text{NH}_2)_3)_2[(\text{UO}_2)_2(\text{NCS})_2(\text{H}_2\text{O})_2\text{edta}]$	[83SHC/MIK], [85SHC/ORL]
$(\text{C}(\text{NH}_2)_3)_4[(\text{UO}_2)_2(\text{NCS})_4\text{edta}]$	[85SHC/ORL]
$(\text{UO}_2)_2[(\text{CH}_3)_2\text{SO}]_4\text{edta}$	[83SHC/MIK], [85SHC/ORL]
$(\text{UO}_2)_2[(\text{CH}_3)_2\text{SO}]_2\text{edta}$	[85SHC/ORL]
$(\text{C}(\text{NH}_2)_3)_2[(\text{UO}_2)_2(\text{ac})_2\text{edta}]\cdot 3\text{H}_2\text{O}$	[83SHC/MIK], [85SHC/ORL]
$(\text{C}(\text{NH}_2)_3)_3[(\text{UO}_2)_2(\text{ac})_3\text{edta}]\cdot 3\text{H}_2\text{O}$	[83SHC/MIK], [85SHC/ORL]
$(\text{C}(\text{NH}_2)_3)_4[(\text{UO}_2)_2(\text{CO}_3)_2\text{edta}]\cdot 2\text{H}_2\text{O}$	[83SHC/MIK], [85SHC/ORL]
$(\text{C}(\text{NH}_2)_3)_6[(\text{UO}_2)_2(\text{CO}_3)_3\text{edta}]$	[83SHC/MIK], [85SHC/ORL]
$(\text{C}(\text{NH}_2)_3)_6[(\text{UO}_2)_2(\text{ox})_3\text{edta}]\cdot 2\text{H}_2\text{O}$	[83SHC/MIK], [85SHC/ORL]

## VIII.10.2 Uranium edta complexes

### VIII.10.2.1 U(V) edta complexes

No thermodynamic data are available for U(V) edta complexes.

### VIII.10.2.2 U(III) edta complexes

Uranium(III) is not stable in aqueous solution because it is rapidly oxidised (see Section V.4.2.1.2.d, p.200, in [92GRE/FUG]). The stability constant for U(III) edta complexation,  $\log_{10} K_1^\circ = 20.3$ , found in Table 1 of [69MOS], has been “determined by extrapolation, also using the literature data on the stability of acido-complexes of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ ”. This estimated value for an unstable species, which is not based on an actual experimental study, is not credited in this review.

Table VIII-29: Equilibrium data for the U(III) edta system.

Method	Ionic medium	$t$ (°C)	$\log_{10} K$	Reference
$\text{U}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Uedta}^-$				
rev	$I \rightarrow 0$	?	20.3	[69MOS]

### VIII.10.2.3 U(IV) edta complexes

Although already in one of the first papers on aqueous uranium(IV) edta chemistry [61PAL/HSU] the formation of 1:1 and 1:2 U(IV) – edta chelates has been postulated, based on spectrophotometric investigations, we have scarce quantitative information on the composition and on the stability of the formed complexes from only five papers [59KLY/SMI4], [62KRO/ERM], [63ERM/KRO], [68CAR/MAR], [83PER/MIS]. The equilibrium constants reported in these papers are summarised in Table VIII-30.

Table VIII-30: Experimental equilibrium data for the U(IV) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	<i>t</i> (°C)	pH range	log <sub>10</sub> <i>K</i>	Reference
$\text{U}^{4+} + \text{edta}^{4-} \rightleftharpoons \text{Uedta}(\text{aq})$					
titr	~0.025 M	?	1.7	(25.6 ± 0.4)	<a href="#">[59KLY/SMI4]</a>
sp	0.10 M KCl	20.0	1.4 – 1.5	(25.8 ± 0.2)	<a href="#">[68CAR/MAR]</a>
$\text{U}^{4+} + \text{H}_5\text{edta}^+ \rightleftharpoons \text{Uedta}(\text{aq}) + 5 \text{H}^+$					
sp	1.0 M (H <sub>3</sub> Na)ClO <sub>4</sub>	25	– 0.2 – 0.4	(2.28 ± 0.04)	<a href="#">[62KRO/ERM]</a>
	1.5 M (H <sub>3</sub> Na)ClO <sub>4</sub>		– 0.2 – 0.3	(1.98 ± 0.03)	
	2.0 M (H <sub>3</sub> Na)ClO <sub>4</sub>		– 0.2 – 0.3	(1.90 ± 0.03)	
	2.5 M (H <sub>3</sub> Na)ClO <sub>4</sub>		– 0.2 – 0.3	(1.65 ± 0.04)	
	3.0 M (H <sub>3</sub> Na)ClO <sub>4</sub>		0.0 – 0.3	(1.61 ± 0.03)	
$2 \text{Uedta}(\text{aq}) + \text{edta}^{4-} \rightleftharpoons \text{U}_2(\text{edta})_3^{4-}$					
pot	0.1 M KCl	25	3.5 – 5	11.9	<a href="#">[63ERM/KRO]</a>
sp	0.2 M	?	4.5 – 6	(9.25 ± 0.03)	<a href="#">[83PER/MIS]</a>
$2 \text{Uedta}(\text{aq}) + \text{H}_2\text{edta}^{2-} \rightleftharpoons \text{U}_2\text{H}_2(\text{edta})_3^{2-}$					
sp	0.04 M KCl	25	1 – 5	(3.64 ± 0.06)	<a href="#">[63ERM/KRO]</a>
	0.1 M KCl			(3.57 ± 0.09)	
	0.5 M KCl			(2.85 ± 0.11)	
	2.0 M KCl			(3.30 ± 0.16)	

(Continued on next page)

Table VIII-30: (continued)

Method	Ionic medium	<i>t</i> (°C)	pH range	log <sub>10</sub> <i>K</i>	Reference
$2 \text{ Uedta(aq)} + \text{H}_2\text{edta}^{2-} \rightleftharpoons \text{U}_2\text{H(edta)}_3^{3-} + \text{H}^+$					
sp	0.04 M KCl	25	1 – 5	(0.46 ± 0.07)	<a href="#">[63ERM/KRO]</a>
	0.1 M KCl			(0.79 ± 0.03)	
	0.5 M KCl			(0.82 ± 0.06)	
	2.0 M KCl			(1.07 ± 0.04)	
$\text{Uedta(aq)} + \text{H}^+ \rightleftharpoons \text{U(Hedta)}^+$					
sp	1.0–3.0 M	25		≤ 1.5	<a href="#">[62KRO/ERM]</a>
$\text{Uedta(aq)} + \text{OH}^- \rightleftharpoons \text{UedtaOH}^-$					
pot	0.01 M KCl	25	4 – 6	9.00	<a href="#">[63ERM/KRO]</a>
	0.1 M KCl			9.07	
	0.25 M KCl			9.08	
	0.5 M KCl			9.17	
	1.0 M KCl			9.13	
$\text{Uedta(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{UedtaOH}^- + \text{H}^+$					
pot	0.10 M KCl	25.3	3 – 5	– (4.72 ± 0.01)	<a href="#">[68CAR/MAR]</a>
	1.0 M KCl			– (4.58 ± 0.01)	
$2 \text{ UedtaOH}^- \rightleftharpoons (\text{UedtaOH})_2^{2-}$					
pot	0.01 M KCl	25	4 – 6	2.84	<a href="#">[63ERM/KRO]</a>
	0.1 M KCl			2.75	
	0.25 M KCl			2.79	
	0.5 M KCl			2.48	
	1.0 M KCl			2.86	
pot	0.10 M KCl	25.3	3 – 5	(2.91 ± 0.05)	<a href="#">[68CAR/MAR]</a>
	1.0 M KCl			(2.48 ± 0.05)	
$\text{UedtaOH}^- + \text{OH}^- \rightleftharpoons \text{Uedta(OH)}_2^{2-}$					
pot	0.01 M KCl	25	7 – 9	5.91	<a href="#">[63ERM/KRO]</a>
	0.1 M KCl			6.29	
	0.25 M KCl			6.41	
	0.5 M KCl			6.49	
	1.0 M KCl			6.87	

In Table VIII-31, information is summarised about the formation of ternary edta complexes, showing the tendency of Uedta(aq) to bind further complexing agents.

Table VIII-31: Experimental equilibrium data for the U(IV) edta X system where the ligand X forms a ternary complex UedtaX. The uncertainties are given as reported in the references.

X	Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$UX^{3+} + edta^{4-} \rightleftharpoons UedtaX^{-}$					
F <sup>-</sup>	pol	0.1 M NaClO <sub>4</sub>	20	17.50	[59SMI]
$Uedta(aq) + X^{n-} \rightleftharpoons UedtaX^{n-}$					
Oxalic acid	H <sub>2</sub> X	sp	?	(3.00 ± 0.03)	[83PER/MIS]
Iminodiacetic acid	H <sub>2</sub> X	pot	0.1 M KCl	25.3	[67CAR/MAR]
Phthalic acid	H <sub>2</sub> X			(4.2 ± 0.1)	
8-Hydroxyquinoline–5-sulfonic acid	H <sub>2</sub> X <sup>a</sup>			(9.72 ± 0.04)	
1,2-Dihydroxybenzene–3,5-disulfonic acid	H <sub>4</sub> X			(15.61 ± 0.05)	
5-Sulfosalicylic acid	H <sub>2</sub> X			(11.08 ± 0.05)	
1,8-Dihydroxynaphthalen–3,6-disulfonic acid	H <sub>4</sub> X			(16.22 ± 0.01)	
Catechol	H <sub>2</sub> X			(14.16 ± 0.5)	
Benzoylacetone	HX	sp	?	3.22	[80PER/POL]
Thenoyltrifluoroacetone	HX			2.80	
Dibenzoylmethane	HX			2.50	

a: In addition, log<sub>10</sub>*K* = – (7.14 ± 0.01) is reported for  $UedtaX^{2-} + H_2O \rightleftharpoons UedtaXOH^{3-} + H^+$ .

As found by [63ERM/KRO] and [68CAR/MAR], the solution of the 1:1 complex is hydrolysed already in acidic medium at pH > 3, and polynuclear hydroxo complexes are formed. At pH > 7 a pH drifting without precipitation is observed in titration experiments [68CAR/MAR]. This phenomenon is an indication of even further hydrolysis and polymerization of the U(IV) chelate. Probably very complex polynuclear chelates containing hydroxo bridges are produced. When the pH exceeds 11, U(OH)<sub>4</sub>(s) is precipitated [63ERM/KRO]. Apparently the six edta donor atoms are not sufficient for replacing all water molecules coordinated with the U(IV) ion, and more complex polydentate ligands would be needed to avoid these complications. The octadentate dtpa (diethylenetrinitrilopenta-acetate) is better in this respect, but only the decadentate ttha (triethylenetetranitrilo-hexa-acetate) forms a 1:1 complex without hydrolytic products [68CAR/MAR]. In this context, probably not only the number of the donor atoms of the

ligand determines its behavior, but also the steric strains of the formed complexes are important.

In the first quantitative study of the U(IV) edta system [59KLY/SMI4] different quantities of U(IV) sulfate were titrated with edta solution and arsenazo indicator until the color of the solutions changed from blue to pink. However, no background electrolyte was used, causing a varying ionic strength during the titration experiments. For this and other reasons (*cf.* Appendix A) the results of [59KLY/SMI4] are not considered in this review.

The spectrophotometric study of the U(IV) edta system by [62KRO/ERM] in acidic (H,Na)ClO<sub>4</sub> media is considered as reliable by this review. The results have been interpreted in terms of the reaction:



involving equilibrium constants for H<sub>5</sub>edta<sup>+</sup> and H<sub>6</sub>edta<sup>2+</sup> determined by the authors [62KRO/ERM] and for UOH<sup>3+</sup> taken from [50KRA/NEL]. The study of U(IV) hydrolysis by [50KRA/NEL] is one of the best source of data for UOH<sup>3+</sup> and has been accepted, among other studies, for the NEA selection in [92GRE/FUG]. The edta protonation constants reported by [62KRO/ERM] have been re-analysed in this review (*cf.* Appendix A) and differences up to 0.14 log<sub>10</sub> units have been found. Considering these differences, an overall uncertainty of ± 0.2 has been assigned to the experimental data of [62KRO/ERM] shown in Table VIII-30. A weighted SIT least squares regression analysis gives log<sub>10</sub> K° (VIII.23) = (4.80 ± 0.19) and Δε(VIII.23) = − (0.02 ± 0.09).

Combining log<sub>10</sub> K° (VIII.23) = (4.80 ± 0.19) with the edta protonation constant log<sub>10</sub> β<sub>5</sub>° = (24.72 ± 0.12) evaluated in this review (see Section VIII.3.7) results in log<sub>10</sub> K<sub>1</sub>° (VIII.24) = (29.52 ± 0.22) for the equilibrium:



The SIT interaction coefficient Δε(VIII.23) = − (0.02 ± 0.09) allows an estimate of ε(Uedta(aq), NaClO<sub>4</sub>) = Δε(VIII.23) − 5 ε(H<sup>+</sup>, ClO<sub>4</sub><sup>−</sup>) + ε(U<sup>4+</sup>, ClO<sub>4</sub><sup>−</sup>) + ε(H<sub>5</sub>edta<sup>+</sup>, ClO<sub>4</sub><sup>−</sup>) using ε(H<sup>+</sup>, ClO<sub>4</sub><sup>−</sup>) = (0.14 ± 0.02) and ε(U<sup>4+</sup>, ClO<sub>4</sub><sup>−</sup>) = (0.76 ± 0.06) from [92GRE/FUG] and ε(H<sub>5</sub>edta<sup>+</sup>, ClO<sub>4</sub><sup>−</sup>) = − (0.23 ± 0.15) evaluated in this review (see Section VIII.3.7). The result, ε(Uedta(aq), NaClO<sub>4</sub>) = − (0.19 ± 0.19), is consistent with ε(H<sub>4</sub>edta(aq), NaClO<sub>4</sub>) = − (0.29 ± 0.14) (see Section VIII.3.7). However, the deviation of ε(Uedta(aq), NaClO<sub>4</sub>) from zero, as generally assumed for neutral species in this review, is at the verge of statistical significance. Considering the more recently discussed value of ε(U<sup>4+</sup>, ClO<sub>4</sub><sup>−</sup>) = (0.84 ± 0.06), see footnote I on p.818 in [2001LEM/FUG], results in ε(Uedta(aq), NaClO<sub>4</sub>) = − (0.11 ± 0.19). Hence, a statistically significant deviation of ε(Uedta(aq), NaClO<sub>4</sub>) from zero cannot be established from the data of [62KRO/ERM].

Another reliable study of the U(IV) edta system is reported by [68CAR/MAR]. The equilibrium constant  $\log_{10} K_1$  (VIII.24) is obtained from a spectrophotometric study of a cation exchange equilibrium in the system U(IV) – edta – Th(IV). The value accepted in this review is  $\log_{10} K_1$  (VIII.24) =  $(26.1 \pm 0.3)$  at 20°C and  $I = 0.1$  M KCl (see Appendix A). Extrapolation to zero ionic strength according to  $\log_{10} K_1^\circ$  (VIII.24) =  $\log_{10} K_1$  (VIII.24) –  $(\Delta z^2) D + \Delta \varepsilon I_m$  with  $\Delta z^2 = -32$ ,  $\varepsilon(\text{U}^{4+}, \text{Cl}^-) \approx \varepsilon(\text{Th}^{4+}, \text{Cl}^-) = (0.25 \pm 0.03)$  [92GRE/FUG],  $\varepsilon(\text{K}^+, \text{edta}^{4-}) = (1.07 \pm 0.19)$  (see Section VIII.3.7) and  $\varepsilon(\text{Uedta}(\text{aq}), \text{KCl}) \approx -0.2$  gives  $\log_{10} K_1^\circ$  (VIII.24) =  $26.1 + 32 \cdot 0.1092 - 1.5 \cdot 0.1 = (29.4 \pm 0.3)$ .

A weighted mean of the values derived from the two studies [62KRO/ERM] and [68CAR/MAR] is selected in this review:

$$\log_{10} K_1^\circ \text{ (VIII.24)} = (29.5 \pm 0.2).$$

The formation of edta complexes with more than one edta anion was not studied accurately, in spite of the fact that for U(IV) a coordination number of 10 is possible. The data of [63ERM/KRO] for an entire series of species,  $\text{U}_2\text{H}_2(\text{edta})_3^{2-}$ ,  $\text{U}_2\text{H}(\text{edta})_3^{3-}$  and  $\text{U}_2(\text{edta})_3^{4-}$ , are not accepted in this review (*cf.* Appendix A). Perfil'ev *et al.* [83PER/MIS] give a constant for the formation of  $\text{U}_2(\text{edta})_3^{4-}$  (Table VIII-30), but it is not accepted in this review because of the scarce experimental information (*cf.* Appendix A), although the obtained value could be expected in analogy with that given by [67CAR/MAR] for iminodiacetate (Table VIII-31).

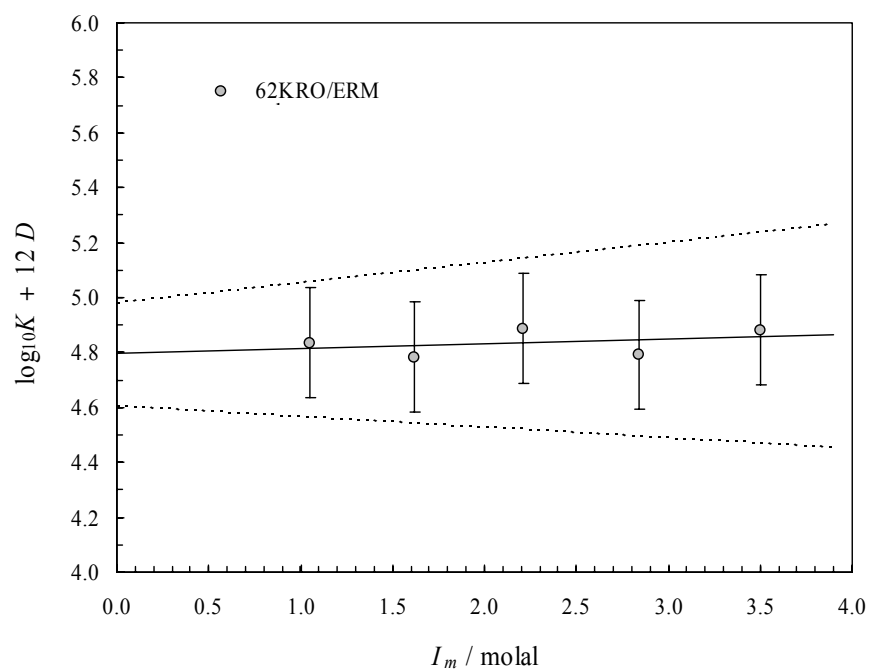
The formation of a protonated edta complex  $\text{U}(\text{Hedta})^+$  has been discussed by [62KRO/ERM] with the following statement: “Allowing for the error in the experiments and calculations, we can say that the equilibrium constant of the reaction  $\text{Uedta}(\text{aq}) + \text{H}^+ \rightleftharpoons \text{U}(\text{Hedta})^+$  at an ionic strength of 1.0 – 3.0 does not exceed 1.5”. No selection is made in this review on the basis of this estimate.

The hydrolysis of  $\text{Uedta}(\text{aq})$  occurs already in acidic medium at  $\text{pH} > 3$  with formation of  $\text{UedtaOH}^-$  and of the dimeric species  $(\text{UedtaOH})_2^{2-}$  [68CAR/MAR]. In addition, the formation of  $\text{Uedta}(\text{OH})_2^{2-}$  has been reported at  $\text{pH} > 7$  [63ERM/KRO]. The equilibrium constants given by [63ERM/KRO] and [68CAR/MAR] for  $\text{UedtaOH}^-$  and  $(\text{UedtaOH})_2^{2-}$  are in agreement if an uncertainty of about half a log unit is assumed. However, considering the shortcomings of [63ERM/KRO] (see Appendix A) this moderate agreement could be just by chance. Nevertheless, the values for U(IV) edta hydrolysis species summarised in Table VIII-30 may serve as qualitative guidelines in modelling exercises. But for a rigorous quantitative evaluation the obtained data need confirmation, especially concerning the formation of polynuclear hydroxo complexes in the millimolar concentration range investigated by [63ERM/KRO] and [68CAR/MAR].

The equilibrium constants reported for the formation of a ternary U(IV) edta fluoride complex [59SMI] and a ternary U(IV) edta oxalate complex [83PER/MIS] (Table VIII-31) are not accepted in this review (*cf.* Appendix A).



Figure VIII-25: Weighted least squares SIT-regression plot of equilibrium data from [\[62KRO/ERM\]](#) for the formation of  $\text{Uedta(aq)}$  according to reaction (VIII.23). The results are  $\log_{10} K^\circ(\text{VIII.23}) = (4.80 \pm 0.19)$  and  $\Delta\varepsilon(\text{VIII.23}) = -(0.02 \pm 0.09)$ .



## VIII.10.2.4 U(VI) edta complexes

The complexation of U(VI) with edta has been studied by various methods over the last four decades. The experimental results as reported in the literature are summarised in Table VIII-32. As can be seen from the table, a variety of U(VI) edta species has been postulated in these studies:  $\text{UO}_2(\text{H}_2\text{edta})(\text{aq})$ ,  $\text{UO}_2(\text{Hedta})^-$ ,  $\text{UO}_2\text{edta}^{2-}$  (also formulated as  $\text{UO}_2(\text{Hedta})\text{OH}^{2-}$ ),  $\text{UO}_2\text{edtaOH}^{3-}$ ,  $(\text{UO}_2\text{edta})_2^{4-}$ ,  $(\text{UO}_2)_2\text{edta}(\text{aq})$ ,  $(\text{UO}_2)_2\text{edtaOH}^-$ ,  $(\text{UO}_2)_2\text{edta}(\text{OH})_2^{2-}$ ,  $(\text{UO}_2)_4(\text{edta})_2(\text{OH})_2^{2-}$ ,  $(\text{UO}_2)_4(\text{edta})_2(\text{OH})_4^{4-}$  and  $(\text{UO}_2)_6(\text{edta})_3(\text{OH})_4^{4-}$ .

Table VIII-32: Experimental equilibrium data for the U(VI) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	$t$ (°C)	pH range	$\log_{10}K$	Reference
$\text{UO}_2^{2+} + \text{H}_2\text{edta}^{2-} \rightleftharpoons \text{UO}_2(\text{H}_2\text{edta})(\text{aq})$					
em	0.1 M KCl	20	1–3.5	$(3.6 \pm 0.2)$	[69STE/MAK2]
$\text{UO}_2^{2+} + \text{Hedta}^{3-} \rightleftharpoons \text{UO}_2(\text{Hedta})^-$					
sol	?	25	6.1–7.5	$(4.13 \pm 0.03)$	[59KLY/SMI3]
dis	0.1 M $\text{NaClO}_4$	20	5–7	$(7.32 \pm 0.02)$	[60STA3]
cix	0.1 M $\text{NaClO}_4$	20	5.3–7	$(7.13 \pm 0.04)$	[61STA/PRA]
sp	0.15 M $\text{NaClO}_4$	25.0	1.8–7	7.96	[64BHA/KRI]
gl	0.1 M $\text{KNO}_3$	25.0	3–7	$(7.40 \pm 0.02)$	[68SIL/SIM]
	1.0 M $\text{KNO}_3$		?	$(7.35 \pm 0.02)$	
em	0.1 M KCl	20	1–3.5	$(6.90 \pm 0.2)$	[69STE/MAK2]
gl	0.1 M $\text{KNO}_3$	25.0	3–7	$(6.9 \pm 0.3)$	[82OVE/LUN]
sp	3 M $\text{NaClO}_4$	25.0	1–3	$(9.55 \pm 0.04)$	[84BRI/LAG]
gl	1.0 M $\text{KNO}_3$	25	?	$(6.35 \pm 0.04)$	[84GON/MOT]
dis	0.3 m NaCl	25	2.2–4.3	$(6.63 \pm 0.03)$	[98POK/BRO]
	1 m		2.2–4.3	$(6.34 \pm 0.03)$	
	2 m		2.2–4.3	$(6.50 \pm 0.02)$	
	3 m		2.8–4.5	$(6.66 \pm 0.02)$	
	4 m		3.0–4.7	$(6.51 \pm 0.02)$	
	5 m		3.3–4.5	$(6.43 \pm 0.02)$	
$\text{UO}_2\text{edta}^{2-} + \text{H}^+ \rightleftharpoons \text{UO}_2(\text{Hedta})^-$					
gl	1.0 M $\text{KNO}_3$	25.0	?	5.62	[68SIL/SIM]
$\text{UO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons \text{UO}_2\text{edta}^{2-}$					
sp	0.1 M $\text{NH}_4\text{Cl}$	24	4.3–5.3	$(10.4 \pm 0.3)$	[60KOZ/KRO]
sp	0.15 M $\text{NaClO}_4$	25.0	1.8–7	12.3	[64BHA/KRI]
gl	0.1 M $\text{KNO}_3$	25.0	3–7	$(11.4 \pm 0.3)$	[82OVE/LUN]

(Continued on next page)

Table VIII-32: (continued)

Method	Ionic medium	$t$ (°C)	pH range	$\log_{10}K$	Reference
$\text{UO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons \text{UO}_2\text{edta}^{2-}$					
sp	3 M NaClO <sub>4</sub>	25.0	1–3	$(15.65 \pm 0.04)$	[84BRI/LAG]
dis	5.0 m NaCl	25	$5.8 \pm 0.1$	$(3.68 \pm 0.03)$	[96BOR/LIS]
dis	0.3 m NaCl	25	2.2–4.3	$(10.72 \pm 0.25)$	[98POK/BRO]
	1 m		2.2–4.3	$(9.82 \pm 0.04)$	
	2 m		2.2–4.3	$(10.08 \pm 0.10)$	
	3 m		2.8–4.5	$(10.20 \pm 0.06)$	
	4 m		3.0–4.7	$(10.27 \pm 0.05)$	
	5 m		3.3–4.5	$(10.48 \pm 0.15)$	
$\text{UO}_2\text{edtaOH}^{3-} + \text{H}^+ \rightleftharpoons \text{UO}_2\text{edta}^{2-} + \text{H}_2\text{O}$					
gl	1.0 M KNO <sub>3</sub>	25.0	?	6.30	[68SIL/SIM]
$2 \text{UO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons (\text{UO}_2)_2\text{edta}(\text{aq})$					
sp	0.1 M NH <sub>4</sub> Cl	24	2–6	$(15.2 \pm 0.3)$	[60KOZ/KRO]
sp	0.15 M NaClO <sub>4</sub>	25.0	1.8–7	18.01	[64BHA/KRI]
gl	0.1 M KNO <sub>3</sub>	25.0	3–7	$(17.87 \pm 0.03)$	[68SIL/SIM]
	1.0 M KNO <sub>3</sub>		?	$(17.77 \pm 0.04)$	
gl	0.1 M KNO <sub>3</sub>	25.0	3–7	$(17.8 \pm 0.3)$	[82OVE/LUN]
sp	3 M NaClO <sub>4</sub>	25.0	1–3	$(20.24 \pm 0.10)$	[84BRI/LAG]
gl	1.0 M KNO <sub>3</sub>	25	?	$(16.14 \pm 0.02)$	[84GON/MOT]
$2 \text{UO}_2^{2+} + \text{edta}^{4-} + \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2\text{edtaOH}^- + \text{H}^+$					
gl	0.1 M KNO <sub>3</sub>	25.0	3–7	$(12.4 \pm 0.3)$	[82OVE/LUN]
gl	1.0 M KNO <sub>3</sub>	25	?	$(11.33 \pm 0.03)$	[84GON/MOT]
$2 \text{UO}_2^{2+} + \text{edta}^{4-} + 2 \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2\text{edta}(\text{OH})_2^{2-} + 2 \text{H}^+$					
gl	0.1 M KNO <sub>3</sub>	25.0	3–7	$(6.8 \pm 0.4)$	[82OVE/LUN]
$2 \text{UO}_2\text{edta}^{2-} \rightleftharpoons (\text{UO}_2\text{edta})_2^{4-}$					
gl	1.0 M KNO <sub>3</sub>	25	?	3.27	[68SIL/SIM]
$2 \text{UO}_2^{2+} + 2 \text{edta}^{4-} \rightleftharpoons (\text{UO}_2\text{edta})_2^{4-}$					
gl	1.00 M KNO <sub>3</sub>	25	?	$(25.04 \pm 0.01)$	[84GON/MOT]
$2 (\text{UO}_2)_2\text{edta}(\text{aq}) + 2 \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_4\text{edta}(\text{OH})_2^{2-} + 2 \text{H}^+$					
gl	1.0 M KNO <sub>3</sub>	25	?	–7.38	[68SIL/SIM]
$4 \text{UO}_2^{2+} + 2 \text{edta}^{4-} + 4 \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_4(\text{edta})_2(\text{OH})_2^{4-} + 4 \text{H}^+$					
gl	1.0 M KNO <sub>3</sub>	25	?	$(15.34 \pm 0.04)$	[84GON/MOT]
$(\text{UO}_2)_4(\text{edta})_2(\text{OH})_2^{4-} + (\text{UO}_2)_2\text{edta}(\text{aq}) + 2 \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_6(\text{edta})_3(\text{OH})_4^{4-} + 2 \text{H}^+$					
gl	1.0 M KNO <sub>3</sub>	25	?	–7.08	[68SIL/SIM]
$6 \text{UO}_2^{2+} + 3 \text{edta}^{4-} + 4 \text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_6(\text{edta})_3(\text{OH})_4^{4-} + 4 \text{H}^+$					
gl	1.0 M KNO <sub>3</sub>	25	?	$(34.3 \pm 0.1)$	[84GON/MOT]

Studies of the complex formation of uranyl ions with edta have revealed a pronounced tendency to form dinuclear complexes [\[60KOZ/KRO\]](#), [\[64BHA/KRI\]](#), [\[68SIL/SIM\]](#), [\[82OVE/LUN\]](#), [\[84BRI/LAG\]](#), [\[84GON/MOT\]](#), which is rather unusual, considering that edta shows a strong preference to form mononuclear complexes with most other metals (*e.g.* Sections VIII.5 and VIII.7). The linear O–U–O configuration of the uranyl ion allows edta to coordinate this ion only in the equatorial plane, which results in decreased stability of the mononuclear complexes, and a preference for dinuclear complexes.

The structure of such a complex,  $(\text{UO}_2)_2\text{edtaF}_4^{4-}$ , is shown in Figure VIII-4-b (Section VIII.1). In this case, the coordination number in the equatorial plane of the linear  $\text{UO}_2^{2+}$  ion reaches 5. As a consequence of this special configuration, only one aminodicarboxyl group can be expected to coordinate the uranyl ion in the mononuclear complex  $\text{UO}_2(\text{Hedta})^-$ . This leaves at least one position in the equatorial plane of the uranyl ion for the coordination of water. The dissociation of a proton from this water molecule leads to the formation of the complex  $\text{UO}_2(\text{Hedta})\text{OH}^{2-}$ . This reaction, which takes place above pH 5, is more likely than the dissociation of the last proton from the uncoordinated part of edta to form the complex  $\text{UO}_2\text{edta}^{2-}$ . However, there is no way to distinguish between these two reactions by potentiometry, spectrophotometry or solvent extraction methods.

The tendency to form the dinuclear complex  $(\text{UO}_2)_2\text{edta}(\text{aq})$  complicates the investigation of solutions with metal to ligand molar ratios 2:1, because  $(\text{UO}_2)_2\text{edta}(\text{aq})$  forms hydroxo species and higher polymers by strong base addition. These polymeric species have a very limited concentration range of stability. At edta concentrations below  $5 \cdot 10^{-4}$  M no polymeric species are formed, and at concentrations above  $5 \cdot 10^{-3}$  M the polymeric species precipitate as soon as they are formed [\[84GON/MOT\]](#).

The results of [\[59KLY/SMI3\]](#), [\[60KOZ/KRO\]](#), [\[60STA3\]](#), [\[61STA/PRA\]](#), [\[64BHA/KRI\]](#) and [\[84BRI/LAG\]](#) are not considered in this review because of various shortcomings, which are discussed in detail in Appendix A.

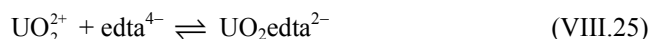
Da Silva and coworkers [\[68SIL/SIM\]](#), [\[70SIL/SIM\]](#), [\[70SIL/SIM2\]](#), [\[83LUR/GON\]](#), [\[84GON/MOT\]](#) studied the U(VI) edta system by potentiometric titrations. The original data [\[68SIL/SIM\]](#) have been further discussed [\[70SIL/SIM\]](#), [\[70SIL/SIM2\]](#), [\[83LUR/GON\]](#) and finally re-evaluated [\[84GON/MOT\]](#). However, as discussed in detail in Appendix A, neither the original data of [\[68SIL/SIM\]](#) nor the new refinement of these data by [\[84GON/MOT\]](#) has been considered in this review.

The studies of [\[69STE/MAK2\]](#), [\[82OVE/LUN\]](#) and the recent work of [\[98POK/BRO\]](#) are considered as reliable by this review (*cf.* Appendix A). Note that the rather erratic value reported for  $\text{UO}_2\text{edta}^{2-}$  in [\[96BOR/LIS\]](#) is rejected in this review. As discussed in Appendix A, the oxalate, citrate and edta protonation constants obtained by [\[96BOR/LIS\]](#) are largely at variance with all other experimental data and have been rejected in this review. Consequently, the metal complexation constants derived on the

basis of these protonation constants are also out of range. In [98POK/BRO] it is claimed that the constant reported by [96BOR/LIS] actually refers to the formation of  $\text{UO}_2(\text{H}_2\text{edta})(\text{aq})$ , but also this re-interpretation is rejected in this review (*cf.* Appendix A).

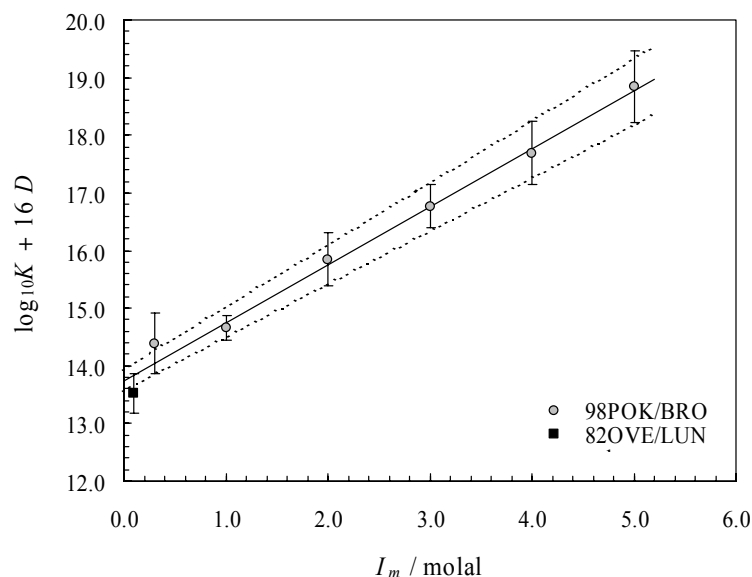
At  $I = 0.1 \text{ M KNO}_3$  remain only the values of [69STE/MAK2] and [82OVE/LUN], further those of [98POK/BRO] at high NaCl concentrations. The data of [98POK/BRO] have been corrected for  $\text{Na}(\text{edta})^{3-}$ ,  $\text{UO}_2\text{Cl}^+$  and  $\text{UO}_2\text{Cl}_2(\text{aq})$  complex formation (see Appendix A) and extrapolated to zero ionic strength by SIT (Figure VIII-26 and Figure VIII-27).

The results of the SIT extrapolation of [98POK/BRO] data to  $I = 0$  for reaction:



are  $\log_{10} K_1^\circ (\text{VIII.25}) = (13.75 \pm 0.18)$  and  $\Delta\epsilon(\text{VIII.25}) = -(1.00 \pm 0.11)$ . The SIT interaction coefficient allows an estimate of  $\epsilon(\text{UO}_2\text{edta}^{2-}, \text{Na}^+) = \Delta\epsilon(\text{VIII.25}) + \epsilon(\text{UO}_2^{2+}, \text{Cl}^-) + \epsilon(\text{edta}^{4-}, \text{Na}^+)$  using  $\epsilon(\text{UO}_2^{2+}, \text{Cl}^-) = \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03)$  from [92GRE/FUG] and  $\epsilon(\text{edta}^{4-}, \text{Na}^+) = (0.32 \pm 0.14)$  evaluated in this review (see Section VIII.3.7). The result,  $\epsilon(\text{UO}_2\text{edta}^{2-}, \text{Na}^+) = -(0.22 \pm 0.18)$ , is compatible with  $\epsilon(\text{H}_2\text{edta}^{2-}, \text{Na}^+) = -(0.37 \pm 0.14)$ .

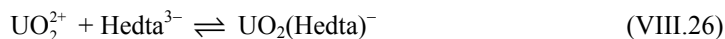
Figure VIII-26: Weighted least squares SIT-regression plot of equilibrium data from [98POK/BRO] for the formation of  $\text{UO}_2\text{edta}^{2-}$  according to Reaction (VIII.25). The results are  $\log_{10} K_1^\circ (\text{VIII.25}) = (13.75 \pm 0.18)$  and  $\Delta\epsilon(\text{VIII.25}) = -(1.00 \pm 0.11)$ . The data of [82OVE/LUN] is shown for comparison only.



For reaction (VIII.25) at  $I = 0.1$  M  $\text{KNO}_3$  the value of [82OVE/LUN] is selected,  $\log_{10} K_1$  (VIII.25) =  $(11.8 \pm 0.3)$ , corrected by + 0.1 log units for the protonation constant used by [82OVE/LUN] (*cf.* Appendix A) and by + 0.3 log units to account for the effect of  $\text{Kedta}^{3-}$  complexation. Extrapolation to zero ionic strength according to equation  $\log_{10} K_1^\circ$  (VIII.25) =  $\log_{10} K_1$  (VIII.25) +  $16D + \Delta\epsilon I_m$  with  $\Delta\epsilon$  (VIII.25) =  $-(1.00 \pm 0.11)$  for NaCl taken as an approximation for  $\text{KNO}_3$  gives  $\log_{10} K_1^\circ$  (VIII.25) =  $11.8 + 16 \cdot 0.1092 - 1.0 \cdot 0.1 = (13.5 \pm 0.3)$ . A weighted mean of this result and the value derived from [98POK/BRO] gives the value selected in this review:

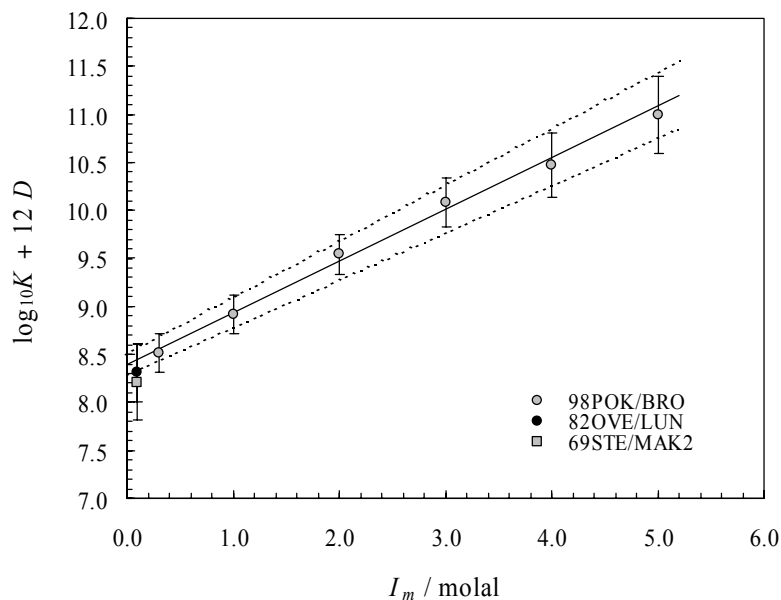
$$\log_{10} K_1^\circ \text{ (VIII.25)} = (13.7 \pm 0.2).$$

The results of the SIT extrapolation of [98POK/BRO] data to  $I = 0$  for reaction:



are  $\log_{10} K^\circ$  (VIII.26) =  $(8.39 \pm 0.11)$  and  $\Delta\epsilon$  (VIII.26) =  $-(0.54 \pm 0.07)$ . The SIT interaction coefficient allows an estimate of  $\epsilon(\text{UO}_2(\text{Hedta})^-, \text{Na}^+) = \Delta\epsilon$  (VIII.26) +  $\epsilon(\text{UO}_2^{2+}, \text{Cl}^-) + \epsilon(\text{Hedta}^{3-}, \text{Na}^+)$  using  $\epsilon(\text{Hedta}^{3-}, \text{Na}^+) = -(0.10 \pm 0.14)$  evaluated in this review (see Section VIII.3.7). The result,  $\epsilon(\text{UO}_2(\text{Hedta})^-, \text{Na}^+) = -(0.18 \pm 0.16)$ , perfectly agrees with  $\epsilon(\text{NpO}_2(\text{H}_2\text{edta})^-, \text{Na}^+) = -(0.18 \pm 0.16)$  (see Section VIII.11.2.3).

Figure VIII-27: Weighted least squares SIT-regression plot of equilibrium data from [98POK/BRO] for the formation of  $\text{UO}_2(\text{Hedta})^-$  according to Reaction (VIII.26). The results are  $\log_{10} K^\circ$  (VIII.26) =  $(8.39 \pm 0.11)$  and  $\Delta\epsilon$  (VIII.26) =  $-(0.54 \pm 0.07)$ . The data of [69STE/MAK2] and [82OVE/LUN] are shown for comparison only.



For Reaction (VIII.26) at  $I = 0.1$  M  $\text{KNO}_3$  the values of [69STE/MAK2] and [82OVE/LUN] are selected,  $\log_{10} K_1(\text{VIII.26}) = (6.9 \pm 0.4)$  and  $(7.0 \pm 0.3)$ , respectively. The latter value has been corrected by  $+0.1$  log units for the protonation constant used by [82OVE/LUN] (*cf.* Appendix A). Extrapolation to zero ionic strength according to equation  $\log_{10} K_1^\circ(\text{VIII.26}) = \log_{10} K_1(\text{VIII.26}) + 12D + \Delta\epsilon I_m$  with  $\Delta\epsilon(\text{VIII.26}) = -(0.54 \pm 0.07)$  for NaCl taken as an approximation for  $\text{KNO}_3$  gives  $\log_{10} K_1^\circ(\text{VIII.25}) = (8.2 \pm 0.4)$  and  $(8.3 \pm 0.3)$ . A weighted mean of these results and the value derived from [98POK/BRO] gives the value selected in this review:

$$\log_{10} K_1^\circ(\text{VIII.26}) = (8.37 \pm 0.10).$$

For reaction



at  $I = 0.1$  M  $\text{KNO}_3$  the value of [82OVE/LUN] is selected,  $\log_{10} K_1(\text{VIII.27}) = (18.2 \pm 0.3)$ , corrected by  $+0.1$  log units for the protonation constant used by [82OVE/LUN] (*cf.* Appendix A) and by  $+0.3$   $\log_{10}$ -units to account for the effect of  $\text{Kedta}^{3-}$  complexation. Extrapolation to zero ionic strength according to equation  $\log_{10} K_1^\circ(\text{VIII.27}) = \log_{10} K_1(\text{VIII.27}) + 24D + \Delta\epsilon I_m$  with  $\epsilon(\text{UO}_2^{2+}, \text{NO}_3^-) \approx \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03)$  from [92GRE/FUG],  $\epsilon(\text{K}^+, \text{edta}^{4-}) = (1.07 \pm 0.19)$  (see Section VIII.3.7) and  $\epsilon((\text{UO}_2)_2\text{edta}(\text{aq}), \text{KNO}_3) \approx 0$  gives  $\log_{10} K_1^\circ(\text{VIII.27}) = 18.2 + 24 \cdot 0.1092 - 2.0 \cdot 0.1 = (20.6 \pm 0.4)$ . The uncertainty of the selected value is increased to account for the ambiguity in the SIT coefficients:

$$\log_{10} K_1^\circ(\text{VIII.27}) = (20.6 \pm 0.4).$$

The complex  $\text{UO}_2(\text{H}_2\text{edta})(\text{aq})$  has been investigated by [69STE/MAK2] only. Although the result of [69STE/MAK2] seems to be reasonable, due to shortcomings discussed in Appendix A no value is selected in this review.

The polynuclear species shown in Table VIII-32 are never present in solutions where edta is in excess with respect to uranium. The only possible exception would be the species  $(\text{UO}_2\text{edta})_2^{4-}$ , proposed in [84GON/MOT]. However, considering the careful measurements of [82OVE/LUN], only monomeric U(VI) edta species are formed in solutions with total edta concentration of  $5 \cdot 10^{-4}$  M and corresponding cation concentrations to obtain mixtures with metal to ligand molar ratios 2:1, 1.5:1 and 1:1. Thus, the existence of the species  $(\text{UO}_2\text{edta})_2^{4-}$  remains doubtful. No values for polymeric U(VI) edta species other than  $(\text{UO}_2)_2\text{edta}(\text{aq})$  are selected in this review, but as long as systems are modelled where edta is in excess with respect to uranium, these complexes are not of importance.

### VIII.10.3 Enthalpy of uranium edta complex formation

No calorimetric data could be identified by this review for the uranium edta system. As can be seen from Table VIII-30 and Table VIII-32, all equilibrium constants reported for the uranium edta system have been obtained in the temperature range  $20 - 25^\circ\text{C}$  by

different authors. This very limited temperature range does not allow the derivation of enthalpy values.

## VIII.11 Neptunium edta compounds and complexes

### VIII.11.1 Neptunium edta compounds

The following solid neptunium edta compounds are mentioned in [76MEF/BLO] and [87MEF/KRO], (p. 259-260):  $\text{Np}(\text{edta}) \cdot 3\text{H}_2\text{O}$ ,  $\text{Ba}_2\text{Np}_2(\text{edta})_3 \cdot n\text{H}_2\text{O}$  ( $n = 12$  and  $18$ ),  $(\text{NpO}_2)_2\text{H}_2\text{edta} \cdot 5\text{H}_2\text{O}$  and  $[\text{Co}(\text{NH}_3)_6]\text{NpO}_2\text{edta} \cdot 3\text{H}_2\text{O}$ . Edta may be oxidised by oxygen (e.g., from air) in the presence of  $\text{Np}(\text{V})$  that acts as a catalyst, and this reaction is quite fast at  $60^\circ\text{C}$  [79SHI/STE2]. Because of this, compounds of edta are unstable when standing for long periods of time in air and moist conditions [76MEF/BLO]. No thermodynamic data are available for neptunium edta compounds.

### VIII.11.2 Neptunium edta complexes

#### VIII.11.2.1 $\text{Np}(\text{III})$ edta complexes

The stability constant for  $\text{Np}(\text{III})$  edta complexation,  $\log_{10} K_1^\circ = 20.5$ , found in Table 1 of [69MOS], has been “determined by extrapolation, also using the literature data on the stability of acido-complexes of  $\text{Am}^{3+}$  and  $\text{Cm}^{3+}$ ”. This estimated value, which is not based on an actual experimental study, is not credited in this review.

The only experimental study of the neptunium(III) edta system [74KRO/MEF] reports spectrophotometric measurements of the exchange equilibrium  $\text{Np}^{3+} + \text{Medta}^- \rightleftharpoons \text{M}^{3+} + \text{Np}(\text{edta})^-$  with  $\text{M}^{3+} = \text{Pr}^{3+}$  and  $\text{Nd}^{3+}$ . As [74KRO/MEF] state, the experiments on determining the exchange equilibria were run only at  $\approx 20^\circ\text{C}$  (i.e.  $21\text{--}24^\circ\text{C}$ ), without strictly controlling the constancy of the ionic strength of the solutions, which varied in the limits  $0.08\text{--}0.12\text{ M}$ . The pH of the measured solutions and the medium responsible for the (varying) ionic strength are not reported. The values  $\log_{10} K_1 = (17.21 \pm 0.08)$  (from Pr) and  $(17.24 \pm 0.18)$  (from Nd) have been derived by [74KRO/MEF] from the exchange equilibria, using auxiliary data taken from [54SCH/GUT]. The reported details about the measurements are too poor in order to base a selection on this single experimental study. Hence, no value for  $\text{Np}(\text{III})$  edta complexation is selected in this review. For environmental modeling studies, the data selected in this review for  $\text{Pu}(\text{III})$  edta (Section VIII.12.2.1) and  $\text{Am}(\text{III})$  edta (Section VIII.13.2.1) might be considered as guidelines for data estimation procedures concerning  $\text{Np}(\text{III})$  edta complexes.



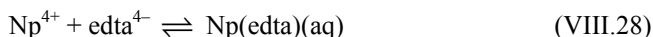
Table VIII-33: Equilibrium data for the Np(III) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Np}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Np}(\text{edta})^{-}$				
rev	$I \rightarrow 0$	?	20.5	[69MOS]
sp	0.08–0.12 M	21–24	$(17.21 \pm 0.08)$ $(17.24 \pm 0.18)$	[74KRO/MEF]

### VIII.11.2.2 Np(IV) edta complexes

In the first quantitative study of the Np(IV) edta system [59GEL/MEF] the experimental data have been interpreted in terms of  $\text{Np}(\text{H}_2\text{edta})^{2+}$  as the only complex forming in a rather wide pH range. However, the results of [59GEL/MEF] are rejected in this review because of various shortcomings, as discussed in Appendix A.

The only complex investigated in [62ISH/NAK], [71CHA/LIA], [71EBE/PAU] is  $\text{Np}(\text{edta})(\text{aq})$ , which is formed in strong acid solutions around 1 M  $[\text{H}^+]$ .



The results reported by [62ISH/NAK] and [71CHA/LIA] are rejected in this review (*cf.* Appendix A). Only the value of [71EBE/PAU] is considered reliable, although the investigation is limited because of  $\text{H}_4\text{edta}(\text{cr})$  solubility problems. Because of the limited pH range of this study, more investigations are necessary to elucidate Np(IV) edta equilibria in less acidic aqueous solutions, as it has been done for  $\text{Am}^{3+}$  by combining spectrophotometric measurements and alkalimetric titrations (Section VIII.13).

Table VIII-34: Experimental equilibrium data for the Np(IV) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	$t$ (°C)	pH range	$\log_{10}K$	Reference
$\text{Np}^{4+} + \text{H}_2\text{edta}^{2-} \rightleftharpoons \text{Np}(\text{H}_2\text{edta})^{2+}$					
sp	1 M (H,K)Cl	?	– 0.3 – 2.0	$(7.8 \pm 0.3)$	[59GEL/MEF]
$\text{Np}^{4+} + \text{edta}^{4-} \rightleftharpoons \text{Np}(\text{edta})(\text{aq})$					
dis	0.5 M HCl	room temperature	?	24.4	[62ISH/NAK]
dis	> 0.45 M $\text{HNO}_3$	25	< 0.35	22.9	[71CHA/LIA]
sp	1 M (H,Na) $\text{ClO}_4$	$(25 \pm 0.2)$	< 0.3	$(24.55 \pm 0.03)$	[71EBE/PAU]

For reaction (VIII.28) the value of [71EBE/PAU] is selected,  $\log_{10}K_1(\text{VIII.28}) = (26.03 \pm 0.53)$ , corrected by + 1.48 log units to account for the effect of  $\text{Na}(\text{edta})^{3-}$  complexation according to  $\log_{10}K_1(\text{VIII.28}) = 24.55 + \log_{10}(1 + K_{\text{Na}} [\text{Na}^+])$  with

$\log_{10}K_{Na} = (1.44 \pm 0.53)$  for  $I = 1.0$  M NaClO<sub>4</sub> and 25°C (see Table VIII-8a). Extrapolation to zero ionic strength according to  $\log_{10} K_1^0$  (VIII.28) =  $\log_{10}K_1$ (VIII.28) +  $32D + \Delta\varepsilon I_m = 26.03 + 32 \times 0.2057 - 1.35 \times 1.05 = (31.19 \pm 0.58)$  with  $\Delta\varepsilon$ (VIII.28) =  $-(1.35 \pm 0.24)$  using  $\varepsilon(\text{Np}^{4+}, \text{ClO}_4^-) = (0.84 \pm 0.06)$  [2001LEM/FUG],  $\varepsilon(\text{Na}^+, \text{edta}^{4-}) = (0.32 \pm 0.14)$  as evaluated in this review (see Section VIII.3.7), and  $\varepsilon(\text{Np}(\text{edta})(\text{aq}), \text{NaClO}_4) \approx \varepsilon(\text{Uedta}(\text{aq}), \text{NaClO}_4) = -(0.19 \pm 0.19)$ , see Section VIII.10.2.3. Hence, the selected value is:

$$\log_{10} K_1^0 \text{ (VIII.28)} = (31.2 \pm 0.6).$$

Note that the value selected for Np(edta)(aq),  $\log_{10} K_1^0$  (VIII.28) =  $(31.2 \pm 0.6)$ , is concordant with the value selected for Uedta(aq),  $\log_{10} K_1^0$  (VIII.24) =  $(29.5 \pm 0.2)$ , as a moderate increase in  $\log_{10}K$  with decreasing ionic radius from U(IV) to Np(IV) is expected.

### VIII.11.2.3 Np(V) edta complexes

The complexation of Np(V) with edta has been studied by spectrophotometry [59GEL/MEF], [70EBE/WED], cation exchange [61ZOL/MAR2] and solvent extraction [71CHA/LIA2], [83INO/TOC], [94TOC/SIR], [96BOR/LIS] and [98POK/BRO]. The experimental results as reported in the literature are summarised in Table VIII-35. As can be seen from the table, several Np(V) edta species have been postulated in these studies:  $\text{NpO}_2(\text{H}_2\text{edta})^-$ ,  $\text{NpO}_2(\text{Hedta})^{2-}$ ,  $\text{NpO}_2\text{edta}^{3-}$ ,  $\text{NpO}_2\text{edtaOH}^{4-}$ ,  $(\text{NpO}_2)_2\text{edta}^{2-}$ .

Table VIII-35: Experimental equilibrium data for the Np(V) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	$t$ (°C)	pH range	$\log_{10}K$	Reference
$\text{NpO}_2^+ + 2 \text{H}^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2(\text{H}_2\text{edta})^-$					
dis	0.3 m NaCl	$(25 \pm 0.5)$	3.0–6.9	$(18.03 \pm 0.05)$	[98POK/BRO]
	1 m		3.3–6.7	$(18.10 \pm 0.05)$	
	2 m		3.6–6.9	$(18.40 \pm 0.05)$	
	3 m		3.6–8.2	$(18.55 \pm 0.07)$	
	4 m		3.6–8.0	$(18.75 \pm 0.08)$	
	5 m		3.6–8.7	$(19.10 \pm 0.10)$	
$\text{NpO}_2^+ + \text{Hedta}^{3-} \rightleftharpoons \text{NpO}_2(\text{Hedta})^{2-}$					
sp	0.1M NaClO <sub>4</sub>	$(25 \pm 0.5)$	1–13	$(5.30 \pm 0.08)$	[70EBE/WED]
dis	1M NaClO <sub>4</sub>	$(25 \pm 1)$	6.6–6.7	$(4.49 \pm 0.05)$	[83INO/TOC]
dis	1M NaClO <sub>4</sub>	$(25 \pm 1)$	5.1–7.2	$(4.89 \pm 0.01)$	[94TOC/SIR]

(Continued on next page)

Table VIII-35: (continued)

Method	Ionic medium	<i>t</i> (°C)	pH range	log <sub>10</sub> <i>K</i>	Reference
$\text{NpO}_2^+ + \text{H}^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2(\text{Hedta})^{2-}$					
dis	0.3 m NaCl	(25 ± 0.5)	3.0–6.9	(13.48 ± 0.06)	[98POK/BRO]
	1 m		3.3–6.7	(13.21 ± 0.03)	
	2 m		3.6–6.9	(13.10 ± 0.05)	
	3 m		3.6–8.2	(12.90 ± 0.05)	
	4 m		3.6–8.0	(12.86 ± 0.06)	
	5 m		3.6–8.7	(12.95 ± 0.05)	
$\text{NpO}_2^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2\text{edta}^{3-}$					
sp	1 M KNO <sub>3</sub>	?	3.2–4.5	(10.35 ± 0.07)	[59GEL/MEF]
			5.5	(9.57 ± 0.23)	
cix	0.05M NH <sub>4</sub> ClO <sub>4</sub>	(20 ± 2)	5.3–5.7	(9.69 ± 0.08)	[61ZOL/MAR2]
sp	0.1M NaClO <sub>4</sub>	(25 ± 0.5)	1–13	(7.33 ± 0.06)	[70EBE/WED]
dis	1 M	?	4–6	9.05	[71CHA/LIA2]
dis	5m NaCl	25	5.8	(3.56 ± 0.04)	[96BOR/LIS]
dis	0.3 m NaCl	(25 ± 0.5)	3.0–6.9	(7.10 ± 0.10)	[98POK/BRO]
	1 m		3.3–6.7	(6.30 ± 0.10)	
	2 m		3.6–6.9	(6.00 ± 0.10)	
	3 m		3.6–8.2	(5.80 ± 0.10)	
	4 m		3.6–8.0	(5.66 ± 0.10)	
	5 m		3.6–8.7	(5.45 ± 0.10)	
$\text{NpO}_2\text{edta}^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{NpO}_2\text{edtaOH}^{4-} + \text{H}^+$					
sp	0.1M NaClO <sub>4</sub>	(25 ± 0.5)	1–13	– (11.51 ± 0.08)	[70EBE/WED]
$2 \text{NpO}_2^+ + \text{edta}^{4-} \rightleftharpoons (\text{NpO}_2)_2\text{edta}^{2-}$					
sp	1 M KNO <sub>3</sub>	?	3.3–4.4	(15.35 ± 0.02)	[59GEL/MEF]

This is a small set of species compared with the U(VI) – edta system (Section VIII.10.2.4), a fact which can be attributed to the lower charge of  $\text{NpO}_2^+$  and its weaker tendency to form hydroxo species.

In the first quantitative study of the Np(V) edta system [59GEL/MEF] the experimental data have been interpreted in terms of the formation of  $\text{NpO}_2\text{edta}^{3-}$  and  $(\text{NpO}_2)_2\text{edta}^{2-}$ . As the results of [59GEL/MEF] are rejected in this review because of various shortcomings (*cf.* Appendix A), we have no reliable experimental evidence for the formation of  $(\text{NpO}_2)_2\text{edta}^{2-}$ .

Evidence for the composition of the other complexes mentioned above is given in the reliable studies of [70EBE/WED] and [98POK/BRO].

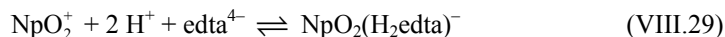
In [59GEL/MEF], [61ZOL/MAR2], [63ZOL/ALI] and [71CHA/LIA2] the complex  $\text{NpO}_2(\text{Hedta})^{2-}$  has been ignored, although it is an important species in the pH

ranges investigated in these studies. Furthermore, the pH measurements are not described. In [83INO/TOC] and [94TOC/SIR] the complex  $\text{NpO}_2(\text{Hedta})^{2-}$  has been included in the data analysis, but unfortunately the pH measurements are also not described. As a consequence of these shortcomings, all these studies could not be considered in this review (*cf.* Appendix A).

The rather erratic value reported for  $\text{NpO}_2\text{edta}^{3-}$  in [96BOR/LIS] is rejected in this review. As discussed in Appendix A, the oxalate, citrate and edta protonation constants obtained by [96BOR/LIS] are largely at variance with all other experimental data and have been rejected in this review. Consequently, the metal complexation constants derived on the basis of these protonation constants are also out of range. In [98POK/BRO] it is claimed that the constant reported by [96BOR/LIS] actually refers to the formation of  $\text{NpO}_2(\text{H}_2\text{edta})^-$ , but also this statement, which is not supported by any further reasoning in [98POK/BRO] is not accepted by this review.

Thus, only the results of [98POK/BRO] are further considered in the data evaluation of this review (see Appendix A) and compared with the values from [70EBE/WED].

For the reaction:



only the data of [98POK/BRO] are available (Figure VIII-28).

The results of the SIT extrapolation of [98POK/BRO] data to  $I = 0$  for reaction (VIII.29) are  $\log_{10} K^\circ (\text{VIII.29}) = (22.51 \pm 0.13)$  and  $\Delta\epsilon (\text{VIII.29}) = -(0.83 \pm 0.06)$ . The SIT interaction coefficient allows an estimate of  $\epsilon(\text{NpO}_2(\text{H}_2\text{edta})^-, \text{Na}^+) = \Delta\epsilon (\text{VIII.29}) + \epsilon(\text{NpO}_2^+, \text{Cl}^-) + 2\epsilon(\text{H}^+, \text{Cl}^-) + \epsilon(\text{edta}^{4-}, \text{Na}^+)$  using  $\epsilon(\text{NpO}_2^+, \text{Cl}^-) = (0.09 \pm 0.05)$  and  $\epsilon(\text{H}^+, \text{Cl}^-) = (0.12 \pm 0.01)$  from [2001LEM/FUG] and  $\epsilon(\text{edta}^{4-}, \text{Na}^+) = (0.32 \pm 0.14)$  evaluated in this review (see Section VIII.3.7). The result,  $\epsilon(\text{NpO}_2(\text{H}_2\text{edta})^-, \text{Na}^+) = -(0.18 \pm 0.16)$ , is in perfect agreement with  $\epsilon(\text{UO}_2(\text{Hedta})^-, \text{Na}^+) = -(0.18 \pm 0.16)$  (see Section VIII.10.2.4).

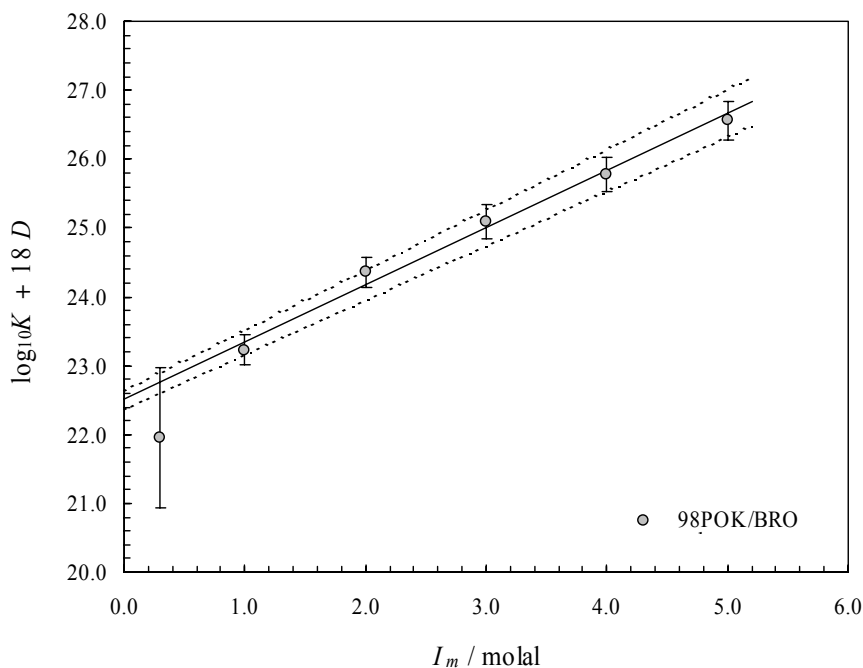
Combining  $\log_{10} K^\circ (\text{VIII.29}) = (22.51 \pm 0.13)$  with the edta protonation constant  $\log_{10} \beta_2^\circ = (18.04 \pm 0.04)$  as evaluated in this review (see Section VIII.3.7) gives for the equilibrium:



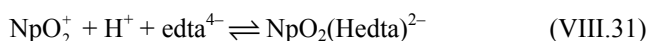
the selected value:

$$\log_{10} K^\circ (\text{VIII.30}) = (4.47 \pm 0.14).$$

Figure VIII-28: Weighted least squares SIT-regression plot of equilibrium data from [98POK/BRO] for the formation of  $\text{NpO}_2(\text{H}_2\text{edta})^-$  according to Reaction (VIII.29). The results are  $\log_{10} K^\circ$  (VIII.29) =  $(22.51 \pm 0.13)$  and  $\Delta\epsilon$ (VIII.29) =  $-(0.83 \pm 0.06)$ .



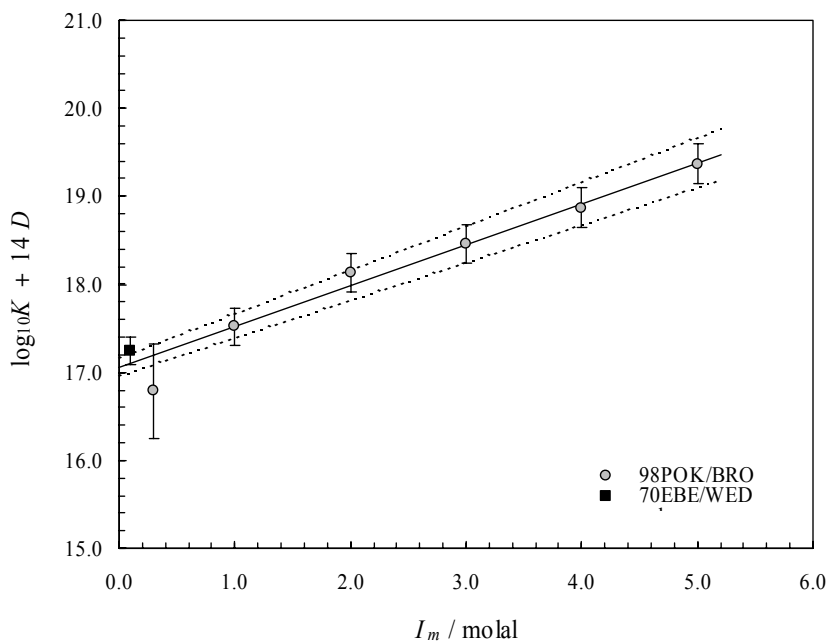
For the reaction



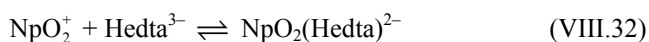
the data of [98POK/BRO] and [70EBE/WED] are available (Figure VIII-29). Considering only the [98POK/BRO] data for the SIT extrapolation to  $I = 0$  results in  $\log_{10} K^\circ$  (VIII.31) =  $(17.06 \pm 0.11)$  and  $\Delta\epsilon$ (VIII.31) =  $-(0.46 \pm 0.05)$ . The SIT interaction coefficient allows an estimate of  $\epsilon(\text{NpO}_2(\text{Hedta})^{2-}, \text{Na}^+) = \Delta\epsilon$ (VIII.31) +  $\epsilon(\text{NpO}_2^+, \text{Cl}^-) + \epsilon(\text{H}^+, \text{Cl}^-) + \epsilon(\text{edta}^{4-}, \text{Na}^+) = (0.07 \pm 0.16)$ . This result is compatible with  $\epsilon(\text{UO}_2\text{edta}^{2-}, \text{Na}^+) = -(0.22 \pm 0.18)$ , as evaluated in Section VIII.10.2.4.

Combining  $\log_{10}K$ (VIII.32) =  $(5.30 \pm 0.16)$  of [70EBE/WED] with the edta protonation constant  $\log_{10}\beta_1 = (10.42 \pm 0.03)$  as evaluated in this review for  $I = 0.1$  M  $\text{NaClO}_4$  at  $25^\circ\text{C}$  (see Section VIII.3.7) gives  $\log_{10}K$ (VIII.31) +  $14 D = (17.25 \pm 0.16)$ . This value is in agreement with the data of [98POK/BRO] as can be seen in Figure VIII-29.

Figure VIII-29: Weighted least squares SIT-regression plot of equilibrium data from [98POK/BRO] for the formation of  $\text{NpO}_2(\text{Hedta})^{2-}$  according to reaction (VIII.31). The results are  $\log_{10} K^\circ(\text{VIII.31}) = (17.06 \pm 0.11)$  and  $\Delta\epsilon(\text{VIII.31}) = -(0.46 \pm 0.05)$ . The data of [70EBE/WED] is shown for comparison only.



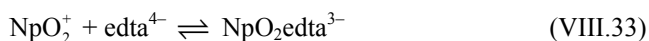
Combining  $\log_{10} K^\circ(\text{VIII.31}) = (17.06 \pm 0.11)$  with the edta protonation constant  $\log_{10} \beta_1^\circ = (11.24 \pm 0.03)$  as evaluated in this review (see Section VIII.3.7) gives for the equilibrium:



the selected value:

$$\log_{10} K^\circ(\text{VIII.32}) = (5.82 \pm 0.11).$$

For the reaction



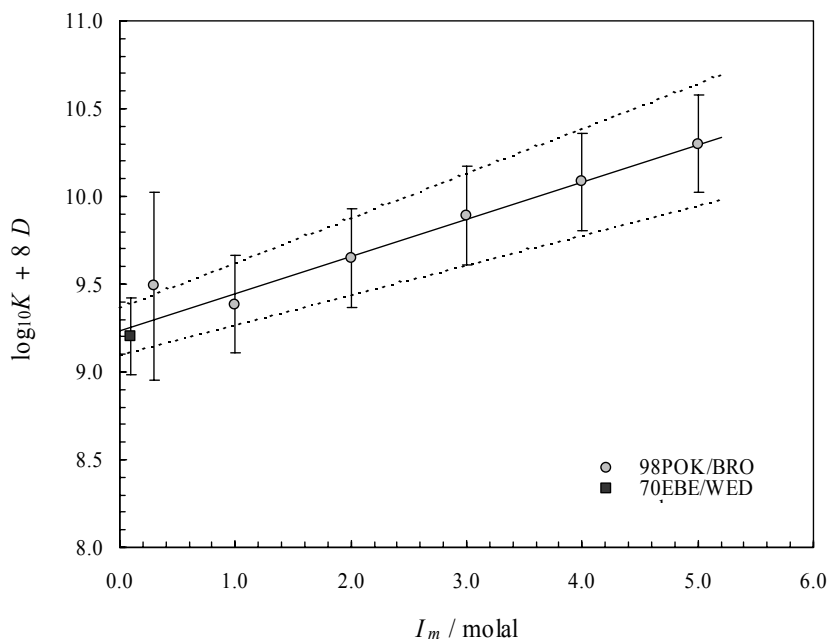
also the data of [98POK/BRO] and [70EBE/WED] are available (Figure VIII-30). Considering only the [98POK/BRO] data for the SIT extrapolation to  $I = 0$  results in  $\log_{10} K^\circ(\text{VIII.33}) = (9.23 \pm 0.13)$  and  $\Delta\epsilon(\text{VIII.33}) = -(0.21 \pm 0.06)$ . The SIT interaction coefficient allows an estimate of  $\epsilon(\text{NpO}_2\text{edta}^{3-}, \text{Na}^+) = \Delta\epsilon(\text{VIII.33}) + \epsilon(\text{NpO}_2^+, \text{Cl}^-) + \epsilon(\text{edta}^{4-}, \text{Na}^+) = (0.20 \pm 0.16)$ .

If the value  $\log_{10}K(\text{VIII.33}) = (7.33 \pm 0.12)$  as reported by [70EBE/WED] is corrected for  $\text{Na}(\text{edta})^{3-}$  complexation, it perfectly agrees with the values of [98POK/BRO] as can be seen in Figure VIII-30. However, due to the ambiguities discussed in Appendix A, it is not clear whether this is a valid procedure and hence, the value of [70EBE/WED] has not been considered for the final data selection. Thus, the selected value is:

$$\log_{10} K^{\circ}(\text{VIII.33}) = (9.23 \pm 0.13).$$

The value  $\log_{10}K = -(11.51 \pm 0.08)$  reported by [70EBE/WED] for the hydrolysis equilibrium  $\text{NpO}_2\text{edta}^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{NpO}_2\text{edtaOH}^{4-} + \text{H}^{+}$  has not yet been confirmed by any other study. Although the stability constant does not look unreasonable, no value is selected in this review.

Figure VIII-30: Weighted least squares SIT-regression plot of equilibrium data from [98POK/BRO] for the formation of  $\text{NpO}_2\text{edta}^{3-}$  according to Reaction (VIII.33). The results are  $\log_{10}K^{\circ}(\text{VIII.33}) = (9.23 \pm 0.13)$  and  $\Delta\epsilon(\text{VIII.33}) = -(0.21 \pm 0.06)$ . The data of [70EBE/WED] is shown for comparison only.



#### VIII.11.2.4 Np(VI) edta complexes

No thermodynamic data have been found in this review for Np(VI) edta complexes. This is no surprise, as according to the study of [\[98REE/WYG\]](#) Np(VI) is reduced almost instantaneously to Np(V) in the presence of edta. The formed Np(V) edta complexes are stable, and [\[98REE/WYG\]](#) found no spectral evidence for reduction to Np(IV) edta complexes, even after about 200 days. Hence, the lack of experimental data for the Np(VI) – edta system is of no importance for environmental modelling studies, and there is no need to estimate values for highly unstable Np(VI) edta complexes.

#### VIII.11.3 Enthalpy of neptunium edta complex formation

No calorimetric data for Np edta complexation could be identified by this review, and no temperature variations of complexation constants have been reported in the literature. Hence, no enthalpy values are available for the Np – edta system.

### VIII.12 Plutonium edta compounds and complexes

#### VIII.12.1 Plutonium edta compounds

No thermodynamic data for Pu edta compounds could be identified in this review.

#### VIII.12.2 Plutonium edta complexes

Already in 1957 Foreman and Smith published two papers [\[57FOR/SMI\]](#), [\[57FOR/SMI2\]](#) on the plutonium edta complex formation. They considered the Pu(III), Pu(IV) and Pu(VI) oxidation states of this metal and used alkalimetric titrations to show that in all cases 1:1 complexes are formed. The stability constants of these complexes were then investigated by a cation-exchange technique and by spectrophotometric measurements. However, as discussed in Appendix A, all results of [\[57FOR/SMI\]](#) and [\[57FOR/SMI2\]](#) and also later attempts to “correct” these results have not been credited in this review.

##### VIII.12.2.1 Pu(III) edta complexes

The complexation of Pu(III) with edta has been studied by various methods over more than three decades. The experimental results as reported in the literature are summarised in Table VIII-36. As can be seen from the table, a variety of Pu(III) edta species has been postulated in these studies:  $\text{Pu}(\text{H}_2\text{edta})^+$ ,  $\text{Pu}(\text{Hedta})(\text{aq})$ ,  $\text{Pu}(\text{edta})^-$ ,  $\text{Pu}(\text{edta})_2^{5-}$ ,  $\text{Pu}(\text{edta})(\text{Hedta})^{4-}$ ,  $\text{Pu}(\text{edta})(\text{H}_2\text{edta})^{3-}$ ,  $\text{Pu}(\text{edta})(\text{H}_3\text{edta})^{2-}$ .



Table VIII-36: Experimental equilibrium data for the Pu(III) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	<i>t</i> (°C)	pH range	log <sub>10</sub> <i>K</i>	Reference
$\text{Pu}^{3+} + \text{H}_2\text{edta}^{2-} \rightleftharpoons \text{Pu}(\text{H}_2\text{edta})^+$					
dis	0.1 M KCl	25	2–5	5.01	[91POC]
$\text{Pu}^{3+} + \text{Hedta}^{3-} \rightleftharpoons \text{Pu}(\text{Hedta})(\text{aq})$					
cix	1 M NH <sub>4</sub> Cl	r. t.	1.2–3.4	9.21	[59MOS/ART]
dis	0.1 M KCl	25	2–5	8.79	[91POC]
$\text{Pu}(\text{edta})^- + \text{H}^+ \rightleftharpoons \text{Pu}(\text{Hedta})(\text{aq})$					
em	0.1 (H,K)Cl	25	1.1–3.5	(4.6 ± 0.3)	[65STE/MAK2]
ise-H	1 M KCl	(25.00 ± 0.01)	1.56–2.39	(1.58 ± 0.06)	[78MER/GAT]
pol, sp	0.1–0.7 M NaClO <sub>4</sub>	(20 ± 1)	2–4	(4.2 ± 0.3)	[73CAU/GUI]
$\text{Pu}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Pu}(\text{edta})^-$					
cix	0.1 M KCl	20	3.3	18.12	[57FOR/SMI]
sp	0.1 M KCl / KNO <sub>3</sub>	?	1.5	18.59	[57FOR/SMI2]
cix	1 M NH <sub>4</sub> Cl	r. t.	1.2–3.4	17.36	[59MOS/ART]
em	0.1 (H,K)Cl	25	1.1–3.5	(15.0 ± 0.3)	[65STE/MAK2]
ise-H	1 M KCl	(25.00 ± 0.01)	1.56–2.39	(16.04 ± 0.01)	[78MER/GAT]
pol, sp	0.1–0.7 M NaClO <sub>4</sub>	(20 ± 1)	2–4	(12.2 ± 0.7)	[73CAU/GUI]
gl	0.1 M KCl	r. t.	2.6–3.7	(16.14 ± 0.56)	[89POC]
dis	0.1 M KCl	25	2–5	16.07	[91POC]
$\text{Pu}(\text{edta})^- + \text{edta}^{4-} \rightleftharpoons \text{Pu}(\text{edta})_2^{5-}$					
ise-H	1 M KCl	(25.00 ± 0.01)		(4.27 ± 0.01)	[78MER/GAT]
$\text{Pu}(\text{edta})^- + \text{Hedta}^{3-} \rightleftharpoons \text{Pu}(\text{edta})(\text{Hedta})^{4-}$					
ise-H	1 M KCl	(25.00 ± 0.01)		(2.60 ± 0.04)	[78MER/GAT]
$\text{Pu}(\text{edta})^- + \text{H}_2\text{edta}^{2-} \rightleftharpoons \text{Pu}(\text{edta})(\text{H}_2\text{edta})^{3-}$					
ise-H	1 M KCl	(25.00 ± 0.01)		(1.83 ± 0.08)	[78MER/GAT]
$\text{Pu}(\text{edta})^- + \text{H}_3\text{edta}^{2-} \rightleftharpoons \text{Pu}(\text{edta})(\text{H}_3\text{edta})^{2-}$					
ise-H	1 M KCl	(25.00 ± 0.01)		(1.6 ± 0.1)	[78MER/GAT]

r. t.: room temperature

The results of [57FOR/SMI], [57FOR/SMI2], [59MOS/ART], [65STE/MAK2], [73CAU/GUI], [89POC] and [91POC] are not considered in this review because of various shortcomings, which are discussed in detail in Appendix A.

Hence, among the data for Pu<sup>3+</sup> only those of [78MER/GAT] are considered adequate for data selection in this review. The outstanding papers of Merciny *et al.* [75MER/GAT], [78MER/GAT] are the best encountered in this review, reporting an unexpectedly detailed and exact description of all needed information.

For the reaction:



the value  $\log_{10} K_1(\text{VIII.34}) = (16.04 \pm 0.01)$  determined in 1 M KCl [78MER/GAT] needs several corrections.

First, the stability constant has to be converted from the molar to the molal scale, giving  $\log_{10} K_1((\text{VIII.34}), \text{molal}) = (16.026 \pm 0.01)$  in 1.033 m KCl.

Then the complexation of  $\text{edta}^{4-}$  with  $\text{K}^+$  of the inert salt, and the complexation of  $\text{Pu}^{3+}$  with  $\text{Cl}^-$  has to be taken into account. For  $\text{Kedta}^{3-}$  the constants  $\log_{10} K_K^{\circ} = (1.8 \pm 0.3)$  and  $\Delta\epsilon = -0.50$  were used (see Section VIII.4.1), and for  $\text{PuCl}_2^{2+}$  the constants  $\log_{10} K_{\text{Cl}_1}^{\circ} = (0.24 \pm 0.03)$  and  $\Delta\epsilon = -0.13$  from the analogous reaction  $\text{Am}^{3+} + \text{Cl}^- \rightleftharpoons \text{AmCl}^{2+}$  have been taken. In analogy with Am in NaCl, the effect of  $\text{PuCl}_2^{2+}$  can be neglected in 1.033 m KCl (for a detailed discussion of Am chloride complexation see Section V.4). Hence, the correction for  $\text{K}^+$  and  $\text{Cl}^-$  effects results in:

$$\log_{10} K_{1,\text{corr}}(\text{VIII.34}) = \log_{10} K_1((\text{VIII.34}), \text{molal}) + \log_{10}(1 + K_K[\text{K}^+]) + \log_{10}(1 + K_{\text{Cl}_1}[\text{Cl}^-])$$

$$\log_{10} K_{1,\text{corr}}(\text{VIII.34}) = 16.026 + \log_{10}(1 + 4.91) + \log_{10}(1 + 0.14) = (16.86 \pm 0.27).$$

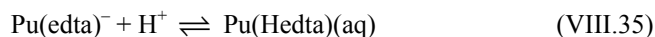
In a last step, this value is extrapolated to zero ionic strength using the SIT interaction parameters  $\epsilon(\text{edta}^{4-}, \text{K}^+) = (1.07 \pm 0.19)$ ,  $\epsilon(\text{Pu}^{3+}, \text{Cl}^-) \approx \epsilon(\text{Am}^{3+}, \text{Cl}^-) \approx \epsilon(\text{Am}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.03)$ , and  $\epsilon(\text{Pu}(\text{edta})^{-}, \text{K}^+) \approx \epsilon(\text{Am}(\text{edta})^{-}, \text{Na}^+) = (0.01 \pm 0.16)$ , resulting in  $\Delta\epsilon(\text{VIII.34}) = -(1.55 \pm 0.25)$ . Therefore,

$$\begin{aligned} \log_{10} K_{1,\text{corr}}^{\circ}(\text{VIII.34}) &= \log_{10} K_{1,\text{corr}}(\text{VIII.34}) - \Delta z^2 D + \Delta\epsilon I_m \\ &= 16.86 + 24 \times 0.205 - 1.55 \times 1.033 \end{aligned}$$

and the selected value is:

$$\log_{10} K_{1,\text{corr}}^{\circ}(\text{VIII.34}) = (20.18 \pm 0.37).$$

For the reaction:



the value  $\log_{10} K_1(\text{VIII.35}) = (1.58 \pm 0.06)$  determined in 1 M KCl [78MER/GAT] does not need corrections for  $\text{K}^+$  and  $\text{Cl}^-$  effects. The selected constant is extrapolated to zero ionic strength assuming  $\epsilon(\text{Pu}(\text{Hedta})(\text{aq}), \text{KCl}) = (0.0 \pm 0.2)$ ,

$$\begin{aligned} \log_{10} K_1^{\circ}(\text{VIII.35}) &= \log_{10} K_1((\text{VIII.35}), \text{molal}) - \Delta z^2 D + \Delta\epsilon I_m \\ &= 1.566 + 2 \times 0.205 - 0.13 \times 1.033 \end{aligned}$$

$$\log_{10} K_1^{\circ}(\text{VIII.35}) = (1.84 \pm 0.26).$$

The paper of Merciny *et al.* [78MER/GAT] gives some details for the formation of the 1:2 species  $\text{Pu}(\text{edta})_2^{5-}$  and of three protonated 1:2 species  $\text{Pu}(\text{edta})(\text{Hedta})^{4-}$ ,

$\text{Pu}(\text{edta})(\text{H}_2\text{edta})^{3-}$  and  $\text{Pu}(\text{edta})(\text{H}_3\text{edta})^{2-}$ . For the reaction  $\text{Pu}(\text{edta})^- + \text{H}_n\text{edta}^{n-4} \rightleftharpoons \text{Pu}(\text{edta})(\text{H}_n\text{edta})^{n-5}$  the values  $\log_{10}K_n = 4.3, 2.6, 1.8$  and  $1.6$  are reported for  $n = 0, 1, 2$  and  $3$ , respectively, *i.e.* showing a weak tendency of  $\text{Pu}(\text{edta})^-$  to form 1:2 complexes from the 1:1 complex. This review considers the results of [78MER/GAT] as reliable. However, in view of the weak complexation effects, the ambiguities involved in extrapolating highly charged species from 1 M KCl to zero ionic strength using estimated SIT interaction parameters, and the fact that no other reliable study has yet confirmed the results of [78MER/GAT], no values are selected in this review for 1:2 complexes.

### VIII.12.2.2 Pu(IV) edta complexes

Stability constants reported for Pu(IV) edta complexes are summarised in Table VIII-37. The Pu(IV) edta system has been studied by three groups of investigators, Forman and Smith [57FOR/SMI], [57FOR/SMI2], Mikhailov [69MIK] and Cauchetier and Guichard [73CAU/GUI]. However, as detailed in Appendix A, none of these studies is credited by this review and hence, no values are selected for the Pu(IV) edta system. For environmental modelling studies, the data selected in this review for U(IV) edta (Section VIII.10.2.3) and Np(IV) edta (Section VIII.11.2.2) might be considered as guidelines for data estimation procedures concerning Pu(IV) edta complexes.<sup>1</sup>

Table VIII-37: Experimental equilibrium data for the Pu(IV) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	$t$ (°C)	pH range	$\log_{10}K$	Reference
$\text{Pu}(\text{edta})(\text{aq}) + \text{H}^+ \rightleftharpoons \text{PuHedta}^+$					
pol, sp	0.1 M $\text{NaClO}_4$	$(20 \pm 1)$	1.4–4.6	$(2.6 \pm 0.2)$	[73CAU/GUI]
$\text{Pu}^{4+} + \text{edta}^{4-} \rightleftharpoons \text{Pu}(\text{edta})(\text{aq})$					
cix	0.1 M KCl	20	3.3	17.66	[57FOR/SMI]
sp	0.1 M KCl / $\text{KNO}_3$	?	3.3	17.10	[57FOR/SMI2]
	1M $\text{HNO}_3$	?	0	24.2 – 24.3	
sol	0.1–0.3 M $\text{HNO}_3$	$(18 \pm 3)$	?	$(26.0 \pm 0.5)$	[69MIK]
pol, sp	0.1–0.7 M $\text{NaClO}_4$	$(20 \pm 1)$	1.4–4.6	$(25.6 \pm 0.6)$	[73CAU/GUI]

<sup>1</sup> A paper by Boukhalfa *et al.* [2004BOU/REI], available to the reviewers only in the final stage of preparation of this book, reports measurements by spectrophotometry, potentiometry and cyclic voltammetry which were performed to evaluate the formation of Pu(IV) – edta, Pu(IV) – edta – carbonate, Pu(IV) – edta – citrate and Pu(III) – edta complexes. The experimental procedures and results reported in this paper seem to be reliable. However, the obtained stability constants need to be re-evaluated using NEA selected auxiliary constants for edta and citrate protonation and Pu hydrolysis, and the SIT approach to take care of the different electrolyte media and concentrations used in the experiments. The experimental raw data needed for recalculations are not published in this paper, but the authors agreed to do these recalculations using auxiliary data provided by the reviewers. All results will be archived by NEA for later use.

### VIII.12.2.3 Pu(V) and Pu(VI) edta complexes

Stability constants reported for Pu(V) and Pu(VI) edta complexes are summarised in Table VIII-38 and Table VIII-39, respectively.

Table VIII-38: Experimental equilibrium data for the Pu(V) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	<i>t</i> (°C)	pH range	log <sub>10</sub> <i>K</i>	Reference
$\text{PuO}_2^+ + \text{Hedta}^{3-} \rightleftharpoons \text{PuO}_2\text{Hedta}^{2-}$					
cix	0.1M NH <sub>4</sub> ClO <sub>4</sub>	25		(4.80 ± 0.01)	<a href="#">[70EBE/WED]</a>
$\text{PuO}_2^+ + \text{edta}^{4-} \rightleftharpoons \text{PuO}_2\text{edta}^{3-}$					
cix	≈ 0.05 M NH <sub>4</sub> Cl	?	3–5	(10.17 ± 0.22)	<a href="#">[59GEL/ART]</a>
gl	0.1 M KCl	r. t.	3–5	(12.9 ± 0.1)	<a href="#">[61KAB]</a>
pol, sp	0.01–0.1M NaClO <sub>4</sub>	(20 ± 1)		(12.6 ± 1.0)	<a href="#">[75CAU/GUI]</a>

r. t.: room temperature

Table VIII-39: Experimental equilibrium data for the Pu(VI) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	<i>t</i> (°C)	pH range	log <sub>10</sub> <i>K</i>	Reference
$\text{PuO}_2^{2+} + \text{H}_2\text{edta}^{2-} \rightleftharpoons \text{PuO}_2\text{H}_2\text{edta}(\text{aq})$					
pol, sp	0.01–0.1M NaClO <sub>4</sub>	(20 ± 1)	1.5–4.0	(3.2 ± 0.3)	<a href="#">[75CAU/GUI]</a>
$\text{PuO}_2^{2+} + \text{Hedta}^{3-} \rightleftharpoons \text{PuO}_2\text{Hedta}^-$					
pol, sp	0.01–0.1M NaClO <sub>4</sub>	(20 ± 1)	1.5–4.0	(8.3 ± 0.7)	<a href="#">[75CAU/GUI]</a>
$\text{PuO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons \text{PuO}_2\text{edta}^{2-}$					
cix	0.1 M KCl	20	3.3	16.39	<a href="#">[57FOR/SMI]</a>
sp	0.1 M KCl / KNO <sub>3</sub>	?	4.0	16.03	<a href="#">[57FOR/SMI2]</a>
pol, sp	0.01–0.1M NaClO <sub>4</sub>	(20 ± 1)		(14.6 ± 0.9)	<a href="#">[75CAU/GUI]</a>

Pu(VI) is reduced by edta to Pu(V) and finally to Pu(IV) in acidic solutions as soon as the pH reaches 1, and the rate of reduction at pH 3 is so large that complete reduction of Pu(VI) to Pu(V) is observed within some minutes, even if the molar amount of edta is lower than that of the metal ion. At pH 4 one mol of edta reduces 6 to 7 moles of Pu(VI) [\[75CAU/GUI\]](#). At pH 6 an instantaneous reduction of Pu(VI) to Pu(V) was observed [\[98REE/WYG\]](#). For this reason, no spectral data on the Pu(VI) edta complex could be obtained by Reed *et al.*, the predominant product was the Pu(V) edta complex, which was reduced further to form a Pu(IV) edta complex [\[98REE/WYG\]](#).

Among the studies mentioned in Table VIII-38 and Table VIII-39 only Eberle and Wede [70EBE/WED] reported clearly depicted details about their experimental procedures, but Pu(V) reduction effects have been ignored by the authors. Only the data of Cauchetier and Guichard [75CAU/GUI] are obtained by considering the Pu(VI) and Pu(V) reduction processes. The instability of the solutions caused large standard deviations of their obtained equilibrium constants.

Hence, no reliable stability constants are available and no values are selected in this review for these systems. Considering the instability of Pu(VI) and Pu(V) edta solutions, this non-selection has no consequences for environmental modelling studies. There is no need to estimate values for highly unstable Pu(VI) and Pu(V) edta complexes, except perhaps for short term laboratory studies involving the kinetics of Pu(VI) and Pu(V) reduction in the presence of edta.

### VIII.12.3 Enthalpy of plutonium edta complex formation

For the formation of  $\text{Pu}(\text{edta})^-$  Fuger and Cunningham [65FUG/CUN] determined  $\Delta_r H_m^\circ(\text{VIII.34}) = -(17.7 \pm 1.0) \text{ kJ}\cdot\text{mol}^{-1}$  at  $I = 0.16 \text{ M KCl}$ . The study of Fuger and Cunningham is considered as reliable (*cf.* Appendix A) and their results are accepted in this review. Extrapolation of the above value to zero ionic strength  $\Delta_r H_m^\circ(\text{VIII.34}) = \Delta_r H_m^\circ(\text{VIII.34}) + 24D_L - RT^2 \cdot \Delta \epsilon_L \cdot I_m$ , using  $\Delta \epsilon_L = (0 \pm 1) \times 10^{-3} \text{ kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , gives the selected value:

$$\Delta_r H_m^\circ(\text{VIII.34}) = -(8.7 \pm 1.2) \text{ kJ}\cdot\text{mol}^{-1}.$$

This selection yields:

$$\Delta_r H_m^\circ(\text{Pu}(\text{edta})^-) = -(2305.3 \pm 4.4) \text{ kJ}\cdot\text{mol}^{-1}.$$

No other calorimetric data could be identified by this review for the plutonium edta system. As can be seen from Table VIII-36 to Table VIII-39, all equilibrium constants reported for the plutonium edta system have been obtained in the temperature range 18 – 25°C by different authors. This very limited temperature range would not allow the derivation of enthalpy values, even if this review would have credited other papers besides [78MER/GAT].

## VIII.13 Americium edta compounds and complexes

### VIII.13.1 Americium edta compounds

No thermodynamic data for Am edta compounds could be identified in this review.

### VIII.13.2 Americium edta complexes

In aqueous media, americium exists as trivalent ion except under strongly oxidising conditions, where the penta- and hexavalent dioxoamericium ions  $\text{AmO}_2^+$  and  $\text{AmO}_2^{2+}$

are formed [95SIL/BID]. As discussed later (Section VIII.13.2.2), the higher oxidation states of Am are not stable in the presence of edta.

### VIII.13.2.1 Am(III) edta complexes

Based on the knowledge of edta complex formation with Pu(III) (Section VIII.12.2.1) and the trivalent lanthanide cations the formation of the following Am(III) edta complexes is expected: Am(Hedta)(aq), Am(edta)<sup>-</sup>, Am(edta)OH<sup>2-</sup>, but also Am(edta)<sub>2</sub><sup>5-</sup>. Eventually protonated 1:2 complexes are possible because of the large coordination number of the actinides, as observed in the case of Pu<sup>3+</sup> [78MER/GAT]. Am<sup>3+</sup> is among the actinide trivalent cations a very important point of reference because of its redox stability, which facilitates an exact determination of the involved equilibrium constants.

The coordination of the first edta ligand occurs in quite strong acidic solution, that of the second one above pH 4 [69DEL/BAY]. However, Delle Site and Baybarz [69DEL/BAY] mention a considerable uncertainty in their experimental data concerning the formation of 2:3 and 1:2 Am edta species. The experimental difficulties are probably connected with the extensive overlapping of the spectral bands in the case of the 2:3 complex, and with the low stability of the 1:2 complex. Delle Site and Baybarz could not derive any stability constants for 2:3 and 1:2 Am edta complexes. In general, in all other papers only the formation of 1:1 Am edta complexes is considered.

The experimental equilibrium constants reported in the literature are collected in Table VIII-40, together with the pH range of the investigations.

Table VIII-40: Experimental equilibrium data for the Am(III) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	<i>t</i> (°C)	pH range	log <sub>10</sub> <i>K</i>	Reference
$\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^{-}$					
cix	0.1 M NH <sub>4</sub> ClO <sub>4</sub>	25	2–3.3	(18.16 ± 0.10)	[58FUG]
cix	1M NH <sub>4</sub> Cl	?	1–2.2	(18.03 ± 0.13)	[60MOS/KHA]
dis	0.1 M NH <sub>4</sub> Cl	20	3.8–5.6	(16.91 ± 0.04)	[66STA]
em	0.1 M KCl	25	1–3	(17.00 ± 0.05)	[67LEB/MAK]
sp	0.1 M NH <sub>4</sub> ClO <sub>4</sub>	25	1–2.1	18.06	[69DEL/BAY]
cix	0.1 M NH <sub>4</sub> ClO <sub>4</sub>	?	4.1	17.38	[71ELE/ZAI]
kin	0.5 M NaClO <sub>4</sub>	24	5.45	18.0	[71OLI/CHO]
dis	6 M LiNO <sub>3</sub>	room temperature	3–4	17.38	[75KOR/PAT]
dis	0.30 m NaCl	25	2.4	(15.10 ± 0.11)	[99CHE/CHO]
	1.0			(13.96 ± 0.07)	
	2.0			(14.04 ± 0.09)	
	3.0			(13.76 ± 0.02)	
	4.0			(13.89 ± 0.03)	
	5.0			(14.38 ± 0.05)	

(Continued on next page)

Table VIII-40 (continued)

Method	Ionic medium	<i>t</i> (°C)	pH range	log <sub>10</sub> <i>K</i>	Reference
$\text{Am}(\text{edta})^- + \text{H}^+ \rightleftharpoons \text{Am}(\text{Hedta})(\text{aq})$					
cix	1M NH <sub>4</sub> Cl	?	1–2.2	(1.94 ± 0.02)	[60MOS/KHA]
em	0.1 M KCl	25	1–3	(2.4 ± 0.2)	[67LEB/MAK]
$\text{Am}^{3+} + \text{edta}^{4-} + \text{OH}^- \rightleftharpoons \text{Am}(\text{edta})\text{OH}^{2-}$					
em	0.1 M KNO <sub>3</sub>	25	9–13	(19.98 ± 0.07)	[72SHA]

The results of [58FUG], [60MOS/KHA], [71ELE/ZAI], [71SHA], [71OLI/CHO] and [75KOR/PAT] are not considered in this review because of various shortcomings, which are discussed in detail in Appendix A.

The accepted values of [66STA], [67LEB/MAK], [69DEL/BAY] and [99CHE/CHO], summarised in Table VIII-41, have all been recalculated in this review (*cf.* Appendix A).

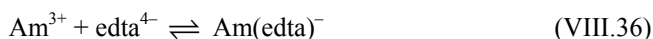
Table VIII-41: Accepted formation constants for the Am edta system to derive the selected values. Uncertainties have been estimated in this review.

Method	Ionic medium	<i>t</i> (°C)	pH range	log <sub>10</sub> <i>K</i>	Reference
$\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$					
dis	0.1 M NH <sub>4</sub> Cl	25	3.8–5.6	(17.08 ± 0.27) <sup>a</sup>	[66STA]
em	0.1 M KCl	25	1–3	(17.59 ± 0.43) <sup>a</sup>	[67LEB/MAK]
dis	0.30 m NaCl	25	2.4	(16.29 ± 0.29) <sup>b</sup>	[99CHE/CHO]
	1.0			(15.48 ± 0.24) <sup>b</sup>	
	2.0			(15.95 ± 0.28) <sup>b</sup>	
	3.0			(16.07 ± 0.26) <sup>b</sup>	
	4.0			(16.63 ± 0.31) <sup>b</sup>	
	5.0			(17.60 ± 0.38) <sup>b</sup>	
$\text{Am}(\text{edta})^- + \text{H}^+ \rightleftharpoons \text{Am}(\text{Hedta})(\text{aq})$					
em	0.1 M KCl	25	1–3	(2.20 ± 0.40) <sup>a</sup>	[67LEB/MAK]
$\text{Am}^{3+} + \text{Hedta}^{3-} \rightleftharpoons \text{Am}(\text{Hedta})(\text{aq})$					
sp	0.1 M NH <sub>4</sub> ClO <sub>4</sub>	25	1–2.1	(8.57 ± 0.30) <sup>a</sup>	[69DEL/BAY]

a: Experimental data re-evaluated in this review (see Appendix A).

b: Stability constants corrected for the complexation effects of Na(edta)<sup>−</sup>, AmCl<sup>2+</sup> and AmCl<sub>2</sub><sup>+</sup> (see Appendix A).

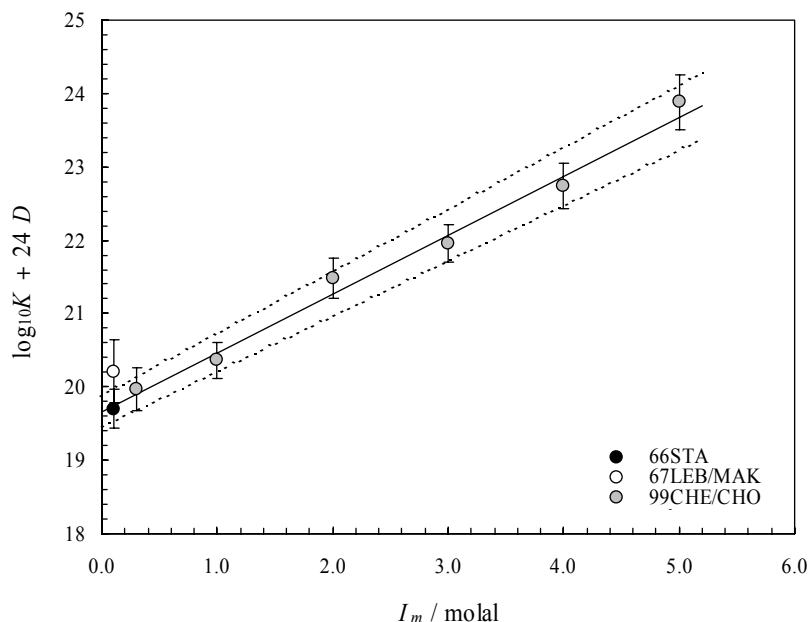
For the reaction:



the results of [66STA], [67LEB/MAK] and [99CHE/CHO] have been considered in the final data evaluation. Weighted least squares SIT regression analysis of equilibrium data from [99CHE/CHO] results in  $\log_{10} K_1^\circ (\text{VIII.36}) = (19.66 \pm 0.13)$  and  $\Delta\epsilon(\text{VIII.36}) = -(0.80 \pm 0.07)$  (Figure VIII-31). The SIT interaction coefficient allows an estimate of  $\epsilon(\text{Am}(\text{edta})^{-}, \text{Na}^{+}) = \Delta\epsilon(\text{VIII.36}) + \epsilon(\text{Am}^{3+}, \text{Cl}^{-}) + \epsilon(\text{edta}^{4-}, \text{Na}^{+}) = -(0.80 \pm 0.07) + (0.49 \pm 0.03) + (0.32 \pm 0.14) = (0.01 \pm 0.16)$ . If we assume that  $\epsilon(\text{Am}(\text{edta})^{-}, \text{Na}^{+}) \approx \epsilon(\text{Am}(\text{edta})^{-}, \text{K}^{+}) \approx \epsilon(\text{Am}(\text{edta})^{-}, \text{NH}_4^{+})$ , and  $\epsilon(\text{edta}^{4-}, \text{K}^{+}) \approx \epsilon(\text{edta}^{4-}, \text{NH}_4^{+})$ ,  $\Delta\epsilon(\text{VIII.36}) = -(1.55 \pm 0.25)$  is obtained for KCl and  $\text{NH}_4\text{Cl}$  media. Using this latter estimate and the re-evaluated values of [66STA] and [67LEB/MAK] according to Table VIII-41, the constants  $\log_{10} K_1^\circ (\text{VIII.36}) = (19.55 \pm 0.27)$  and  $\log_{10} K_1^\circ (\text{VIII.36}) = (20.06 \pm 0.43)$ , respectively, are obtained. A weighted mean of the values of [66STA], [67LEB/MAK] and [99CHE/CHO] extrapolated to  $I = 0$  gives the following selected value:

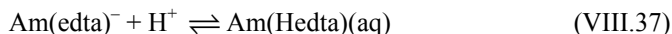
$$\log_{10} K_1^\circ (\text{VIII.36}) = (19.67 \pm 0.11).$$

Figure VIII-31: Weighted least squares SIT-regression plot of equilibrium data from [99CHE/CHO] for the formation of  $\text{Am}(\text{edta})^{-}$  according to Reaction (VIII.36). The results are  $\log_{10} K_1^\circ (\text{VIII.36}) = (19.66 \pm 0.13)$  and  $\Delta\epsilon(\text{VIII.36}) = -(0.80 \pm 0.07)$ . The data of [66STA] and [67LEB/MAK] are shown for comparison only.





For deriving the equilibrium constant of the reaction



the results of [67LEB/MAK] and [69DEL/BAY] as re-evaluated in this review (Table VIII-41) can be used. Assuming that  $\varepsilon(\text{Am}(\text{Hedta})(\text{aq}), \text{KCl}) = \varepsilon(\text{Am}(\text{Hedta})(\text{aq}), \text{NH}_4\text{ClO}_4) = 0$ , and  $\varepsilon(\text{Am}(\text{edta})^-, \text{K}^+) \approx \varepsilon(\text{Am}(\text{edta})^-, \text{Na}^+) = (0.01 \pm 0.16)$ , the value of [67LEB/MAK] extrapolated to  $I = 0$  is  $\log_{10} K^\circ (\text{VIII.37}) = (2.4 \pm 0.4)$ . Assuming that  $\varepsilon(\text{Hedta}^{3-}, \text{NH}_4^+) \approx \varepsilon(\text{Hedta}^{3-}, \text{K}^+) = (0.31 \pm 0.18)$ , the value of [69DEL/BAY] extrapolated to  $I = 0$  is  $\log_{10} K^\circ = (10.46 \pm 0.30)$ . Taking the first edta protonation constant  $\log_{10} K_1^\circ = (11.24 \pm 0.03)$  and  $\log_{10} K_1^\circ (\text{VIII.36}) = (19.67 \pm 0.11)$ , both selected in this review,  $\log_{10} K^\circ (\text{VIII.37}) = (2.03 \pm 0.32)$  is obtained from [69DEL/BAY]. A weighted mean of the values of [67LEB/MAK] and [69DEL/BAY] results in the selected value:

$$\log_{10} K^\circ (\text{VIII.37}) = (2.17 \pm 0.25).$$

Shalinets [72SHA] assumed, based on electromigration data, that a mixed hydroxo complex  $\text{Am}(\text{edta})(\text{OH})^{2-}$  is formed in strongly alkaline solutions (Table VIII-40). Although the data interpretation and the derived constant are not unreasonable, this review does not select a value based on this single study of uncertain accuracy (see Appendix A).

#### VIII.13.2.2 Am(V) edta complexes

Complex formation in the Am(V) edta system has been studied by only two groups of investigators. The experimental equilibrium data are summarised in Table VIII-42. In all cases, only one equilibrium,



has been proposed to interpret the experimental data. In all papers referred to in Table VIII-42, the pH scale has not been defined and the calibration of the pH meter is not described. The papers [78MOS/POZ] and [79MOS/POZ] report identical results obtained by a coprecipitation method. There, the dependence of the coprecipitation of actinides with iron(III) hydroxide on the concentration of various ligands has been studied, and the composition and stability of the complexes formed has been inferred from experimental distribution coefficients. In [79MOS/POZ4] “the methods of carrying out the experiments and calculations were similar to those described in the previous paper [78MOS/POZ]”.

Considering these very limited and poor studies, confirmation is needed concerning the stoichiometry of the complexes formed and the redox state of Am in these systems. Hence, no value is selected in this review.

Nikolaevskii *et al.* [74NIK/SHI] report that by preliminary experiments they established that in edta solutions Am(V) slowly changes into the trivalent state. The rate of reduction of 1 mM solution of Am(V) at 25°C with a concentration of edta of 5 mM is 2 to 3% per hour and depends little on the pH. This information is confirmed by [78MOS/POZ] who report that the Am(V) prepared for their studies was stable for about one hour. Thus, stability constants for the Am(V) edta system may only be needed for short-term experimental investigations, but they are of no importance in any long-term study.

Table VIII-42: Experimental equilibrium data for the Am(V) edta system. The uncertainties are given as reported in the references.

Method	Ionic medium	$t$ (°C)	pH range	$\log_{10}K$	Reference
$\text{AmO}_2^+ + \text{Hedta}^{3-} \rightleftharpoons \text{AmO}_2\text{Hedta}^{2-}$					
sp	0.1 M KNO <sub>3</sub>	25	2–7	$(4.88 \pm 0.05)$	[74NIK/SHI]
coprecip	0.1 M NH <sub>4</sub> Cl	$(20 \pm 2)$	$\approx 8.5$	$(4.73 \pm 0.11)$	[78MOS/POZ], [79MOS/POZ]
coprecip	0.1 M NH <sub>4</sub> Cl	r. t.	8.5	$(4.83 \pm 0.10)$	[79MOS/POZ4]
			$\neq \text{const}$	$(4.81 \pm 0.10)$	

r. t.: room temperature

### VIII.13.3 Enthalpy of americium edta complex formation

Two calorimetric studies [65FUG/CUN], [89RIZ/SUL] report the enthalpy of formation of Am(edta)<sup>−</sup> (Table VIII-43). The results of [89RIZ/SUL] are not credited in this review (*cf.* Appendix A). Fuger and Cunningham [65FUG/CUN] used AmCl<sub>3</sub> solutions in their experiments without correcting for the presence of  $\approx 4\%$  AmCl<sub>2</sub><sup>2+</sup>, as expected from the composition of the used solutions. Otherwise this study is reliable and the result is extrapolated to zero ionic strength by assuming  $\Delta\epsilon_L = (0 \pm 5) \cdot 10^{-3} \text{ kg} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ :  $\Delta_r H_m^\circ(\text{VIII.36}) = \Delta_r H_m(\text{VIII.36}) - \Delta z^2 D_L(I = 0.16) + RT^2 m \Delta\epsilon_L = -(19.5 \pm 1.0) + 24 \times 0.372 + (0 \pm 0.6) = -(10.6 \pm 1.2) \text{ kJ mol}^{-1}$ . Considering the ambiguity with respect to the effect of AmCl<sub>2</sub><sup>2+</sup>, this review increases the uncertainty of the selected value:

$$\Delta_r H_m^\circ(\text{VIII.36}) = -(10.6 \pm 2.0) \text{ kJ mol}^{-1}.$$

For temperature corrections at  $I = 0.1 \text{ M KCl}$  this review calculates  $\Delta_r H_m((\text{VIII.36}), 298.15 \text{ K}, I = 0.1\text{M}) = -(18.3 \pm 2.0) \text{ kJ} \cdot \text{mol}^{-1}$ . This leads to  $\Delta\log_{10}K = -(0.055 \pm 0.006)$  using the van't Hoff equation for a temperature correction from 20 to 25°C.

This selection yields:

$$\Delta_r H_m^\circ(\text{Am(edta)}^-) = -(2332.1 \pm 4.5) \text{ kJ} \cdot \text{mol}^{-1}.$$

Table VIII-43: Experimental enthalpy data for the Am edta system. The uncertainties are given as reported in the references (it refers to a 95% confidence interval in [\[65FUG/CUN\]](#)). If the ionic medium is shown in parenthesis, the contribution of the reacting species to the total ionic strength has been considered.

Method	Ionic medium	$t$ (°C)	$\Delta_t H_m$ kJ mol <sup>-1</sup>	Reference
$\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$				
cal	0.16 M (KCl)	25	$-(19.5 \pm 1.0)$	<a href="#">[65FUG/CUN]</a>
cal	0.50 M NaClO <sub>4</sub>	25	$(23.9 \pm 1.0)$ or $-(23.9 \pm 1.0)$ ?	<a href="#">[89RIZ/SUL]</a>



## Chapter IX

# Discussion of data selection for isosaccharinic acid (isa) compounds and complexes

### IX.1 Introduction

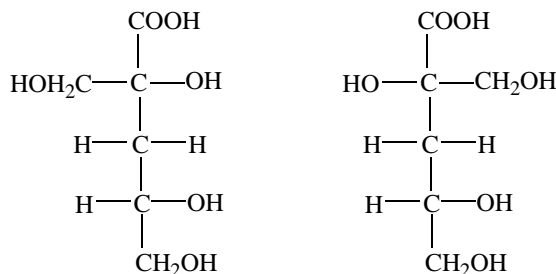
Isosaccharinic acid is considered to be one of the most important products of cellulose degradation under alkaline conditions [\[89CRO/EWA\]](#), [\[92GRE/MOR\]](#), [\[93GRE/HAR\]](#), [\[93MOR\]](#), [\[94GRE/HUR\]](#), [\[94GRE/LIN\]](#), [\[95GRE/HOL\]](#), [\[97HAG\]](#), [\[99PAV\]](#), [\[2000ASK/CHA\]](#), [\[2000VER\]](#), [\[2002TIT/WIE\]](#). As a polyhydroxycarboxylic acid, isosaccharinic acid forms complexes with metal ions in solutions of wide pH, as well as participates in redox reactions involving metal ions. A number of studies revealed a strong influence of isosaccharinic acid on the solubility and sorption, and thus on the mobility of radionuclides [\[89CRO/EWA\]](#), [\[92GRE/MOR\]](#), [\[93GRE/HAR\]](#), [\[93MOR\]](#), [\[94GRE/HUR\]](#), [\[94GRE/LIN\]](#), [\[95GRE/HOL\]](#), [\[97GRE/HUR\]](#), [\[2000VER\]](#), [\[2002TIT/WIE\]](#). It is noted by the present review that the solubility of radionuclides in the presence of isosaccharinic acid reported in the earlier literature is not strictly thermodynamic solubilities. Instead, it was the measured maximum concentration of an element over a solubility-limiting phase [\[97GRE/HUR\]](#). The solid phase was seldom well identified and the final oxidation state of the element in the solution was uncertain. A more detailed discussion of this earlier literature is given in Section IX.12.

Information about the thermodynamics of isosaccharinic acid and its complexes and compounds is scarce. The first study reporting the constants of protonation and metal complexation was published in 1997 [\[97HAG\]](#). Since then, approximately thirty publications on the protonation of isosaccharinate and its complexes and compounds have become available in the literature. This review covers the publications available in the literature up to the year of 2004. In addition to the review of already published information, the authors of some of these publications have been contacted to receive additional and more up-to-date information about ongoing projects.

## IX.2 Isosaccharinic acid

Isosaccharinic acid, or 2,4,5-trihydroxy-2-hydroxymethyl-pentonic acid, has two diastereomers: the erythro- and threo-forms, also called  $\alpha$ -isosaccharinic acid and  $\beta$ -isosaccharinic acid, respectively. Both diastereomers are shown in Figure IX-1. Approximately equal amounts of  $\alpha$ -isosaccharinic acid and  $\beta$ -isosaccharinic acid are generated in the degradation of cellulose along with minor amounts of small organic acids. However, in the synthesis of calcium isosaccharinate as described by [63WHI/BEM], only the  $\alpha$ -form of isosaccharinic acid is produced. In the present review, only the thermodynamics concerning  $\alpha$ -isosaccharinic acid, denoted as isa, is discussed.

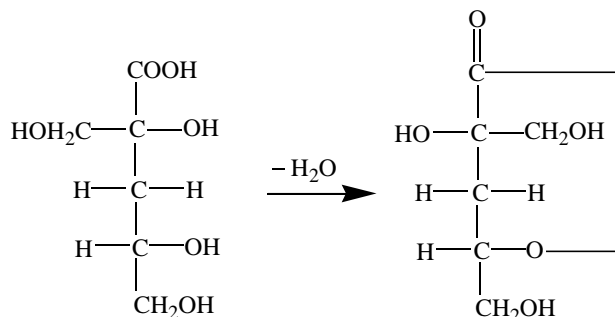
Figure IX-1: (a)  $\alpha$ -isosaccharinic acid      (b)  $\beta$ -isosaccharinic acid.



Isa contains one carboxyl group and four aliphatic hydroxyl groups. It could form complexes with metal ions *via* the interactions with the carboxylate group in acidic solutions or, with both the carboxylate and the hydroxyl group(s) if the acidity is low or the metal ion has higher charge.

Like other polyhydroxycarboxylic acids such as gluconic acid, isa undergoes dehydration to form a lactone as shown in Figure IX-2. The lactonisation reaction is catalysed by the proton. Because the lactonisation reaction affects the speciation of isa and the determination of the protonation constant in acidic solutions, more discussions concerning lactonisation are provided in the next section.

Figure IX-2: Dehydration of  $\alpha$ -isosaccharinic acid to form  $\alpha$ -isosaccharinate-1,4-lactone.



No thermodynamic data on crystalline isosaccharinic acid is identified in the literature by this review.

### IX.3 Protonation of isosaccharinate

It is noteworthy to point out three aspects concerning the protonation of isosaccharinate:

- The deprotonation of the carboxyl group is expected to occur in a pH range comparable to other polyhydroxy-carboxylic acids like gluconic or glycolic acid, but in a pH range lower than simple monocarboxylate such as acetate because the adjacent hydroxyl group(s) of isa could form hydrogen bonding with the deprotonated carboxylate group and stabilise the deprotonated form of isa, *i.e.*,  $\text{isa}^-$ .
- In the absence of interactions with metal ions, the deprotonation of the hydroxyl groups requires extremely high pH and the constants may not be accurately measured in aqueous solution. Interactions with metal ions, especially the ions with higher positive charges, could facilitate the deprotonation of the hydroxyl groups and result in the formation of metal isa chelate complexes.
- The lactonisation reaction is coupled with the protonation and affects the speciation of isa and the determination of the protonation constant in acidic solutions.

In this review, the fully protonated isosaccharinic acid is denoted as  $\text{Hisa}(\text{aq})$  and its lactone form is denoted as  $\text{isa}_\text{L}(\text{aq})$ . When forming a 1:1 complex with a metal cation ( $\text{M}^{m+}$ ) in which  $n$  hydroxyl groups of  $\text{isa}^-$  are deprotonated, the complex is denoted as  $\text{M}(\text{isa}_{-n\text{H}})^{(m-n-1)+}$ .

Since the reactions of lactonisation and protonation of isosaccharinic acid are coupled, they need to be discussed together in this section. The lactonisation and the carboxylate protonation are represented by Reactions (IX.1) and (IX.2), respectively.



The lactonisation reaction (IX.1) is catalysed by protons and becomes important in acidic solutions. It complicates the determination of the protonation constant of isa in several ways. First, the total concentration of isosaccharinic acid in acidic solutions should be expressed as  $\{[\text{isa}^-] + [\text{Hisa}(\text{aq})] + [\text{isa}_\text{L}(\text{aq})]\}$ . Secondly, the lactonisation reaction “regulates” the concentration of  $\text{Hisa}(\text{aq})$  if the time is sufficient for both reactions to achieve equilibrium, since  $K(\text{IX.1}) = [\text{isa}_\text{L}(\text{aq})]/[\text{Hisa}(\text{aq})]$ . However, because the lactonisation involves ring closure and the formation and breaking of chemical bonds (see Figure IX-2), it is kinetically slow so that its effect on the concentration of  $\text{Hisa}(\text{aq})$  may be difficult to quantify. As a result, it is important to evaluate the lactonisation of isa, both thermodynamically and kinetically, in order to understand the protonation of isa and accurately determine the protonation constant.

### IX.3.1 Lactonisation of isosaccharinic acid

Only two studies have reported the lactonisation constant of isa [2003RAI/HES], [2004EKB/EKB]. Rai *et al.* [2003RAI/HES] obtained a value of  $(0.37 \pm 0.07)$  for  $\log_{10} K$  (IX.1) by fitting the solubility data of  $\text{Ca(isa)}_2(\text{s})$  with a protonation constant  $\log_{10} K$  (IX.2) = 3.27 from [2003CHO/RAI]. Ekberg *et al.* [2004EKB/EKB] used ion chromatography to selectively detect  $\text{isa}^-$  to study the equilibrium and the transformation rates of lactonisation. The study of [2004EKB/EKB] appears to be well designed and conducted. The authors obtained two values of  $\log_{10} K$  (IX.1) from the equilibrium data and the kinetic data, respectively.

Calculation of  $\log_{10} K$  (IX.1) =  $\log_{10}([\text{isa}_\text{L}(\text{aq})]/[\text{Hisa}(\text{aq})])$  from the equilibrium data requires the value of  $\log_{10} K$  (IX.2) =  $\log_{10}\{[\text{Hisa}(\text{aq})]/([\text{H}^+][\text{isa}^-])\}$  as well as the  $[\text{H}^+]$ . However, as described in [2004EKB/EKB], the  $\text{isa}^-$  detected by ion chromatography is actually the sum of  $\text{isa}^-$  and  $\text{Hisa}(\text{aq})$  in the analysed sample, as  $\text{Hisa}(\text{aq})$  is deprotonated in the suppressor. Consequently, the authors used a value of  $\log_{10} K$  (IX.2) =  $(3.86 \pm 0.05)$ , extrapolated from the data in [2003EKB/EKB], and tentatively determined  $\log_{10} K$  (IX.1) =  $(0.84 \pm 0.04)$ . Obviously, the reliability of  $\log_{10} K$  (IX.1) from [2004EKB/EKB] depends on that of  $\log_{10} K$  (IX.2) from [2003EKB/EKB]. According to the authors, the uncertainty in  $\log_{10} K$  (IX.2) (even at the level of  $\pm 0.1$ ) would not noticeably change the value of  $\log_{10} K$  (IX.1).

The transformation rates from  $\text{Hisa}(\text{aq})$  to  $\text{isa}_\text{L}(\text{aq})$  (forward) and from  $\text{isa}_\text{L}(\text{aq})$  to  $\text{Hisa}(\text{aq})$  (backward) are also calculated from the ion chromatographic data [2004EKB/EKB]. The rate constants are:  $k(\text{IX.1}, \text{forward}) = (4.85 \pm 0.03) \times 10^{-3} \text{ min}^{-1}$  and  $k(\text{IX.1}, \text{backward}) = (7.35 \pm 0.04) \times 10^{-4} \text{ min}^{-1}$ . These results show that the lactonisation reaction is very slow compared to simple protonation or deprotonation reactions. From these two kinetic constants, an independent value for  $\log_{10} K$  (IX.1) was calculated to be  $\log_{10} K$  (IX.1) =  $(0.820 \pm 0.005)$  [2004EKB/EKB]. This value is in excellent agreement with the value obtained from the equilibrium data. Both values from [2004EKB/EKB] are listed in Table IX-1.

No value for the lactonisation constant is selected by this review. Additional studies are needed to reliably evaluate the lactonisation of isa.

Table IX-1: Lactonisation constant of isosaccharinic acid in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10} K$	Reference
$\text{Hisa}(\text{aq}) \rightleftharpoons \text{isa}_\text{L}(\text{aq}) + \text{H}_2\text{O}(\text{l})$				
sol	$I \rightarrow 0$	23	$(0.37 \pm 0.07)$	[2003RAI/HES]
chr	$I = 0.1 \text{ M NaClO}_4$	23	$(0.84 \pm 0.04)$	[2004EKB/EKB]
chr	$I = 0.1 \text{ M NaClO}_4$	23	$(0.820 \pm 0.005)$	[2004EKB/EKB]



### IX.3.2 Protonation of isosaccharinate

In contrast to the other ligands covered by this review, *i.e.*, oxalate, citrate and edta, where information about protonation constants is abundant, data on the protonation constant of isa (Reaction (IX.2)) is very scarce. The protonation constants of isa reported in the literature are summarised in Table IX-2.

Table IX-2: Protonation constants of isosaccharinic acid in the literature.

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{H}^+ + \text{isa}^- \rightleftharpoons \text{Hisa}(\text{aq})$				
pot	<i>I</i> = 0.01 M NaClO <sub>4</sub>	25	3.75	<a href="#">[97HAG]</a>
	<i>I</i> = 0.1 M NaClO <sub>4</sub>	25	3.83	
em	6×10 <sup>-4</sup> - 4×10 <sup>-3</sup> M, mixed	?	4.02	<a href="#">[98MOT/CHA]</a>
em	<i>I</i> = ? (low), mixed	?	4.05	<a href="#">[98MOT/RIC]</a>
sol	<i>I</i> → 0	23	4.46	<a href="#">[98RAI/RAO2]</a>
em	<i>I</i> → 0	25	3.87	<a href="#">[2002HAG/DUK]</a>
pot	<i>I</i> = 0.1 M KCl → 0	25	3.98	<a href="#">[2002HAG/DUK]</a>
NMR	<i>I</i> = 0, Na(isa)	22.0	(3.27 ± 0.01)	<a href="#">[2003CHO/RAI]</a>
NMR	<i>I</i> = 0, Ca(isa) <sub>2</sub>	22.0	(3.36 ± 0.02)	<a href="#">[2003CHO/RAI]</a>
pot	<i>I</i> = 1.0 M NaClO <sub>4</sub>	22.8	(3.78 ± 0.05)	<a href="#">[2003EKB/EKB]</a>
		34.5	(3.64 ± 0.02)	
		44.2	(3.53 ± 0.03)	
pot	<i>I</i> = 1.0 M NaClO <sub>4</sub>	25	(3.65 ± 0.05)	<a href="#">[2004RAO/GAR]</a>

Because the protonation reaction (IX.2) is coupled with the lactonisation reaction (IX.1), determination of *K*(IX.2) requires taking into consideration the effect of lactonisation. If appropriate techniques and experimental conditions are selected to allow sufficient time for both reactions to achieve equilibrium, both *K*(IX.1) and *K*(IX.2) may be evaluated simultaneously. However, if equilibria are achieved but the experimental techniques do not allow to distinguish between Hisa(aq) and isa<sub>L</sub>(aq), a “composite” protonation constant *K*(IX.3) is determined according to the reaction:



where [Hisa(aq)\*] = [Hisa(aq)] + [isa<sub>L</sub>(aq)] and *K*(IX.3) = *K*(IX.2) × (1 + *K*(IX.1)). The “composite” protonation constant *K*(IX.3) has a higher value than the “intrinsic” protonation constant *K*(IX.2). The concept of a “composite” constant for isa is similar to that for carbonic acid discussed by [\[96STU/MOR\]](#) p. 150-157.

However, the conditions of complete equilibrium of both Reactions (IX.1) and (IX.2) are usually difficult to meet, considering the slow kinetics of lactonisation.

As an alternative and approximate approach, the experiments may be conducted at a fast rate (*i.e.* completion of an experiment in the order of one hour) so that the concentration of  $\text{isa}_L(\text{aq})$  could be considered unchanged during the experiments. If the fast experiment (of about one hour) is conducted from alkaline or neutral to acidic pH, the  $[\text{isa}_L(\text{aq})]$  might be ignored and the mass balance of isosaccharinic acid in solution is:  $C_{\text{total}} \approx [\text{isa}^-] + [\text{Hisa}(\text{aq})]$ , where  $C_{\text{total}}$  is the total concentration of isosaccharinic acid. In this case the determined constant is close to the “intrinsic” protonation constant  $K(\text{IX.2})$ . If the fast experiment (of about one hour) is conducted from acidic to neutral or alkaline pH, the concentration of  $\text{isa}_L(\text{aq})$  can still be assumed unchanged during the experiments but should be known from independent measurements. In this case, the mass balance of isosaccharinic acid in solution should be expressed as:  $C_{\text{total}} = [\text{isa}^-] + [\text{Hisa}(\text{aq})] + [\text{isa}_L(\text{aq})]$ . If the experimental techniques do not allow to distinguish between  $\text{Hisa}(\text{aq})$  and  $\text{isa}_L(\text{aq})$  the protonation constant determined is somewhere in between the “intrinsic” protonation constant  $K(\text{IX.2})$  and the “composite” protonation constant  $K(\text{IX.3})$ .

In reviewing the data on the protonation of isa in the literature, it is found that there is a general lack of consideration of the effect of lactonisation in most of the studies (Table IX-2). The data from these studies are discussed individually as follows.

Protonation constants at two different ionic strengths (0.1 and 0.01 M  $\text{NaClO}_4$ ) derived from potentiometric titrations have been reported by [97HAG]. The results in this report are presented as two numbers without uncertainty estimates and as a plot of  $\text{p}K_a$  versus the degree of neutralisation. In the present review, the constants have been re-evaluated from this plot and extrapolated to zero ionic strength using the Debye-Hückel term of the SIT equation. The result is  $\log_{10} K^\circ(\text{IX.2}) = (4.0 \pm 0.2)$ .

The experimental information given by [97HAG] is rather limited and possible effects of the ring closure reaction of isa at low pH on the potentiometric titration data is not mentioned. The titrations were carried out by adding standardised NaOH to a solution of isosaccharinic acid, starting at pH 3, but no information is given in [97HAG] about titration times. Hence, the derived protonation constant is assumed by this review to represent something in between the “intrinsic” protonation constant  $K(\text{IX.2})$  and the “composite” protonation constant  $K(\text{IX.3})$ .

Estimates of the isa protonation constant have been reported by [98MOT/CHA] and [98MOT/RIC]. These estimates have been derived from electrophoretic mobility data measured by capillary electrophoresis. The values given by [98MOT/CHA] and [98MOT/RIC], 4.02 and 4.05, respectively (no uncertainty estimates given by the authors), seem to be in good agreement with the potentiometric data. However, the electrophoretic data have been measured at low but varying ionic strength, and no correction has been made for these ionic strength effects by deriving the protonation constants from electrophoretic mobility data. Although the ionic strength effect is estimated to be not larger than 0.1  $\log_{10}$ -units, these data are not used

in the present review. However, they are within the uncertainty range of the potentiometric data, and a direct comparison of the reported values for isa, glycolate and lactate corroborates the assumption that the protonation constant of isa is very close to other polyhydroxy-carboxylic acids (3.8 - 3.9).

The value of 4.47 (no uncertainty estimate given by the authors) by [\[98RAI/RAO2\]](#) is exceptionally high compared with constants of other polyhydroxy-carboxylic acids. It was obtained by fitting Ca - isa solubility data under specific model assumptions including the formation of  $\text{Ca(isa)}_2(\text{aq})$ . A more recent study by the same group [\[2003RAI/HES\]](#) revised that model and excluded  $\text{Ca(isa)}_2(\text{aq})$ . The value of 4.47 is shown to be erroneous in [\[2003RAI/HES\]](#), and is rejected by the present review.

Hagberg *et al.* [\[2002HAG/DUK\]](#) determined the protonation constant by potentiometry (pH 2.5 – 5) and capillary zone electrophoresis. The values of  $\log_{10} K^\circ$  (IX.2) obtained by the two methods (3.87 by electrophoresis and 3.98 by potentiometry) differ by about 0.1, but are both comparable to the values reported by [\[97HAG\]](#), [\[98MOT/CHA\]](#) and [\[98MOT/RIC\]](#). The effect of lactonisation on the measurement of  $\log_{10} K^\circ$  (IX.2) was not considered in [\[2002HAG/DUK\]](#). The titrations were carried out in both directions, by adding HCl to solutions of  $\text{Na(isa)}$ , and by adding NaOH to solutions of isosaccharinic acid, but no experimental details nor any data are given by [\[2002HAG/DUK\]](#), only a single value extrapolated to zero ionic strength is reported. The migration time in the electrophoresis experiments varied with pH, up to 25 minutes at pH 5.1. However, in all cases the reaction times were probably too short to reach complete equilibrium of both Reactions (IX.1) and (IX.2). Thus, the protonation constants derived by [\[2002HAG/DUK\]](#) are assumed by this review to represent something in between the “intrinsic” protonation constant  $K(\text{IX.2})$  and the “composite” protonation constant  $K(\text{IX.3})$ .

Cho *et al.* [\[2003CHO/RAI\]](#) studied the speciation of isosaccharinic acid in solution over a wide pH (1 – 13) using  $^1\text{H}$  and  $^{13}\text{C}$  NMR. Six lines were observed in the  $^{13}\text{C}$  NMR spectra of all solutions (pH = 1 – 13), corresponding to the average chemical shifts ( $\delta$ ) of the six carbon atoms of  $\text{Hisa}(\text{aq})$  and  $\text{isa}^-$  in fast exchange. In solutions with pH < 4, six additional lines appeared, that were assigned to  $\text{isa}_\text{L}(\text{aq})$ . The NMR data showed that sharp changes in the average  $\delta$  of  $\text{Hisa}(\text{aq})$  and  $\text{isa}^-$  occurred as the pH was increased from 2 to 5.3. When pH  $\geq$  5.3, no further change in  $\delta$  was observed, indicating  $\text{Hisa}(\text{aq})$  was completely deprotonated. From these data, the protonation constant of isa is calculated and extrapolated to  $I = 0$  by the Davies equation. The values of  $\log_{10} K^\circ$  (IX.2) obtained from the solutions of sodium or calcium isosaccharinic acid are slightly different ( $3.27 \pm 0.01$ ) for sodium and ( $3.36 \pm 0.02$ ) for calcium media), but both are significantly lower than the values obtained by potentiometry [\[97HAG\]](#), [\[2002HAG/DUK\]](#), [\[2003EKB/EKB\]](#), [\[2004RAO/GAR\]](#) or electrophoresis [\[98MOT/CHA\]](#), [\[98MOT/RIC\]](#), [\[2002HAG/DUK\]](#). The values derived from NMR data by [\[2003CHO/RAI\]](#) may represent the “intrinsic” protonation constant  $K(\text{IX.2})$  where

the lactonisation effect is taken care of. However, this assumption needs to be confirmed by other experimental methods before a value can be selected.

The values of  $\log_{10} K$  (IX.2) at  $I = 1.0$  NaClO<sub>4</sub> and three temperatures (22.8, 34.5 and 44.2°C) were determined by potentiometry in [2003EKB/EKB]. The authors were aware of the transformation of isosaccharinic acid into lactone and its effect on the determination of the protonation constant by titration potentiometry. Instead of allowing the protonation and lactonisation reactions to achieve equilibrium in sufficient time, the authors took advantage of the difference in the rate of the reactions. Based on the information in the literature that the transformation to lactone occurred at approximately pH 8 (which is questionable according to the present review) and the transformation was quite slow with a reaction time similar to that of an analogous polyhydroxycarboxylic acid (~ 16 hours), (note that according to [2004EKB/EKB] a 90% transformation to *isa<sub>L</sub>* takes ~ 7 hours based on a half-life of  $t_{1/2} = 122$  minutes), the authors conducted the titrations from high pH to low pH (~ 3) using 0.1 M HCl as the titrant and assumed that the *Hisa*(aq) form would prevail during the titrations which lasted for about 1.5 hours. Thus, in the data treatment, the mass balance of isosaccharinic acid was expressed as  $C_{\text{total}} = [\text{isa}^-] + [\text{Hisa}(\text{aq})]$ , neglecting the presence of *isa<sub>L</sub>*(aq). This is the alternative and approximate method to determine the protonation constant of isosaccharinate previously mentioned in this review. The  $\log_{10} K$  (IX.2) was calculated to be  $(3.78 \pm 0.05)$  (22.8°C),  $(3.64 \pm 0.02)$  (34.5°C), and  $(3.53 \pm 0.03)$  (44.2°C), respectively. These values appear to be comparable with the other values in Table IX-2 except those by NMR. However, it should be pointed out by this review that the assumption of the transformation to lactone to occur at pH 8 seems incorrect, though the calculated results from [2003EKB/EKB] were not affected by this assumption. The NMR data indicate that such transformation probably occur at and below pH 4 - 5. The value  $\log_{10} K = (3.78 \pm 0.05)$  at 22.8°C has been extrapolated to zero ionic strength in this review using  $\Delta\epsilon = -(0.07 \pm 0.10)$  in analogy with the value derived for the reaction  $\text{Hox}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{ox}(\text{aq})$  in NaClO<sub>4</sub> (*cf.* Section VI.3.3) resulting in  $\log_{10} K^\circ = (4.10 \pm 0.10)$ .

Rao *et al.* [2004RAO/GAR] determined a value of  $\log_{10} K$  (IX.2) at 25°C in  $I = 1.0$  M NaClO<sub>4</sub> by potentiometry. The titrations have been carried out in the pH region 2.5 to 5.0 in both directions using NaOH and HClO<sub>4</sub> as titrant, and a common value  $\log_{10} K$  (IX.2) =  $(3.65 \pm 0.05)$  has been derived by the authors from both titrations. This value is extrapolated to zero ionic strength in this review using  $\Delta\epsilon = -(0.07 \pm 0.10)$  in analogy with the value derived for the reaction  $\text{Hox}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{ox}(\text{aq})$  in NaClO<sub>4</sub> (*cf.* Section VI.3.3) resulting in  $\log_{10} K^\circ = (3.97 \pm 0.10)$ . The titration experiments and the subsequent data evaluation are considered reliable by this review. However, the two reactions (IX.1) and (IX.2) were not allowed to achieve equilibrium, and hence, the protonation constant is assumed to represent something in between the “intrinsic” protonation constant  $K(\text{IX.2})$  and the “composite” protonation constant  $K(\text{IX.3})$ .

Considering the ambiguities of the lactonisation constant  $K(\text{IX.1})$  (cf. Section IX.3.1) and the need of confirmation of the “intrinsic” protonation constant  $K(\text{IX.2})$  reported in [2003CHO/RAI], this review selects a “composite” protonation constant:

$$\log_{10} K^\circ (\text{IX.3}) = (4.0 \pm 0.5)$$

with an enlarged uncertainty to cover the whole range of expectation. This value is recommended as a first approximation to be applied in (geo)chemical systems with equilibrium times of several days to geological time scales.

### IX.3.3 Enthalpy and entropy of protonation of isosaccharinate

The enthalpy of protonation of isa was determined by fitting the protonation constants at variable temperatures (22 – 44°C) with the van’t Hoff equation [2003EKB/EKB] and by direct calorimetric titrations at 25°C [2004RAO/GAR]. The entropy of protonation of isa was also obtained in both studies. The values of  $\Delta_r H_m$  (IX.2) and  $\Delta_r S_m$  (IX.2) are  $-(21.51 \pm 1.50) \text{ kJ}\cdot\text{mol}^{-1}$  and  $(2.13 \pm 4.19) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  at 22 – 44°C [2003EKB/EKB], and  $-(7.94 \pm 1.50) \text{ kJ}\cdot\text{mol}^{-1}$  and  $(43 \pm 1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  at 25°C [2004RAO/GAR]. Both studies show that the protonation of isa at 25°C is exothermic, but the values of enthalpy differ significantly. Though the enthalpy and entropy of protonation of isa from [2004RAO/GAR] appear to be more consistent with the corresponding values for other  $\alpha$ -hydroxycarboxylates ( $\Delta_r H_m$  (IX.2)  $\approx -2 \text{ kJ}\cdot\text{mol}^{-1}$  for hydroxyacetic and 2-hydroxy-2-methylpropanoic acids,  $\Delta_r S_m$  (IX.2)  $\approx 70 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for hydroxyacetic and 2-hydroxy-propanoic acids [77MAR/SMI]), additional studies are needed for reliable evaluation. Accordingly, no values of enthalpy or entropy of protonation of isa are selected by this review.

## IX.4 Alkali metal isa compounds and complexes

The structure of sodium isosaccharinate,  $\text{Na(isa)}\cdot\text{H}_2\text{O}$ , was determined by single crystal X-ray diffraction [2004BON/MOO]. It crystallises in the monoclinic space group  $P2_1$  (#4) with cell parameters  $a = 9.2267(11) \text{ \AA}$ ,  $b = 5.0765(6) \text{ \AA}$ ,  $c = 9.7435(11) \text{ \AA}$ ,  $\beta = 103.304(2)^\circ$ ,  $V = 444.13(9) \text{ \AA}^3$ ,  $Z = 2$ . The structure of sodium isosaccharinate consists of  $\text{isa}^-$  anions arranged in layers parallel to the  $bc$  plane. An extended network of  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds links the  $\text{isa}^-$  anion and the crystal water molecules. Each sodium atom is coordinated by four oxygen atoms belonging to four different  $\text{isa}^-$  anions and by one water molecule. The resulting “ $\text{NaO}_5$ ” polyhedra are linked by sharing common corners in zigzag chains running parallel to the  $b$ -axis [2004BON/MOO].

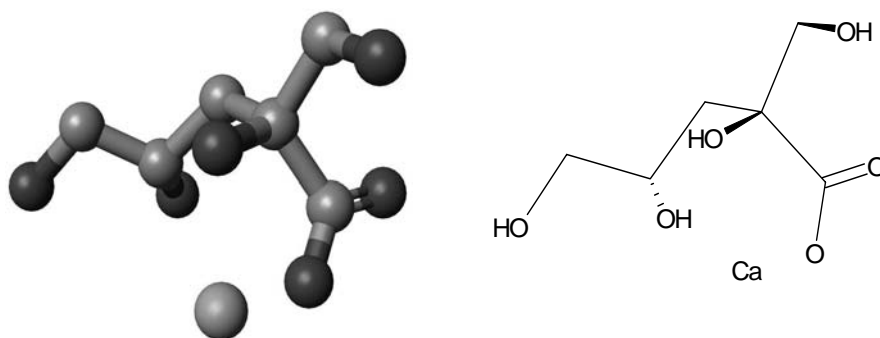
As indicated in [2004BON/MOO], in addition to the crystal structure the solubility of  $\text{Na(isa)}\cdot\text{H}_2\text{O}$  has been determined by the authors. In the pH range of the measurements (pH 4.5 – 10) the rather high solubility of  $\text{Na(isa)}\cdot\text{H}_2\text{O}$ , 1.7 – 1.9 M, has been found to be independent of pH (Bontchev, personal communication).

No thermodynamic data on alkali metal isa compounds or complexes are identified in the literature by this review.

### IX.5 Alkaline earth metal isa compounds and complexes

The crystal and molecular structures of calcium  $\alpha$ -isosaccharinate,  $\text{Ca(isa)}_2(\text{cr})$  [68NOR/WER], and the isomorphous strontium  $\alpha$ -isosaccharinate,  $\text{Sr(isa)}_2(\text{cr})$  [69WER/NOR], have been determined by single crystal X-ray diffraction. The molecular structure of Ca isa in the solid  $\text{Ca(isa)}_2(\text{cr})$  is shown in Figure IX-3.

Figure IX-3: Two representations of the calcium  $\alpha$ -isosaccharinate structure in the solid  $\text{Ca(isa)}_2(\text{cr})$  [68NOR/WER].



However, except for calcium, no thermodynamic data on the isa compounds or complexes with alkaline earth metals are identified in the literature by this review.

The  $\text{Ca(II)}$  - isa system has been investigated independently by two groups and their results have been published recently: [98RAI/RAO2], [2003RAI/HES] and [99LOO/GLA], [99VER/GLA], [2000VER], [2004LOO/GLA]. Both groups studied the solubility of the sparingly soluble compound  $\text{Ca(isa)}_2(\text{cr})$  over a wide range of pH and isa concentration. The study of  $\text{Ca(isa)}_2(\text{cr})$  solubility was conducted by [98RAI/RAO2] and [2003RAI/HES] in a wide pH range from very acidic ( $\text{pH} \approx 1 - 2$ ) to strongly basic (up to 1 m NaOH). Van Loon *et al.* [99LOO/GLA] studied the  $\text{Ca(isa)}_2(\text{cr})$  solubility at near neutral pH (6 – 8) while [99VER/GLA] and [2000VER] put special emphasis on the solubility behaviour in the alkaline region beyond pH 12, in order to evaluate the formation of aqueous  $\text{Ca(II)}$  - isa complexes. There is considerable overlap in the parameter space of the studies from the two groups and the agreement of experimental solubility data is excellent in this range. This considerable overlap in the parameter space and the agreement of the obtained solubility data enabled this review to select equilibrium constants as discussed in the following.

Rai and co-workers [98RAI/RAO2], [2003RAI/HES] employed the Pitzer formalism in their fitting procedures despite the fact that all their data had been measured at very low ionic strength. [99LOO/GLA], [99VER/GLA], [2000VER] and [2004LOO/GLA] used the Davies equation in their fitting procedures. [2004LOO/GLA] studied the Ca(II) - isa complexation by two independent methods: ion-exchange and potentiometry with a Ca-selective electrode. The solubility constants of Ca(isa)<sub>2</sub>(s) and the stability constants of Ca(II) - isa complexes in the literature are summarised in Table IX-3 and Table IX-4.

Table IX-3: Solubility constants of calcium isosaccharinate compounds in the literature.

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K<sub>s</sub></i>	Reference
$\text{Ca(isa)}_2(\text{cr}) + 2 \text{H}^+ \rightleftharpoons \text{Ca}^{2+} + 2 \text{Hisa}(\text{aq})$				
sol	$I \rightarrow 0$	23	1.30	[98RAI/RAO2]
$\text{Ca(isa)}_2(\text{cr}) \rightleftharpoons \text{Ca(isa)}_2(\text{aq})$				
sol	$I \rightarrow 0$	23	- 2.22	[98RAI/RAO2]
$\text{Ca(isa)}_2(\text{cr}) \rightleftharpoons \text{Ca}^{2+} + 2 \text{isa}^-$				
sol	$I \rightarrow 0$	(20 ± 1)	– (6.22 ± 0.03)	[99LOO/GLA] <sup>a</sup>
		25	– 6.14	
		2.6	– 7.10	
		7.8	– 6.77	
		10	– 6.51	
		12.7	– 6.54	
		15.7	– 6.35	
		20.3	– 6.21	
		25.8	– 6.15	
		30.4	– 5.96	
		36	– 5.85	
		42	– 5.77	
		50.4	– 5.64	
sol	$I \rightarrow 0$	(25 ± 2)	– (6.36 ± 0.10)	[99VER/GLA], [2000VER]
sol	$I \rightarrow 0$	23	– (6.26 ± 0.07)	[2003RAI/HES]

a: The solubility products reported here were calculated in [99LOO/GLA] ignoring the Ca(isa)<sup>+</sup> complex. If this complexation reaction is taken into account with an estimated value log<sub>10</sub> *K*<sup>o</sup> = 1.7 a solubility product log<sub>10</sub> *K<sub>s,0</sub>* = – (6.53 ± 0.02) at *I* = 0 and (20 ± 1)°C is reported by [99LOO/GLA]. The uncertainty of this value should be increased to ± 0.10 according to [2004LOO/GLA].

Table IX-4: Stability constants of calcium isosaccharinate complexes in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Ca}^{2+} + \text{isa}^- \rightleftharpoons \text{Ca(isa)}^+$				
sol	$I \rightarrow 0$	23	$(1.44 \pm 0.07)$	[2003RAI/HES]
ix	$I \rightarrow 0$	$(22 \pm 1)$	$(1.8 \pm 0.1)$	[2004LOO/GLA]
pot, ise-Ca	$I \rightarrow 0$	$(22 \pm 1)$	$(1.78 \pm 0.04)$	[2004LOO/GLA]
$\text{Ca}^{2+} + 2 \text{isa}^- \rightleftharpoons \text{Ca(isa)}_2(\text{aq})$				
sol	$I \rightarrow 0$	23	5.4	[98RAI/RAO2]
$\text{Ca}^{2+} + \text{isa}^- \rightleftharpoons \text{Ca(isa}_\text{H})(\text{aq}) + \text{H}^+$				
sol	$I \rightarrow 0$	$(25 \pm 2)$	$-(10.4 \pm 0.2)$	[99VER/GLA], [2000VER]

The speciation models proposed by the two groups for interpretation of their solubility data are different. Rai *et al.* [98RAI/RAO2] described their solubility data by two equilibria:



Equation (IX.4) accounts for the solubility of  $\text{Ca(isa)}_2(\text{cr})$  at  $2 < \text{pH} < 4$ , whereas Eq. (IX.5) describes the pH independent solubility at  $4 < \text{pH} < 11$ . Combining the isa protonation reaction, Eq. (IX.2), the two equilibria can be rewritten as:



The stability constant derived by [98RAI/RAO2] for the Ca - isa 1:2 complex,  $\log_{10} \beta_2^\circ$  (IX.7) = 5.40, is exceptionally high for the coordination of two single carboxyl groups to Ca(II). This value was associated with an erroneous high value of  $\log_{10} K^\circ$  (IX.2) = 4.46 that is rejected by this review (*cf.* Section IX.3.2). In conjunction with results obtained in further solubility experiments and using a new  $\text{p}K_\text{a}$  of isa obtained by NMR [2003CHO/RAI] coupled with an equilibrium constant of Hisa lactonisation, the data from [98RAI/RAO2] were reanalysed in [2003RAI/HES]. The new model from [2003RAI/HES] excluded the  $\text{Ca(isa)}_2(\text{aq})$  complex. As a result, the formation of  $\text{Ca(isa)}_2(\text{aq})$  is considered to be questionable and the values of  $\log_{10} K_s^\circ$  (IX.5) and  $\log_{10} \beta_2^\circ$  (IX.7) from [98RAI/RAO2] are rejected by this review.

Van Loon *et al.* [99LOO/GLA], Vercammen *et al.* [99VER/GLA], [2000VER] interpreted their solubility data in terms of three equilibria, the solubility product, Eq. (IX.6) and two Ca - isa complexes:





The solubility product, Eq. (IX.6) and the simple Ca - isa 1:1 complex, Eq. (IX.8), account for the pH independent solubility effects measured at  $6 < \text{pH} < 12$ , whereas the solubility product and the complexation Eq. (IX.9) explain the increase in solubility found at  $\text{pH} > 12$ . Concerning the structure of the complex  $\text{Ca}(\text{isa}_{\text{H}})(\text{aq})$  it is assumed that Ca is bound in a bidentate manner by the carboxyl group and the  $\alpha$ -hydroxyl group. In the process of complex formation this hydroxyl group is deprotonated.

With the speciation model proposed by [98RAI/RAO2] it is not possible to model all experimental data of [99LOO/GLA], [99VER/GLA], [2000VER]. However, the later results in [2003RAI/HES] agree with those in [99LOO/GLA], [99VER/GLA], [2000VER]. The speciation model comprising the equilibria (IX.2), (IX.6), (IX.8) and (IX.9), proposed by [99LOO/GLA], [99VER/GLA] and [2000VER] appears to be able to describe the solubility data in the entire pH region.

Because the complexation of  $\text{Ca}(\text{II})$  with  $\text{isa}^-$  is weak and there is a strong correlation in the solubility measurements between the value of  $K(\text{IX.8})$  and the solubility product of  $\text{Ca}(\text{isa})_2(\text{cr})$ , it is difficult to evaluate  $\beta_1^\circ$  by the solubility experiments and such evaluation is usually associated with large uncertainties. As a result, in their original data treatment, [99LOO/GLA], [99VER/GLA] and [2000VER] estimated and fixed the value of Eq. (IX.8) by taking a value from the literature for the similar Ca - gluconate 1:1 complex:  $\log_{10} K^\circ(\text{IX.8}) = 1.7$ . Using this estimated value [99LOO/GLA] derived  $\log_{10} K^\circ(\text{IX.6}) = -(6.53 \pm 0.10)$ , [99VER/GLA], [2000VER] derived  $\log_{10} K^\circ(\text{IX.6}) = -(6.36 \pm 0.10)$  and  $\log_{10} K^\circ(\text{IX.9}) = -(10.4 \pm 0.2)$ . Meanwhile, additional measurements have been made to determine the value of the Ca - isa 1:1 complex (Reaction (IX.8)) in [2004LOO/GLA], using ion exchange and potentiometry. The two independent methods gave very close values of  $\log_{10} K^\circ(\text{IX.8})$ :  $(1.8 \pm 0.1)$  and  $(1.78 \pm 0.04)$  at  $22^\circ\text{C}$ . These new values are in good agreement with the original estimate from the  $\text{Ca}(\text{II})$  - glucolate complex and close to the value obtained by [2003RAI/HES] ( $\log_{10} K^\circ(\text{IX.8}) = (1.44 \pm 0.07)$  at  $23^\circ\text{C}$ ). As a result, the three values of  $\log_{10} K^\circ(\text{IX.8})$  from [2004LOO/GLA] and [2003RAI/HES] are accepted by this review. A weighted average  $\log_{10} K^\circ(\text{IX.8})$  is selected by this review with an enlarged uncertainty to cover the whole range of expectation:

$$\log_{10} K^\circ((\text{IX.8}), 298.15 \text{ K}) = (1.7 \pm 0.3).$$

The correction for the effect of temperature change from  $22 - 23^\circ\text{C}$  to  $25^\circ\text{C}$  on  $\log_{10} K^\circ(\text{IX.8})$  is ignored because it is expected to be small and insignificant compared with the large uncertainty.

Combination of Reactions (IX.8) and (IX.9) would result in Reaction (IX.10):



This reaction represents the deprotonation of a hydroxyl group in  $\text{Ca}(\text{isa})^+$ . Using the selected  $\log_{10} K^\circ((\text{IX.8}), 298.15 \text{ K}) = (1.7 \pm 0.3)$  in this review and the value of  $\log_{10} K(\text{IX.9}) = -(10.4 \pm 0.2)$  at  $25^\circ\text{C}$  ( $I \rightarrow 0$ ) from [99VER/GLA] and [2000VER],

the equilibrium constant for Reaction (IX.10) is calculated to be  $\log_{10} K$  (IX.10) =  $-12.1$ . Considering that the deprotonation of a hydroxyl group in an uncomplexed isa requires extremely high pH ( $> 13$  or  $14$ ) but could occur at lower pH due to the complexation with metal ions, the value of  $\log_{10} K$  (IX.10) =  $-12.1$  appears reasonable. Thus, the value of  $\log_{10} K$  (IX.9) =  $-(10.4 \pm 0.2)$  at  $25^\circ\text{C}$  ( $I \rightarrow 0$ ) from [99VER/GLA] and [2000VER] is also considered to be reasonable by this review. A value of  $\log_{10} K^\circ$  (IX.9), 298.15 K) with an enlarged uncertainty is selected by this review, taking into consideration of the uncertainties in temperature and ionic strength in [99VER/GLA] and [2000VER]:

$$\log_{10} K^\circ \text{ (IX.9), 298.15 K) } = -(10.4 \pm 0.5).$$

In order to describe their solubility data at  $\text{pH} < 5$ , [2003RAI/HES] used the “intrinsic” protonation constant  $\log_{10} K^\circ$  (IX.2) =  $(3.27 \pm 0.02)$  from [2003CHO/RAI] and developed a lactonisation constant  $\log_{10} K^\circ$  (IX.1) =  $(0.37 \pm 0.07)$ . Combination of these two constants would result in  $\log_{10} K^\circ$  (IX.3) =  $(3.79 \pm 0.07)$ , compatible with the “composite” protonation constant  $\log_{10} K^\circ$  (IX.3) =  $(4.0 \pm 0.5)$  selected in this review.

The pH independent solubility data reported in [99LOO/GLA], [99VER/GLA] [2000VER] and [2003RAI/HES] for the pH range 5 to 12 agree well and can be interpreted in terms of the solubility product (IX.6) and the complexation equilibrium (IX.8). The estimated value  $\log_{10} K^\circ$  (IX.8) =  $1.7$  used by [99LOO/GLA] [99VER/GLA] [2000VER] perfectly agrees with the value  $\log_{10} K^\circ$  (IX.8) =  $(1.7 \pm 0.3)$  selected in this review. Hence, the solubility products  $\log_{10} K^\circ$  (IX.6) =  $-(6.53 \pm 0.10)$  at  $20^\circ\text{C}$  [99LOO/GLA] and  $\log_{10} K^\circ$  (IX.6) =  $-(6.36 \pm 0.10)$  at  $25^\circ\text{C}$  [99VER/GLA] [2000VER] are considered in this review. Rai *et al.* [2003RAI/HES] used a lower complexation constant  $\log_{10} K^\circ$  (IX.8) =  $(1.44 \pm 0.07)$  and consequently a higher solubility product  $\log_{10} K^\circ$  (IX.6) =  $-(6.26 \pm 0.07)$  to describe the same solubility data. A solubility product consistent with the selected equilibrium constants (IX.3) and (IX.8) and the reported experimental data is selected by this review:

$$\log_{10} K^\circ \text{ (IX.6), 298.15 K) } = -(6.4 \pm 0.2).$$

Van Loon *et al.* [99LOO/GLA] conducted the solubility experiments at variable temperatures ( $2.6 - 50.4^\circ\text{C}$ ) so that the enthalpy for the dissolution reaction (IX.6),



was calculated by using the integrated van't Hoff equation:  $\Delta_r H_m^\circ$  (IX.6), 298.15 K) =  $(40 \pm 1) \text{ kJ}\cdot\text{mol}^{-1}$  [99LOO/GLA].

## IX.6 Selenium isa compounds and complexes

No thermodynamic data on selenium isa compounds or complexes are identified in the literature by this review.

## IX.7 Nickel isa compounds and complexes

Stability constants of Ni(II) - isa complexes have been determined by capillary electrophoresis [98MOT/CHA] and by ion exchange and differential pulse polarography [2003WAR/EVA]. The stability constants of Ni(II) - isa complexes from [98MOT/CHA] and [2003WAR/EVA] are summarised in Table IX-5. The stability constant of a Cu(II) - isa complex from [97HAG] is also listed for comparison.

Table IX-5: Stability constants of isa complexes with Ni(II) and Cu(II) in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Ni}^{2+} + \text{isa}^- \rightleftharpoons \text{Ni(isa)}^+$				
em	$I$ (low, varying), pH = 6.2	?	1.99	[98MOT/CHA]
ion ex	$I = ?$ , pH = 7	25	$(2.20 \pm 0.36)$	[2003WAR/EVA]
pol.	$I = ?$ , pH = 7	25	$(2.58 \pm 0.07)$	[2003WAR/EVA]
$2 \text{Ni}^{2+} + \text{isa}^- + 4 \text{OH}^- \rightleftharpoons \text{Ni}_2\text{isa(OH)}_4^-$				
ion ex	$I = ?$ , pH = 7	25	$(29.85 \pm 0.89)$	[2003WAR/EVA]
$\text{Cu}^{2+} + \text{isa}^- \rightleftharpoons \text{Cu(isa)}^+$				
pot	$I = 0.1 \text{ M NaClO}_4$	?	$(2.7 \pm 0.6)$	[97HAG]

The capillary electrophoresis experiments in [98MOT/CHA] were conducted at a single pH (6.2) and low ionic strength. In [2003WAR/EVA], a combination of techniques including pH measurements, conductometric titrations, and spectrophotometry were used to obtain the stoichiometry of Ni(II) isa complexes in different pH regions:  $\text{Ni(isa)}^+$  at pH < 7,  $\text{Ni}_2\text{isa(OH)}_3(\text{aq})$  at pH between 7 and 10,  $\text{Ni}_2\text{isa(OH)}_4^-$  at pH > 10. The stability constants of the complexes were determined by ion exchange and differential pulse polarography.

The value for  $\text{Ni(isa)}^+$  from [98MOT/CHA] ( $\log_{10} K = 1.99$ , no uncertainty estimate given by the authors) compares reasonably well with the stability constant of 1:1 Ca – isa complex selected by this review,  $\log_{10} K^\circ (\text{IX.8}) = (1.7 \pm 0.3)$ . However, the electrophoretic data were obtained at low but varying ionic strength, and no correction was made by the authors for the effect of ionic strength while deriving the stability constant. Somewhat higher values are obtained in [2003WAR/EVA] ( $\log_{10} K = (2.20 \pm 0.36)$  by ion exchange and  $\log_{10} K = (2.58 \pm 0.07)$  by polarography). The ionic strength in the ion exchange or polarographic experiments was not clearly described in the paper [2003WAR/EVA].

The results in [2003WAR/EVA] indicate that different complexes form in different pH regions. As pH is increased, the hydroxyl groups of isa could deprotonate to form different Ni(II) complexes. Besides, mixed complexes containing isa and hydroxide could form. These observations are similar to the results on Cu(II) - isa complexa-

tion studied by potentiometry, capillary electrophoresis, FTIR and UV/Vis [97HAG]. The Cu(II) - isa complexation was found to be independent of pH at pH < 6, which could be interpreted by assuming the formation of Cu(isa)<sup>+</sup> with  $\log_{10} K^{\circ} = (2.7 \pm 0.6)$  [97HAG]. However, at pH > 6, the Cu(II) - isa complexation was found to depend on pH and the complexation strength increased with pH reaching a slope of about 2 at pH > 8. This behaviour can either be interpreted in terms of a ternary complex Cu(isa<sub>-H</sub>)OH<sup>-</sup> with one isa hydroxyl group deprotonated or as Cu(isa<sub>-2H</sub>)<sup>-</sup> where two hydroxyl groups are deprotonated. The results from [2003WAR/EVA] and [97HAG] demonstrated the importance of determining the stoichiometry of complexes with independent techniques, and possible co-existence of different complexes in solution at a given pH region. Based on this point of view, the assignment of a single Ni(isa)<sup>+</sup> species at pH 6.2 [98MOT/CHA] or pH < 7 [2003WAR/EVA] cannot be taken for granted, though we can assume by means of chemical systematics that an increase in complexation strength in the case of Ni(II) may commence at higher pH values than in the case of Cu(II).

Due to the scarcity and difference in the stability constants and the varying [98MOT/CHA] or uncertain [2003WAR/EVA] ionic strength in the experiments, no value for Ni(II) - isa complexes is selected by the present review. Nevertheless, the values reported in the literature may serve as a guideline for Ni - isa complexation around neutral pH.

### IX.8 Technetium isa compounds and complexes

No thermodynamic data on technetium isa compounds or complexes are identified in the literature by this review.

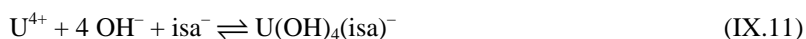
### IX.9 Zirconium isa compounds and complexes

No thermodynamic data on zirconium isa compounds or complexes are identified in the literature by this review.

### IX.10 Uranium isa compounds and complexes

Warwick *et al.* [2004WAR/EVA] determined the solubility of hydrous UO<sub>2</sub>(am) in the absence and in the presence of isa and gluconic acid at three different pH values (acidic, near-neutral and alkaline solutions) at 25°C and *I* = 0.3 M. The total concentration of isa was 0.0444 M at pH 3.3 and 6.5, and 0.0615 M at pH 13.5.

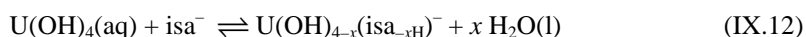
The solubility data measured in the three pH regions were interpreted by [2004WAR/EVA] in terms of the reaction:



The stability constants were found to increase with pH (see Table IX-6), and the authors proposed a mean value of  $\log_{10} K$  (IX.11) =  $(49 \pm 2)$ . The same constant was determined by [2004WAR/EVA] from results provided by UK-Nirex [97GRE/HUR]. These data had originated from an investigation into the effect of Na(isa) on uranium solubility, at pH 12.

Although all experiments were carried out at  $I = 0.3$  M, the ionic medium is not specified in [2004WAR/EVA] but it can be inferred from the description of the experimental procedures that it changed considerably, from almost pure NaOH at pH 13.5 – 13.8 to a non-specified mixture at low pH. In addition, the effect of isa protonation at pH 3.2 has not been considered in the data analysis of [2004WAR/EVA].

The solubility data in the pH range from 3 to 14 have been modelled by [2004WAR/EVA] solely with the species  $\text{U}(\text{OH})_4(\text{isa})^-$ . However, it would seem very likely that there are more than one complex present in equilibrium within this large pH range. Furthermore, this complex is just one of several possible complexes according to the overall reaction:



The formula  $\text{U}(\text{OH})_4(\text{isa})^-$  implicitly assumes that isa forms a U(IV) complex with its carboxyl group (and probably still protonated hydroxyl groups). On the other hand, [2004WAR/EVA] postulate a structure for the U(IV) isa complex compatible with the formula  $\text{U}(\text{isa}_{-4\text{H}})^-$  with  $x = 4$ , where isa coordinates to U(IV) with four deprotonated hydroxyl groups (Note that there are some errors in Figs. 7 and 8 in [2004WAR/EVA]: The figure captions say that U(IV) isa complexes are shown, but actually they are gluconate complexes). However, this question cannot be decided by interpreting solubility data as the resulting reactions differ only in the number of moles of water released during complex formation.

Considering the observed pH dependence of the postulated reaction (IX.11) and the discussion of the analogous case of Np(IV) isa complexation (*cf.* Section IX.11) it seems doubtful that the U(IV) isa system can be described by just one complex in the entire pH range from 3 to 14.

Due to the shortcomings in the experimental procedure and data evaluation, and the uncertainty in defining the reaction stoichiometry, no thermodynamic value for U(IV) - isa is selected by this review.

Table IX-6: Stability constants of U(IV) - isa complexes in the literature [2004WAR/EVA].

Method	Ionic medium	$t$ (°C)	$\log_{10} K$
$U^{4+} + 4 OH^- + isa^- \rightleftharpoons U(OH)_4(isa)^-$			
sol	$I = 0.3$ M, pH = 3.3	25.0	$(48 \pm 0.3)$
sol	$I = 0.3$ M, pH = 6.2	25.0	$(49 \pm 0.2)$
sol	$I = 0.3$ M, pH = 13.5	25.0	$(50 \pm 0.1)$

Rao *et al.* [2004RAO/GAR] studied the complexation of isa with U(VI) in acidic solutions at 25.0°C and  $I = 1.0$  M NaClO<sub>4</sub> by potentiometry and calorimetry. Three monomeric successive complexes,  $UO_2(isa)_j^{(2-j)+}$  where  $j = 1 - 3$ , were identified. The stability constants were calculated from the potentiometric titration data, using a  $pK_a$  of isa ( $3.65 \pm 0.05$ ) also determined in this work by potentiometry (Table IX-7).

Table IX-7: Stability constants of U(VI) - isa complexes in the literature [2004RAO/GAR].

Method	Ionic medium	$t$ (°C)	$\log_{10} K$
$UO_2^{2+} + isa^- \rightleftharpoons UO_2isa^+$			
pot	$I = 1.0$ M NaClO <sub>4</sub>	25.0	$(2.91 \pm 0.15)$
$UO_2^{2+} + 2 isa^- \rightleftharpoons UO_2(isa)_2(aq)$			
pot	$I = 1.0$ M NaClO <sub>4</sub>	25.0	$(5.37 \pm 0.07)$
$UO_2^{2+} + 3 isa^- \rightleftharpoons UO_2(isa)_3^-$			
pot	$I = 1.0$ M NaClO <sub>4</sub>	25.0	$(7.25 \pm 0.18)$

The stability constant of  $UO_2isa^+$  ( $2.91 \pm 0.15$ ) is comparable to those of U(VI)  $\alpha$ -hydroxycarboxylate complexes (*e.g.*, hydroxyacetate), but stronger than those of simple monocarboxylate complexes (*e.g.*, acetate). As shown in Figure IX-4 from [2004RAO/GAR], the stability constant of  $UO_2isa^+$ , as well as the constants of U(VI) complexes with other  $\alpha$ -hydroxycarboxylates, is significantly above the  $\log_{10} \beta - pK_a$  correlation for the simple carboxylates, indicating that the U(VI) complexes with  $\alpha$ -hydroxycarboxylates (including isa) have “enhanced” stability with respect to the  $\log_{10} \beta - pK_a$  correlation. Such enhancement, according to the authors, suggests that the  $\alpha$ -hydroxyl group in isa probably participates in the complexation with U(VI) to form chelate complexes [2004RAO/GAR].

Although these values appear reasonable and compare well with other hydroxycarboxylate systems, more studies are needed to confirm these, especially the formation of rather strong  $UO_2(isa)_2(aq)$  and  $UO_2(isa)_3^-$  complexes, before the values can be recommended. It should be noted that the values of [2004RAO/GAR] may be used for scoping calculations, but they only describe the U(VI) – isa system in acidic

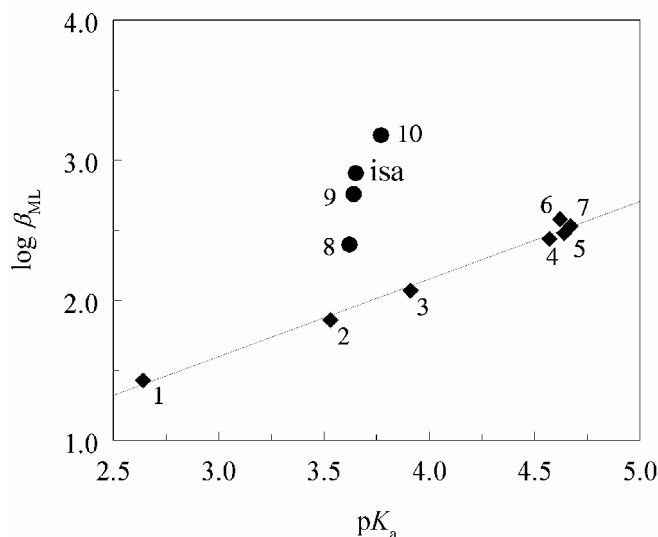
solutions. In alkaline solutions other complexes of the type  $\text{UO}_2(\text{OH})_x(\text{isa}_{-y\text{H}})^{(1-x-y)}$  may dominate the U(VI) – isa system.

Values of the enthalpy of complexation, determined by calorimetry [2004RAO/GAR] are summarised in Table IX-8. These values indicate that the enthalpies of complexation of U(VI) with isa are quite small, comparable with or even smaller than the uncertainties. No obvious trend could be derived for the enthalpies of the successive 1:1, 1:2 and 1:3 complexes. However, the entropies of complexation (Table IX-8), calculated with the enthalpies (Table IX-8) and the formation constants (Table IX-7), are all positive, suggesting that the complexation is, at least partially, entropy-driven. Because of the high uncertainties of the enthalpies in Table IX-8 and the concern about the accuracy of the formation constant of a rather strong  $\text{UO}_2(\text{isa})_3^-$  complex discussed above, no values of enthalpy of U(VI) isa complexation are recommended by this review.

Table IX-8: Enthalpy and entropy of U(VI) isa complexation in the literature [2004RAO/GAR].

Method	Ionic medium	$t$ (°C)	$\Delta_r H_m$ kJ·mol <sup>-1</sup>	$\Delta_r S_m$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
	$\text{UO}_2^{2+} + \text{isa}^- \rightleftharpoons \text{UO}_2\text{isa}^+$			
cal	$I = 1.0 \text{ M NaClO}_4$	25.0	$-(1.0 \pm 1.0)$	$(52 \pm 4)$
	$\text{UO}_2^{2+} + 2 \text{ isa}^- \rightleftharpoons \text{UO}_2(\text{isa})_2(\text{aq})$			
cal	$I = 1.0 \text{ M NaClO}_4$	25.0	$(1.4 \pm 1.8)$	$(108 \pm 6)$
	$\text{UO}_2^{2+} + 3 \text{ isa}^- \rightleftharpoons \text{UO}_2(\text{isa})_3^-$			
cal	$I = 1.0 \text{ M NaClO}_4$	25.0	$-(6.2 \pm 3.0)$	$(118 \pm 10)$

Figure IX-4: Correlation between the stability constants of U(VI) carboxylate complexes and the  $\text{p}K_a$  of carboxylic acids ( $t = 20 - 25^\circ\text{C}$ ,  $I = 1.0 \text{ M}$ ). Symbols: ◆ simple carboxylates, 1: chloroacetate, 2: formate, 3: 3-chloropropanoate, 4: acetate, 5: isobutyrate, 6: butanoate, 7: propanoate; ●  $\alpha$ -hydroxycarboxylates, 8: hydroxyacetate, 9: 2-hydroxypropanoate, 10: 2-hydroxy-2-methylpropanoate. The straight line is an unweighted linear regression of the data for simple carboxylates (data points 1 – 7) [2004RAO/GAR].



### IX.11 Neptunium isa compounds and complexes

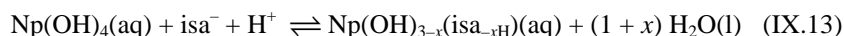
The Np(IV) - isa system has been investigated by [98RAI/RAO] and [2003RAI/HES]. The constants on Np(IV) isa complexes as reported by [98RAI/RAO] and [2003RAI/HES] are summarized in Table IX-9.

Table IX-9: Stability constants of Np(IV) isosaccharinate complexes in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10} K$	Reference
$\text{Np}^{4+} + 2 \text{OH}^- + 2 \text{isa}^- \rightleftharpoons \text{Np}(\text{OH})_2(\text{isa})_2(\text{aq})$				
sol	$I \rightarrow 0$	23	36.9	[98RAI/RAO]
$\text{Np}^{4+} + 3 \text{OH}^- + \text{isa}^- \rightleftharpoons \text{Np}(\text{OH})_3(\text{isa})(\text{aq})$				
sol	$I \rightarrow 0$	23	43.2	[98RAI/RAO]
sol	$I \rightarrow 0$	23	43.47	[2003RAI/HES]
$\text{Np}(\text{OH})_3(\text{isa})(\text{aq}) + \text{isa}^- \rightleftharpoons \text{Np}(\text{OH})_3(\text{isa})_2^-$				
sol	$I \rightarrow 0$	23	2.11	[2003RAI/HES]
$\text{Np}^{4+} + 4 \text{OH}^- + \text{isa}^- \rightleftharpoons \text{Np}(\text{OH})_4(\text{isa})^-$				
sol	$I \rightarrow 0$	23	50.14	[2003RAI/HES]
$\text{Np}(\text{OH})_4(\text{isa})^- + \text{isa}^- \rightleftharpoons \text{Np}(\text{OH})_4(\text{isa})_2^{2-}$				
sol	$I \rightarrow 0$	23	1.86	[2003RAI/HES]

The influence of isa on the solubility of Np(IV) hydrous oxide was studied in the acidic region ( $2 < \text{pH} < 7$ ) in [98RAI/RAO], while it is extended to the alkaline region (up to 1 m NaOH) in [2003RAI/HES]. It was observed that the presence of isa significantly increased the solubility of  $\text{NpO}_2(\text{am})$  in the entire region from acidic to basic conditions.

The increase in solubility in the acidic region ( $2 < \text{pH} < 7$ ) was interpreted in terms of the formation of two Np(IV) hydroxyl isa complexes:  $\text{Np}(\text{OH})_2(\text{isa})_2(\text{aq})$  and  $\text{Np}(\text{OH})_3\text{isa}(\text{aq})$  in [98RAI/RAO]. Formation constants of the complexes were calculated to be 43.2 and 36.9 at  $I = 0$ , respectively. A detailed inspection of the solubility data reported by [98RAI/RAO] indicates that the complex  $\text{Np}(\text{OH})_2(\text{isa})_2(\text{aq})$  mainly had to be introduced to compensate for the exceptionally high isa protonation constant (4.47, see discussion in Section IX.3). It is questionable whether the species  $\text{Np}(\text{OH})_2(\text{isa})_2(\text{aq})$  is justified to explain the solubility data at  $\text{pH} < 4$  and high isa concentration. The majority of solubility data has been modelled by [98RAI/RAO] with the species  $\text{Np}(\text{OH})_3\text{isa}(\text{aq})$ . This complex is just one of several possible complexes according to the overall reaction:



with  $\log_{10} K^\circ = 11.0$  (no uncertainty estimate given by the authors). The variant chosen by [98RAI/RAO],  $\text{Np}(\text{OH})_3\text{isa}(\text{aq})$ , implicitly assumes that isa forms a Np(IV) complex



with its carboxyl group (and probably a still protonated hydroxyl group). It is highly unlikely that such a weak interaction is responsible for the observed increase in solubility. More probable candidates are complexes with  $x = 1$  or 2, where isa coordinates to Np(IV) with one or two deprotonated hydroxyl groups. However, this question cannot be decided by interpreting solubility data as the resulting reactions differ only in the number of moles of water released during complex formation.

In [2003RAI/HES], the data of the solubility of hydrous  $\text{NpO}_2(\text{am})$  in the presence of isa in a wide pH region (from acidic to 1 M NaOH) was evaluated. A new  $\text{p}K_{\text{a}}$  of isa (3.27) obtained by NMR [2003CHO/RAI] and coupled with an equilibrium constant for the lactonisation of Hisa ( $\log_{10} K (\text{IX.1}) = (0.37 \pm 0.07)$ ) was used in the evaluation. The authors found that one of the Np(IV) hydroxyl isa complexes defined in [98RAI/RAO],  $\text{Np}(\text{OH})_2(\text{isa})_2(\text{aq})$ , was unnecessary to fit the data in the entire pH region. Instead, four Np(IV) hydroxyl isa complexes were included in the new model:  $\text{Np}(\text{OH})_3\text{isa}(\text{aq})$ ,  $\text{Np}(\text{OH})_3(\text{isa})_2^-$ ,  $\text{Np}(\text{OH})_4(\text{isa})^-$ , and  $\text{Np}(\text{OH})_4(\text{isa})_2^{2-}$  [2003RAI/HES]. Using the solubility product of  $\text{NpO}_2(\text{am})$  ( $\log_{10} K_{\text{s},0}^\circ = -54.9$  at  $I = 0$ ), stability constants of the four complexes were calculated to be 43.47, 45.58, 50.14 and 52.00, respectively.

In the solubility experiments with Np(IV), it is always a concern that Np(IV) could be oxidised to Np(V), especially in neutral to basic media. If the oxidation occurs, the measured aqueous concentration of Np will be significantly higher than that for Np(IV). Rai *et al.* [98RAI/RAO], [2003RAI/HES] recognised such concern and took precautions to prevent the oxidation. The oxidation states of Np in the aqueous samples were analysed by a solvent extraction method and the concentrations of Np(IV) were used in the modelling calculations of the solubility data [2003RAI/HES]. This approach appears valid. However, there could be large uncertainties in the oxidation state analysis of solutions with isa and extremely low concentrations of Np. Due to the uncertainties in oxidation state analysis, the scarcity of data and the uncertainty in defining the reaction stoichiometries in alkaline solutions, no thermodynamic values for Np(IV) - isa are selected by this review. However, the results of [2003RAI/HES] give an indication of the order of magnitude of Np(IV) - isa complexation and their values may be used for scoping calculations.

## IX.12 Plutonium isa compounds and complexes

A number of studies were devoted to the influence of isosaccharinic acid on the solubility of Pu(IV) [89CRO/EWA], [92GRE/MOR], [93GRE/HAR], [93MOR], [94GRE/HUR], [94GRE/LIN], [95GRE/HOL], [97GRE/HUR]. All these studies have been carried out in the context of cellulose degradation under alkaline conditions, and isosaccharinic acid was considered to be one of the most important degradation products. The set-up of all experiments described in the above cited reports has been the same: an alkaline solution, usually at pH 12, containing cellulose degradation products, or containing a selected organic ligand like isa, has been spiked with plutonium(IV)

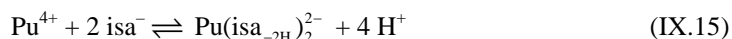
nitrate solution, and after a certain time the concentration of the dissolved plutonium has been measured. In a series of experiments the pH of the alkaline solution has been kept constant while the concentration of the organic ligand was varied. From the effect of the presence of isa on the “solubility” of plutonium, stability constants of plutonium complexes with isa,  $\text{Pu(isa}_{-4\text{H}})^{-}$  and  $\text{Pu(isa}_{-2\text{H}})_2^{2-}$ , were calculated (Table IX-10).

It is noted by the present review that the quantity reported in the studies cited above as “plutonium solubility” in the presence of isosaccharinic acid is not strictly a thermodynamic solubility. Instead, it was the measured maximum concentration of plutonium over a solubility-limiting phase. The solid phase formed in these oversaturation experiments was assumed to be  $\text{Pu(OH)}_4(\text{s})$  but was not characterised and the final oxidation state of plutonium in the solution was uncertain. Furthermore, the effect of Pu(IV) colloid formation in oversaturation experiments at pH 12 is not addressed in any of the above cited reports and papers. No experiments starting from undersaturation with a well-characterised plutonium solid phase have been reported in the studies cited above.

Table IX-10: Stability constants of Pu(IV) isosaccharinate complexes in the literature.

Method	Ionic medium	$t$ (°C)	$\log_{10}K$	Reference
$\text{Pu}^{4+} + \text{isa}^{-} \rightleftharpoons \text{Pu(isa}_{-4\text{H}})^{-} + 4 \text{H}^{+}$				
sol	NaOH, pH = 12	?	− 3.50	[93MOR], [94GRE/LIN]
$\text{Pu}^{4+} + 2 \text{isa}^{-} \rightleftharpoons \text{Pu(isa}_{-2\text{H}})_2^{2-} + 4 \text{H}^{+}$				
sol	NaOH, pH = 12	?	− 0.20	[93MOR], [94GRE/LIN]

The measured maximum concentrations of plutonium have been interpreted [93MOR], [94GRE/LIN] in terms of the reactions:



The values listed in Table IX-10 are not credited by this review because of the shortcomings in the experiments as discussed above.

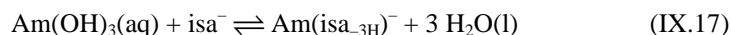
### IX.13 Americium isa compounds and complexes

Tits *et al.* [2004TIT/WIE] conducted batch-type sorption experiments to investigate the effect of isa on the sorption of  $^{241}\text{Am(III)}$  by calcite. The sorption experiments were conducted in 0.3 M NaOH at  $(23 \pm 3)^{\circ}\text{C}$ . It was found that the sorption of Am(III) by calcite decreased significantly when the concentration of isa was above  $10^{-5}$  M. Such effect was interpreted in terms of the formation of a 1:1 Am(III) - isa complex in solution. Assuming that the only “inorganic” Am species is  $\text{Am(OH)}_3(\text{aq})$  with  $\log_{10} \beta^{\circ} = -(26.2 \pm 0.5)$  [2003GUI/FAN], and the only “organic” Am species is  $\text{Am(isa}_{-3\text{H}})^{-}$ , the equilibrium constant of Reaction (IX.16) was derived from the experimental sorption data [2004TIT/WIE]:  $\log_{10} K (\text{IX.16}) = -(22.2 \pm 1)$  ( $I = 0.3$  M) and  $\log_{10} K^{\circ} (\text{IX.16}) =$

–  $(21.4 \pm 1)$  ( $I = 0$  M), obtained by extrapolation using the Davies equation [2004TIT/WIE].

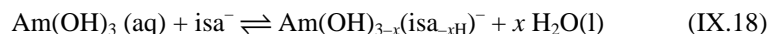


Reaction (IX.16) can be converted back to Reaction (IX.17) that was thought to reflect the actual equilibrium in alkaline solutions [2004TIT/WIE]:



The equilibrium constant of Reaction (IX.17) is calculated to be  $\log_{10} K^\circ (\text{IX.17}) = (4.8 \pm 1.1)$  ( $I = 0$  M) from  $\log_{10} K^\circ (\text{IX.16}) = -(21.4 \pm 1)$ , using  $\log_{10} \beta^\circ (\text{Am}(\text{OH})_3, \text{aq}) = -(26.2 \pm 0.5)$ .

Reactions (IX.16) and (IX.17) are based on the assumption that three protons dissociated from  $\text{isa}^-$  to form the Am(III) - isa complex in alkaline solutions. Such assumption cannot be verified by the experiments in [2004TIT/WIE]. Taking this uncertainty into consideration, the experimental data may be more appropriately represented by the following reaction:



The value of  $x$  in Reaction (IX.18) cannot be determined by standard thermodynamic methods as the resulting models differ only in the number of moles of water released during complex formation.

The values of  $\log_{10} K$  (IX.16) from [2004TIT/WIE],  $-(22.2 \pm 1)$  for  $I = 0.3$  M and  $-(21.4 \pm 1)$  for  $I = 0$  M, are the only stability constants of Am(III) - isa complexes that have been reported in the literature. These should be considered as approximate values, as pointed out by [2004TIT/WIE], because the quality of the experimental data is not high due to the extremely low concentration of Am(III) used in the experiments. Nevertheless, they are of value by providing “first estimates” of Am(III) isa complexation in alkaline solutions in the absence of more reliable data. It should be pointed out that the values of the stability constant of Am(III) - isa complex from [2004TIT/WIE],  $\log_{10} K$  (IX.16), are comparable to the value of corresponding Eu(III) - isa complex that was determined from experimental data of higher quality with higher concentrations of Eu(III) [2004TIT/WIE]. The data on Eu(III) - isa complexes are discussed in Section IX.14.1.2.

## IX.14 Other compounds and complexes of isa

In contrast to the ligands oxalate, citrate and edta discussed in this review (*cf.* Chapters VI, VII and VIII) the thermodynamic data published for isa is rather limited, and thus it might be useful to provide a comprehensive overview of isa data available to the reviewers, and to include elements somewhat outside the scope of this review. In this section isa complexation data found for trivalent lanthanides, iron and thorium are discussed.

The experimental work on trivalent lanthanides was mainly carried out to obtain data for chemical analogues of trivalent actinides, such as Np(III), Pu(III) and Am(III). Lanthanides are not included in the list of elements reviewed in the NEA TDB project, and therefore lanthanide data are discussed here only with the aim to provide guidelines for scoping calculations but no thermodynamic values have been selected.

Thermodynamic data for inorganic compounds and complexes of iron and thorium are currently reviewed within the scope of the NEA TDB Project Phase III. Hence, it might be useful to include here data available for iron and thorium complexes with isa, which will be discussed more thoroughly in a future update.

### IX.14.1 Trivalent lanthanide isa compounds and complexes

Stability constants of isa complexes with a few trivalent lanthanides, including La(III), Eu(III) and Tb(III), were reported in [98MOT/CHA], [2000VER], [2001VER/GLA], [2002TIT/WIE], [2003ZHE/MAU] and [2004TIT/WIE]. The values are summarised in Table IX-11.

Table IX-11: Stability constants of isa complexes with Ln(III) in the literature.

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{La}^{3+} + \text{isa}^- \rightleftharpoons \text{La(isa)}^{2+}$				
em	<i>I</i> (low, varying), pH = 6.2	?	3.09	[98MOT/CHA]
$\text{Eu}^{3+} + \text{isa}^- \rightleftharpoons \text{Eu(isa}_{-4\text{H}})^{2-} + 4 \text{H}^+$				
sorption	<i>I</i> = 0.3 M, pH = 10.7 – 13.3	(23 ± 2)	– (30.6 ± 0.2)	[2000VER], [2001VER/GLA]
sorption	<i>I</i> = 0.3 M, pH = 13.3	23 (?)	– (31.4 ± 0.2)	[2002TIT/WIE]
$\text{Eu}^{3+} + \text{isa}^- \rightleftharpoons \text{Eu(isa}_{-3\text{H}})^{2-} + 3 \text{H}^+$				
sorption	<i>I</i> = 0.3 M, pH = 13.3	(23 ± 2)	– (19.2 ± 0.2) – (21.7 ± 0.2)	[2004TIT/WIE]
$\text{Tb}^{3+} + \text{isa}^- \rightleftharpoons \text{Tb(isa)}^{2+}$				
em	<i>I</i> = 0.1 M Na(OH/ClO <sub>4</sub> )	25.0	(3.07 ± 0.08)	[2003ZHE/MAU]
$\text{Tb(isa)}^{2+} + \text{isa}^- \rightleftharpoons \text{Tb(isa)}_2^+$				
em	<i>I</i> = 0.1 M Na(OH/ClO <sub>4</sub> )	25.0	(2.69 ± 0.11)	[2003ZHE/MAU]
$\text{Tb(isa)}_2^+ + \text{isa}^- \rightleftharpoons \text{Tb(isa)}_3(\text{aq})$				
em	<i>I</i> = 0.1 M Na(OH/ClO <sub>4</sub> )	25.0	(1.80 ± 0.12)	[2003ZHE/MAU]

#### IX.14.1.1 La(III) isa complex

La(III) - isa complexation was investigated solely by capillary electrophoresis at pH 6.2 and an estimate of the stability constant of La - isa 1:1 complex has been reported [98MOT/CHA]. The constant on the La(III) isa complex from [98MOT/CHA] is included in Table IX-11.

The value given by [98MOT/CHA], 3.09 (no uncertainty estimate given by the authors), appears to be reasonable – higher than that for La(III) complexes with single monocarboxylate (*e.g.*,  $\log_{10} K \sim 1.8$  for La(III) acetate at  $I = 0.1$  M) but comparable to that for La(III)  $\alpha$ -hydroxycarboxylate complexes (*e.g.*,  $\log_{10} K \sim 2.6$  for La(III) glycolate and lactate at  $I = 0.1$  M), suggesting possible participation of the hydroxyl group in forming a chelate. However, the same objections as discussed in the case of Ni(II) (*cf.* Section IX.7) apply to the La(III) data of [98MOT/CHA], *i.e.*, the varying ionic strength and the uncertainty in assigning the stoichiometry of  $\text{La(isa)}^{2+}$ . Besides, with a constant of  $10^{3.09}$  for the first complex, the presence of the second or even the third complex,  $\text{La(isa)}_2^+$  and  $\text{La(isa)}_3(\text{aq})$ , may not be neglected in fitting the data. Moreover, in the case of M(III) - isa interaction, complexes like  $\text{M(III)(isa-H)}^+$  may form even under acidic conditions, and no conclusions can be drawn from measurements at a single pH.

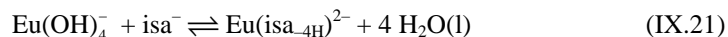
#### IX.14.1.2 Eu(III) isa complexes

The constants on Eu(III) - isa complexes from the literature are summarised in Table IX-11. Data on the isa complexation with Eu(III) under alkaline conditions have been reported in [2000VER], [2001VER/GLA], [2002TIT/WIE] and [2004TIT/WIE]. Sorption experiments were performed at pH 10.7, 12.0 and 13.3 in [2000VER] and [2001VER/GLA], and at pH 13.3 in [2002TIT/WIE] and [2004TIT/WIE], using carrier-free  $^{152}\text{Eu}$  radiotracer. Strong effects on the sorption due to Eu(III) - isa complexation have been found.

Data were evaluated by [2000VER], [2001VER/GLA] and [2002TIT/WIE] to obtain the stability constant of an Eu - isa 1:1 complex in terms of Reaction (IX.19):



where  $\log_{10} K$  (IX.19) =  $-(30.6 \pm 0.2)$  [2000VER], [2001VER/GLA], and  $\log_{10} K = -(31.4 \pm 0.2)$  [2002TIT/WIE] at  $I = 0.3$  M. In all cases, *i.e.* at pH 10.7, 12.0 and 13.3,  $\text{Eu(OH)}_4^-$  (whose existence is doubtful as discussed below) was assumed to be the dominant hydrolysis species of Eu(III) and different values of the hydrolysis constant for Reaction (IX.20):  $\text{Eu}^{3+} + 4 \text{OH}^- \rightleftharpoons \text{Eu(OH)}_4^-$ ,  $\log_{10} \beta_4$  (IX.20) = 19.89 [2000VER], [2001VER/GLA] and  $\log_{10} \beta_4$  (IX.20) = 18.2 [2002TIT/WIE] were used in the evaluation of sorption data. Reaction (IX.19) can be converted back to the following reaction that was thought to reflect the actual equilibrium in alkaline solutions:



The equilibrium constant of Reaction (IX.21) can be derived directly from series of sorption data at constant pH as reported in [2000VER], [2001VER/GLA] and [2002TIT/WIE] by assuming that the only “inorganic” Eu species is  $\text{Eu(OH)}_4^-$ , and the only “organic” Eu species is  $\text{Eu(isa}_{-4\text{H}})^{2-}$  (an assumption which might be too simplistic, not considering the possible formation of mixed Eu - OH - isa complexes) :

$\log_{10} K$  (IX.21) =  $(4.5 \pm 1.1)$  ( $I = 0.3$  M) [2000VER], [2001VER/GLA], and  $\log_{10} K$  (IX.21) =  $(5.3 \pm 0.2)$  ( $I = 0.3$  M) [2002TIT/WIE].

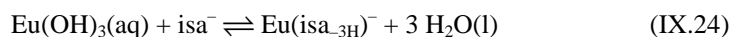
However, the existence of the negatively charged tetrahydroxo species  $\text{Eu}(\text{OH})_4^-$  in alkaline solutions is not proven. For example, the value recommended in [2002HUM/BER] is based solely upon a single solubility study [84BER/KIM]. In contrast, the hydrolysis of the trivalent actinides Am(III) and Cm(III) has been investigated in the alkaline range up to pH 13 in numerous studies, which could all be interpreted without assuming the existence of tetrahydroxo complexes [2003GUI/FAN].

Considering this ambiguity data were evaluated by [2004TIT/WIE] to obtain the stability constant of an Eu - isa 1:1 complex in terms of Reaction (IX.22):



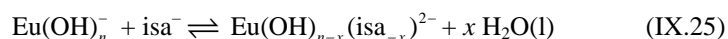
However, not only the situation regarding the existence of  $\text{Eu}(\text{OH})_4^-$  is unclear, but also the value of the formation constant for the trihydroxo complex  $\text{Eu}(\text{OH})_3(\text{aq})$  is not well known. In their data analysis [2004TIT/WIE] used two different stability constants for  $\text{Eu}(\text{OH})_3(\text{aq})$  (Reaction (IX.23),  $\text{Eu}^{3+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Eu}(\text{OH})_3(\text{aq}) + 3 \text{H}^+$ ),  $\log_{10} \beta_3^0$  (IX.23) =  $-23.7$  and  $\log_{10} \beta_3^0$  (IX.23) =  $-26.2$ . The first value is taken from [2002HUM/BER], based on the solubility study of [84BER/KIM] but neglecting the species  $\text{Eu}(\text{OH})_4^-$ , and the second value was selected on the basis of the chemical analogy between Eu(III) and Am(III)/Cm(III) [2003GUI/FAN]. This results in two different constants:  $\log_{10} K$  (IX.22) =  $-(19.2 \pm 0.2)$  ( $I = 0.3$  M) and  $\log_{10} K$  (IX.22) =  $-(21.7 \pm 0.2)$  ( $I = 0.3$  M), respectively.

Reaction (IX.22) can be converted back to the following reaction that was thought to reflect the actual equilibrium in alkaline solutions [2004TIT/WIE]:



The equilibrium constant of Reaction (IX.24) is derived from the experimental sorption data [2004TIT/WIE]:  $\log_{10} K$  (IX.24) =  $(5.4 \pm 0.2)$  ( $I = 0.3$  M).

Reactions (IX.19), (IX.21), (IX.22), (IX.24) are based on the assumption that in order to form the Eu(III) - isa complex in alkaline solutions four or three protons dissociated from  $\text{isa}^-$ , respectively. Such assumptions cannot be verified by the experiments in [2000VER], [2001VER/GLA], [2002TIT/WIE] and [2004TIT/WIE]. Taking this uncertainty into consideration, the experimental data may be more appropriately represented by the following reaction:



In order to determine the dominating hydrolysis species, *i.e.*, to determine the value of  $n$  in Reaction (IX.25), reliable studies of the Eu hydrolysis at high pH would be necessary. The value of  $x$  in Reaction (IX.25) cannot be determined by standard thermodynamic methods as the resulting models differ only in the number of moles of

water released during complex formation. In both cases, reliable values of the number of hydroxyl groups coordinated to the Eu might be determined by suitable spectroscopic methods.

#### IX.14.1.3 Tb(III) isa complexes

The complexation of isa with Tb(III) was studied by electromigration at pH 7 and 25.0°C, using  $^{160}\text{Tb}$  radiotracer [2003ZHE/MAU]. The constants on Tb(III) isa complexes from [2003ZHE/MAU] are summarised in Table IX-11.

Statistically, the ratio of the stepwise stability constants (Table IX-11) is quite reasonable. Moreover, the stability constant of  $\text{Tb(isa)}^{2+}$  is higher than that for Tb(III) complexes with single monocarboxylate (*e.g.*,  $\log_{10} K \sim 1.9$  for Tb(III) acetate at  $I = 0.1$  M) but comparable to that for Tb(III)  $\alpha$ -hydroxycarboxylate complexes (*e.g.*,  $\log_{10} K \sim 2.8$  for Tb(III) glycolate and 2.9 for Tb(III) lactate at  $I = 0.1$  M), suggesting the participation of the hydroxyl group in forming chelate complexes. However, as already discussed in Section IX.14.1.1, in the case of M(III) - isa interaction, complexes like  $\text{M(III)(isa-H)}^+$  may form even under acidic conditions, and no conclusions can be drawn from measurements at a single pH.

#### IX.14.2 Iron(III) isa compounds and complexes

Rao *et al.* [2004RAO/GAR] studied the complexation of isa with Fe(III) in acidic solutions (pH 1.5 – 4.5) at 25.0°C and  $I = 1.0$  M  $\text{NaClO}_4$  by potentiometry and calorimetry. Four monomeric successive complexes,  $\text{Fe(isa)}_j^{(3-j)+}$  where  $j = 1 - 4$ , were identified. The stability constants were calculated from the potentiometric titration data, using a “composite”  $\text{p}K_a$  of isa ( $3.65 \pm 0.05$ ) also determined in this work by potentiometry (Table IX-12). Values of the enthalpy of complexation, determined by calorimetry are summarised in Table IX-13.

The experimental procedures and the results obtained by Rao *et al.* [2004RAO/GAR] seem to be reliable. However, it is outside the scope of the present review to recommend data for iron complexes with organic ligands, as thermodynamic data for inorganic compounds and complexes of iron are currently reviewed within the scope of the NEA TDB Project Phase III. Hence, the iron isa data of [2004RAO/GAR] are included here for the sake of completeness; they will be discussed more thoroughly in a future update.

Table IX-12: Stability constants of Fe(III) isa complexes in the literature [2004RAO/GAR].

Method	Ionic medium	$t$ (°C)	$\log_{10}K$
$\text{Fe}^{3+} + \text{isa}^- \rightleftharpoons \text{Fe(isa)}^{2+}$			
pot	$I = 1.0 \text{ M NaClO}_4$	25.0	$(5.06 \pm 0.17)$
$\text{Fe}^{3+} + 2 \text{ isa}^- \rightleftharpoons \text{Fe(isa)}_2^+$			
pot	$I = 1.0 \text{ M NaClO}_4$	25.0	$(8.51 \pm 0.15)$
$\text{Fe}^{3+} + 3 \text{ isa}^- \rightleftharpoons \text{Fe(isa)}_3(\text{aq})$			
pot	$I = 1.0 \text{ M NaClO}_4$	25.0	$(11.00 \pm 0.16)$
$\text{Fe}^{3+} + 4 \text{ isa}^- \rightleftharpoons \text{Fe(isa)}_4^-$			
pot	$I = 1.0 \text{ M NaClO}_4$	25.0	$(12.99 \pm 0.17)$

Table IX-13: Enthalpy of Fe(III) isa complexation in the literature [2004RAO/GAR].

Method	Ionic medium	$t$ (°C)	$\Delta_r H_m$ kJ·mol <sup>-1</sup>
$\text{Fe}^{3+} + \text{isa}^- \rightleftharpoons \text{Fe(isa)}^{2+}$			
cal	$I = 1.0 \text{ M NaClO}_4$	25.0	$(3.4 \pm 0.5)$
$\text{Fe}^{3+} + 2 \text{ isa}^- \rightleftharpoons \text{Fe(isa)}_2^+$			
cal	$I = 1.0 \text{ M NaClO}_4$	25.0	$(7.8 \pm 1.3)$
$\text{Fe}^{3+} + 3 \text{ isa}^- \rightleftharpoons \text{Fe(isa)}_3(\text{aq})$			
cal	$I = 1.0 \text{ M NaClO}_4$	25.0	$-(18.3 \pm 2.0)$
$\text{Fe}^{3+} + 4 \text{ isa}^- \rightleftharpoons \text{Fe(isa)}_4^-$			
cal	$I = 1.0 \text{ M NaClO}_4$	25.0	$-(23.3 \pm 3.0)$

### IX.14.3 Th(IV) isa compounds and complexes

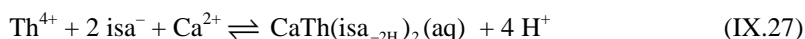
The Th - isa system has been studied by [99VER/GLA2], [2000VER], [2001VER/GLA], [2002TIT/WIE] and [2004TIT/WIE] under alkaline conditions. Strong effects on the sorption of Th(IV) on solid phases due to Th - isa complexation have been found at pH 10.7, 12.0 and 13.3. The constants on Th(IV) isa complexes from [2000VER], [2001VER/GLA], [2002TIT/WIE] and [2004TIT/WIE] are summarised in Table IX-14.



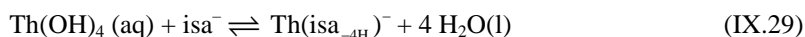
Table IX-14: Stability constants of Th(IV) isosaccharinate complexes in the literature.

Method	Ionic medium	<i>t</i> (°C)	log <sub>10</sub> <i>K</i>	Reference
$\text{Th}^{4+} + \text{isa}^- \rightleftharpoons \text{Th}(\text{isa}_{-4\text{H}})^- + 4 \text{H}^+$				
sorption	<i>I</i> = 0.3 M Na(ClO <sub>4</sub> /OH)	(23 ± 2)	– (10.1 ± 0.2)	[2000VER], [2001VER/GLA]
$\text{Th}^{4+} + 2 \text{isa}^- + \text{Ca}^{2+} \rightleftharpoons \text{CaTh}(\text{isa}_{-2\text{H}})_2(\text{aq}) + 4 \text{H}^+$				
sorption	<i>I</i> = 0.3 M Na(ClO <sub>4</sub> /OH)	(23 ± 2)	– (3.6 ± 0.2)	[2000VER], [2001VER/GLA]
sorption	<i>I</i> = 0.3 M Na(ClO <sub>4</sub> /OH)	23 ?	– (7.4 ± 0.3)	[2002TIT/WIE]
sorption	<i>I</i> = 0.3 M Na(ClO <sub>4</sub> /OH)	(23 ± 2)	– (7.4 ± 0.3)	[2004TIT/WIE]

Vercammen and co-workers [2000VER] and [2001VER/GLA] include data of Th(IV) sorption on different solids in the absence and presence of Ca. The data were evaluated by [2000VER] and [2001VER/GLA] to obtain the stability constant of a Th – isa 1:1 complex ( $\log_{10} K$  (IX.26) = – (10.1 ± 0.2) at *I* = 0.3 M) in the absence of Ca, and the stability constant of a Th - isa - Ca 1:2:1 complex ( $\log_{10} K$  (IX.27) = – (3.6 ± 0.2) at *I* = 0.3 M) in the presence of Ca:



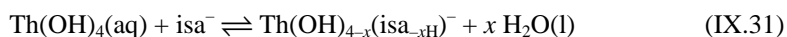
In the evaluation, the authors assumed that Th(OH)<sub>4</sub>(aq) is the dominant hydrolysis species of Th(IV) and used a hydrolysis constant for Reaction (IX.28),  $\text{Th}^{4+} + 4 \text{OH}^- \rightleftharpoons \text{Th}(\text{OH})_4(\text{aq})$ ,  $\log_{10} \beta_4$  (IX.28) = 39.44. Reactions (IX.26) and (IX.27) can be converted back to the following reactions that may reflect the actual reaction in alkaline solutions:



The equilibrium constants of Reactions (IX.29) and (IX.30) can be derived directly from series of sorption data at constant pH as reported in [2000VER] and [2001VER/GLA] by assuming that the only “inorganic” Th species is Th(OH)<sub>4</sub>(aq), and the only “organic” Th species are Th(isa<sub>-4H</sub>)<sup>–</sup> and CaTh(isa<sub>-2H</sub>)<sub>2</sub>(aq), respectively:  $\log_{10} K$  (IX.29) = (5.4 ± 0.2) and  $\log_{10} K$  (IX.30) = (11.9 ± 0.2) (*I* = 0.3 M). Reaction (IX.29) is an isocoulombic reaction so that the ionic strength dependence of its equilibrium constant is expected to be small.

Reactions (IX.26) and (IX.27), and accordingly Reactions (IX.29) and (IX.30), are based on the assumption that four (Reactions (IX.26) and (IX.29)) or two protons dissociated (Reactions (IX.27) and (IX.30)) from isa<sup>–</sup> in alkaline solutions to form the Th(IV) - isa or Th(IV) - Ca(II) - isa complexes. Such assumption cannot be verified by the experiments in [2000VER] and [2001VER/GLA]. Taking into consideration of this

uncertainty, the experimental data in [2000VER] and [2001VER/GLA] may be more appropriately represented by the following reactions:



The value of  $x$  and  $y$  in Reactions (IX.31) and (IX.32) cannot be determined by standard thermodynamic methods as the resulting models differ only in the number of moles of water released during complex formation.

The sorption experiments reported in [2002TIT/WIE] are similar to those in [2000VER] and [2001VER/GLA], but are conducted only on calcite and at pH 13.3. The data were evaluated by [2002TIT/WIE] in terms of Reaction (IX.27) as in [2001VER/GLA], to obtain the stability constant of a Th - isa - Ca 1:2:1 complex ( $\log_{10} K = -(7.4 \pm 0.3)$  at  $I = 0.3$  M, and  $\log_{10} K^\circ = -(5.0 \pm 0.3)$  at  $I \rightarrow 0$  using Davies equation). The value of  $-(7.4 \pm 0.3)$  from [2002TIT/WIE], [2004TIT/WIE] differs from that  $-(3.6 \pm 0.3)$  from [2001VER/GLA]. The difference is due to the use of different hydrolysis constants for  $\text{Th}(\text{OH})_4(\text{aq})$ :  $\log_{10} K$  (IX.28) = 39.44 [2001VER/GLA] and  $\log_{10} K$  (IX.28) = 34.9 [2002TIT/WIE], [2004TIT/WIE]. If the equilibrium constant of Reaction (IX.30) is derived directly from series of sorption data at constant pH as reported in [2002TIT/WIE], [2004TIT/WIE] this difference vanishes  $\log_{10} K$  (IX.30) =  $(9.4 \pm 0.3)$  ( $I = 0.3$  M) [2002TIT/WIE], [2004TIT/WIE] and  $\log_{10} K$  (IX.30) =  $(9.4 \pm 0.2)$  ( $I = 0.3$  M) [2000VER], [2001VER/GLA].

It is outside the scope of the present review to recommend data for thorium complexes with organic ligands, as thermodynamic data for inorganic compounds and complexes of thorium are currently reviewed within the scope of the NEA TDB Project Phase III. Hence, the thorium isa data are included here for the sake of completeness; they will be discussed more thoroughly in a future update based on NEA selected values for thorium hydrolysis.

# Appendices



## Appendix A

### Discussion of selected references

#### [\[1820DUB/SIL\]](#)

To obtain pure zirconium oxide, zirconium oxalate was precipitated from acid solution. The oldest paper reporting the insoluble zirconium oxalate but its composition and solubility are not mentioned.

#### [\[1842EBE\]](#)

The author precipitated solid U(VI) oxalate solids by adding a hot concentrated solution of oxalic acid into a concentrated solution of  $\text{UO}_2(\text{NO}_3)_2$ . The solubility of the solid in water was determined to be 0.8 g salt ( $14^\circ\text{C}$ ) and 3.4 g salt ( $100^\circ\text{C}$ ) in 100 g of water. The paper did not specify clearly whether the salt is  $\text{UO}_2(\text{ox})\cdot 3\text{H}_2\text{O}$  or  $\text{UO}_2(\text{ox})$ . However, based on the comparison of the data from different studies, it is assumed by this review that the salt is  $\text{UO}_2(\text{ox})\cdot 3\text{H}_2\text{O}$ . So, the solubility of  $\text{UO}_2(\text{ox})\cdot 3\text{H}_2\text{O}$  in water from this study is  $0.019 \text{ mol}\cdot\text{kg}^{-1}$  at  $14^\circ\text{C}$  and  $0.082 \text{ mol}\cdot\text{kg}^{-1}$  at  $100^\circ\text{C}$ . As shown in Figure VI-26, the value at  $100^\circ\text{C}$  agrees fairly well with the data from other studies but the value at  $14^\circ\text{C}$  from this study seems erroneously high. As a result, only the solubility data at  $100^\circ\text{C}$  from this study is accepted by this review.

#### [\[1894NAS\]](#)

Nass reports in this paper his investigations concerning the “oxalate method” proposed in a textbook by Classen (4<sup>th</sup> edition, 1891) for quantitative analytical determination of the concentration of Mn, Mg, Zn, Co and Ni. The reported concentrations of Ni in oxalate solutions would be of interest for this review if they reflected the equilibrium solubility in water.

In the case of Ni the recipe tested is the following: 25 mL of Ni acetate solutions (containing 0.2414 and 0.2413 g Ni) were mixed with 15 mL K oxalate solution (K oxalate – water ratio 1:3), heated to the boiling point, and then 75 mL acetic acid (85%) have been added. This resulted in the precipitation of Ni oxalate. The solution with the precipitate was left at  $50^\circ\text{C}$  for 6 hours and then filtrated. The filtered solution exhibited a clearly visible green colour, and determination of its Ni content by electrolysis resulted in 0.0068 and 0.0065 g Ni. The conclusion of Nass is that the “oxalate

method” is not suitable for quantitative determination of Ni concentrations. He did not intend to determine the solubility of Ni oxalate, but merely tested a proposed analytical method and reports its failure in the case of Ni.

In support of his findings, Nass cites the results of a PhD thesis by Kofahl (1890). These results are summarised on p.508 of [\[1894NAS\]](#) in tables reporting: “solubility of Ni oxalate in acetic acid (85%)”, “solubility of Ni oxalate in the rinsing fluid”, “solubility of Ni oxalate in water” and “solubility of Ni oxalate in alcohol (90%)”. It is not clear what the numbers cited by [\[1894NAS\]](#) under the heading “solubility of Ni oxalate in water” actually mean. However, the PhD thesis of Kofahl also is devoted to a critical investigation of the “oxalate method” proposed by Classen, and for sure, Kofahl did not either intend to measure the solubility of Ni oxalate but to test an analytical method.

#### [\[02ORL\]](#)

The solubility of  $K_4U(ox)_4$  in water was measured to be 21.73 g “salt” in 100 g  $H_2O$  at  $17^\circ C$ . The composition of the salt was assumed to be  $K_4U(ox)_4 \cdot 6H_2O$ , but not confirmed. As a result, the data are rejected by this review.

#### [\[16COL\]](#)

The solid phases in equilibrium with solutions containing various concentrations of  $UO_2(ox)$  and  $K_2(ox)$  at 15 and  $50^\circ C$  were identified in this study. The solid phase in the solution without  $K_2(ox)$  was  $UO_2(ox) \cdot 3H_2O$ . As the concentration of  $K_2(ox)$  was increased from 0 to 24% (by mass of the solution) at  $15^\circ C$  and from 0 to 33% (by mass of the solution) at  $50^\circ C$ , the solid phase was transformed from pure  $UO_2(ox) \cdot 3H_2O$ , through mixtures of  $UO_2(ox) \cdot 3H_2O + K_2[(UO_2)_2(ox)_3] \cdot 4H_2O$ ,  $K_2[(UO_2)_2(ox)_3] \cdot 4H_2O + K_2[UO_2(ox)_2] \cdot 3.5H_2O$ ,  $K_2[UO_2(ox)_2] \cdot 3.5H_2O + K_6[(UO_2)_2(ox)_5] \cdot 10H_2O$ ,  $K_6[(UO_2)_2(ox)_5] \cdot 10H_2O + K_2ox \cdot H_2O$ , and finally into the pure  $K_2ox \cdot H_2O$ . From these data, a phase diagram of the  $UO_2(ox) - K_2ox - H_2O$  system at 15 and  $50^\circ C$  was obtained.

The solubility data from this study, except the data in water ( $[K_2(ox)] = 0$ ) for the pure solid phase of  $UO_2(ox) \cdot 3H_2O$ , are not accepted by this review because the equilibrium phases are mixed solids. The solubility of  $UO_2(ox) \cdot 3H_2O$  in water was reported to be 0.47 g and 1.00 g  $UO_2(ox)$  in 100 g solution at 15 and  $50^\circ C$ , respectively. The same values appear repeatedly in a few later papers including [\[17COL\]](#), [\[17COL2\]](#) and [\[25COL\]](#). These values are consistent with the data at other temperatures [\[25COL\]](#), [\[57BOL/KOR3\]](#) (Figure VI-26) and they are discussed in Section VI.10.1.2.2.1.

#### [\[17COL\]](#)

The solid phases in equilibrium with solutions containing various concentrations of  $UO_2(ox)$  and  $Na_2(ox)$  at 15 and  $50^\circ C$  were identified in this study. The solid phase in the solution without  $Na_2(ox)$  was  $UO_2(ox) \cdot 3H_2O$ . As the concentration of  $Na_2(ox)$  was increased from 0 to 3% (by mass of the solution) at  $15^\circ C$  and from 0 to 4% (by mass of

the solution) at 50°C, the solid phase was transformed from pure  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ , through mixtures of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ ,  $\text{Na}_2[(\text{UO}_2)_4(\text{ox})_5] \cdot 11\text{H}_2\text{O}$ ,  $\text{Na}_2[(\text{UO}_2)_2(\text{ox})_3] \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2[\text{UO}_2(\text{ox})_2] \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{ox} \cdot \text{H}_2\text{O}$ , and finally into the pure  $\text{Na}_2\text{ox}$ . From these data, a phase diagram of the  $\text{UO}_2(\text{ox})$ - $\text{Na}_2\text{ox}$ - $\text{H}_2\text{O}$  system at 15 and 50°C was obtained.

The solubility data from this study, except the data in water ( $[\text{Na}_2(\text{ox})] = 0$ ) for the pure solid phase of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ , are not accepted by this review because the equilibrium phases are mixed solids. The solubilities of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in water at 15 and 50°C are identical to those from [\[16COL\]](#).

#### [\[17COL2\]](#)

The solid phases in equilibrium with solutions containing various concentrations of  $\text{UO}_2(\text{ox})$  and  $(\text{NH}_4)_2(\text{ox})$  at 15 and 50°C were identified in this study. The solid phase in the solution without  $(\text{NH}_4)_2(\text{ox})$  was  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ . As the concentration of  $(\text{NH}_4)_2(\text{ox})$  was increased from 0 to 4% (by mass of the solution) at 15°C and from 0 to 9% (by mass of the solution) at 50°C, the solid phase was transformed from pure  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ , through mixtures of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2[(\text{UO}_2)_2(\text{ox})_3] \cdot 3\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2[\text{UO}_2(\text{ox})_2] \cdot 2\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{ox} \cdot \text{H}_2\text{O}$  at 15°C, and mixtures of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2[(\text{UO}_2)_2(\text{ox})_3]$ ,  $(\text{NH}_4)_2[\text{UO}_2(\text{ox})_2]$ ,  $(\text{NH}_4)_2\text{ox} \cdot \text{H}_2\text{O}$  at 50°C, and finally into the pure  $(\text{NH}_4)_2\text{ox} \cdot \text{H}_2\text{O}$ .

The solubility data from this study, except the data in water ( $[(\text{NH}_4)_2(\text{ox})] = 0$ ) for the pure solid phase of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ , are not accepted by this review because the equilibrium phases are mixed solids. The solubilities of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in water at 15 and 50°C are identical to those from [\[16COL\]](#).

#### [\[25COL\]](#)

The solubilities of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in water at variable temperatures (11-100°C), in solutions of  $\text{HCl}$  at 11°C, in solutions of  $\text{H}_2\text{ox}$  at 15°C, and in solutions of  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$  at 20°C were determined in this study. The content of uranium in the equilibrium solid phase was determined by gravimetric analysis.

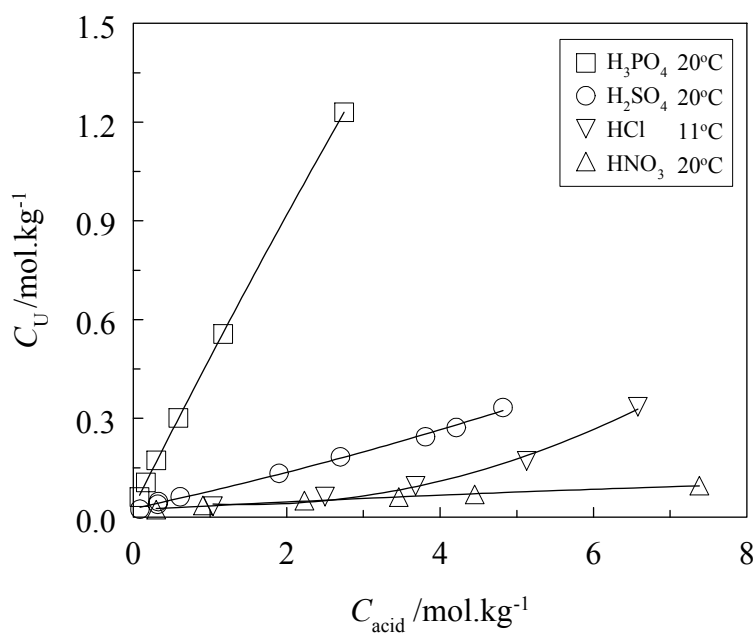
The data from this work on the solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in water from 11 to 100°C are in good agreement with the results in the temperature range of 0 – 70°C from [\[57BOL/KOR3\]](#). These data are considered by this review (Section VI.10.1.2.2.1). A summary of the raw data from [\[25COL\]](#) and [\[57BOL/KOR3\]](#) is shown in Table A-1 (page 570) under [\[57BOL/KOR3\]](#).

The data on the solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in  $\text{HNO}_3$  at 20°C from this work are in good agreement with the results from [\[52AMP/DAV\]](#) and [\[59MOS/ZAK\]](#). These data are considered by this review (Section VI.10.1.2.2.2).

The data on the solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in  $\text{H}_2\text{Ox}$  at  $15^\circ\text{C}$  from this work fit fairly well with the results at  $0 - 70^\circ\text{C}$  from [57BOL/KOR3]. A comparison is given in Figure A-8 under [57BOL/KOR3].

The solubilities of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in solutions of the mineral acids ( $\text{HCl}$  at  $11^\circ\text{C}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{H}_3\text{PO}_4$  at  $20^\circ\text{C}$ ) from this study were summarised in Figure A-1, where the concentrations are in molalities converted from the mass percentages in the paper by this review. The data indicate that the presence of mineral acids enhances the solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ . The magnitude of the enhancement follows the order:  $\text{H}_3\text{PO}_4 > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$ , probably consistent with the order of the complexing ability of the anions with  $\text{U(VI)}$ . Due to the high concentrations used in these experiments and the lack of accurate data to account for the complexation of the anions with  $\text{U(VI)}$  at these temperatures, further analysis of the data to derive thermodynamic constants for  $\text{U(VI)}$  oxalates is not pursued in this review.

Figure A-1: Solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in solutions of mineral acids.





[\[27DAV\]](#)

The author used the conductivity data then available in the literature to derive dissociation constants of weak electrolytes. Activity coefficients were estimated with a Debye-Hückel equation of the type:  $\log_{10} \gamma_{\pm} = -|z_+ z_-| \sqrt{c_i}$ . Among others, magnesium oxalate data was analysed. The conductivity data used for estimating the magnesium oxalate dissociation constant are not reported, and also the source of the data is not given in the paper. Hence, the equilibrium constant is not included in the present review.

[\[27SCH3\]](#)

Scholder investigated the complex formation of divalent metal – oxalates by measuring the specific conductivity and the metal concentration of saturated solutions, calculating the equivalent conductivity (the ratio of these two quantities), and comparing the equivalent conductivities at infinite dilution. The possible complex formation is discussed in qualitative terms only. However, solubility data are reported for all investigated solids, including Ca, Mg and Ni oxalate.

In order to get reliable results for sparingly soluble solids Scholder worked with 5 L bottles at 18°C. Specific conductivity was measured in these bottles, and these *in situ* measurements were used to monitor the attainment of solubility equilibrium. Solubility equilibria were investigated from undersaturation in all experiments by adding the respective solids to pure water. The pH of the resulting solutions has not been measured. The dissolved oxalate concentrations were determined by titration with permanganate,  $\text{KMnO}_4$ . The procedure is described as follows: The saturated solutions were filtered using membrane filters, and several quantities of 0.5 to 1 L solution were subsequently reduced by boiling to 50 mL, then 15 mL  $\text{H}_2\text{SO}_4$  (15%) added, and the resulting solutions titrated with 0.001 N permanganate.

The results as reported by Scholder are the mean values of  $6.0 \text{ mg}\cdot\text{L}^{-1}$ ,  $296.0 \text{ mg}\cdot\text{L}^{-1}$  and  $3.0 \text{ mg}\cdot\text{L}^{-1}$  for Ca, Mg and Ni oxalate, respectively. All these concentrations refer to the anhydrous oxalates “Ca(ox)”, “Mg(ox)” and “Ni(ox)”, and therefore they are equivalent to 47, 2640 and  $20 \text{ }\mu\text{mol}\cdot\text{dm}^{-3}$  for Ca, Mg and Ni oxalate, respectively. In the case of Ca and Ni oxalate also the individual analytical results are reported: 5.93, 6.05, 6.1, 6.03,  $5.9 \text{ mg}\cdot\text{L}^{-1}$  for Ca, and 3.05, 3.03, 3.01,  $2.97 \text{ mg}\cdot\text{L}^{-1}$  for Ni.

In the case of Ni oxalate Scholder reports that attaining constant conductivity (which is interpreted as reaching solubility equilibrium) took more than 100 hours, an exceptionally long time compared with all other systems investigated. In an experiment lasting just 3 hours only  $0.56 \text{ mg}\cdot\text{L}^{-1}$  “Ni(ox)” were found in solution, and in an experiment stopped after 24 hours the concentration was  $1.6 \text{ mg}\cdot\text{L}^{-1}$ .

[\[28FLO\]](#)

The solubility of  $\text{Na}_2\text{ox(s)}$  and  $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O(cr)}$  in water at 15, 20 and 25°C has been determined by titration of oxalate with  $\text{KMnO}_4$ . The solubility of  $\text{Na}_2\text{ox(s)}$  in pure water is reported to be 3.125 mass-% ( $= 0.241 \text{ mol}\cdot\text{kg}^{-1}$ ), 3.302 mass-% ( $= 0.255 \text{ mol}\cdot\text{kg}^{-1}$ ) and 3.475 mass-% ( $= 0.269 \text{ mol}\cdot\text{kg}^{-1}$ ) at 15, 20, and 25°C, respectively. The density of the saturated solutions is reported as 1.0253, 1.0255 and 1.0254 at 15, 20, and 25°C, respectively. The solubility of  $\text{H}_2\text{ox}\cdot 2\text{H}_2\text{O(cr)}$  in pure water is reported to be 6.71 mass-% ( $= 0.80 \text{ mol}\cdot\text{kg}^{-1}$ ), 8.34 mass-% ( $= 1.01 \text{ mol}\cdot\text{kg}^{-1}$ ) and 9.81 mass-% ( $= 1.21 \text{ mol}\cdot\text{kg}^{-1}$ ) at 15, 20, and 25°C, respectively. The density of the saturated solutions is reported as 1.0318, 1.0383 and 1.0437 at 15, 20, and 25°C, respectively.

[\[31BAN/RIG\]](#)

In this paper the dissociation constants of several salts in water were calculated from conductivity data. Stability constants for the complex  $\text{Kox}^-$  have been derived from conductivity and viscosity data of  $\text{K}_2\text{ox}$  taken from “International Critical Tables” Vols. V and VI. Three values for the formation constant of  $\text{Kox}^-$  are reported in Table III of [\[31BAN/RIG\]](#), namely  $\log_{10}K = -0.42$ ,  $-0.59$  and  $-0.62$  for ionic strength 0.07, 0.15 and 0.29 M  $\text{K}_2\text{ox}$ , respectively. Some of the data in this paper refer to 25°C, others to 18°C, but for the  $\text{K}_2\text{ox}$  data no information is given about the temperature. Using a special variant of the Debye-Hückel equation, Banks *et al.* extrapolated these numbers to zero ionic strength resulting in  $\log_{10} K^\circ = 0.25$ , 0.03 and 0.15. In [\[77MAR/SMI\]](#) a value of  $-0.8$  (18°C,  $I = 0$ ) is reported with reference to [\[31BAN/RIG\]](#), but this number obviously is erroneous.

No further details are reported by Banks *et al.* concerning the experimental data used in their calculations, except a general comment: “Complete reliance cannot be placed on several of the series of measurements reported since they fail, on extrapolation, to give additive values for the mobilities of the ions”. Considering the fact that conductivity measurements of unsymmetrical electrolytes are difficult to interpret unambiguously since the metal complex is itself charged and contributes to the measured conductivity, and the complete lack of details in this paper, the values reported for  $\text{Kox}^-$  complexation are not credited in this review.

[\[31GAB\]](#)

$\text{Zr(ox)}_2$  was prepared by adding methyl alcoholic solution of oxalic acid to the methyl alcoholic solution of zirconium tetrachloride. From the analysis of the obtained salt (Zr found was 35.08 weight-% as compared to the calculated value of 34.80 (this value is wrong as compared to 34.13)), the author concluded that the salt was  $\text{Zr(ox)}_2$ . The salt was found to be very soluble in water and insoluble in  $\text{HCl}$  and in  $\text{HNO}_3$ . No other analyses have been carried out for the structure of the solid and for the reaction with water. This review considers that the result is only very qualitative and not useful for the reactions in water.

[\[32MON/DAV\]](#)

The authors used the conductivity data then available in the literature to derive dissociation constants of weak electrolytes. Activity coefficients were estimated with a Debye-Hückel equation of the type:  $\log_{10} \gamma_{\pm} = -|z_+ z_-| \sqrt{c_i}$ . Among others, the calcium-oxalate and nickel-oxalate systems were analysed. The estimated complex dissociation constants in these systems were based on few data only. In the case of  $\text{Ca(ox)(aq)}$  the value was obtained from conductivity measurements on only two saturated solutions [\[27SCH3\]](#) where equilibrated water was used and thus large solvent and hydrolysis corrections were involved. The formation constant of  $\text{Ni(ox)(aq)}$  showed a decreasing tendency with the Ni-oxalate concentration, and Money and Davies concluded that  $K_{\text{Ni(ox)}} > 2 \times 10^5 \text{ M}^{-1}$ . The formation constant for  $\text{Mg(ox)(aq)}$  has been taken from [\[27DAV\]](#). The equilibrium constants reported in this paper are not included in the present review.

[\[33FOO/VAN\]](#)

The aim of this investigation was to obtain information about the solubility of  $\text{Na}_2\text{ox(s)}$  in  $\text{NaIO}_3$  solutions. The solubility isotherm in the  $\text{Na}_2\text{ox-NaIO}_3\text{-H}_2\text{O}$  system at 0, 25, 40 and 50°C has been determined, from pure  $\text{Na}_2\text{ox}$  to pure  $\text{NaIO}_3$ . The solubility of  $\text{Na}_2\text{ox(s)}$  in pure water is reported to be 2.62 mass-% ( $= 0.201 \text{ mol}\cdot\text{kg}^{-1}$ ), 3.56 mass-% ( $= 0.275 \text{ mol}\cdot\text{kg}^{-1}$ ), 4.09 mass-% ( $= 0.318 \text{ mol}\cdot\text{kg}^{-1}$ ) and 4.37 mass-% ( $= 0.341 \text{ mol}\cdot\text{kg}^{-1}$ ) at 0, 25, 40 and 50°C, respectively.

[\[33LAT/SCH\]](#)

In this careful low-temperature calorimetric study the heat capacity and entropy of calcium oxalate monohydrate has been determined in the range 19 to 300 K. The experimental data are given in tabular form as  $C_{p,m}^{\circ}$  in  $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  versus temperature. The authors used a molecular weight of  $146.09 \text{ g}\cdot\text{mol}^{-1}$  for calcium oxalate monohydrate to convert their data from  $\text{cal}\cdot\text{g}^{-1}\cdot\text{K}^{-1}$  to  $\text{cal}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . In this review a molecular weight of  $146.1154 \text{ g}\cdot\text{mol}^{-1}$  has been used and the data have been converted from cal to J using the factor 4.184. The data in the range 19.31 to 299.78 K have been fitted by a polynomial expression based on Eq. X.8 in [\[97PUI/RAR\]](#). The optimal representation of the experimental data has been reached using the polynomial expression  $C_{p,m}^{\circ}(T) = a + b \cdot T + c \cdot T^2 + j \cdot T^3 + d \cdot T^{-1} + e \cdot T^{-2}$  with the parameters  $a = -56.29$ ,  $b = 1.5431$ ,  $c = -4.960 \cdot 10^{-3}$ ,  $j = 7.070 \cdot 10^{-6}$ ,  $d = 9.357 \cdot 10^2$  and  $e = -6.637 \cdot 10^3$ . The curve below 19.31 K was extrapolated by means of a  $T^3$  dependence using  $C_{p,m}^{\circ}(T) = 3.285 \cdot 10^{-4} \cdot T^3$ . The experimental data and the fitted curves are shown in Figure A-2 for the entire temperature range and in Figure A-3 for  $T < 50 \text{ K}$ .

Figure A-2: Heat capacity of calcium oxalate monohydrate as a function of temperature. Symbols represent the experimental data of [33LAT/SCH] and the line shows the polynomial function fitted by this review.

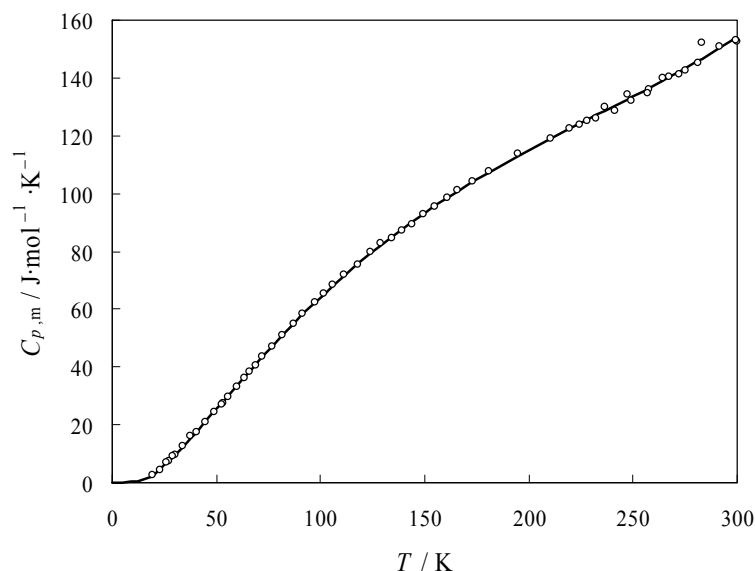


Figure A-3: Heat capacity of calcium oxalate monohydrate as a function of temperature. Symbols represent the experimental data of [33LAT/SCH] and the line shows the polynomial function fitted by this review. Below 19.31 K the heat capacity is extrapolated assuming a  $T^3$  dependence.

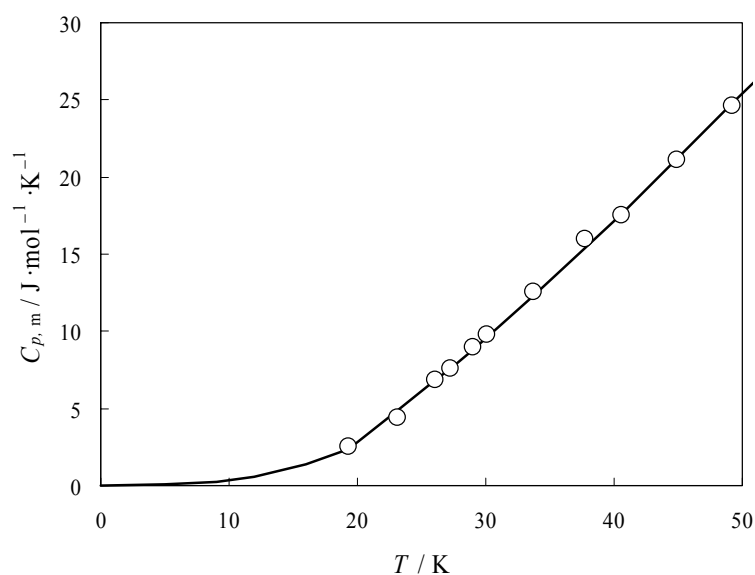
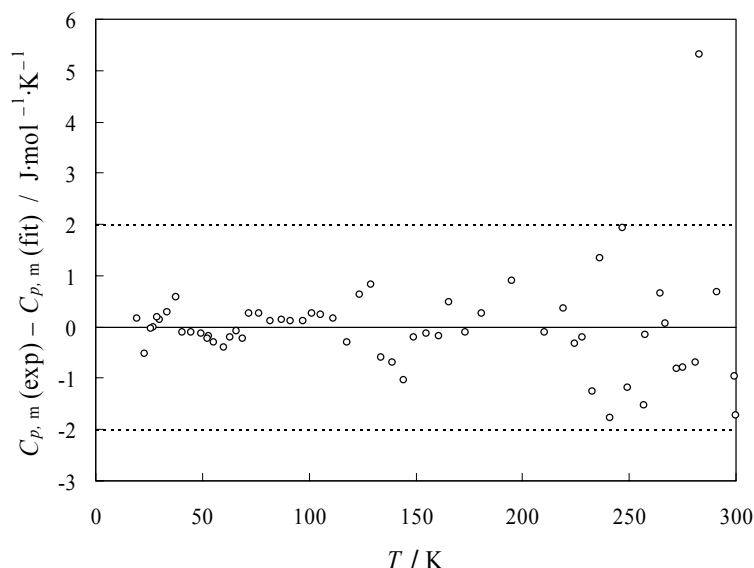


Figure A-4: Deviations of observed heat capacities of calcium oxalate monohydrate [33LAT/SCH] from the values of the polynomial function fitted by this review. Dotted lines represent the 95% confidence interval.



The results of these fitting procedures are:  $C_{p,m}^{\circ}(\text{Ca(ox)}\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (153.34 \pm 2.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $S_{\text{m}}^{\circ}(\text{Ca(ox)}\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = (156.37 \pm 2.0) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The entropy has been calculated from the fitted parameters of the heat capacity functions using analytical integration according to Eq. X.10 in [97PUI/RAR]. The original entropy value  $S_{\text{m}}^{\circ}(\text{Ca(ox)}\cdot\text{H}_2\text{O}, \text{cr}, 298.1 \text{ K}) = 156.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , obtained by graphical integration in [33LAT/SCH], is in good agreement with the value re-evaluated in this review. Note that the heat capacity and entropy values given in the NBS tables [82WAG/EVA],  $C_{p,m}^{\circ}(\text{Ca(ox)}\cdot\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K}) = 152.80 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $S_{\text{m}}^{\circ}(\text{Ca(ox)}\cdot\text{H}_2\text{O}, \text{cr}, 298.1 \text{ K}) = 156.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , most probably have been derived from the data set of [33LAT/SCH].

#### [34COL]

The solid phases in equilibrium with solutions containing various concentrations of  $\text{UO}_2(\text{ox})$  and  $\text{M(ox)}$  ( $\text{M} = \text{Ca}, \text{Sr}$  and  $\text{Ba}$ ) at 15 and 50°C were identified in this study. Depending on the alkaline earths used in the study, the concentrations of the alkaline earth oxalates ranged from 0 to 0.5% (by mass of the solution). Only in water and the solutions with low concentrations of  $\text{Mox}$ , the solid phase was found to be pure  $\text{UO}_2(\text{ox})\cdot 3\text{H}_2\text{O}$ . As the concentration of  $\text{Mox}$  was increased, the solid phases were transformed into mixtures of double salts ( $\text{U/M(ox)}$ ) or pure alkaline earth oxalates. Phase diagrams for the systems of  $\text{UO}_2(\text{ox})$ -  $\text{Mox}$ -  $\text{H}_2\text{O}$  at 15 and 50°C were obtained.

The solubility data from this study, except the data in water ( $[M(ox)] = 0$ ) for the pure solid phase of  $UO_2(ox) \cdot 3H_2O$ , are not accepted by this review because the equilibrium phases are mixed solids. The solubilities of  $UO_2(ox) \cdot 3H_2O$  in water at 15 and 50°C are identical to those from [16COL].

#### [34HAS/MCL]

Free concentration of  $Ca^{2+}$  in the solution containing  $CaCl_2$  and  $Na_3cit$  has been determined by the frog heart method at  $I = 0.155$  to  $0.163$  M (NaCl), pH 7.4 and 22°C. The authors claimed that the amplitude of contraction of the ventricle of the isolated heart of the frog, as recorded on a drum is dependent on  $[Ca^{2+}]$  without the effect of  $[Ca(cit)^-]$  and  $[cit^{3-}]$ . Total calcium was determined gravimetrically and total citrate was determined by oxidation by  $KMnO_4$  following the measurement of  $CO_2$  pressure. The values of the constant for  $M^{2+} + cit^{3-} \rightleftharpoons M(cit)^-$  ( $M = Mg$  or  $Ca$ ) has been determined to be  $\log_{10} \beta_1 = (3.22 \pm 0.025)$  for  $Ca(cit)^-$ . Also, by an indirect method, a value of approximately  $\log_{10} \beta_1 = 3.22$  for  $Mg(cit)^-$  has been derived. Since the effect of the frog heart method on the equilibrium of  $Ca^{2+} + cit^{3-} \rightleftharpoons Ca(cit)^-$  is unknown, this review does not accept these values.

#### [34SAR]

The author performed polarographic measurements, probably at room temperature, of  $Cd(II)$ ,  $Zn(II)$  and  $Ni(II)$  sulphates in  $KCl$ ,  $LiCl$  and  $NH_4Cl$  solutions and in the presence of sodium pyrophosphate ( $Na_4P_2O_7$ ) or ammonium oxalate. The system nickel oxalate was studied by measuring five solutions containing high concentrations of background electrolyte: either saturated  $NH_4Cl$  ( $\approx 5.4$  M), or 6.2 M  $LiCl$ . Sartori indicates in [34SAR] that the polarographic data for nickel was problematic, and the results involving this metal were only qualitative. From the data in  $LiCl$  the author estimated the value of  $\log_{10} \beta_2 = 13.7$ . This value is not included in the review procedure.

#### [36BOU]

The solubility of zirconium oxalate has been studied in solutions containing variable amounts of potassium oxalate (at 19, 35 and 52°C), rubidium and caesium oxalate (at 19°C), and in an accompanying paper [36BOU2] in sodium oxalate (at 39 and 52°C), ammonium oxalate (at 19 and 39°C), and lithium oxalate (at 19°C). The solubility of  $Na_2ox(s)$  in pure water is reported [36BOU2] to be 4.0 mass-% ( $= 0.31 \text{ mol} \cdot \text{kg}^{-1}$ ), and 4.40 mass-% ( $= 0.34 \text{ mol} \cdot \text{kg}^{-1}$ ) at 39 and 52°C, respectively. The solubility of  $K_2ox(s)$  in pure water is reported [36BOU] to be 24.5 mass-% ( $= 1.95 \text{ mol} \cdot \text{kg}^{-1}$ ), 28.42 mass-% ( $= 2.39 \text{ mol} \cdot \text{kg}^{-1}$ ) and 34.25 mass-% ( $= 3.13 \text{ mol} \cdot \text{kg}^{-1}$ ) at 19, 35, and 52°C, respectively.

Besides tables of results in mass-%, no details are given in [36BOU] and [36BOU2] about the solubility experiments and the analytical methods used to measure concentrations or to determine the composition of the solid phases. The author assumed

that pure zirconyl oxalate is  $\text{ZrO(ox)} \cdot 4\text{H}_2\text{O}$ , and the salts formed might correspond to  $3\text{Na}_2\text{ox} \cdot 2\text{ZrO(ox)} \cdot \text{H}_2\text{ox} \cdot 8\text{H}_2\text{O}$  or  $2\text{Na}_2\text{ox} \cdot \text{ZrO(ox)} \cdot \text{H}_2\text{ox} \cdot 2\text{H}_2\text{O}$  and  $2\text{K}_2\text{ox} \cdot \text{ZrO(ox)} \cdot \text{H}_2\text{ox} \cdot 4\text{H}_2\text{O}$ . Due to the complete lack of any experimental details, the results reported in [36BOU] and [36BOU2] are not credited in this review.

#### [36BOU2]

See comments to [36BOU].

#### [36MUU/LEB]

Solubility of  $\text{Ca(IO}_3)_2$  in the presence of excess amount of  $\text{KIO}_3$  was measured in the absence and presence of  $\text{Na}_3\text{cit}$  at  $I = 0.155 - 0.163$  M ( $\text{NaCl} + \text{KIO}_3$ ) and  $25^\circ\text{C}$ . The value of  $\log_{10} \beta_1$  for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca(cit)}^-$  was determined to be 3.21. By measuring the solubility at lower pH and using the value of  $\log_{10} \beta_1$  for  $\text{Ca(cit)}^-$ ,  $\log_{10} \beta_1$  for  $\text{Ca}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Ca(Hcit)(aq)}$  was obtained to be 2.3 at  $I = 0.110$ . Considering the low degree of purity in the reagents used and uncertainties in the pH measurement by indicator at that time of age, this review does not accept these values.

#### [38CAN/KIB]

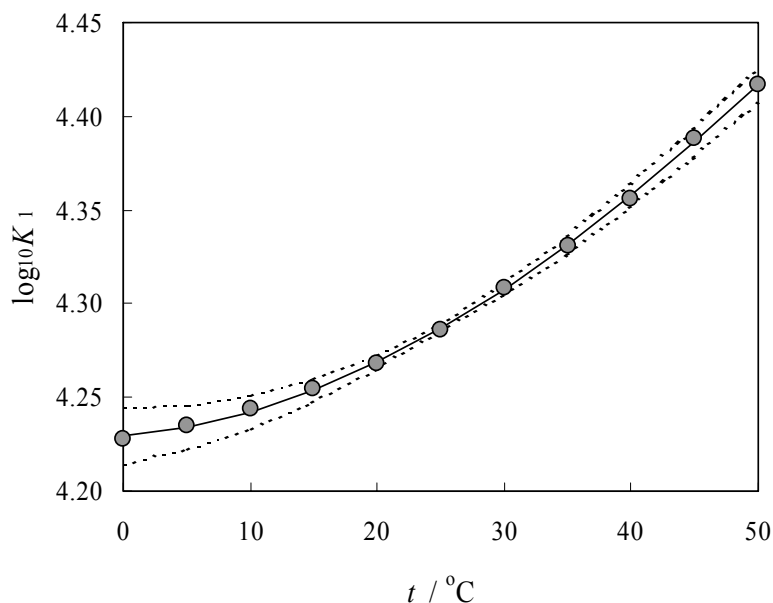
The results of titration using a hydrogen electrode are reported in this paper for a series of divalent metals and carboxylic acids, including Mg oxalate. Amounts of 1 M KCl and of 0.33 M  $\text{MCl}_2$  ( $\text{M} = \text{Zn, Mg, Ca, Sr, Ba}$ ) were added to give the desired cation mixtures, and the whole was diluted to  $I = 0.2$  M (calculated from  $\text{KCl} - \text{MCl}_2$  only). In this way the concentration of divalent cation was varied while approximate constancy of the ionic strength was maintained. The concentration of dicarboxylic acids was 0.01 M. The ionic strength would increase with the degree of neutralisation and decrease with the extent of complex formation. Actual calculations using the association constants found showed that  $I$  seldom fell outside of the range 0.19 – 0.21 M. For  $\text{Mg(ox)(aq)}$  the authors report  $\log_{10} K = 2.55$ . Considering that their oxalate protonation constants,  $\log_{10} K_1 = 3.85$  (3.75) and  $\log_{10} K_2 = 1.14$  (1.15), are somewhat different from the ones selected in this review (in parentheses), this review accepts the value  $\log_{10} K_1 = 2.55$  with an uncertainty of  $\pm 0.2$ . The authors also report a value  $\log_{10} K = \approx 0.5$  for  $\text{Mg(Hox)}^+$  but state that this value is “highly tentative” because it was not possible to make accurate calculations from observations at the low pH range in which this complex might dominate. This value is not credited in this review, and it remains to be shown that  $\text{Mg(Hox)}^+$  really exists.

[\[39HAR/FAL\]](#)

The second dissociation constant of oxalic acid was determined at intervals of 5 degrees from 0 to 50°C by measurement of the electromotive force of cells without liquid junction. Hydrogen and silver – silver chloride electrodes were employed. The solutions were composed of NaHox, Na<sub>2</sub>ox and NaCl with an ionic strength ranging from 0.03 to 0.17 mol·kg<sup>-1</sup>. The data set comprises 87 measurements made at 11 different temperatures. Each solution had the same ratio of oxalate to chloride (2:1) so that all data can be treated as a single set. The experimental emf data reported in [\[39HAR/FAL\]](#) have been later refitted together with new measurements by Kettler *et al.* [\[98KET/WES\]](#). The log<sub>10</sub>*K*<sub>1</sub> values at 25°C included in Table VI-4 have kindly been provided by R.M. Kettler (private communication) for this review.

In order to estimate the temperature variation of log<sub>10</sub>*K*<sub>1</sub> values extrapolated to zero ionic strength as reported in [\[39HAR/FAL\]](#) (Table VI-2) have been fitted in this review to a temperature function assuming  $\Delta_r C_{p,m} = \text{const}$ . The results are  $\Delta_r H_m = (6.66 \pm 0.09) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r C_{p,m} = (241 \pm 13) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . According to the rules of error propagation discussed in Section VI.3, assuming an uncertainty of  $\pm 0.02$  in the log<sub>10</sub>*K*<sub>1</sub> values, determined over the temperature range 0 to 50°C, the total uncertainty in  $\Delta_r H_m$  was estimated to be  $\Delta_r H_m = (6.7 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$ . No increase of the total uncertainty of  $\Delta_r C_{p,m}$  was necessary.

Figure A-5: First protonation constant for oxalate determined and extrapolated to *I* = 0 by [\[39HAR/FAL\]](#) and the constant  $\Delta_r C_{p,m}$  model with the parameters determined in this review.





[\[39NOR\]](#)

The solution containing various ratios of  $MCl_2$  ( $M = Mg$  or  $Ca$ ) and  $Na_3cit$  was equilibrated with the calcium and magnesium compound of tropeolin OO ( $M(Trop)_2$ ) at  $I = 0.08$  M ( $NaCl$  and  $K_2SO_4$ ) and  $37^\circ C$ . The concentration of the dye dissolved was determined colorimetrically and  $[M^{2+}]$  was calculated using the solubility product  $K_{s,0} = [M^{2+}] \times [Trop^-]^2$  ( $1.60 \times 10^{-13}$  for  $Mg(Trop)_2$  and  $2.42 \times 10^{-11}$  for  $Ca(Trop)_2$ ) obtained by separate experiments. Using the relation,  $[MCl_2]_T + (1/2)[Trop^-] = [M^{2+}] + [M(cit)^-]$  and  $[Na_3cit]_T = [cit^{3-}] + [M(cit)^-]$  where subscript T denotes the initially added concentrations, the constants for  $M^{2+} + cit^{3-} \rightleftharpoons Mcit^-$  were calculated to be  $\log_{10} \beta_1 = 3.58$  for  $Mg(cit)^-$  and 3.50 for  $Ca(cit)^-$ . Considering the difficulty in the determination of the solubility products (the values found indicate that  $Ca(Trop)_2$  is more soluble than  $Mg(Trop)_2$ , but usually magnesium salts are more soluble than calcium salts) and the uncertainty in the establishment of solubility equilibria, this review does not accept these values.

[\[39PAR/GIB\]](#)

Parton and Gibbons [\[39PAR/GIB\]](#) used a cell without a liquid junction to determine the first and second dissociation constant of oxalic acid. For determining the first dissociation constant at  $25^\circ C$  mixtures of  $H_2ox$ ,  $KHox$  and  $KCl$  were studied at very low ionic strength ( $0.12 > I > 0.007$ ). For determining the second dissociation constant at 25, 30 and  $35^\circ C$  mixtures of  $KHox$ ,  $K_2ox$ , and  $KCl$  were studied at similar low ionic strength ( $0.26 > I > 0.016$ ). In all cases the reported protonation constants systematically decrease with decreasing ionic strength, reaching their lowest values at  $I \rightarrow 0$ . These results are in marked contrast to the well-established Debye-Hückel behaviour of increasing constants at  $I \rightarrow 0$  [\[39HAR/FAL\]](#), [\[48PIN/BAT\]](#). Hence, the results of [\[39PAR/GIB\]](#) are not accepted in this review.

[\[39PAR/NIC\]](#)

Parton and Nicholson [\[39PAR/NIC\]](#) used the same method as [\[39PAR/GIB\]](#) except that a hydrogen electrode was used instead of quinhydrone, and sodium salts replaced the potassium salts. For determining the first dissociation constant of oxalic acid at 25, 30 and  $35^\circ C$  mixtures of  $HCl$ ,  $NaHox$  and  $NaCl$  were studied at very low ionic strength ( $0.13 > I > 0.005$ ). In all cases the reported protonation constants systematically decrease with decreasing ionic strength, reaching their lowest values at  $I \rightarrow 0$ . These results are in marked contrast to the well-established Debye-Hückel behaviour of increasing constants at  $I \rightarrow 0$  [\[39HAR/FAL\]](#), [\[48PIN/BAT\]](#). Hence, the results of [\[39PAR/NIC\]](#) are not accepted in this review.

[\[39PED\]](#)

Solubility and conductivity data taken from the literature [\[03KOH\]](#), [\[08KOH\]](#), [\[29HAM\]](#) are re-evaluated by Pedersen. Greta Hammarsten [\[29HAM\]](#) carried out two

sets of determinations of the solubility of calcium oxalate,  $\text{Ca(ox)} \cdot \text{H}_2\text{O}$ , in solutions of  $\text{MgCl}_2$  at  $37^\circ\text{C}$ . In the first series the solvent contained only  $\text{MgCl}_2$ , in the second it contained in addition 0.32 M  $\text{NaCl}$ . Both series have been evaluated by Pedersen assuming either that only  $\text{Mg(ox)(aq)}$  is forming, or that only  $\text{Mg(ox)}_2^{2-}$  is forming. From the results he concluded that  $\text{Mg(ox)(aq)}$  is the dominating complex in these solutions. In the first series containing only  $\text{MgCl}_2$ , the calculated ionic strength varies from 0.003 to 0.1 M due to variable amounts of  $\text{Mg}^{2+}$  and  $\text{ox}^{2-}$ . The results of this series are not included in the final data analysis of this review. In the second series the ionic strength is close to 0.32 M  $\text{NaCl}$ , and the calculated stability constant is in the range  $\log_{10} K_1 = 2.23 - 2.31$ . This review accepts the mean value  $\log_{10} K_1 = 2.28$  with an uncertainty of  $\pm 0.10$ .

Conductivity data of Kohlrausch [03KOH], [08KOH] were re-evaluated using the same method as Davies [27DAV], [32MON/DAV]. The results are similar, and also the criticism is the same. The equilibrium constant derived from conductivity data is not included in the present review.

#### [42HEI]

From the measurement of the quantum yield of photolysis and the absorption spectra of uranyl oxalate solutions, the photosensitive species were identified as  $\text{UO}_2(\text{H}_2\text{ox})^{2+}$ ,  $\text{UO}_2\text{ox(aq)}$  and  $\text{UO}_2(\text{ox})_2^{2-}$ . Results of potentiometric measurements were consistent with the presence of these species. The experiments were conducted at  $25\text{--}26^\circ\text{C}$  in solutions of low ionic strength. The concentrations and concentration quotients in the solutions are summarised in Table A-2 by this review. In the calculation of the concentration of various species, the first and the second ionisation constants of oxalic acid ( $0.0536$  and  $5.18 \times 10^{-5}$ ) were used and taken from [41DAR] and [39HAR/FAL]. The activity coefficient of the ionic species in dilute solutions was calculated by the equation:  $\log_{10} \gamma = -0.5089 \cdot z^2 \cdot \sqrt{I} / (1 + 1.5 \cdot \sqrt{I})$ . This appears to be a carefully conducted study. However, without using a more concentrated background electrolyte, the ionic strength was not maintained constant in the experiments. Besides, the presence of the protonated U(VI) oxalate complex,  $\text{UO}_2(\text{H}_2\text{ox})^{2+}$ , remains to be confirmed by independent studies and/or techniques. Therefore, the data are not selected by this review.

Table A-2: Concentrations and concentration quotients of the U(VI) oxalate system in [42HEI].

	$I \approx 0.08 \text{ M}$	$I \approx 0.05 \text{ M}$	$I = 0$
$C_{\text{UO}_2\text{SO}_4}, \text{ M}$	0.02	0.0143	
$C_{\text{H}_2\text{ox}}, \text{ M}$	0.05	0.0143	
$a_{\text{H}^+}$	0.045	0.018	
$[\text{UO}_2^{2+}], \text{ M}$	0.00147	0.00488	
$[\text{UO}_2(\text{H}_2\text{ox})^{2+}], \text{ M}$	0.00503	0.000814	
$[\text{UO}_2\text{ox}(\text{aq})], \text{ M}$	0.00488	0.00582	
$[\text{UO}_2(\text{ox})_2^{2-}], \text{ M}$	0.00862	0.00279	
$[\text{H}_2\text{ox}(\text{aq})], \text{ M}$	0.00915	0.00045	
$[\text{Hox}^-], \text{ M}$	0.0137	0.00164	
$[\text{ox}^{2-}], \text{ M}$	$3.18 \times 10^{-5}$	$8.5 \times 10^{-6}$	
$([\text{UO}_2^{2+}][\text{H}_2\text{ox}(\text{aq})]) / [\text{UO}_2(\text{H}_2\text{ox})^{2+}]$	$2.7 \times 10^{-3}$	$2.7 \times 10^{-3}$	$2.7 \times 10^{-3}$
$([\text{UO}_2\text{ox}(\text{aq})][\text{ox}^{2-})] / [\text{UO}_2(\text{ox})_2^{2-}]$	$1.8 \times 10^{-5}$	$1.8 \times 10^{-5}$	$1.8 \times 10^{-5}$
$([\text{UO}_2^{2+}][\text{ox}^{2-})] / [\text{UO}_2\text{ox}(\text{aq})]$	$9.6 \times 10^{-6}$	$7.1 \times 10^{-6}$	$1.5 \times 10^{-5}$

**[45BOB/JOR]**

By measuring the conductivity, absorbance, and pH of the solution containing 0.02 M  $\text{NiSO}_4$  and a variable amount of  $\text{Na}_3\text{cit}$  (or 0.02 M  $\text{Na}_3\text{cit}$  and variable amount of  $\text{NiSO}_4$ ), it has been shown that the molar ratio of  $\text{Ni}^{2+}$  to citrate in the complex is always 1:1 and that this complex behaves as if it were a monobasic acid and is neutralised by one equivalent of alkali at pH 6 – 8. Although this observation is qualitatively reasonable, the stability constant  $\log_{10} \beta_1 = 3.39$  reported for  $\text{Ni}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})^-$  is not accepted by this review since the solution conditions such as pH and ionic strength were not maintained constant in the experiment.

**[46JOS]**

The amalgam electrode of the third kind,  $\text{Pb}(\text{Hg}) | \text{PbC}_2\text{O}_4, \text{CaC}_2\text{O}_4 | \text{Ca}^{2+}$  has been used to determine the concentration of  $\text{Ca}^{2+}$ . The relation between the activity (electrode potential) and concentration was established at NaCl up to 3 M. Then  $[\text{Ca}^{2+}]$  was measured in the mixtures of 0.0025 or 0.005 M  $\text{CaCl}_2$  and 0 to 0.0025 or 0.005 M  $\text{K}_3\text{cit}$ , and the constant for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$  was calculated to be  $\log_{10} \beta_1 = 3.17$  at  $I = 0.15$  M NaCl, and 25°C. Considering the scatter in the calculated  $\log_{10} \beta_1$  and the scarcity of the data points, this review accepts this value with assigning a large uncertainty of  $\pm 0.4$ .

[\[47SCH/ACK\]](#)

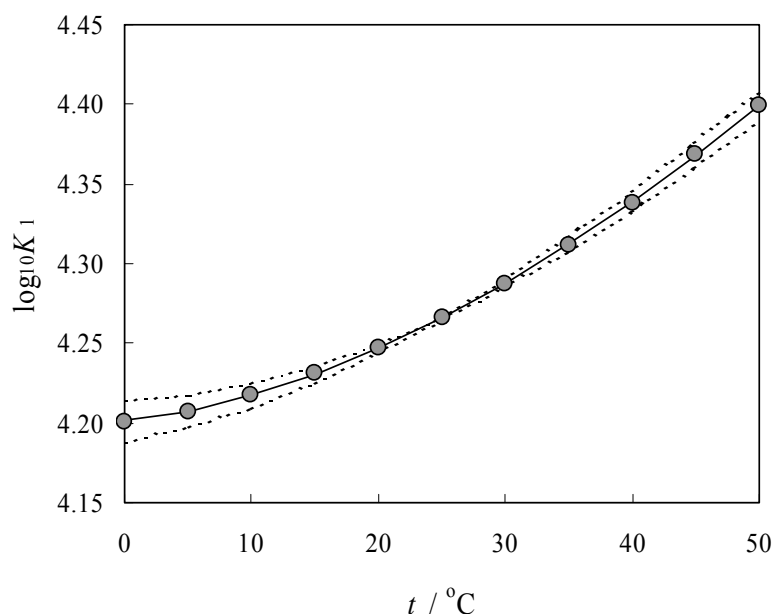
Alkalimetric titrations are reported of H<sub>4</sub>edta alone and in the presence of Li, Na, Mg, Ca, Sr and Ba chlorides. The pH measurements were carried out with a hydrogen electrode (for more experimental details, see [\[47SCH/WIL\]](#)). The solutions used in this study for metal complex formation contained 0.1 M KCl, [H<sub>4</sub>edta]<sub>total</sub> = 1×10<sup>-3</sup> M and [MeCl]<sub>total</sub> = 10×10<sup>-3</sup> M (Me = Li, Na) or [MeCl<sub>2</sub>]<sub>total</sub> = 15×10<sup>-3</sup> M (Me = Mg, Ca, Sr, Ba). In the latter case this results in an actual ionic strength of  $I = 0.145$  M, instead of 0.100 M if solely the contribution of KCl alone would be considered. This introduces systematic errors in the reported data. Therefore, this review does not include the stability constants reported for Mg(edta)<sup>2-</sup> and Ca(edta)<sup>2-</sup> in the final evaluation of recommended values. However, in the cases of log<sub>10</sub>K<sub>1</sub>(Na(edta)<sup>3-</sup>) and, log<sub>10</sub>K(Mg(Hedta)<sup>-</sup>) and log<sub>10</sub>K(Ca(Hedta)<sup>-</sup>), this ionic strength ambiguity is less important and the values have been considered in this review with an uncertainty of ± 0.2 log<sub>10</sub>-units.

[\[48PIN/BAT\]](#)

The second dissociation constant of oxalic acid was determined at intervals of 5 degrees from 0° to 50°C by measurement of the electromotive force of cells without liquid junction. Hydrogen and silver – silver chloride electrodes were employed. The solutions were composed of KHox, Na<sub>2</sub>ox and NaCl with an ionic strength ranging from 0.05 to 0.75 mol·kg<sup>-1</sup>. The data collection comprises 617 measurements made at 11 temperatures and 4 different ionic media with respect to the ratio of KHox, Na<sub>2</sub>ox and NaCl. The experimental emf data reported in [\[48PIN/BAT\]](#) have been later refitted together with new measurements by [\[98KET/WES\]](#). The log<sub>10</sub>K<sub>1</sub> values at 25°C included in Table VI-4 have kindly been provided by R.M. Kettler (private communication) for this review.

In order to estimate the temperature variation of log<sub>10</sub>K<sub>1</sub>, values extrapolated to zero ionic strength as reported in [\[48PIN/BAT\]](#) (Table VI-2) have been fitted in this review to a temperature function assuming  $\Delta_r C_{p,m} = \text{const}$ . The results are  $\Delta_r H_m = (7.00 \pm 0.05) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r C_{p,m} = (231 \pm 6) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . According to the rules of error propagation discussed in Section VI.3, assuming an uncertainty of ± 0.02 in the log<sub>10</sub>K<sub>1</sub> values, determined over the temperature range 0 to 50°C, the total uncertainty in  $\Delta_r H_m$  was estimated to be  $\Delta_r H_m = (7.0 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$ . Consequently, the total uncertainty of  $\Delta_r C_{p,m}$  was estimated to be  $\Delta_r C_{p,m} = (231 \pm 13) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

Figure A-6: First protonation constant for oxalate determined and extrapolated to  $I = 0$  by [48PIN/BAT] and the constant  $\Delta_r C_{p,m}$  model with the parameters determined in this review.



#### [48PYN]

The constant for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$  has been determined to be  $\log_{10} \beta_1 = 3.46$  at  $I = 0.03 \text{ M}$  and  $2^\circ\text{C}$  by dialysis. The details of the experiment such as pH measurement, concentrations of the reagents and the method of calculation are not given. This review does not accept this value.

#### [48SCH/ACK]

The same type of study as reported in [47SCH/ACK] has been extended to higher homologues of edta. From the results obtained for these homologues the authors estimate an upper limit of  $\log_{10} K < 0.7$  for the reaction  $\text{Ca}(\text{edta})^{2-} + \text{Ca}^{2+} \rightleftharpoons \text{Ca}_2\text{edta}(\text{aq})$ .

#### [49CON/MCV]

Zirconium species in acidic solutions have been investigated by using two phase distribution with TTA. From the distribution behaviour of zirconium, zirconium was shown to exist as  $\text{Zr}^{4+}$  and/or  $\text{ZrOH}^{3+}$  in  $2 \text{ M HClO}_4$  at low zirconium concentrations. The composition was not known precisely because of the interference of an unidentified

impurity in the experiments. This paper gives useful information that hydrolysis and/or polymerisation of zirconium can be avoided only at acidities higher than 2 M at low zirconium concentrations.

#### [49REA]

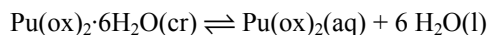
In this article the author reports the solubility of Pu(IV)-oxalate in solutions containing oxalic acid and 0.75 M HNO<sub>3</sub>. To interpret these data the equilibrium constants for the following reactions,

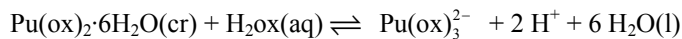


were also determined at 25°C. Values for reactions (A.1) and (A.2) were estimated from data in the literature, and then three solutions were prepared in which the ionic strength was calculated to be constant ( $I = 0.84$  M), containing 0.4 to 0.75 M HNO<sub>3</sub>, LiNO<sub>3</sub> and H<sub>2</sub>ox, and saturated with solid oxalic acid dihydrate. After three days of equilibration time the total oxalate in the solution was determined by titration with (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub>. The values of  $\log_{10} K$  at  $I = 0.84$  M are  $-0.967$  and  $-0.0685$  for reactions (A.1) and (A.2), respectively. However, the author does not provide any information on the quality of the solid oxalic acid used, or about the separation method to obtain aliquots (*e.g.*, filtration or centrifugation). Furthermore, the composition of the three different solutions and the final concentration of oxalate in the solubility experiments are not reported. This complete lack of experimental data precludes any plausibility check or recalculation of the reported stability constants. Hence, these values are not credited by this review.

The solubility of Pu(IV) oxalate was obtained in 0.75 M HNO<sub>3</sub> solutions containing up to 0.4 M H<sub>2</sub>ox at  $(25 \pm 0.05)^\circ\text{C}$ . The solid was reported to be Pu(ox)<sub>2</sub>·6H<sub>2</sub>O, although a characterisation of the solid phase either before or after the equilibration is not reported. The author states that equilibration time was at least 10 days, and checks were performed after additionally  $\approx 5$  days for changes. However, in the most diluted samples the solubility was determined after two hours of mechanical stirring, possibly to avoid the effect of oxidation of oxalic acid by Pu(IV). The plutonium contents of aliquots were determined radiometrically, but again the author does not provide any information on the separation method to obtain the aliquots (*e.g.*, filtration or centrifugation), although it is mentioned that spectrophotometric measurements were made after centrifugation.

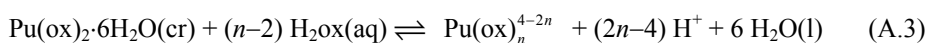
The author used the protonation constant obtained at  $I = 0.84$  M to evaluate the solubility data determined at  $I = 0.75$  M. Solubility constants were derived for the following reactions:





No equilibrium constant could be determined involving the formation of  $\text{Pu(ox)}_4^{4-}$ , although the author found spectroscopic evidence for its formation. The equilibrium constants reported in this article are not accepted by this review because side reactions were not considered: hydrolysis and nitrate complexation of Pu(IV).

An exact re-evaluation of the data is not possible because ionic medium effects of  $\text{HNO}_3$  on either the dissociation of oxalic acid or the formation of  $\text{PuNO}_3^{3+}$ ,  $\text{PuOH}^{3+}$  and  $\text{Pu(OH)}_2^{2+}$  are not known. The tabulated solubility values are re-evaluated assuming that the solid phase is indeed  $\text{Pu(ox)}_2 \cdot 6\text{H}_2\text{O}$  in these experiments, and that perchlorate specific ion interaction coefficients may be used as an approximation instead of nitrate:  $\varepsilon(\text{PuNO}_3^{3+}, \text{NO}_3^-) = \varepsilon(\text{PuNO}_3^{3+}, \text{ClO}_4^-) = (0.70 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}$  (from the value of  $\Delta\varepsilon$  selected in [2001LEM/FUG] for  $\text{HClO}_4$  media); and the  $\varepsilon$ -values in perchlorate media for  $\text{PuOH}^{3+}$  and  $\text{Pu(OH)}_2^{2+}$  from [2001NEC/KIM]. For all other ions the following approximation was used:  $\varepsilon(\text{M}^{Z_M}, \text{X}^{Z_X}) = 0.15 + 0.15 \times ((Z_M - 1) + (Z_X + 1))$ . Values of  $\varepsilon(\text{H}^+, \text{Hox}^-)$  in the range  $(+0.15 \text{ to } -0.15) \text{ kg} \cdot \text{mol}^{-1}$  were tested, giving  $\log_{10} K$  values for the first dissociation constant of oxalic acid ( $\text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Hox}^- + \text{H}^+$ ) in the range  $-(0.97 \pm 0.08)$  to  $-(1.20 \pm 0.08)$  (for 0.7 M  $\text{HNO}_3$ , in molar units), corresponding to  $\approx 12\%$  and  $\approx 8\%$  dissociation, respectively. The data with  $[\text{H}_2\text{ox}] \geq 0.003 \text{ M}$  were used in the least-squares regression using the following equilibria:

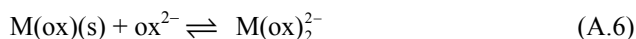


resulting in:  $\log_{10} K_s^\circ((\text{A.3}); n=0) \leq -13$ ;  $\log_{10} K_s^\circ((\text{A.3}); n=1) = -(8.1 \pm 0.3)$ ;  $\log_{10} K_s^\circ((\text{A.3}); n=2) = -(4.58 \pm 0.04)$ ;  $\log_{10} K_s^\circ((\text{A.3}); n=3) = -(4.26 \pm 0.03)$ ;  $\log_{10} K_s^\circ((\text{A.3}); n=4) = -(8.2 \pm 0.5)$ . The concentrations of  $\text{Pu(ox)}^{2+}$  and  $\text{Pu(ox)}_4^{4-}$  are less than 10% and 6%, respectively, of the total plutonium in these experiments.

#### [51BAR/ARG]

This study reports solubility measurements at  $(25 \pm 0.3)^\circ\text{C}$  of several metal ion oxalates, including  $\text{Mg(ox)}(\text{s})$  and  $\text{Ni(ox)}(\text{s})$ , with increasing potassium oxalate concentrations. Solubilities were measured after 4 days equilibration time, and the samples were filtered a number of times through “very fine” sintered glass. Magnesium was measured colorimetrically with Titan yellow, and nickel was also analysed colorimetrically using dimethylglyoxime. The solubility of  $\text{Mg(ox)}(\text{s})$  in water is reported to be  $3.20 \times 10^{-3} \text{ M}$ , and the dissociation constant of  $\text{Mg(ox)}_2^{2-}$  was reported to be  $4.2 \times 10^{-5}$ . For nickel, the solubility of the oxalate in distilled water was found to be  $7.15 \times 10^{-5} \text{ M}$  and the dissociation constant of  $\text{Ni(ox)}_2^{2-}$  was reported to be  $3.1 \times 10^{-7}$ . Although the solids were chemically analysed, the number of hydration waters is not reported. No attempt was made to control the ionic strength, and no information is given on the pH of the solutions.

The reported solubility curves for  $\text{Mg(ox)}$  and  $\text{Ni(ox)}$  as a function of added  $\text{K}_2\text{ox}$  might provide values for the equilibrium constants of the following reactions:



provided that the solid remains unchanged between experiments.

For magnesium it may be assumed that  $\text{Mg(ox)} \cdot 2\text{H}_2\text{O(cr)}$  was present in all experiments performed by Barney *et al.* [51BAR/ARG], see [2004FRO/ADE], therefore the solubility data in Fig.3 of [51BAR/ARG] were digitised by this review, and the data fitted using a least squares procedure to a model including the three reactions listed above, with  $\text{M} = \text{Mg}^{2+}$ , neglecting protonation and hydrolysis reactions. The SIT model described in Appendix B was used to estimate single-ion activity coefficients with  $\epsilon(\text{K}^+, \text{ox}^{2-}) = 0.07 \text{ kg} \cdot \text{mol}^{-1}$ , while for all other ions the following approximation was used:  $\epsilon(\text{M}^{Z_M}, \text{X}^{Z_X}) = 0.15 + 0.15 \times ((Z_M - 1) + (Z_X + 1))$ . Because the calculated ionic strength for these aqueous solutions was  $\leq 0.1 \text{ M}$  for all data points, the exact magnitude of the specific ion interaction parameters does not affect the results. The fitting of the data resulted in the following equilibrium constants:

$$\log_{10} K^\circ ((\text{A.4}), \text{M} = \text{Mg}) = -(5.90 \pm 0.08);$$

$$\log_{10} K^\circ ((\text{A.5}), \text{M} = \text{Mg}) = -(2.82 \pm 0.05);$$

$$\log_{10} K^\circ ((\text{A.6}), \text{M} = \text{Mg}) = -(1.26 \pm 0.05).$$

However, due to the ambiguities caused by the slow reaction kinetics of  $\text{Mg(ox)} \cdot 2\text{H}_2\text{O(cr)}$ , as discussed in Section VI.5.1, these fitting parameters are not considered in the final evaluation of Mg oxalate complexation constants.

In the case of nickel oxalate the formation of solid solutions with potassium oxalate (*cf.* [09DEA/SCO], [36VOS/ISR]) precludes the interpretation of the solubility data unless the solid phase present in the equilibrium solutions is thoroughly analysed. The authors stated that analysis of the solid phase showed that no solid solutions were formed at  $[\text{K}_2\text{ox}] < 0.002 \text{ M}$ , but no details are given about the analytical technique employed. Furthermore, the solid phase was most probably a dihydrate, but the authors failed to report the water contents of their solid, indicating that they had little control on the nature of the solid phase used in their experiments. The solubility for “ $\text{Ni(ox)(s)}$ ” given in Fig. 4 of [51BAR/ARG] exhibits an abrupt decrease at very low oxalate concentrations (Figure VI-18-a). This review is not able to interpret the data using reactions (A.4) to (A.6). There is no apparent reason for this peculiar behaviour, although it is possible that either solid solutions were nevertheless formed in this study, or that there was a change in the crystalline form (there are two  $\text{Ni(ox)} \cdot 2\text{H}_2\text{O}$  forms:  $\alpha$  and  $\beta$ ). The equilibrium constant reported by Barney *et al.* for  $\text{Ni(ox)}_2^{2-}$  is not credited by this review.



[\[51CON/REA\]](#)

The polymerisation of Zr(IV) in 1 M and 2 M HClO<sub>4</sub> solutions has been investigated by measurement of the extraction of Zr(IV) with TTA in benzene as a function of zirconium concentration. In 2 M HClO<sub>4</sub> solution, polymers were found to begin to form at zirconium concentration of approximately  $2 \times 10^{-3}$  M while in 1 M HClO<sub>4</sub> solution, they appeared at concentrations as low as  $2 \times 10^{-4}$  M. Dimers containing 3 and 5 hydroxide groups were shown to exist. Higher polymers were formed. At low zirconium concentrations in 1 M and 2 M HClO<sub>4</sub> solutions, zirconium is mainly present as unhydrolysed Zr<sup>4+</sup>. This experiment has been carried out carefully and the result is considered reliable giving important basic information for the study of complex formation of Zr(IV).

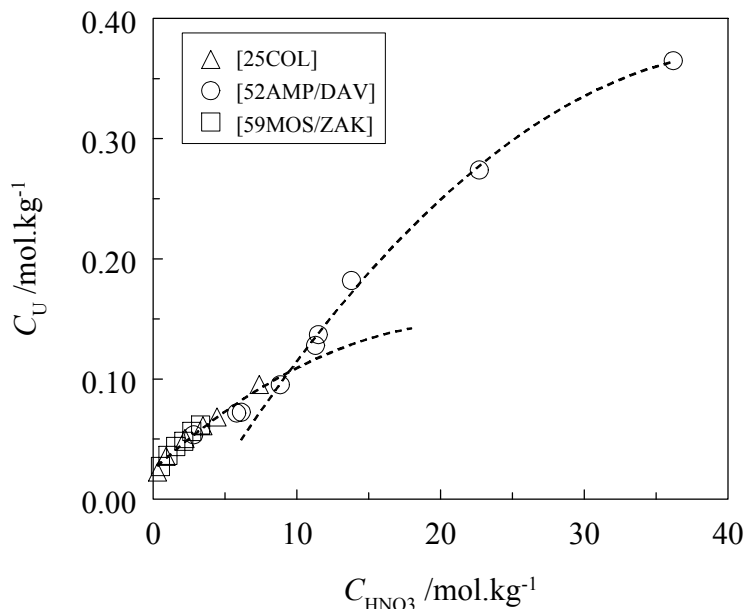
[\[51HEI\]](#)

Potentiometric titration of 0.0025 M citric acid has been conducted in the presence of 0.0075 M KCl or 0.0025 M CaCl<sub>2</sub> at room temperature. Protonation constants obtained are  $\log_{10} K_1^o = 6.38$ ,  $\log_{10} K_2^o = 4.66$  and  $\log_{10} K_3^o = 3.08$ , and the constants for  $\text{Ca}^{2+} + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{Ca}(\text{H}_r\text{cit})^{r-1}$  are  $\log_{10} \beta_1^o = (4.84 \pm 0.008)$  for  $\text{Ca}(\text{cit})^-$ , and  $(3.29 \pm 0.013)$  for  $\text{Ca}(\text{Hcit})(\text{aq})$ . Since the Debye-Hückel limiting equation used to estimate the activity coefficients may have introduced uncertainties, this review does not accept these values.

[\[52AMP/DAV\]](#)

The solubility of solid UO<sub>2</sub>(ox)·3H<sub>2</sub>O was studied in concentrated nitric acid (15-70% by mass of the solutions of HNO<sub>3</sub> + H<sub>2</sub>O, equivalent to 2.8-36 mol·kg<sup>-1</sup> H<sub>2</sub>O) at  $(20 \pm 1)^\circ\text{C}$ . The data are compared in Figure A-7 by this review with the results from other studies [\[25COL\]](#), [\[59MOS/ZAK\]](#). The concentrations of U(VI) and HNO<sub>3</sub> in the figure were in molalities, converted by this review from the mass percentages reported in the paper. The obvious “break” between the values at lower and higher concentrations of HNO<sub>3</sub> suggests possible changes in the solid phase. The solid phase in the region of lower [HNO<sub>3</sub>] was identified to be UO<sub>2</sub>(ox)·3H<sub>2</sub>O, which is consistent with other studies [\[25COL\]](#). In the region of higher [HNO<sub>3</sub>], the authors assumed that the solid phase was UO<sub>2</sub>(ox) based on limited experimental evidence.

The solubility data in solutions with  $[\text{HNO}_3] > 5 \text{ mol}\cdot\text{kg}^{-1} \text{ H}_2\text{O}$  from this study are rejected by this review due to possible changes and uncertainty in the nature of the solid phase. The solubility data at  $[\text{HNO}_3] < 5 \text{ mol}\cdot\text{kg}^{-1} \text{ H}_2\text{O}$  (only one data point) are in agreement with those from [\[25COL\]](#) and included in the discussions in Section VI.10.1.2.2.2.

Figure A-7: Solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in nitric acid at 20°C reported in the literature.**[52SCH/LIN]**

Distribution coefficients ( $K_d$ ) of  $^{45}\text{Ca}$  between a cation exchanger (Dowex 50) and an aqueous solution containing various concentrations of citrate ( $2 \times 10^{-4} - 4 \times 10^{-3}$  M) and 0.16 M NaCl were measured at pH 7.2 – 7.3 (adjusted by acetate and diethylbarbiturate, each 0.02856 M) and 25°C. Distribution coefficients of  $^{45}\text{Ca}$  can be expressed by:

$$K_d = \frac{K_d^0}{1 + \beta_1 [\text{cit}^{3-}]},$$

where  $K_d^0$  is the distribution coefficient in the absence of citrate and  $\beta_1$  is the constant for the reaction  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$ . Two series of experiment ( $[\text{cit}^{3-}] = 2 \times 10^{-4} - 4 \times 10^{-3}$  M and  $8 \times 10^{-4} - 2 \times 10^{-3}$  M) yielded the values of  $\log_{10} \beta_1$  as 3.15 and 3.16 from the plots of  $1/K_d$  versus  $[\text{cit}^{3-}]$ . The effect of the complex formation of  $\text{Ca}^{2+}$  with buffer components was estimated by assuming the formation constants of Ca-acetate and Ca-diethylbarbiturate were equal to 4.3. At most, this effect underestimates the value of  $\beta_1$  about 12%. However, the authors have not included the correction factors for the constant because these factors usually fall within the range of experimental uncertainty in the value of the constant itself. The assumption that the total citrate concentration is equal to  $[\text{cit}^{3-}]$  would overestimate  $[\text{cit}^{3-}]$  about 3% at this experimental pH. With considering these uncertainties, this review accepts the value as  $\log_{10} \beta_1 = (3.15 \pm 0.2)$ .

[\[53DAV/HOY\]](#)

The solubility of calcium iodate in the presence of citrate has been measured. pH measurements were carried out colorimetrically by comparison with the succinic acid-borax standards. A standard solution of methyl-red was used as an indicator. Using the values of  $\log_{10} K_1^o = 6.396$ ,  $\log_{10} K_2^o = 4.761$ ,  $\log_{10} K_3^o = 3.128$  for citrate protonation [\[49BAT/PIN\]](#) and  $\log_{10} \beta_1^o = 4.68$  (corrected to zero ionic strength from 3.15 at  $I = 0.16$  [\[52SCH/LIN\]](#)) for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$ , the constants for  $\text{Ca}^{2+} + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{Ca}(\text{H}_r\text{cit})^{r-1}$  were obtained to be  $\log_{10} \beta_1^o = 3.09$  for  $\text{Ca}(\text{Hcit})(\text{aq})$  and 1.10 for  $\text{Ca}(\text{H}_2\text{cit})^+$ . In the calculation, the effect of ionic strength (changed from 0.03 to 0.06) was corrected using  $\log_{10} \gamma = -0.5 z^2 (\sqrt{I_m}/(1 + \sqrt{I_m}) - 0.2 I_m)$ . Considering the uncertainties in the pH measurements, activity correction and  $\log_{10} \beta_1^o$  for  $\text{Ca}(\text{cit})^-$  used in the calculation, this review does not accept these values.

[\[53GRU/KAT\]](#)

A spectrophotometric study at  $I = 0.5 \text{ M}$  ( $\text{NaClO}_4$ ) of the complex equilibria between  $^{237}\text{Np}(\text{V})$  and oxalate was carried out at wavelengths of 983, 989 and 999 nm. Titrations were performed directly in thermostated spectrophotometric cells. The authors studied the change of absorbance of solutions as a function of the total concentration of oxalate (up to  $\approx 0.016 \text{ M}$ ) at three pH values (1.26, 3.20 and 4.87) at room temperature and also at 10, 29 and  $47^\circ\text{C}$  at pH = 3.2. Only the experimental optical densities at pH = 3.20 and room temperature are presented in a graph. The authors interpreted the data with the formation of  $\text{NpO}_2\text{ox}^-$  and  $\text{NpO}_2(\text{ox})_2^{3-}$  using the following protonation constants for oxalate:  $\log_{10} K_1^o = 4.27$  and  $\log_{10} K_2^o = 1.27$ . The pH of the solutions was measured using either a pH-meter with a glass electrode (at pH 1 to 2), or spectrophotometrically using pH-indicator dyes: methyl orange and methyl red at pH 3.1 to 4.4 and pH 4.2 to 6.3, respectively. According to the authors the pH was maintained constant within  $\pm 0.1$  units during a titration. No details are given about the calibration of the pH meter, or on the temperature effects on the pH measurements and on the protonation constants of oxalate. Because of this, the reported temperature effects on complex formation are not credited by this review.

Equilibrium constant at room temperature for the formation of the two complexes  $\text{NpO}_2\text{ox}^-$  and  $\text{NpO}_2(\text{ox})_2^{3-}$  were determined at the three pH values, and the average of these values is:  $\log_{10} K_1 = 3.29$  and  $\log_{10} K_2 = 3.77$  ( $\log_{10} \beta_2 = 7.06$ ). As pointed out in several later studies of this system (for example [\[72MAG/BIS\]](#)) the fact that  $K_2$  is larger than  $K_1$  is unexpected according to models of stepwise complex formation. The reason for this might be the values for the protonation constants for oxalate used by the authors in combination with their activity coefficient corrections.

In order to give uncertainty estimates for the results of this study the experimental data in Fig.2 of [\[53GRU/KAT\]](#) for  $[\text{NpO}_2^+] \approx 1 \times 10^{-3} \text{ M}$  and pH =  $(3.2 \pm 0.1)$  were digitalised and re-analysed by this review. Unfortunately the original experimental data at the other pH-values were not reported. Values of  $[\text{H}^+]$  for our recalculation were

obtained from  $a_{\text{H}^+}$  by estimating  $\gamma_{\text{H}^+}$  with the SIT model (Appendix B). Our analysis using the Letagrop-Spefo software [69SIL/WAR2] gave  $\log_{10} K_1 = (3.27 \pm 0.15)$  and  $\log_{10} \beta_2 = (6.4 \pm 0.2)$ . No protonated species  $\text{NpO}_2\text{Hox}(\text{aq})$  was found in our analysis. The results of the recalculation also showed that the reported values of  $K_2$  were overestimated, in agreement with a similar re-analysis of these data in [67KRO/MEF2]. Because not all original experimental data in [53GRU/KAT] could be re-analysed, the original values of  $K_1$  are accepted in this review with an uncertainty of  $\pm 0.15$   $\log_{10}$ -units, while the value of  $K_2$  is not included in the review procedure.

Experiments at  $\text{pH} = 3.2$  were also performed by Gruen and Katz at 10, 29 and 47°C. The individual values of the equilibrium constants at these temperatures are not reported. The data was interpreted in the same way as the data at room temperature. The authors calculated that the heat of formation for  $\text{NpO}_2\text{ox}^-$  was  $(0 \pm 1.3) \text{ kJ}\cdot\text{mol}^{-1}$ . A temperature function was reported for  $\log_{10} K_2$  which corresponds to  $\log_{10} K_2 = -4.27$  and  $\Delta_f H_m = +6.9 \text{ kJ}\cdot\text{mol}^{-1}$ . There is evidently an error in the sign of the  $\log_{10} K_2$  value and, as the equilibrium constants at these temperatures are not reported, it is not clear if the enthalpy change that corresponds to  $K_2$  is positive or negative.

#### [53HUG/MAR]

In this spectrophotometric study the dissociation of the complex  $\text{Ni}(\text{edta})^{2-}$  was investigated by increasing  $[\text{H}^+]$  at 30°C and  $I = 0.1 \text{ M}$  obtained with  $\text{KClO}_4$  or  $\text{KNO}_3$ . The edta protonation constants determined for other conditions (25°C and  $I = 0.2 \text{ M KCl}$ ) were used. Although the authors carried out their experiments at high  $[\text{H}^+]$  concentrations ( $\text{pH} < 3$ ) where the protonation of  $\text{Ni}(\text{edta})^{2-}$  to  $\text{Ni}(\text{Hedta})^-$  occurs, the formation of  $\text{Ni}(\text{Hedta})^-$  was neglected in their data analysis. The value  $\log_{10} K_1 = 17.5$  for the complex  $\text{Ni}(\text{edta})^{2-}$  is given without any indication of its precision. It is outside the range of expectation compared with results obtained under similar conditions [51SCH/FRE], [54SCH/GUT], [75AND/POD]. The value reported by [53HUG/MAR] is not considered in this review.

#### [54CAR/MAR]

This paper reports a potentiometric study of the systems Mg, Ca, Sr, Ba and edta in a temperature range  $(0 - 30)^\circ\text{C}$ . However, the measurements were carried out at low and varying ionic strengths without using a background electrolyte. The results have been extrapolated to zero ionic strength by the authors using the extended Debye-Hückel equation. From the temperature variation of these stability constants the authors derived enthalpy values. Note that the stability constants of  $\text{Mg}(\text{edta})^{2-}$  show the opposite temperature trend than found in other experimental studies [60BOH/MAR], [83ARE/MUS] and hence, the derived enthalpy value has a negative sign in contrast with all other reported data. The stability constants and enthalpy values of [54CAR/MAR] have not been considered further in this review.

[\[54HEI/BOB\]](#)

In this study  $0.1 \text{ mol} \cdot \text{kg}^{-1} \text{UO}_2(\text{NO}_3)_2$  solution and  $0.1 \text{ mol} \cdot \text{kg}^{-1} \text{Na}_3\text{cit}$  solution were mixed in various proportions and the mixtures were diluted to 10 mL in the absence and presence of various concentrations of NaOH. Spectrophotometric, potentiometric, and conductometric measurements have been carried out for the solutions. By observing the change in the absorption spectrum with the solution composition, the peaks at 430 nm and 450 nm were assigned to the formation of  $\text{UO}_2(\text{cit})^-$  and  $(\text{UO}_2)_2(\text{cit})_3^{5-}$ , respectively. The former complex prevails at pH lower than 7 and the latter at pH 7 to 9. At pH 9, the complex decomposes and the precipitation of hydroxide occurs. The constants were calculated to be  $\log_{10} K = 3.165$  for the reaction  $\text{UO}_2^{2+} + \text{cit}^{3-} \rightleftharpoons \text{UO}_2(\text{cit})^-$  and  $\log_{10} K = 6.095$  for  $2 \text{UO}_2^{2+} + 3 \text{cit}^{3-} \rightleftharpoons (\text{UO}_2)_2(\text{cit})_3^{5-}$ .

The ionic strength was not controlled and the calibration from pH to  $\log_{10}[\text{H}^+]$  was not carried out. The complex speciation seems uncertain since the separation of the peaks at 430 nm, 450 nm and those of  $\text{UO}_2^{2+}$  is not good and no isosbestic points are observed in the reported spectra. This review does not accept the results of this paper.

[\[54YAT/ZOL\]](#)

The heat of complexation of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) nitrates with potassium or ammonium oxalate was measured using microcalorimetry at 25°C. The experiments were performed in solutions containing  $[\text{ox}]_{\text{TOT}} = 0.25, 0.35$  and  $0.8 \text{ M}$ . In the first stage of the experiments a precipitate of  $\text{M}(\text{ox})(\text{s})$  may be formed, although it would then dissolve in the excess of oxalate. However, the amount of metal ion is not reported in the paper, and the ionic strength was not maintained constant. The enthalpy change for the reaction  $\text{Ni}^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Ni}(\text{ox})_2^{2-}$  was reported to be  $-5.15 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\log_{10} \beta_2$  was estimated from a correlation between enthalpy changes and formation constants to be 7.2. Because only three concentrations were investigated and given the experimental uncertainties, the data can not be re-calculated, and the values of  $\Delta_r H_m$  and  $\log_{10} \beta_2$  are not considered by this review.

[\[55DAV/HOY\]](#)

This is the correction of the calculation in [\[53DAV/HOY\]](#).

[\[55MOH/SIN\]](#)

$\text{Zr}(\text{NO}_3)_4$  was dissolved to form  $0.1 \text{ M}$  solution. A given volume of the solution was taken in a Pyrex vessel, and the following cell was formed:  $\text{Hg} \mid \text{Hg}_2\text{Cl}_2, \text{KCl sat.} \parallel \text{KCl sat.} \parallel \text{Zr}(\text{NO}_3)_4 \mid \text{Pt}$ . The e.m.f. of the cell was determined after successive addition of small amounts of a standard solution of  $\text{Na}_2\text{ox}$ . The plots of  $\Delta E/\Delta V$  against the added volume of  $\text{Na}_2\text{ox}$  showed four well-defined peaks, which were assigned to correspond respectively to quantitative precipitation of zirconium as  $\text{Zr}(\text{ox})_2$  and three oxalate complexes in which zirconium is associated with 4, 6 and 8 oxalate ions. The formation of the first complex was reported to be accompanied by complete dissolution of the pre-

precipitated  $\text{Zr(ox)}_2$ . This report gives only qualitative information that zirconium reacts with 2, 4, 6 and 8 equivalents of oxalate and cannot give any information about actual chemical species since  $\text{Zr(NO}_3)_4$  cannot be monomeric in 0.1 M solution. Solution conditions are not given and the effect of pH and zirconium concentration was not studied. This paper is not considered in this review.

#### [\[56CAR/STA\]](#)

Calorimetric measurements have been made in order to investigate the heats of formation of the complexation of edta with nine bivalent cations ( $\text{Me}^{2+} = \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}$  and  $\text{Pb}^{2+}$ ). A constant background concentration of a neutral salt was achieved by making both, the metal solution (0.01 M  $\text{Me(NO}_3)_2$  resulting in  $I = 0.13$  M) and the more concentrated solution of the complexing agent (0.1 M  $\text{K}_4\text{edta}$  resulting in  $I = 1.1$  M) always 0.1 M in potassium nitrate. By complexation the ionic strength of the mixture decreases from 0.24 M to approximately 0.17 M. Unfortunately aqueous  $\text{MeSO}_4$  solutions were used in the cases of  $\text{Mg}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ , causing additional unknown heat effects. Hence, the values reported by [\[56CAR/STA\]](#) for Mg and Ni edta are rejected by this review, and only the value of Ca edta is accepted.

#### [\[56GRI/PET2\]](#)

The solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in water,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$  and acetic acid at  $(25 \pm 0.1)^\circ\text{C}$  was measured. The solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in water at  $(25 \pm 0.1)^\circ\text{C}$  was 0.051 g  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in 1 kg of solution ( $\sim 23 \text{ mg} \cdot \text{L}^{-1}$  or  $0.097 \text{ mmol} \cdot \text{kg}^{-1}$  U-238). The solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in acetic acid was lower than that in water when the concentration of acetic acid was in the range of 0.1 – 1 N. The solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in the mineral acids first decreased when the concentration of the acids was increased ( $[\text{acid}] < 0.1$  N), then gradually increased with the further increase in the acid concentration ( $[\text{acid}] = 0.1 - 1$  N).

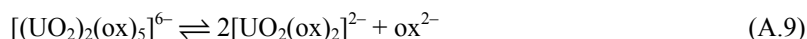
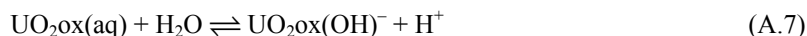
The same authors pointed out, in a later publication [\[63GRI/PET\]](#), partial oxidation of U(IV) by either the oxygen or the products of  $\alpha$ -radiolysis (from  $^{233}\text{U}$ ) occurred in the solubility experiments with mineral acids except HCl. Such oxidation casts serious doubts on the results from the solubility experiments where the oxidation state of uranium (IV) in the solid phase and aqueous species are not confirmed. In fact, the solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in water at  $25^\circ\text{C}$  from this reference ( $0.097 \text{ mmol} \cdot \text{kg}^{-1}$  U-238) is much higher than that from [\[60ZAK/MOS\]](#) ( $0.043 \text{ mmol} \cdot \text{kg}^{-1}$  U-238) (Figure VI-23). Data from this reference are not accepted in this review.

#### [\[56GRI/PTI\]](#)

Three types of compounds,  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ ,  $\text{M}_2[\text{UO}_2(\text{ox})_2] \cdot 3(2)\text{H}_2\text{O}$  ( $\text{M} = \text{K}^+, \text{NH}_4^+$ ), and  $\text{K}_6[(\text{UO}_2)_2(\text{ox})_5] \cdot 10\text{H}_2\text{O}$  were prepared in this study. The compositions of the compounds were analysed with two methods:

- (1) volumetric determination of oxalate and U(IV) with  $\text{KMnO}_4$  after U(VI) was reduced to U(IV) with Zn or by electrolysis;
- (2) volumetric determination of oxalate by titration with  $\text{KMnO}_4$  and gravimetric determination of uranium as  $\text{U}_3\text{O}_8$ .

The water content was determined at 110, 160, and 230°C. Electric conductivity measurements and potentiometry were used to study the dissolution reactions and the equilibria in solution. The equilibrium constants for the reactions:



were determined to be  $K(\text{A.7}) \sim 5 \times 10^{-7}$ ,  $K(\text{A.8}) = 3.5 \times 10^{-5}$ ,  $K(\text{A.9}) \sim 5 \times 10^{-7}$  at 25°C. The ionic strength was not maintained constant, but it appears to be  $< 0.1 \text{ mol} \cdot \text{kg}^{-1}$  according to the conditions given in the paper. Though similar dinuclear U(VI) oxalate complexes were reported later in [59TEK/VIN2] and [2002HAV/SOT], there is lack of supporting evidence for the significant presence of such complexes in solution and the obtained stability constants are highly uncertain. Therefore, the stability constants from this work are not accepted by this review.

#### [56MAR]

This paper is a summary of the investigations of Martell's research group. No new experimental results are reported. The entropy value for Ni edta complexation listed in [56MAR] was taken from [54CHA2].

#### [56MOR/JUS]

In this spectrophotometric study of zirconium edta complexation the authors did not use the direct spectrophotometric determination of the species because the difference between the curve for the Zr-edta mixture and the curve of the zirconium salt was small. The results were obtained in competition with  $\text{Cu}^{2+}$  by taking into consideration only the equilibrated clear solutions. The measurements were carried out at pH 2, but hydrolytic processes have been completely neglected in the data analysis. The resulting Zr-edta complexation constant is orders of magnitude outside the expectation range for this complex. However, the information given by [56MOR/JUS] is too scarce to allow any re-evaluation of their experimental data using edta protonation values selected in this review and proper Zr hydrolysis constants.

#### [56ZIE/CON]

Zirconium species in 1 M and 2 M  $\text{HClO}_4$  solutions has been investigated by using two phase distribution with TTA. From the distribution behaviour of zirconium, monomeric zirconium was shown to undergo hydrolytic polymerisation at  $5 \times 10^{-4} \text{ M}$  zirconium in 2

M HClO<sub>4</sub> and 10<sup>-4</sup> M zirconium in 1 M HClO<sub>4</sub>. Until ~0.02 M zirconium, data could be explained by a trimer (and a tetramer) and they are shown to hydrolyse to species containing 4 and 8 hydroxyl groups, respectively.

### [\[57BOL/KOR3\]](#)

The solubility of UO<sub>2</sub>(ox)·3H<sub>2</sub>O in water and in aqueous solutions of oxalic acid was determined at 0, 25, 40, 50 and 70°C in this study. It is stated in the paper that the temperature precision was ± 0.5°C at low temperatures and ± 0.1°C at high temperatures. The composition of the solid phases was confirmed by chemical analysis. The authors took the precautions to shield the sample solutions from sunlight so as to prevent photochemical reduction of U(VI) to U(IV). The equilibrium was found to achieve within 4-5 days at 25°C and 10-12 hours at 70°C. For all the temperatures, as the concentration of oxalic acid was increased, the solid phase was transformed from pure UO<sub>2</sub>(ox)·3H<sub>2</sub>O, through a mixture of UO<sub>2</sub>(ox)·3H<sub>2</sub>O and H<sub>2</sub>(ox)·2H<sub>2</sub>O, and finally into pure H<sub>2</sub>(ox)·2H<sub>2</sub>O. Only the results for pure UO<sub>2</sub>(ox)·3H<sub>2</sub>O are considered by this review.

The results are summarised and compared with the results at 15°C from [\[25COL\]](#) in Figure A-8, where the concentrations were in molality, converted by this review from the mass percentages reported in the paper. As shown in Figure A-8, the solubility of UO<sub>2</sub>(ox)·3H<sub>2</sub>O increased as the temperature was increased and, at each temperature, the solubility of UO<sub>2</sub>(ox)·3H<sub>2</sub>O increased as the concentration of oxalic acid was increased from 0 to ~ 1.5 mol·kg<sup>-1</sup>. At higher concentrations of oxalic acid, the solubilities decreased. The data from [\[25COL\]](#) fit fairly well with the results from this study.

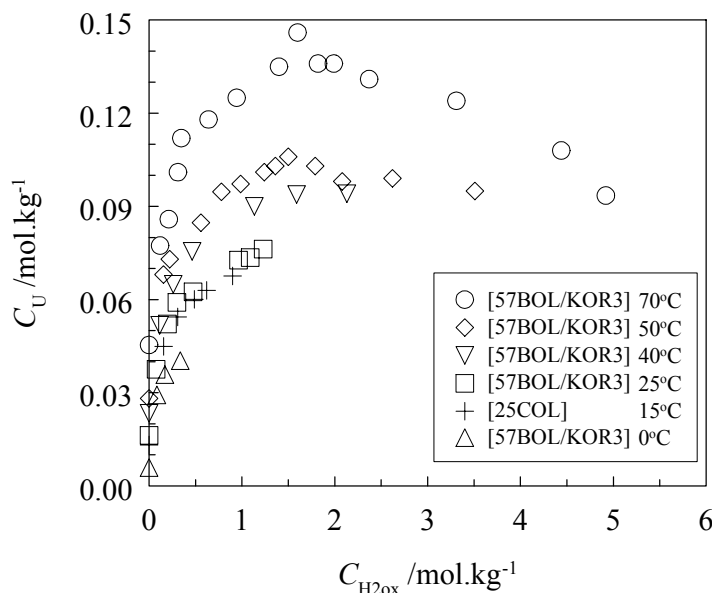
This study appears to be carefully conducted. The solubilities of UO<sub>2</sub>(ox)·3H<sub>2</sub>O in water ([H<sub>2</sub>ox] = 0) at 0, 25, 40, 50 and 70°C from this study, together with the data at 11, 15, 20, 50, 75 and 100°C from [\[25COL\]](#), are considered by this review (Section VI.10.1.2.2.1). Table A-1 summarises the results.

Table A-1: Solubility of UO<sub>2</sub>(ox)·3H<sub>2</sub>O in water at variable temperatures.

<i>t</i> °C	UO <sub>2</sub> (ox) g/100g solution	UO <sub>2</sub> (ox) mol·kg <sup>-1</sup>	Reference
11	0.45	0.0126	<a href="#">[25COL]</a>
15	0.47	0.0132	
20	0.50	0.0140	
50	1.00	0.0282	
75	1.65	0.0469	
100	3.06	0.0882	
0	0.21	0.00588	<a href="#">[57BOL/KOR3]</a>
25	0.58	0.0163	
40	0.83	0.0234	
50	1.00	0.0282	
70	1.60	0.0454	



Figure A-8: Solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in aqueous solutions of oxalic acid at variable temperatures.



#### [57BOL/KOR4]

The solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in the solutions of  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{UO}_2(\text{NO}_3)_2 + \text{H}_2\text{ox}$  was determined at 25°C. The concentrations of  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{HNO}_3$  varied from 0 to 56% and 0 to 65% (by mass of the solution), respectively. Several solid phases were observed in the experiments, including  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{H}_2(\text{ox}) \cdot 2\text{H}_2\text{O}$ . It was observed that  $\text{UO}_2(\text{NO}_3)_2$  has a salting-out effect on the solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  due to the common ion  $\text{UO}_2^{2+}$ .

Data obtained at very high concentrations of multiple electrolytes ( $\text{UO}_2(\text{NO}_3)_2$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{ox}$ ) are not particularly useful to derive thermodynamic solubilities. Besides, there seems to be inconsistent information on the composition of the solid phase in the paper (Table II, p.368). As a result, the solubility data from this paper are rejected by this review.

#### [57FOR/SMI]

Foreman and Smith inferred from potentiometric titrations of the plutonium edta system that  $\text{Pu(III)}$ ,  $\text{Pu(IV)}$  and  $\text{Pu(VI)}$  ions form 1:1 complexes with edta. The  $\text{Pu} : \text{edta}$  molar ratios in these titrations have been 1:0.5, 1:1, 1:2 and 1:4 in the case of  $\text{Pu(III)}$  and  $\text{Pu(IV)}$ , and 1:1 and 1:2 in the case of  $\text{Pu(VI)}$ .

The stability constants for these 1:1 Pu edta complexes in the three redox states

have been determined by a cation exchange technique. All solutions were made up in 0.1 M KCl solution and were about  $10^{-7}$  M in plutonium. The concentration range of the chelating agent edta was  $10^{-6}$  to  $10^{-4}$  M. As the authors report, at pH 3.3 it was possible to vary the edta concentrations obtaining reasonable values for the Pu distribution coefficients between the solution and the cation exchange resin in presence ( $\lambda$ ) and in absence ( $\lambda_0$ ) of edta. This was reached without the use of pH buffers, and the resin was conditioned at this pH before use. Foreman and Smith report  $\log_{10} K (\text{Pu}(\text{edta})^-) = 18.12$ ,  $\log_{10} K (\text{Pu}(\text{edta}), \text{aq}) = 17.86$ , and  $\log_{10} K (\text{PuO}_2\text{edta}^{2-}) = 16.39$ , and state that “it is unlikely that these values are in error by more than  $\pm 3\%$ , except in the case of plutonium(IV), where the calculated values for  $\lambda_0$  showed an overall spread of about 10%, and the total error in  $\log_{10} K$  could be  $\pm 3\%$ ”.

All experimental cation exchange results are reported as a plot of  $\log_{10}(\lambda_0/\lambda - 1)$  versus  $-\log_{10}[\text{edta}^{4-}]$ . The edta protonation constants used to calculate  $[\text{edta}^{4-}]$  from the total analytical concentration of edta have been taken from [\[51CAB\]](#). Note that the results of [\[51CAB\]](#) have been rejected in this review. The values for  $\lambda$ ,  $\lambda_0$  and the total edta concentrations are not reported and hence, no re-evaluation of the data is possible.

In the case of Pu(III), the authors ignored the possible presence of Pu(Hedta)(aq) at pH 3.3, and doing measurements just at a single pH, the contributions of Pu(Hedta)(aq) and  $\text{Pu}(\text{edta})^-$  to the resulting distribution coefficients cannot be de-convoluted. Moreover, the authors did not investigate to which extent Pu(III) could have been oxidised to Pu(IV) by water in edta free solutions used to determine  $\lambda_0$ .

In the case of Pu(IV) the authors themselves worry about the anomalously low stability constant obtained from their cation exchange measurements. They state that “in the case of plutonium(IV) a direct determination at this pH of  $\lambda_0$  in the absence of edta is impossible owing to hydrolysis of the  $\text{Pu}^{4+}$  ion;  $\lambda_0$  was therefore calculated by solving equation  $\log_{10}(\lambda_0/\lambda - 1) = \log_{10} K + \log_{10}[\text{edta}^{4-}]$  from pairs of edta concentration”. Having measured only 4 experimental points, this is an unreliable fitting exercise. But much more seriously, the authors completely ignored Pu(IV) hydrolysis as an important side reaction in their cation exchange experiments. This renders their Pu(IV) results wrong by orders of magnitude.

In the case of Pu(VI) the authors have not been aware of the instantaneous reduction of Pu(VI) to Pu(V) and further reduction to Pu(IV) in the presence of edta [\[98REE/WYG\]](#). Hence, their 3 experimental cation exchange measurements refer to an undetermined Pu redox state.

In summary, all results of [\[57FOR/SMI\]](#) are rejected in this review.

#### [\[57FOR/SMI2\]](#)

Absorption spectra of the edta complexes of Pu(III), Pu(IV) and Pu(VI) are presented by Foreman and Smith, and the stability constants of Pu – edta 1:1 complexes obtained

from these measurements are reported. Solutions of plutonium were used at concentrations of  $0.7 - 3.0 \times 10^{-2}$  M. Constant ionic strength of 0.1 M KNO<sub>3</sub> or KCl was maintained. The temperature of the measurements is not reported. The edta protonation constants used to calculate [edta<sup>4-</sup>] from the total analytical concentration of edta have been taken from [51CAB]. Note that the results of [51CAB] have been rejected in this review. No details about the measured values, or the calculations done to derive stability constants are given by Foreman and Smith.

The same shortcomings as discussed for the cation exchange study of Foreman and Smith [57FOR/SMI] apply to this spectrophotometric study. In the case of Pu(III), the authors ignored the presence of Pu(Hedta)(aq), an important species at pH 1.5 [78MER/GAT], in their data analysis. In the case of Pu(IV) the authors pretend having evaluated the constant  $K = [\text{Pu}(\text{edta})(\text{aq})] \cdot [\text{Cd}^{2+}] / ([\text{Cd}(\text{edta})^{2-}] \cdot [\text{Pu}^{4+}])$  at pH 3.3 but completely ignored the effects of Pu(IV) hydrolysis at that pH. In the case of Pu(VI) the authors realised that the Pu(VI) – edta solution is unstable and decomposes during a period of several days to Pu(IV) (from pH 6.5 to 8.1 in three days, and at pH 9.1 in six days) but they missed the observation that a Pu(VI) – edta solution is almost instantaneously reduced to Pu(V) in a first step [98REE/WYG]. Hence, all data reported by [57FOR/SMI2] at  $I = 0.1$  M KCl / KNO<sub>3</sub> are rejected in this review.

Foreman and Smith were aware of the Pu(IV) hydrolysis problems and thus, they carried out another experiment at 1 M HNO<sub>3</sub>. They state that “it is not possible to obtain an accurate value for the stability constant of the complex since its spectrum is not known and cannot be isolated”. Assuming that the molecular absorbance values for the Pu(IV) chelate measured at pH 3.3 can also be applied in 1 M HNO<sub>3</sub>, the authors report as a first approximation  $\log_{10} K (\text{Pu}(\text{edta}), \text{aq})$  values in the range of 24.2 – 24.3. No experimental data are given and especially, the edta protonation constants used for 1 M HNO<sub>3</sub> are not reported. Hence, also the value reported by [57FOR/SMI2] at 1 M HNO<sub>3</sub> is rejected in this review.

Klygin *et al.* [59KLY/SMI4] used their edta protonation constants to correct the Pu(IV) edta stability constant obtained in 1 M HNO<sub>3</sub> by [57FOR/SMI2] with respect to the presence of H<sub>6</sub>edta<sup>2+</sup> and obtained a value  $\log_{10} K (\text{Pu}(\text{edta}), \text{aq}) = 26.1$ . This correction is not accepted in this review. First of all, [59KLY/SMI4] ignored the presence of H<sub>5</sub>edta<sup>+</sup> in their correction, and secondly, this correction is applied to a value obtained by [57FOR/SMI2] using unknown edta protonation constants.

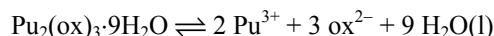
Krot *et al.* [62KRO/ERM] also used their edta protonation constants to correct the Pu(IV) edta stability constant obtained in 1 M HNO<sub>3</sub> by [57FOR/SMI2] considering both, the presence of H<sub>6</sub>edta<sup>2+</sup> and H<sub>5</sub>edta<sup>+</sup>, and obtained a value  $\log_{10} K (\text{Pu}(\text{edta}), \text{aq}) = 25.75$ . This value was then extrapolated to  $I = 0.1$  by means of the Davies equation. Also this correction is not accepted in this review. Although [62KRO/ERM] used the correct set of edta protonation species and their protonation data have been considered in this review, this correction still is applied to a value obtained by [57FOR/SMI2] using unknown edta protonation constants in the first place.

ing unknown edta protonation constants in the first place.

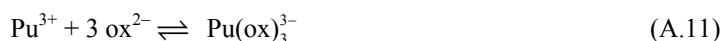
### [\[57GEL/MAT2\]](#)

The authors determined the solubility of Pu(III)-oxalate in water and in near neutral solutions (pH  $\approx$  8) of K<sub>2</sub>ox and (NH<sub>4</sub>)<sub>2</sub>ox at 20 and 70°C, respectively. Although the formula Pu<sub>2</sub>(ox)<sub>3</sub>·9H<sub>2</sub>O is given in the paper, no characterisation of the solid phase is reported. The solubilities were obtained from experiments without control of the ionic strength, except for data in [K<sub>2</sub>ox] = 0.01 to 1.5 M at 20°C which are reported both at varying and at constant ionic strength adjusted with KCl. The authors do not state however the value of the ionic strength (it may be estimated to be 4.5 M for a 1.5 M solution of potassium oxalate). The oxidation of Pu(III) to Pu(IV) was avoided by using a nitrogen atmosphere and at 20°C also by adding 10-15 g·L<sup>-1</sup> of NaHSO<sub>3</sub>·CH<sub>2</sub>O·2H<sub>2</sub>O (sodium formaldehyde sulfoxylate). The precipitate was equilibrated for 4-6 hours, and plutonium was analysed radiometrically. However, the method used for the phase separation (*e.g.*, filtration or centrifugation) is not reported.

From the solubility of Pu(III)-oxalate in water the authors deduced  $\log_{10} K_s = -24.8$  and  $-21.6$  at 20 and at 70°C, respectively, for the following reaction:



The variation of the solubility values with the concentration of oxalate was interpreted with reactions:



with the following values for the equilibrium constants at 20 and 70°C, respectively:  $\log_{10} \beta_2$  (A.10) = 9.31 and 7.94;  $\log_{10} \beta_3$  (A.11) = 18.70 and 16.19; and  $\log_{10} \beta_4$  (A.12) = 28.62 and 24.79. From the temperature variation of these constants, the authors calculated the enthalpy changes for reactions (A.10) to (A.12). All experimental data were used in these evaluations without correction for changes in activity coefficients. However, the equilibrium constants and  $\Delta_r H_m^\circ$  values reported in this paper are excluded from the review procedure because of lack of experimental details.

### [\[57GEL/MAT3\]](#)

The authors report the same solubility values for Pu<sub>2</sub>(ox)<sub>3</sub>·9H<sub>2</sub>O in near neutral solutions (pH  $\approx$  8) of K<sub>2</sub>ox and (NH<sub>4</sub>)<sub>2</sub>ox at 20 and 70°C, respectively, as those published in [\[57GEL/MAT2\]](#). In addition the ion-exchange measurements at pH 1.4-3.0 that are reported in this paper have also been published in [\[58GEL/MAT\]](#). See the comments in this appendix for these other two references, for which English translations are available.

[\[57JOR/ALL\]](#)

Enthalpy titrations have been carried out for the accurate evaluation of the heat of chelation of the divalent cations  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  with edta. Solutions of 0.01 M  $\text{Me}^{2+}$  (the nature of the anion is not reported in the paper) have been titrated with a 1.00 M  $\text{Na}_4\text{edta}$  solution. As no inert salt had been present in the solution, this procedure caused an increase of the ionic strength from 0.03 to 0.05 M. In addition to this variation in ionic strength, possible heat effects of  $\text{Na}^+$  (from  $\text{Na}_4\text{edta}$ ) reacting with the unknown anions of the metal salts cannot be judged and hence, the values reported by [\[57JOR/ALL\]](#) are not accepted by this review.

[\[57LEF\]](#)

Potentiometric titration experiments of a number of systems are described including Mg oxalate and Ca citrate. In the latter two cases the method consists of comparing, by pH titration with a strong acid, a state where the totally deprotonated ligand complexes with a cation, with a state where the totally protonated ligand does not form any complexes with the cation. This “integrating” method avoids the need to analyse the shape of the pH titration curve in detail involving protonation constants, but as a drawback does not provide information about metal complexation with protonated forms of the ligand.

In the case of the Mg oxalate titrations the total concentration of oxalate was 0.01 M whereas the total concentration of magnesium was varied from 0.0025 to 0.12 M at 27°C in 1 M  $\text{KNO}_3$ . The formation constant  $\log_{10} K_1 = (1.99 \pm 0.03)$  (95% statistical uncertainty, estimated in this review) for the  $\text{Mg}(\text{ox})(\text{aq})$  complex has been derived by the authors from their measurements. The nature of the Mg and oxalate salts used in the experiments is not reported. Within the pH range of the titrations,  $6 > \text{pH} > 2$ , some initial solutions at higher pH values were largely oversaturated with respect to  $\text{Mg}(\text{ox}) \cdot 2\text{H}_2\text{O}$ . Due to the very slow precipitation kinetics of  $\text{Mg}(\text{ox}) \cdot 2\text{H}_2\text{O}$  (see Section VI.5.1) this oversaturation perhaps has not caused problems in the titration experiments. However, this potential problem is not discussed by the author. The value  $\log_{10} K_1 = 1.99$  is included with an increased uncertainty of  $\pm 0.20$  in the final data analysis of this review.

In the case of Ca citrate titrations at 28°C in 0.15 M  $\text{NaCl}$  neither the concentrations of the reactants nor any other experimental detail are given; just the final result of four titrations is reported as  $\log_{10} K_1 = (3.20 \pm 0.10)$  (95% statistical uncertainty, estimated in this review) for the  $\text{Ca}(\text{cit})^-$  complex. Although this constant is in good agreement with values reported for similar conditions (see Section VII.5.1) it has not been included in the final evaluation of this review due to the total lack of experimental details.

[\[57LI/WES\]](#)

The stability constants of the complexes,  $\text{UO}_2(\text{Hox})^+$  and  $\text{UO}_2(\text{Hox})_2(\text{aq})$ , were obtained by an ion exchange method using U-233. The experiments were conducted at

( $25 \pm 1$ )°C in 0.16 M HClO<sub>4</sub> (pH = 0.90), 1 and 2 M HClO<sub>4</sub>, and at pH = 4.5. Using the  $pK_a$ 's of oxalic acid determined in this work (1.28 and 3.75), the stability constants  $K_1(\text{UO}_2^{2+} + \text{Hox}^- \rightleftharpoons \text{UO}_2(\text{Hox})^+)$  and  $K_2(\text{UO}_2^{2+} + 2 \text{Hox}^- \rightleftharpoons \text{UO}_2(\text{Hox})_2(\text{aq}))$  were calculated from the results at pH 0.90 to be 2510 and 360, respectively. The results from the experiments in 1 and 2 M HClO<sub>4</sub> allowed to calculate only  $K_1$  (680 and 780 for 1 and 2 M HClO<sub>4</sub>), but it should be noted that the  $pK_a$ 's of oxalic acid were not determined in these media. The results from the experiments at pH = 4.5 did not justify the calculation of the stability constant for  $\text{UO}_2\text{ox}(\text{aq})$ , though this complex was expected to form under the conditions. Because of the lack of appropriate  $pK_a$ 's, the results obtained in 1 and 2 M HClO<sub>4</sub> were not accepted by this review. The stability constants of  $\text{UO}_2(\text{Hox})^+$  and  $\text{UO}_2(\text{Hox})_2(\text{aq})$  obtained at pH 0.90 appear reasonable and consistent with values from other studies [42HEI], [76BRI/ELD]. However, the formation of protonated U(VI) oxalate complexes is still open for debate. If they form, it is most likely to occur in strongly acidic solutions. Therefore, the stability constants of protonated U(VI) oxalate complexes are not selected by this review.

#### [57PAT/PAN2]

Potentiometric titrations of 0.055 M citric acid with and without 0.045 M NiSO<sub>4</sub> by 1 M NaOH were conducted at 32.5°C (ionic strength was not maintained constant). At pH  $\leq 3.10$ , the authors assumed the formation of  $\text{Ni}(\text{Hcit})(\text{aq})$  only and obtained the value of  $^*K_1 = 7.97 \times 10^{-5}$  for the reaction  $\text{Ni}^{2+} + \text{H}_3\text{cit} \rightleftharpoons \text{Ni}(\text{Hcit})(\text{aq}) + 2\text{H}^+$ . At  $3.70 \leq \text{pH} \leq 4.20$ , they assumed the existence of  $\text{Ni}(\text{Hcit})(\text{aq})$  and  $\text{Ni}(\text{cit})^-$  and obtained the value of  $^*K = 1.75 \times 10^{-4}$  for the reaction  $\text{Ni}(\text{Hcit})(\text{aq}) \rightleftharpoons \text{Ni}(\text{cit})^- + \text{H}^+$ . Moreover, from the potentiometric titrations of 0.25 M KNO<sub>3</sub> with and without 0.0125 M NiSO<sub>4</sub> by 0.1 M Na<sub>3</sub>(cit) at 32°C, the value of  $^*K = 1.35 \times 10^{-8}$  was obtained for the reaction  $\text{Ni}(\text{cit})^- + \text{H}_2\text{O} \rightleftharpoons \text{Ni}(\text{cit})(\text{OH})^{2-} + \text{H}^+$ , where  $\text{Ni}(\text{cit})^-$  and  $\text{Ni}(\text{cit})(\text{OH})^{2-}$  were assumed to be present at  $6.2 \leq \text{pH} \leq 6.6$ . Ionic strength was not maintained constant in the former experiments, and measured pH was not corrected to  $\text{pH}_c$ . Moreover, the values of  $\log_{10} K_1^0 = 6.51$ ,  $\log_{10} K_2^0 = 4.39$ ,  $\log_{10} K_3^0 = 3.08$  were used for the protonation of citric acid, which are fairly different from those selected in this review. By these reasons, the reported values are not accepted by the present review.

#### [57SCH/AND]

The complexation of Mg with oxalate has been studied by means of an Hg sensitive electrode at 20°C in 0.1 M NaNO<sub>3</sub>. The stability constant  $\log_{10} K_1 = (2.76 \pm 0.04)$  for the  $\text{Mg}(\text{ox})(\text{aq})$  complex has been derived as the mean value from three titration experiments, and the uncertainty is the standard deviation. No indication has been found for the formation of a  $\text{Mg}(\text{ox})_2^{2-}$  complex even at the highest oxalate : magnesium ratios studied. Thus, [57SCH/AND] estimate an upper limit of  $\log_{10} K_2 < 1$  for  $\text{Mg}(\text{ox})_2^{2-}$ . The study is reliable and this review accepts  $\log_{10} K_1$  with an uncertainty multiplied by a factor 1.96 to obtain error limits closer to a 95% total uncertainty levels.

[\[57ZAI/SHU2\]](#)

Alcohol solutions of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  and oxalic acid were mixed and precipitates were obtained. From the composition analysis and TGA,  $\text{H}_2[\text{ZrO}(\text{ox})_2] \cdot 3\text{H}_2\text{O}$  and  $\text{H}_2[\text{ZrO}(\text{ox})_2] \cdot \text{H}_2\text{O}$  were concluded to be formed. The stoichiometries of the solid species were estimated only from their analytical composition. More recent studies indicate that the unit  $\text{ZrO}^{2+}$  actually does not exist either in aqueous solutions nor in the solid state and that a tetrameric species  $[\text{Zr}_4(\text{OH})_8(\text{OH}_2)_{16}]^{8+}$  is more probable.

[\[58BLU\]](#)

This review paper includes the discussion about the oxalate complex species. From the observations cited therein, it says that oxalate compounds with a relatively small number of oxalate ligands tend to be insoluble while those with a larger number of oxalate ligands tend to be soluble and only exceedingly slightly dissociated. The oxalatozirconic acids tend to hydrolyse in the absence of a substantial concentration of the acid from which they are derived, and the hydrolysates are only sparingly soluble. The oxalate hydrolysates are not well known and understood. When a mole of oxalic acid or an oxalate salt is added to a zirconyl chloride solution, a precipitate of empirical composition  $\text{ZrO}(\text{ox})_2 \cdot x\text{H}_2\text{O}$  is formed. Products in which  $x = 0, 3$  and  $4$  have been reported, and it is probable that  $x$  varies continuously and that there are no true chemical hydrates. The solid  $\text{Zr}(\text{ox})_2$  is prepared by the reaction of zirconium tetrachloride with its equivalence of anhydrous oxalic acid in methanol. Proof of the occurrence of the zirconium atom in the complex anion in the oxalate compounds has been adduced from electrochromatography, which has shown the zirconium to migrate toward the anode in solutions containing oxalate ion [\[52SAT/DIA\]](#). Systematic study has been made of the phases separating from systems containing  $\text{ZrO}(\text{ox})$ ,  $\text{M}_2(\text{ox})$  and  $\text{H}_2\text{O}$  ( $\text{M}_4\text{Zr}(\text{ox})_4 \cdot x\text{H}_2\text{O}$ ), where  $\text{M}$  is lithium, sodium, ammonium, potassium, rubidium or caesium.

[\[58BOB/BEN\]](#)

The authors performed titrations of Zr nitrate using potassium oxalate or *vice-versa*. The experiments were relatively fast: between 10 and 90 minutes. The formation of solid phases and their subsequent dissolution was studied by measuring the optical density photometrically. The authors admitted that in several cases reproducible results could not be obtained. A series of soluble and solid complexes were postulated from the shape of the curves representing optical density (proportional to the amount of precipitate) *versus* the stoichiometric composition of the solutions. Although this experimental method might give some qualitative information, this review does not set any trust in the quantitative value of the data presented.

[\[58BOL/KOR\]](#)

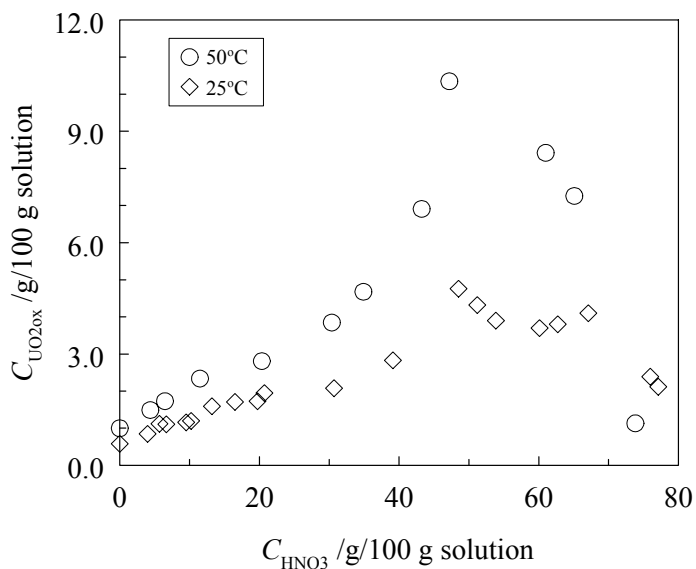
The solubility of  $\text{UO}_2\text{ox} \cdot 3\text{H}_2\text{O}$  in  $\text{HNO}_3$  at 25 and 50°C was studied in this work. As the concentration of  $\text{HNO}_3$  was increased from 0 to over 70 g/100 g solution, the solid

phase was transformed from  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  to  $\text{UO}_2(\text{NO}_3)_2$ . In the intermediate concentration range of  $\text{HNO}_3$  at  $25^\circ\text{C}$ , a solid phase of  $\text{UO}_2\text{ox}\cdot\text{H}_2\text{O}$  was observed. The data from the paper are plotted in Figure A-9.

The data show that the concentration of uranium increased as the concentration of nitric acid was increased from 0 to about 50 g/100 g solution, then decreased as the concentration of nitric acid was further increased. This is consistent with the change in the solid phase. The solubility is higher at  $50^\circ\text{C}$  than  $25^\circ\text{C}$ . Though the information from the paper is not sufficient to allow the estimation of the uncertainty, the data are more scattered, especially at higher concentrations of nitric acid, than the data at  $20^\circ\text{C}$  from [25COL], [52AMP/DAV] and [59MOS/ZAK] (see discussions and Figure A-7 under [52AMP/DAV]).

The solubility data in solutions with high  $[\text{HNO}_3]$  from this study are rejected by this review because of the existence of different solid phase(s) and the scatter of the data at high concentrations of nitric acid. Only the data at  $[\text{HNO}_3] < 5 \text{ mol}\cdot\text{kg}^{-1} \text{ H}_2\text{O}$  ( $\sim 24\%$  by mass) are included in the discussions in Section VI.10.1.2.2.2.

Figure A-9: Solubility of  $\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}$  in  $\text{HNO}_3$  at 25 and  $50^\circ\text{C}$  [58BOL/KOR].

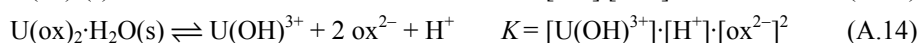




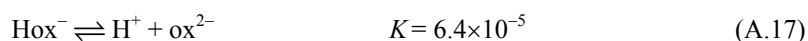
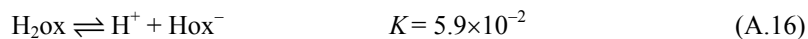
[\[58DOR\]](#)

The authors studied the solubility of  $\text{U(ox)}_2(\text{s})$  in solutions of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and mixtures of  $\text{HCl}/\text{H}_2\text{ox}$  at  $25^\circ\text{C}$ . The concentration of uranium was determined by  $\alpha$ -activity counting using either the electroplating method or the filter paper method. Precautions were taken to prevent oxidation of  $\text{U(IV)}$  oxalate during the experiments, including boiling the solutions to drive out dissolved oxygen and storing and shaking the solutions under a nitrogen atmosphere. The solubility data were taken after three-days shaking. Re-measurement of one sample after 36 days provided identical results as those after 3 days. Based on this, the author claimed that the dissolution equilibrium was reached in three days. No information on the characterisation of the solid phase was given. It is not clear whether the solid phase is  $\text{U(ox)}_2(\text{s})$ ,  $\text{U(ox)}_2\cdot\text{H}_2\text{O}(\text{s})$ , or  $\text{U(ox)}_2\cdot 6\text{H}_2\text{O}(\text{s})$ . However, by comparing with the solubility data from [\[56GRI/PET2\]](#) and [\[60ZAK/MOS\]](#), it appears that the solid phase is  $\text{U(ox)}_2\cdot 6\text{H}_2\text{O}(\text{s})$ .

The data on the solubility of  $\text{U(ox)}_2(\text{s})$  in  $\text{HCl}$  are shown in Figure VI-23. The author tested three reactions to model the dissolution and calculate the solubility product:



Using the following dissociation constants of the reactions:



and the mean ion activities interpolated from the data for hydrochloric acid at  $25^\circ\text{C}$  by Lewis and Randall [\[23LEW/RAN\]](#), the authors derived the values for  $K(\text{A.13})$ ,  $K(\text{A.14})$  and  $K(\text{A.15})$  as shown in Table A-2.

Table A-2: Calculated solubility products for  $\text{U(IV)}$ /oxalate defined by reactions (A.13) (A.14) and (A.15).

Solution $[\text{HCl}]$ , N	Mean activity of $\text{HCl}$	$K$ (A.13) ( $\times 10^{-23}$ )	$K$ (A.14) ( $\times 10^{-22}$ )	$K$ (A.15) ( $\times 10^{-15}$ )
0.118	0.00949	302	2.87	6.63
1.049	0.884	14	1.23	26.6
1.18	1.046	15.8	1.65	45.2
3.09	4.35	1.29	0.56	59.8
3.62	5.90	0.975	0.575	83.0
6.01	20.5	0.331	0.68	283
6.18	22.6	0.225	0.508	235
3.08 + 0.26 % $\text{H}_2\text{ox}$	4.31	21.5	9.24	973
6.05 + 0.268 % $\text{H}_2\text{ox}$	21.0	4.79	1.01	428

Since the results indicate that  $K(A.14)$  is the most consistent for all the solutions, the author concluded that the Reaction (A.14) is the best to describe the dissolution process and the hydrolysis of U(IV) to  $UOH^{3+}$  is roughly complete. The average  $\log_{10} K_2(A.14)$  is included in Table VI-30.

The solubility data in sulfuric acid from this reference is rejected by this review because of the possible oxidation of U(IV) in the system discussed in [63GRI/PET]. The solubility data in hydrochloric acid and oxalic acid are accepted but not recalculated in this review because of the following concerns: 1) the nature of the solid phase (*e.g.*,  $U(ox)_2(s)$  or  $U(ox)_2 \cdot H_2O(s)$  or  $U(ox)_2 \cdot 6H_2O(s)$ ) is unknown. No information on the characterisation of the solid phase is given; 2) it is highly unlikely that hydrolysed species such as  $UOH^{3+}$  would be dominant in concentrated HCl solutions; 3) the effect of chloride ion on the solubility cannot be properly corrected with SIT because the concentrations of HCl in the majority of the samples were too high.

#### [58ERM/BEL]

The distribution coefficient  $K_d$  of Zr(IV) to the anion exchange resin at 0.2 M HCl and at zirconium concentration of  $5 \times 10^{-5}$  M was measured as a function of potassium oxalate concentration. The value of  $\log_{10} K_d$  decreased with a slope of  $-3$  against  $\log_{10}[ox^{2-}]$ . By assuming that the observed distribution is due to reactions of the anionic zirconium complexes  $Zr(ox)_3^{2-}$  and  $Zr(ox)_4^{4-}$  with the resin, the distribution coefficient was formulated to be:

$$K_d = \frac{{}^* \beta_3 K_{3,d} [H_2ox]^3 + {}^* \beta_4 K_{4,d} [H_2ox]^4}{1 + {}^* \beta_1 [H_2ox] + {}^* \beta_2 [H_2ox]^2 + {}^* \beta_3 [H_2ox]^3 + {}^* \beta_4 [H_2ox]^4}$$

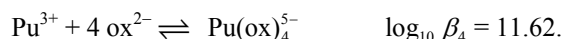
where  $K_{3,d}$  and  $K_{4,d}$  are the constants for the ion exchange reactions and  ${}^* \beta_n$  is the constant for the complex formation  $Zr^{4+} + n H_2ox \rightleftharpoons Zr(ox)_n^{4-2n} + 2n H^+$ . The values of  ${}^* \beta_n$  were obtained to be  ${}^* \beta_1 = 7.08 \times 10^3$ ,  ${}^* \beta_2 = 1 \times 10^8$ ,  ${}^* \beta_3 = 1 \times 10^{10}$  and  ${}^* \beta_4 = 5 \times 10^{11}$ . As the authors indicated in their later paper [59ERM/BEL2], the slope of  $-3$  in the decrease of  $\log_{10} K_d$  against  $\log_{10}[ox^{2-}]$  cannot be explained by assuming the distribution of  $Zr(ox)_3^{2-}$  and  $Zr(ox)_4^{4-}$ . Thus, this paper is not considered in this review.

#### [58FOM/VOR]

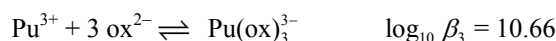
This study reports polarographic data of Pu(IV)/Pu(III) solutions containing potassium oxalate. The experiments were performed at  $(25 \pm 1)^\circ C$  in Ar-purged solutions. The following protonation constants for oxalate were used by the authors:  $\log_{10} K_1 = 4.19$  and  $\log_{10} K_2 = 1.23$ , but corrections for activity coefficients were not applied when calculating the free oxalate concentration. No details are given on the calibration of the pH electrode. From the polarographic data the authors established the differences in coordination number and in stability constants between the Pu(III) and Pu(IV)-oxalate complexes.

Data on the complex formation between Pu(III) and oxalate were obtained by

precipitating Pu(III)-oxalate in the measuring cell and recording immediately polarograms in the solid suspensions. The solubility product of Reas and Connick (*cf.* Table VI-52) was used:  $K_s = [\text{Pu}^{3+}]^2 [\text{H}_2\text{ox}]^3 [\text{H}^+]^{-6} = 2 \times 10^{-10}$ . From data at pH 2.7 to 4.2 without background electrolyte and data at pH  $\approx 4$ ,  $I = 3$  M (KCl) and  $[\text{K}_2\text{ox}]_{\text{TOT}} = 0.35$  to 0.95 M, the authors derived:



From polarographic data of Pu(IV) reduction at pH = 5.5 in  $[\text{K}_2\text{ox}]$  0.001 to 1.2 M (no background electrolyte), and assuming that the composition of the Pu(IV)-oxalate complex did not vary in these conditions, the authors concluded that the Pu(III) complex with lower coordination had an equilibrium constant one order of magnitude lower, *i.e.*,



and that the ratio of equilibrium constants for the Pu(III) and Pu(IV) tetra-oxalate complexes was 15.9  $\log_{10}$ -units, giving:



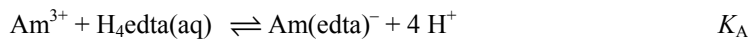
To obtain these constants the authors used several assumptions, *e.g.*, on the stoichiometry of the predominating complexes. Furthermore the authors mixed data from solutions of different ionic strengths and compositions, without considering the effects of changes in activity coefficients. Because of these limitations the equilibrium constants reported in this paper are not credited by this review.

#### [\[58FUG\]](#)

The complexation of Am(III) with edta has been studied by a cation exchange method with static equilibrations in the pH range 2 – 3 at  $(25.00 \pm 0.02)^\circ\text{C}$  in  $I = 0.1$  M  $\text{NH}_4\text{ClO}_4$ . The distribution coefficients  $K_d^\circ$  were obtained in the absence of edta, and  $K_d$  in the presence of  $1 \cdot 10^{-3}$  M edta. The pH meter used was a Beckman Model G, standardised at pH 4.00 with a commercial Beckman buffer and with specially prepared potassium acid phthalate buffer. Special care was taken with pH measurements, because pH is the most important factor in determining  $K_d$  values. The pH meter was standardised several times during each series of measurements. Measurements were taken of each individual solution, after equilibrium had been reached, with an accuracy of 0.01 pH units.

Fuger assumed that the only complex formed is  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$ , and using edta protonation constants of Cabell [\[51CAB\]](#) he obtained  $\log_{10} K_1 = (18.16 \pm 0.10)$ . This value has been criticised as too high, probably caused by neglecting the species  $\text{Am}(\text{Hedta})(\text{aq})$  and  $\text{H}_5\text{edta}^+$  in the data evaluation [\[78MER/GAT\]](#). Merciny *et al.* report a “corrected” value of  $\log_{10} K_1 = 17.40$ . However, no details about this correction procedure are reported and thus, the “corrected” value in [\[78MER/GAT\]](#) is not accepted in this review.

Fuger reports all experimental data (Table 1 in [58FUG]) and thus, a re-evaluation has been carried out in this review. The following reactions were assumed:



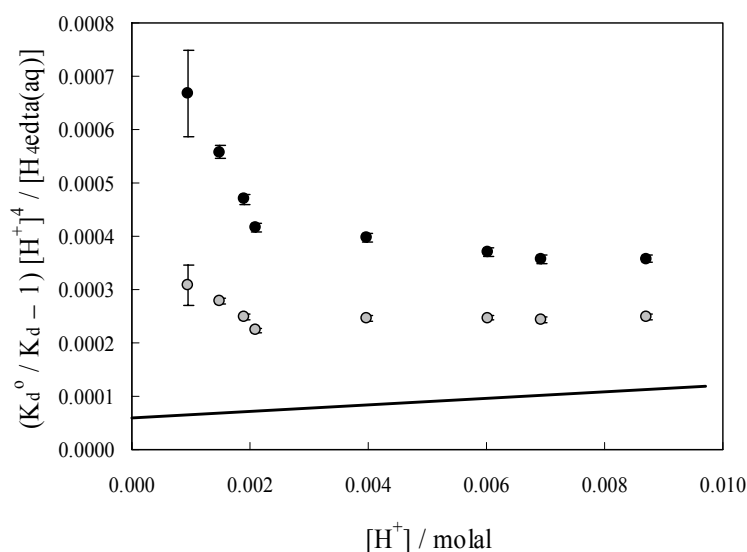
Considering the distribution coefficients  $K_d^\circ$  and  $K_d$ , and the two equilibria  $K_A$  and  $K_B$  the cation exchange data can be expressed in terms of the following equation:

$$(\frac{K_d^\circ}{K_d} - 1) \cdot [\text{H}^+]^4 / [\text{H}_4\text{edta}(\text{aq})] = K_A + K_B \cdot [\text{H}^+]$$

So, if the left hand side of the above equation is plotted against  $[\text{H}^+]$ , the data should increase with slope  $K_B$ , whereas the intercept at  $[\text{H}^+] = 0$  represents  $K_A$ . If the edta protonation constants of Cabell [51CAB] are used, and it is assumed that “pH” in Table 1 of [58FUG] represents  $-\log_{10}[\text{H}^+]$ , the data first slightly decrease with increasing  $[\text{H}^+]$  and then remain constant (grey symbols in Figure A-10). From the mean value of these points the value  $\log_{10}K_1 = 18.16$  of [58FUG] can be reproduced. However, using the edta protonation constants selected in this review for 0.1 M NaClO<sub>4</sub> (Table VIII-8-a, including the species  $\text{H}_5\text{edta}^+$  and  $\text{H}_6\text{edta}^{2+}$ ), all data are shifted towards higher values and an overall negative slope is observed (black symbols in Figure A-10). A negative slope could only be fitted with a physically meaningless negative value for  $K_B$ . Even if we assume that the uncertainties in  $K_d^\circ$  and  $K_d$  are higher than 1% (except for the point at lowest  $[\text{H}^+]$  where it is 10%) [58FUG], the negative slope remains, and the data are far away from the expectations according to the values selected in this review (line in Figure A-10).

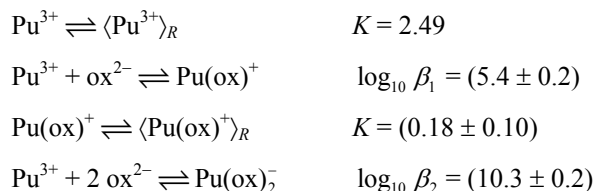
As the experimental work of Fuger is carefully done, a possible explanation of this erratic behaviour may be found in the assumption [58FUG] that only  $\text{Am}^{3+}$  will absorb on the cation exchange resin, while protonated edta species and Am – edta complexes will not absorb. However, according to the edta protonation constants evaluated in this review, a considerable amount of  $\text{H}_5\text{edta}^+$  is formed under the experimental conditions of [58FUG]. This cationic species may very well absorb on the cation exchange resin. Also  $\text{H}_4\text{edta}(\text{aq})$  as a double zwitterion (Figure VIII-1) and the complex  $\text{Am}(\text{Hedta})(\text{aq})$  cannot be assumed a priori not to absorb at all on the cation exchange resin. The combined effects of all these unknown absorption effects could be responsible for the observed behaviour of the system Am – edta – cation exchange resin. Because of these ambiguities, the results of [58FUG] have not been considered in this review.

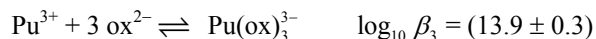
Figure A-10: Experimental data of Fuger [58FUG] evaluated using the edta protonation constants of Cabell [51CAB] (grey symbols), and using protonation constants selected in this review (black symbols). The error bars correspond to uncertainties in  $K_d^0$  and  $K_d$  of 1% (except for the point at lowest  $[H^+]$  where it is 10%). The line is calculated using stability constants for  $\text{Am}(\text{edta})^-$ ,  $\text{Am}(\text{Hedta})(\text{aq})$  and edta protonation selected in this review.



#### [58GEL/MAT]

Gel'man *et al.* studied the complex formation between Pu(III) and oxalate using a cation-exchange resin. The experiments were performed at pH 1.5 to 2.7 and  $(20 \pm 1)^\circ\text{C}$  in 1 M  $\text{NH}_4\text{Cl}$ . Trace amounts of Pu(III) were used, and the solutions were kept under a nitrogen atmosphere. The total oxalate concentration was kept constant to 0.005 M. The protonation constants of the ligand were also determined by separate titrations in the same ionic media. No details are however given on the calibration of the glass electrode. The authors interpreted the ion-exchange data assuming that only anionic complexes were formed:  $\text{Pu}(\text{ox})_2^-$  and  $\text{Pu}(\text{Hox})_4^-$  with  $\log_{10} \beta_2 = 9.15$  and  $\log_{10} \beta_4 = 10.95$ , respectively, for reactions  $\text{Pu}^{3+} + 2 \text{ox}^{2-} \rightleftharpoons \text{Pu}(\text{ox})_2^-$ ; and  $\text{Pu}^{3+} + 4 \text{Hox}^- \rightleftharpoons \text{Pu}(\text{Hox})_4^-$ . Calculations performed by this review show that an equally good fit of the data is obtained assuming the formation of oxalate complexes only:





where  $\langle i \rangle_R$  indicates a species “ $i$ ” bound to the ion-exchange resin. As the data are too scarce to properly define the speciation of the system, no equilibrium constants may be deduced from these distribution coefficients.

#### [\[58GEL/MOS2\]](#)

This article presents solubilities of Pu(IV)-oxalate in different acid media as well as solubility data for Pu(IV)-hydroxide in  $\text{K}_2\text{CO}_3$ . These data were also reported elsewhere [\[58MOS/GEL3\]](#), [\[58MOS/GEL\]](#), see the comments under [\[58MOS/GEL3\]](#) in this Appendix.

#### [\[58GRI/PET2\]](#)

The authors studied solid U(IV) oxalates including  $\text{U}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$  and few ternary compounds containing K, Ba, Pb and Cd. Empirical compositions of the compounds were given. The solubility of  $\text{U}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$  in water and solutions of perchloric, hydrochloric, sulfuric, nitric and acetic acids was measured. The temperature of the experiments is not reported. The solubility of  $\text{U}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$  in water was found to be  $0.05 \text{ g} \cdot \text{L}^{-1}$   $\text{U}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$ . When the concentration of the acids increased, the solubility of  $\text{U}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$  first decreased ( $[\text{acid}] < 0.1 \text{ N}$ ), then gradually increased ( $[\text{acid}] = 0.1 - 1 \text{ N}$ ). The magnitude of increase in the solubility followed the order: sulfuric > nitric > hydrochloric > perchloric > acetic acids. The authors interpreted the order as being consistent with the tendency of forming complexes with U(IV). However, the observation that the solubility of  $\text{U}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$  was the lowest in acetic acid was not explained.

The constant for the reaction:



was estimated by the authors to be of the order of  $10^{-10}$ , by a method of “equilibrium shift”, in which the amount of calcium oxalate salt was determined at varying concentrations of Ca(II). By potentiometry, the constant for the equilibrium:



was estimated to be of the order of  $10^{-4}$ .

Both the solubility data and the dissociation constants for  $\text{U}(\text{ox})_4^{4-}$  from this study are rejected by this review, because no information is provided on the characterisation of the solid phase, the temperature of the experiment is unknown, and the dissociation constants are only rough estimates without supporting information on experimental conditions. In fact, the same authors pointed out, in a later publication [\[63GRI/PET\]](#), partial oxidation of U(IV) by either the oxygen or the products of  $\alpha$ -radiolysis (from  $^{233}\text{U}$ ) occurred in solutions of the mineral acids except HCl. Such oxidation casts serious doubts on the results of solubility experiments where the solid

phase and aqueous species are not confirmed.

#### [\[58HEI/FRI\]](#)

Potentiometry, conductometry and spectrophotometry were conducted to determine the composition of  $\text{Ni}^{2+}$  citrate complexes. From the titrations of the various mixtures of  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Na}_3\text{cit}$ ,  $\text{Na}_2\text{Hcit}$ ,  $\text{NaH}_2\text{cit}$  or  $\text{H}_3\text{cit}$ , three complexes,  $\text{Ni}(\text{Hcit})(\text{aq})$ ,  $\text{Ni}(\text{cit})^-$  and  $\text{Ni}(\text{H}_{-1}\text{cit})^{2-}$  have been claimed to form. The values of the constant for  $\text{Ni}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})^-$  have been reported to be  $\log_{10} \beta_{1,1} = (4.40 \pm 0.12)$  at pH 7 and  $(4.54 \pm 0.08)$  at pH 8. Also, the constant for  $\text{Ni}^{2+} + \text{H}_{-1}\text{cit}^{4-} \rightleftharpoons \text{Ni}(\text{H}_{-1}\text{cit})^{2-}$  was estimated to be  $\log_{10} \beta_{1,-1,1} = 11.22$  by assuming  $\log_{10} K_{0(\text{H})} = 16$ . However, the ionic strength was not controlled and the details for the data analysis are not given. Thus, the reported values are not accepted by this review.

#### [\[58MAR2\]](#)

Thermal decomposition reactions of  $\text{Am}_2(\text{ox})_3 \cdot 7\text{H}_2\text{O}$  were examined by TGA. In air, it decomposes as  $\text{Am}_2(\text{ox})_3 \cdot n\text{H}_2\text{O}$  ( $n = 4 \rightarrow 3 \rightarrow 1 \rightarrow 0.5$ )  $\rightarrow \text{Am}_2(\text{ox})_3 \cdot 0.5\text{H}_2\text{O} \rightarrow \text{Am}_2(\text{ox})_3 \rightarrow \text{AmO}_2$ . The conversion of oxalate to oxide was completed at  $470^\circ\text{C}$  and XRD showed that the final product is  $\text{AmO}_2$ . In vacuo, the heptahydrate began to lose water of hydration at  $50^\circ\text{C}$ . Anhydrous americium oxalate was formed at  $240^\circ\text{C}$ , and decomposition of the oxalate to the red-brown sesquioxide  $\text{Am}_2\text{O}_3$  commenced at  $290^\circ\text{C}$ . The conversion of oxalate to  $\text{Am}_2\text{O}_3$  was completed at  $620^\circ\text{C}$ .

#### [\[58MIG/SYC\]](#)

Potentiometric titrations of citric acid with  $\text{NiSO}_4$  (at  $C_M/C_L = 1, 1/2, 1/3$  and  $1/4$ ) by  $\text{KOH}$  were conducted at  $25^\circ\text{C}$  in  $2\text{ M KNO}_3$ . The titration data before the first end point (at  $C_{\text{KOH}} < 3C_L$ ) were analysed to produce  $\bar{n}$  versus  $\log_{10} [\text{cit}^{3-}]$ , and the constants for  $\text{Ni}^{2+} + q\text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})_q^{2-3q}$  were calculated to be  $\log_{10} \beta_{1,1} = 4.99$  for  $\text{Ni}(\text{cit})^-$  and  $\log_{10} \beta_{2,1} = 7.76$  for  $\text{Ni}(\text{cit})_2^{4-}$ , respectively, and from the data at  $3C_L < C_{\text{KOH}} < 3C_L + C_M$ , the constant  $\text{Ni}^{2+} + \text{H}_{-1}\text{cit}^{4-} \rightleftharpoons \text{Ni}(\text{H}_{-1}\text{cit})^{2-}$  was calculated to be  $\log_{10} \beta_{1,-1,1} = 5.27$ . The measured pH was not corrected to  $\text{pH}_c$ . For the calculation of  $\log_{10} \beta_{1,-1,1}$  for  $\text{Ni}(\text{H}_{-1}\text{cit})^{2-}$  from the data at  $3C_L < C_{\text{KOH}} < 3C_L + C_M$ , the authors used the invalid assumption of  $C_M = [\text{Ni}^{2+}] + [\text{Ni}(\text{H}_{-1}\text{cit})^{2-}]$  instead of  $C_M = [\text{Ni}(\text{cit})^-] + [\text{Ni}(\text{cit})_2^{4-}] + [\text{Ni}(\text{H}_{-1}\text{cit})^{2-}]$ . By these reasons, the reported values are not accepted by this review.

#### [\[58MOS/GEL\]](#)

See comments under [\[58MOS/GEL3\]](#).

#### [\[58MOS/GEL3\]](#)

Solubilities of  $\text{Pu}(\text{IV})$  oxalate were determined in different media by Moskvina and Gel'man and the results were presented and analysed in three papers [\[58GEL/MOS2\]](#),

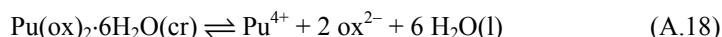
[58MOS/GEL3], [58MOS/GEL]. All these papers are discussed here. The experimental methodology is described in [58MOS/GEL]. Additionally, in [58GEL/MOS2], [58MOS/GEL] the solubilities of Pu(IV) hydroxide in carbonate media are also reported; these values are discussed in the Np/Pu review [2001LEM/FUG].

In a typical solubility experiment with Pu(IV) oxalate an amount of freshly prepared solid was added to solutions containing either:

- HNO<sub>3</sub>, HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> (all with [H<sup>+</sup>] ≤ 1 M)
- (NH<sub>4</sub>)<sub>2</sub>ox (up to 0.35 M), with or without 1 M or 3.8 M HNO<sub>3</sub>.

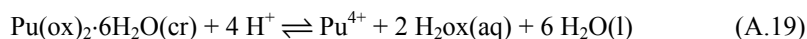
After 4-6 hours of equilibration at (20 ± 0.02)°C the amount of Pu in the solutions was measured radiometrically. There is no indication that the authors characterised the initial or final solid phase(s), but the authors write the formula as Pu(ox)<sub>2</sub>·6H<sub>2</sub>O. The separation of the aqueous solution from the solid (filtration or centrifugation) is not specified.

The solubility constant for:

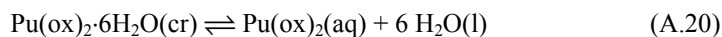


$\log_{10} K_s$  (A.18) = − 21.4, was calculated from the solubilities measured as a function of [(NH<sub>4</sub>)<sub>2</sub>ox] in the presence of 1 M HNO<sub>3</sub>, using the dissociation constants of oxalic acid from the literature ( $\log_{10} K_{a1} = -0.967$  and  $\log_{10} K_{a2} = -4.194$ ). In this case the background electrolyte changed substantially, from [H<sup>+</sup>] = 1 M to ≈ 0.3 M. The same equilibrium constant was evaluated from the solubilities in 3.8 M HNO<sub>3</sub> and varying concentrations of (NH<sub>4</sub>)<sub>2</sub>ox:  $\log_{10} K_s$  (A.18) = − 20.1. Corrections were made in this case for nitrate complex formation with  $\log_{10} K_1(I = 6 \text{ M}) = 0.67$  for  $\text{Pu}^{4+} + \text{NO}_3^- \rightleftharpoons \text{PuNO}_3^{3+}$ , but complex formation between Pu(IV) and oxalate was neglected. No mention is made of ionic medium effects in the calculations.

The solubility constant for:



was obtained from three solubility values measured in 0.5, 0.75 and 1.0 M HClO<sub>4</sub>:  $\log_{10} K_s$  (A.19) = − 11. Using literature constants for the dissociation of H<sub>2</sub>ox, the authors converted this value to:  $\log_{10} K_s$  (A.18) = − 21.3. Again, no mention is made of the influence of the ionic medium. From the same three experimental data in HClO<sub>4</sub> the authors also calculated  $\log_{10} K_s$  (A.20) = − 4.49 for reaction:



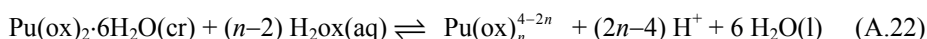
Equilibrium constants for complex formation:



$\log_{10} \beta_1$  ((A.21),  $n = 1$ ) = 8.745;  $\log_{10} \beta_2$  ((A.21),  $n = 2$ ) = 16.92;  $\log_{10} \beta_3$  ((A.21),  $n = 3$ ) = 23.40; and  $\log_{10} \beta_4$  ((A.21),  $n = 4$ ) = 27.5; were obtained from a least squares fit-



ting of the solubilities as a function of  $[(\text{NH}_4)_2\text{ox}]$  in the presence of 1 M  $\text{HNO}_3$ , using dissociation constants of oxalic acid from the literature given above. As mentioned previously, the background electrolyte in these solutions changed substantially, from  $[\text{H}^+] = 1$  M to  $\approx 0.3$  M. In an alternative method of data evaluation the authors used the same data set to obtain solubility constants for reactions:

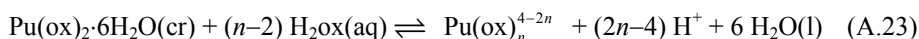


with  $n = 1$  to 4:  $\log_{10} K_s ((\text{A.22}), n = 1) = -7.51$ ;  $\log_{10} K_s ((\text{A.22}), n = 2) = -4.49$ ;  $\log_{10} K_s ((\text{A.22}), n = 3) = -3.17$ ; and  $\log_{10} K_s ((\text{A.22}), n = 4) = -4.15$ .

The authors also measured the solubility of Pu(IV) oxalate in  $\leq 0.26$  M  $(\text{NH}_4)_2\text{ox}$  solutions without any added  $\text{HNO}_3$ . The data in the concentration range 0.02 to 0.14 M  $(\text{NH}_4)_2\text{ox}$  were evaluated with the formation of  $\text{Pu}(\text{ox})_3^{2-}$ :  $\log_{10} \beta_3 ((\text{A.21}), n = 3) = 20.66$ , but the possibility of side reactions was not investigated (partial protonation of the ligand, hydrolysis and disproportionation of Pu(IV), or precipitation of  $\text{Pu}(\text{OH})_4(\text{am})$ ). And again, the effect of changing ionic strength was not mentioned.

Because the solid phase was not characterised, and due to the deficiencies in the data evaluation, *e.g.*, the disregard of ionic medium effects, the equilibrium constants reported in [58MOS/GEL] are not credited by this review.

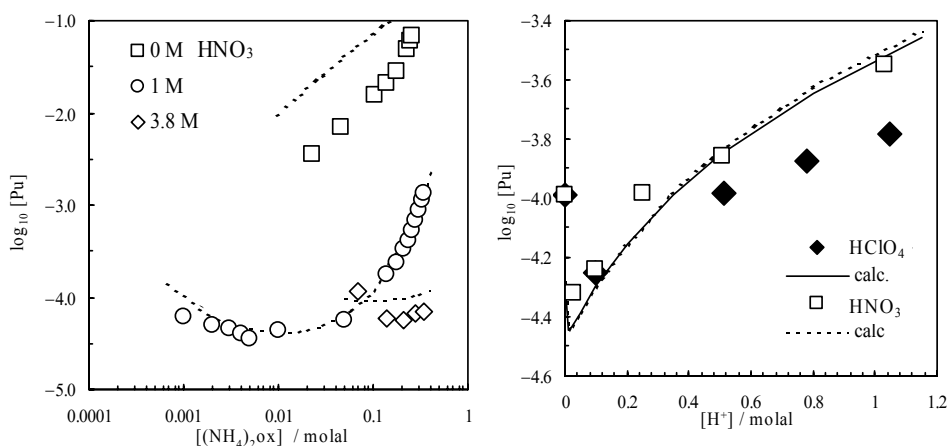
The experimental data is re-evaluated in this review assuming that the solid phase is indeed  $\text{Pu}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$ , and using the SIT method (Appendix B) to estimate activity coefficients. A rigorous analysis is not possible because the experiments were poorly designed, and the ionic medium effects on either the dissociation of oxalic acid or on the formation of  $\text{PuNO}_3^{3+}$ ,  $\text{PuOH}^{3+}$  and  $\text{Pu}(\text{OH})_2^{2+}$  are not precisely known for either  $\text{HNO}_3$  or  $\text{NH}_4^+$ . As an approximation it is assumed that the available ion-interaction coefficients in perchlorate media may be used in nitric acid solutions: the  $\varepsilon$ -values for  $\text{PuOH}^{3+}$  and  $\text{Pu}(\text{OH})_2^{2+}$  with  $\text{ClO}_4^-$  are taken from [2001NEC/KIM]; and  $\varepsilon(\text{PuNO}_3^{3+}, \text{NO}_3^-) = \varepsilon(\text{PuNO}_3^{3+}, \text{ClO}_4^-) = (0.70 \pm 0.08) \text{ kg} \cdot \text{mol}^{-1}$  (from the value of  $\Delta\varepsilon$  selected in [2001LEM/FUG] for  $\text{HClO}_4$  media). Also the values  $\varepsilon(\text{NH}_4^+, \text{Hox}^-)$  and  $\varepsilon(\text{NH}_4^+, \text{ox}^{2-})$  were assumed to be equal to those in  $\text{Na}^+$  media. For all other ions the approximation made was:  $\varepsilon(\text{M}^{Z_M}, \text{X}^{Z_X}) = 0.15 + 0.15 \times ((Z_M - 1) + (Z_X + 1))$ . Values of  $\varepsilon(\text{H}^+, \text{Hox}^-)$  in the range  $(+0.15$  to  $-0.15) \text{ kg} \cdot \text{mol}^{-1}$  were tested, giving  $\log_{10} K$  values for the first dissociation constant of oxalic acid ( $\text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Hox}^- + \text{H}^+$ ) in the range  $-(0.92 \pm 0.11)$  to  $-(1.23 \pm 0.11)$  (for 1 M  $\text{HNO}_3$ , in molar units), corresponding to  $\approx 11\%$  and  $\approx 6\%$  dissociation, respectively. The least-squares evaluation of the data obtained in 1 M  $\text{HNO}_3$  with varying concentrations of  $(\text{NH}_4)_2\text{ox}$ , converted to molal units, using the following equilibria:



gives:  $\log_{10} K_s^\circ ((\text{A.23}), n = 0) \leq -13$ ;  $\log_{10} K_s^\circ ((\text{A.23}), n = 1) = -(7.9 \pm 0.1)$ ;  $\log_{10} K_s^\circ ((\text{A.23}), n = 2) = -(4.6 \pm 0.1)$ ;  $\log_{10} K_s^\circ ((\text{A.23}), n = 3) = -(4.37 \pm 0.05)$ ; and  $\log_{10} K_s^\circ ((\text{A.23}), n = 4) = -(9 \pm 1)$ .

Calculations show that  $\text{Pu}(\text{ox})_4^{4-}$  is never  $> 5\%$  of the total plutonium in these experiments. The results of calculations made using this model are compared in Figure A-11 to the fitted data, as well as to the other data reported by Moskvin and Gel'man in [58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL]. For some unknown reason the agreement with the data in near-neutral solutions of  $(\text{NH}_4)_2\text{ox}$  is not as good, although it should be pointed out that according to the calculations these solutions should be over-saturated with amorphous solid Pu(IV) hydroxide.

Figure A-11: Calculated solubilities of Pu(IV)-ox compared with the experimental data at 20°C reported in [58GEL/MOS2], [58MOS/GEL3], [58MOS/GEL]. See text for [58MOS/GEL3] in this Appendix for details on the model.



#### [58YAT/KAR]

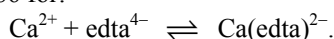
The authors studied with calorimetric techniques several reactions of ethylenediaminetetraacetate ( $\text{edta}^{4-}$ ) and hexamethylenediaminetetraacetate ( $\text{hmdta}^{4-}$ ). Of interest for this review are the following results:

- $\Delta_r H_m = -(41.8 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$  at  $I \approx 1 \text{ M}$  and  $25^\circ\text{C}$  for:  

$$2 \text{ H}^+ + \text{edta}^{4-} \rightleftharpoons \text{H}_2\text{edta}^{2-}.$$

This value was obtained by combining the heat of  $\text{H}_2\text{O}$  dissociation at standard conditions with the heats of dissolution of  $\text{Na}_2\text{H}_2\text{edta} \cdot 2\text{H}_2\text{O}(\text{cr})$  in 1 M NaOH and in acetate buffer ( $\text{pH} = 4.8$ , unknown ionic strength). The reported enthalpy change includes the heat effect due to the formation of  $\text{Na}^+$  complexes.

- The authors report in a table  $\Delta_r H_m = -(19.7 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$  both at  $I = 0.54$  and at  $I = 0.86$  for:



No experimental data are however reported, and it is not clear if these enthalpies were determined in the present study.

#### [\[58YOS/IGU\]](#)

This is a short presentation of the study reported in [\[59IGU/YOS\]](#).

#### [\[59ERM/BEL2\]](#)

The distribution of Pu(IV), Zr(IV) and Hf(IV) to an anion exchange resin were measured. From the slope of minus 3 of the distribution coefficient against  $\log_{10}[\text{ox}]_T$  at pH 6,  $[\text{M}(\text{ox})_5]^{6-}$  is assumed to exist in aqueous solution. The species was estimated simply by this slope and this review considers that more detailed experimental verification is necessary to confirm this conclusion such as the effect of the concentrations of oxalate, metal ion concentration and pH.

#### [\[59GEL/ART\]](#)

A study was made by Gel'man *et al.* of the distribution of Pu(V) (prepared by reducing Pu(VI) with  $\text{H}_2\text{O}_2$  at pH 3 – 4) and the cation exchange resin KU-2 at pH 3 – 5 (ionic strength  $\approx 0.05$ ), and then in the presence of 0.001 M  $\text{Na}_2\text{H}_2\text{edta}$  under the same conditions.

No information is given about the pH measurements (pH scale used and calibration of the pH meter). The authors mention that Pu(V) solution remains stable for 20 – 30 days, and then its own  $\alpha$ -radiation produces other valence states. However, they were not aware of the fast reduction of Pu(V) to Pu(IV) in the presence of edta [\[98REE/WYG\]](#), at least no measures are reported by Gel'man *et al.* to ensure the +V state of their Pu – edta solutions.

#### [\[59GEL/MEF\]](#)

The complex formation of Np(IV) and Np(V) with edta has been studied by spectrophotometric titration. The complex formation of Np(IV) was investigated in HCl solution, and the complex formation of Np(V) in  $\text{HNO}_3$  solution. The ionic strength was kept constant by the addition of KCl and  $\text{KNO}_3$ , respectively. The authors state, that complex formation of  $\text{Np}^{4+}$  with  $\text{Cl}^-$  in 1 M HCl is extremely slight and was neglected. Considering the review of Np(IV) chloride complexation in [\[2001LEM/FUG\]](#) this statement is erroneous. The acidity of the solution was determined either by titration or by measurement on an LP-5 potentiometer. No details are reported about the pH scale used or the calibration of the pH meter. The temperature of the measurements is not given. The edta protonation constants used for deriving stability constants are also not

reported.

In the case of Np(IV), experimental data are reported in the pH range – 0.3 to 1.2 at ionic strength 1 and 2 M (Table 1 in [\[59GEL/MEF\]](#)). The authors state that in all experiments,  $[Cl^-]$  equaled 1 M, and increasing the acidity and ionic strength above 1 was accomplished by adding  $HClO_4$  and  $NaClO_4$ . This would give a  $HCl - HClO_4 - KCl - NaClO_4$  mixture. The data have been interpreted in terms of the formation of  $Np(H_2edta)^{2+}$ . In contrast to other studies of the Np(IV) edta system in the same pH range ([\[71CHA/LIA\]](#) and [\[71EBE/PAU\]](#)), the formation of  $Np(edta)(aq)$  has not been considered by the authors.

In the case of Np(V), the authors report two rather different stability constants for the formation of  $NpO_2edta^{3-}$ ,  $K = (3.73 \pm 1.79) \cdot 10^9$  at pH 5.5 and  $K = (2.26 \pm 0.36) \cdot 10^{10}$  at pH 3.2 – 4.5 and a 200-fold excess of edta. The latter value is commented by the authors as follows: “We were unsuccessful in attempt to calculate the constant, assuming any other composition for the complex”. Hence, the presence of the protonated species  $NpO_2(Hedta)^{2-}$  at the investigated pH range 3.2 – 5.5 has been ignored.

For a similar pH range 3.3 – 4.4 but equimolar amounts of Np(V) and edta the authors calculated the stability constant for the formation of a dinuclear complex  $(NpO_2)_2edta^{2-}$  as  $K = (2.24 \pm 0.08) \cdot 10^{15}$ . The authors remark “although we were unable to obtain spectrophotometric proof of the formation of  $(NpO_2)_2edta^{2-}$ , nonetheless, the high invariability of the constant calculated for  $(NpO_2)_2edta^{2-}$  makes it incorrect to reject the possibility of its existence”.

In view of the numerous shortcomings of this study, all values reported by [\[59GEL/MEF\]](#) are considered as unreliable in this review.

#### [\[59GRI/PET\]](#)

The authors synthesised  $La_4[U(ox)_4]_3 \cdot 22H_2O$ ,  $KLa[U(ox)_4] \cdot 8H_2O$  and  $KCe[U(ox)_4] \cdot 8H_2O$  from  $K_4[U(ox)_4]$  and  $Ln(NO_3)_3$  ( $Ln = La$  or  $Ce$ ). The solubility of  $KCe[U(ox)_4] \cdot 8H_2O$  in water at 25°C was measured by a radiometric method with  $^{144}Ce$ . The amount of Ce(III) in solution was found to be  $(5.0 \pm 0.4) \text{ mg} \cdot \text{L}^{-1}$  after 3 – 149 hours of shaking time. The authors also found that  $KCe[U(ox)_4] \cdot 8H_2O$  underwent decomposition in aqueous solution to generate precipitates of Ce(III) oxalate and U(IV) oxalate.

The concentration of uranium in the solubility experiments was not measured. The decomposition that led to precipitation of different solids complicated the experiments. No thermodynamic information could be extracted from the results. As a result, the solubility data from this reference are not accepted in this review.

[\[59IGU/YOS\]](#)

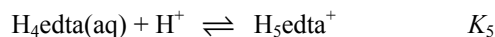
The authors determined the solubility of  $\text{H}_4\text{edta}(\text{cr})$  in various aqueous media and temperatures. From their data the heat of solution in water was found to be  $+28.3 \text{ kJ}\cdot\text{mol}^{-1}$ . This value corresponds to the dissolution of  $\text{H}_4\text{edta}(\text{cr})$  and to the formation of  $\text{H}_4\text{edta}(\text{aq})$ ,  $\text{H}_5\text{edta}^+$ ,  $\text{H}_3\text{edta}^-$ , *etc.* in unknown proportions. Heats of solution in other electrolyte media were also reported.

In their Figure 3, Iguchi *et al.* reported the solubility of  $\text{H}_4\text{edta}(\text{cr})$  *versus*  $[\text{HCl}]_{\text{TOT}}$  at  $30^\circ\text{C}$  and ionic strengths of 0.1 and 0.5 M. These data were used in this review to fit a theoretical solubility curve using a least-squares algorithm. The calculations gave the following equilibrium constants (at  $30^\circ\text{C}$ ):

Table A-3: Solubility constants for  $\text{H}_4\text{edta}(\text{cr})$  at different ionic strengths.

Reaction number	Reaction	$I = 0.1 \text{ M}$	$I = 0.5 \text{ M}$
(A.24)	$\text{H}_4\text{edta}(\text{cr}) + \text{H}^+ \rightleftharpoons \text{H}_5\text{edta}^+$	$-(2.34 \pm 0.07)$	$-(2.30 \pm 0.02)$
(A.25)	$\text{H}_4\text{edta}(\text{cr}) \rightleftharpoons \text{H}_4\text{edta}(\text{aq})$	$-(3.64 \pm 0.08)$	$-(3.57 \pm 0.04)$
(A.26)	$\text{H}_4\text{edta}(\text{cr}) \rightleftharpoons \text{H}_3\text{edta}^- + \text{H}^+$	$-(5.65 \pm 0.06)$	$-(5.39 \pm 0.04)$

Values for  $K_4$  and  $K_5$  at  $30^\circ\text{C}$ , corresponding to reactions:



may be calculated from the data given in Table A-3. The values of  $K_s$  (A.25),  $K_4$  and  $K_5$  were included in the evaluations described in Sections VIII.2.2, VIII.3.2 and VIII.3.3.

The acidity range studied [\[59IGU/YOS\]](#), (their Fig.3) was not large enough to determine the equilibrium constants of the following reactions:

[\[59KIR/TAN\]](#)

The complex formation of zirconium with oxalate, citrate and sulfate was investigated using an ion exchange method. The solutions of  $0.015 - 0.02 \text{ M}$  of  $\text{Zr}(\text{SO}_4)_2$  mixed with  $\text{H}_2\text{ox}$ ,  $\text{H}_3\text{cit}$  or  $\text{H}_2\text{SO}_4$  in various molar ratios were passed through a column packed with a cation exchange resin KU-1 or KU-2 ( $500 - 1000 \mu\text{m}$ ) prepared in the  $\text{H}^+$ ,  $\text{Na}^+$  or  $\text{NH}_4^+$ -form. The zirconium content of the eluates was determined by precipitation with ammonia followed by ignition of the precipitate at  $800 - 1000^\circ\text{C}$ . From the relation between the amount of zirconium adsorbed on the resin and the molar ratio of  $\text{H}_2\text{ox}$ ,  $\text{H}_3\text{cit}$  or  $\text{H}_2\text{SO}_4$  to  $\text{Zr}(\text{SO}_4)_2$ , the formation of  $(\text{Zr}_2\text{O}_3)\text{ox}$ ,  $\text{Zr}(\text{ox})_4^{4-}$  and  $\text{Zr}_2(\text{cit})_7^{x-}$  as well as the slightly stable sulfate complexes of zirconium is inferred.

The paper does not include any information about the stability constants of the complexes. The paper gives qualitative information about the speciation of the complexes, but this review does not accept the speciation since more detailed examination such as the effect of the acidity of the solution and the metal-ion concentration is considered necessary to confirm the conclusions of this paper.

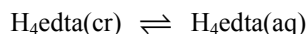
#### [\[59KLY/SMI3\]](#)

The aim of this work has been to study the processes occurring in the  $\text{UO}_2(\text{NO}_3)_2 - \text{edta} - \text{H}_2\text{O}$  system in the pH range 2.0 – 8.0. The authors determined the solubility product of  $\text{UO}_2(\text{H}_2\text{edta}) \cdot \text{H}_2\text{O}$  as  $\log_{10}([\text{UO}_2^{2+}] \cdot [\text{H}_2\text{edta}^{2-}]) = -(5.65 \pm 0.04)$  from solubility measurements in the pH range 3.0 – 4.5. Furthermore, they calculated the stability constant  $\log_{10}K = (4.13 \pm 0.03)$  from solubility measurements at 25°C in the pH range 6.1 – 7.5 assuming the presence of a single 1:1 complex  $\text{UO}_2(\text{Hedta})^-$ .

No background electrolyte has been used in these solubility measurements and hence, the ionic strength of the solutions varied strongly during the experiments. The pH was measured with a quinhydrone electrode and a PPTV-1 potentiometer, and also with a LP-5 potentiometer and a glass electrode. However, the method of pH calibration is not reported by the authors. In the pH range 6.1 – 7.5 investigated for the calculation of the stability constant of  $\text{UO}_2(\text{Hedta})^-$  the presence of other complexes like  $\text{UO}_2\text{edta}^{2-}$  is expected. The complete neglect of other U(VI) edta species may be the main reason for the large discrepancy revealed when we compare the obtained stability constant with the results of all other studies (Table VIII-32). For these reasons the results of this study cannot be further considered in this review.

#### [\[59KLY/SMI4\]](#)

The authors determined the solubility of ethylenediaminetetraacetic acid as a function of pH (in the range  $\approx 0.8$  to  $\approx 2.9$ ) adjusted by the addition of HCl (0.0075 – 0.164 M) or  $\text{NH}_3$  (0.00186 – 0.00734 M). The solutions were shaken automatically in 100 mL graduated flasks in a thermostat (25°C). The pH was measured with a quinhydrone electrode and a PPTV-1 potentiometer. From these data they calculated values for the equilibrium constants for the reactions:



The method of pH calibration and the used reference electrode are not reported. Furthermore, no discussion is found in the paper about the actual ionic strength of the solutions. Since no background medium was used, the ionic strength is approximately identical with the concentration of the added components, *i.e.*, it changes strongly in the HCl solutions from 0.0075 to 0.165 M, and less so in the  $\text{NH}_3$  solutions. This varying ionic strength does not allow to obtain accurate values for equilibrium constants and hence, the protonation constants are not considered in this review.

The authors used their protonation constants to correct the stability constant of Pu(IV) edta, obtained spectrophotometrically in 1 M HNO<sub>3</sub> by [57FOR/SMI2], with respect to the presence of H<sub>6</sub>edta<sup>2+</sup>. This correction is not accepted in this review.

The complex formation of edta<sup>4-</sup> with U(IV) was examined by the authors by complexometric titrations of U(IV) sulphate solutions with edta and arsenazo indicator at constant pH using sulphuric acid as buffer resulting in a varying ionic strength in the range of 0.025 M. The stability constant  $\log_{10}K_1 = (25.6 \pm 0.4)$  was obtained considering the presence of UOH<sup>3+</sup>, USO<sub>4</sub><sup>2+</sup> and HSO<sub>4</sub><sup>-</sup> but neglecting the (varying) ionic strength of the solutions. Moreover, the authors did not consider the contribution of H<sub>5</sub>edta<sup>+</sup> in their data analysis, and the formation of ternary U(IV) edta complexes with sulphate cannot be excluded under these experimental conditions. Thus, the U(IV) edta equilibrium constant is not considered in this review.

#### [59LI/LIN]

In the indirect polarographic method for Mg<sup>2+</sup> citrate complexes, the half wave potentials due to the reduction of cadmium ion were measured for the solution containing  $5 \times 10^{-4}$  M Cd(NO<sub>3</sub>)<sub>2</sub> and 0.05 M Na<sub>3</sub>cit in the absence and presence of 0.05 M Mg(NO<sub>3</sub>)<sub>2</sub> at pH 6.9 and 25°C. Ionic strength was estimated by the concentrations of the species in the solution. The values of  $\log_{10}\beta_{1(cit)}$  for  $Mg^{2+} + cit^{3-} \rightleftharpoons Mg(cit)^-$  and  $\log_{10}\beta_{1(Hcit)}$  for  $Mg^{2+} + Hcit^{2-} \rightleftharpoons Mg(Hcit)(aq)$  were calculated with using the protonation constants,  $\log_{10}K_{(H)} = 5.62, 4.34, 2.94$ , and the constants of  $\log_{10}\beta_{1(cit)} = 3.98$  for  $Cd^{2+} + cit^{3-} \rightleftharpoons Cd(cit)^-$  and  $\log_{10}\beta_{1(Hcit)} = 1.70$  for  $Cd^{2+} + Hcit^{2-} \rightleftharpoons Cd(Hcit)(aq)$  obtained by potentiometry at  $I = 0.15$  M NaCl and 25°C. In the calculation,  $\beta_{1(Hcit)}/\beta_{1(cit)}$  for Mg<sup>2+</sup> citrates were assumed to be equal to that of Cd<sup>2+</sup> citrates, and  $\log_{10}\beta_{1(cit)} = 3.29$  for Mg(cit)<sup>-</sup> and  $\log_{10}\beta_{1(Hcit)} = 1.60$  for Mg(Hcit)(aq) were obtained. Thus, the result totally depends on the values for Cd<sup>2+</sup>-citrates and the assumption used in the calculation. Also, the ionic strength was not well controlled. This review does not accept these values.

From the potentiometric titration of the solution containing 0.005 M citric acid and 0.05 M Ni(NO<sub>3</sub>)<sub>2</sub> at 25°C, the formation constants for  $Ni^{2+} + H_r cit^{r-3} \rightleftharpoons Ni(H_r cit)^{r-1}$  were obtained to be  $\log_{10}\beta_{1(cit)} = (5.11 \pm 0.15)$  for Ni(cit)<sup>-</sup> and  $\log_{10}\beta_{1(Hcit)} = (3.19 \pm 0.15)$  for Ni(Hcit)(aq), respectively. Although the protonation constants,  $\log_{10}K_{(H)} = 5.62, 4.34$  and 2.94, used in the calculation are close to those selected in this review, they may give some errors since the ionic strength is controlled by Ni(NO<sub>3</sub>)<sub>2</sub>. Thus, this review does not accept the reported values.

From the potentiometric titrations of the solutions containing (UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>, H<sub>3</sub>cit) = (0.01 M, 0.01 M), (0.01 M, 0.02 M), (0.04 M, 0.05 M) plus NaCl to give total 0.15 M ionic strength, the authors reported that equimolar concentrations of uranyl ion and citric acid react in the pH region of 1.9 to 2.5 to form only a mononuclear chelate UO<sub>2</sub>(cit)<sup>-</sup> with  $\log_{10}\beta_{1(cit)} = 8.5$  for  $UO_2^{2+} + cit^{3-} \rightleftharpoons UO_2(cit)^-$  (to obtain this

value, the authors used the values of  $\log_{10} K_{(H)} = 5.62, 4.34$  and  $2.94$ ). Feldman *et al.* [60FEL/NOR] showed that their data could be interpreted in terms of the formation of the dimer  $(\text{UO}_2)_2(\text{cit})_2^{2-}$ . Posterior and more elaborate studies [60FEL/NOR], [65RAJ/MAR] and [72MAR/KLO] also revealed that the predominating species should be the dimer  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  under these conditions. Assuming the predominant formation of the dimer, the value of  $\log_{10} \beta_{2,2(\text{cit})} = (18.90 \pm 0.2)$  for  $2\text{UO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons (\text{UO}_2)_2(\text{cit})_2^{2-}$  has been estimated from the data listed in Table 3 of [59LI/LIN] and accepted in this review.

#### [59MOS/ART]

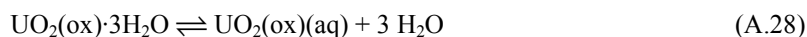
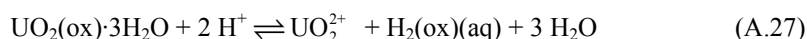
The Pu(III) edta system has been investigated by a cation exchange technique in the pH range 1.2 – 3.4 in 1M  $\text{NH}_4\text{Cl}$  at room temperature. It was shown spectrophotometrically, for solutions containing weighable quantities of  $\text{Pu}^{3+}$ , that under these conditions  $\text{Pu}^{3+}$  is not oxidised to  $\text{Pu}^{4+}$ . The authors used edta protonation constants of [47SCH/ACK], valid for 0.1M  $\text{KNO}_3$  at  $20^\circ\text{C}$ . The presence of  $\text{H}_5\text{edta}^+$  and  $\text{H}_6\text{edta}^{2+}$ , important species at  $\text{pH} < 2$  (see Figure VIII–13), has not been considered in the data analysis.

Unfortunately, no details about the pH measurements are given. Neither the pH scale is mentioned nor the calibration method of the pH meter is reported. Hence, although some experimental data are presented in tabular form by Moskvina and Artyukhin, no reliable re-evaluation of their data is possible, and their results have not been further considered in this review.

#### [59MOS/ZAK]

This is a rather comprehensive study of the solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  at  $(20 \pm 1)^\circ\text{C}$  in a variety of solutions. Solubility constants of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  and the stability constants of aqueous U(VI) oxalate complexes were calculated. However, the confirmation of the solid phase was not reported in the paper. The presentation of the results and the description of the methods for data analysis in the paper are not straightforward or consistent. For example, different values of the solubility products,  $K_s = [\text{UO}_2^{2+}][\text{ox}^{2-}]$ , were obtained from the same set of data but the difference was not explained. In addition, the experimental information in the paper was not sufficient to allow estimation of the uncertainty of the solubility data.

The systems in which the solubilities of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  were studied include  $\text{HClO}_4$  (0.5–3.0 M),  $\text{HNO}_3$  (0.5–3.0 M),  $(\text{NH}_4)_2\text{ox}$  (0–0.28 M),  $\text{HClO}_4$  (0.5 and 1.0 M)/ $\text{H}_2\text{ox}$  (0.08–0.636 M),  $\text{HNO}_3$  (0.5 and 2.0 M)/ $\text{H}_2\text{ox}$  (0.08–0.636 M),  $\text{HClO}_4$  (0.5, 1.0 and 3.0 M)/ $(\text{NH}_4)_2\text{ox}$  (0.07–0.28 M),  $\text{HNO}_3$  (0.5 and 1.0 M)/ $(\text{NH}_4)_2\text{ox}$  (0.07–0.28 M), and  $\text{HNO}_3$  (3.0 M)/ $(\text{NH}_4)_2\text{ox}$  (0.08–0.476 M). The authors assumed two dissolution reactions:





The experimentally observed solubility, ( $s$ ), of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  was thus represented by:

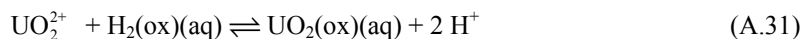
$$s = [\text{UO}_2^{2+}] + [\text{UO}_2(\text{ox})(\text{aq})] = K(\text{A.27}) \times [\text{H}^+]^2 / [\text{H}_2\text{ox}] + K(\text{A.28})$$

By solving sets of equations for  $s$  with the experimental solubility data, the equilibrium constants of  $K(\text{A.27})$  and  $K(\text{A.28})$  were calculated.

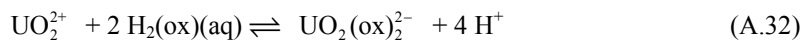
The solubility of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  was found to increase as the concentration of oxalic acid or ammonium oxalate was increased in water, 0.5 – 1.0 M  $\text{HNO}_3$  or  $\text{HClO}_4$ . Such increase was interpreted as reflecting the formation of U(VI) oxalate complexes in the solution. The data were analyzed to obtain the equilibrium constants ( $K(\text{A.29})$  and  $K(\text{A.30})$ ) for reactions:



$K(\text{A.27})$ ,  $K(\text{A.28})$ ,  $K(\text{A.29})$  and  $K(\text{A.30})$  are the “primary” constants directly calculated from the experimental solubility data. From these constants, the equilibrium constants for the formation of aqueous complexes were calculated.

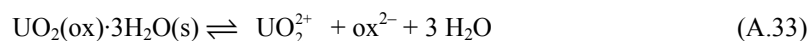


$$K(\text{A.31}) = K(\text{A.28})/K(\text{A.27})$$



$$K(\text{A.32}) = K(\text{A.29})/K(\text{A.27})$$

Using the dissociation constants of  $\text{H}_2\text{ox}$  ( $K' = [\text{H}^+][\text{Hox}^-] / [\text{H}_2\text{ox}] = 0.108$  and  $K'' = [\text{H}^+][\text{ox}^{2-}] / [\text{Hox}^-] = 6.4 \times 10^{-5}$ ), the authors calculated the solubility product of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  (A.33) and the stability constants of the 1:1 and 1:2 U(VI) oxalate complexes ((A.34) and (A.35)).



$$K_s(\text{A.33}) = K(\text{A.27}) \times (K'K'')$$



$$K(\text{A.34}) = (K'K'') / K(\text{A.31})$$



$$K(\text{A.35}) = (K'K'')^2 / K(\text{A.32})$$

The solubility constants for Reactions (A.27) – (A.30) and the stability constants for  $\text{UO}_2(\text{ox})(\text{aq})$  and  $\text{UO}_2(\text{ox})_2^{2-}$  (Reactions (A.34) and (A.35)) are summarised in Table VI-34 and Table VI-38. In addition to the shortcomings associated with the identification of the solid phase and the assignment of uncertainty, inaccurate dissociation constants of oxalic acid were used to derive the solubility product. Besides, the

ionic strength was not maintained constant in the experiments to determine the stability constants of the U(VI) oxalate complexes. Therefore, only the data of solubility constants ( $K(A.27)$  and  $K(A.28)$ ) are accepted by this review (Table VI-35). The data of stability constants of the aqueous U(VI) oxalate complexes from this work are not accepted. Discussions are made in Section VI.10.1.2 and Section VI.10.2.4 on these data.

Some of the data on  $\log_{10} K_s$  (A.27) are obtained in  $\text{HNO}_3$  media and need to be corrected for the complexation of U(VI) by nitrate. The correction is accomplished by the following equation:

$$\log_{10} K_{s,\text{corr.}} = \log_{10} K_{s,\text{exp.}} - \log_{10} (1 + K_{\text{NO}_3^-} [\text{NO}_3^-]) \quad (\text{A.36})$$

where  $K_{\text{NO}_3^-}$  is the equilibrium constant at each ionic strength for the reaction:



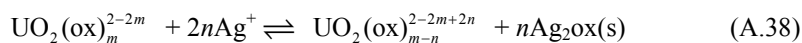
and can be calculated from  $\log_{10} K_{\text{NO}_3^-}^0 = (0.30 \pm 0.15)$  and  $\Delta\epsilon(\text{A.37}) = -(0.02 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$  for the  $\text{KNO}_3$  media, calculated from  $\epsilon(\text{UO}_2^{2+}, \text{NO}_3^-) = \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\epsilon(\text{UO}_2\text{NO}_3^+, \text{ClO}_4^-) = (0.33 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$ , and  $\epsilon(\text{K}^+, \text{NO}_3^-) = (0.11 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$  [2003GUI/FAN]. The corrections are shown in Table A-4. The corrected values are accepted by this review, and included in the SIT analysis in conjunction with other values in Table VI-35.

Table A-4: Corrections of  $\log_{10} K_s$  (A.27) from [59MOS/ZAK] for the complexation of U(VI) with nitrate.

$I_m$	$\log_{10} K_{\text{NO}_3^-}$	$\log_{10} (1 + K_{\text{NO}_3^-} [\text{NO}_3^-])$	$\log_{10} K_s(\text{A.27})$	
			Exp.	Corr.
0.508	$-(0.30 \pm 0.15)$	$(0.10 \pm 0.03)$	$-(3.15 \pm 0.30)$	$-(3.25 \pm 0.30)$
1.032	$-(0.31 \pm 0.16)$	$(0.18 \pm 0.05)$	$-(3.31 \pm 0.30)$	$-(3.49 \pm 0.30)$
1.572	$-(0.27 \pm 0.18)$	$(0.26 \pm 0.08)$	$-(3.44 \pm 0.30)$	$-(3.70 \pm 0.30)$
2.129	$-(0.20 \pm 0.20)$	$(0.37 \pm 0.11)$	$-(3.31 \pm 0.30)$	$-(3.68 \pm 0.31)$
2.707	$-(0.12 \pm 0.22)$	$(0.48 \pm 0.15)$	$-(3.38 \pm 0.30)$	$-(3.86 \pm 0.31)$
3.304	$-(0.03 \pm 0.25)$	$(0.61 \pm 0.19)$	$-(3.48 \pm 0.30)$	$-(4.09 \pm 0.32)$

#### [59PTI/TEK]

The authors used a silver electrode to study the following equilibrium in both forward and backward directions:



From the concentrations of silver in the solutions with different [U(VI)] and [ox], the equilibrium constants at  $(25 \pm 0.1)^\circ\text{C}$  were calculated. The ionic strength varied from 0.002 to 0.2 M. Linear extrapolation was performed to obtain the constants at  $I = 0$ . The constant  $K(\text{UO}_2\text{Ox(aq)} \rightleftharpoons \text{UO}_2^{2+} + \text{ox}^{2-})$  calculated from both directions

of reaction (A.38) is equal to  $1.0 \times 10^{-6}$ , but the constants  $K(\text{UO}_2(\text{ox})_2^{2-} \rightleftharpoons \text{UO}_2\text{ox}(\text{aq}) + \text{ox}^{2-})$  calculated from forward or backward directions are significantly different:  $8.3 \times 10^{-6}$  (forward) or  $3.6 \times 10^{-5}$  (backward). The authors assumed that the latter value is more accurate without convincing reasons. Due to the discrepancy between the data obtained in different directions and the varying ionic strength in the experiments, the data from this work are not accepted by this review.

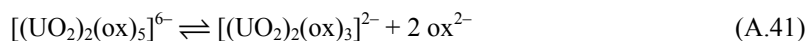
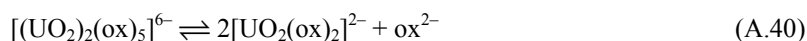
#### [\[59SMI\]](#)

The effect of the fluoride ion upon U(IV) solutions containing edta is explained in terms of the participation of the  $\text{UF}^{3+}$  ion in coordination. The stability constant of this ion with edta has been derived from polarographic determinations of free cadmium ion concentration in the exchange equilibrium:  $\text{UedtaF}^- + \text{Cd}^{2+} \rightleftharpoons \text{UF}^{3+} + \text{Cd}(\text{edta})^{2-}$  in 0.1 M  $\text{NaClO}_4$  at 20°C. The stability constant  $\log_{10}K = 16.1$  for  $\text{Cd}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Cd}(\text{edta})^{2-}$  was taken from [\[54SCH/GUT\]](#). Only the result of this derivation,  $\log_{10}K = 17.5$  for  $\text{UF}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{UedtaF}^-$  is reported by the author.

As a plausibility check, the obtained stability constant is transformed in this review to the equilibrium  $\text{Uedta}(\text{aq}) + \text{F}^- \rightleftharpoons \text{UedtaF}^-$  using two auxiliary equilibria. The first equilibrium is  $\text{U}^{4+} + \text{F}^- \rightleftharpoons \text{UF}^{3+}$  with  $\log_{10}K_1^0 = (9.28 \pm 0.09)$  [\[92GRE/FUG\]](#), extrapolated to 0.1 M  $\text{NaClO}_4$  using SIT interaction parameters given in [\[92GRE/FUG\]](#):  $\log_{10}K_1 = 8.4$ . The second equilibrium is  $\text{U}^{4+} + \text{edta}^{4-} \rightleftharpoons \text{Uedta}(\text{aq})$  with  $\log_{10}K_1^0 = (29.5 \pm 0.2)$  evaluated in this review, extrapolated to 0.1 M  $\text{NaClO}_4$  using SIT interaction parameters also evaluated in this review:  $\log_{10}K_1 = 26.1$ . The stability constant for the equilibrium  $\text{Uedta}(\text{aq}) + \text{F}^- \rightleftharpoons \text{UedtaF}^-$  now is  $\log_{10}K = 17.5 + 8.4 - 26.1 = -0.2$ . Comparing this result with data reported for  $\text{Uedta}(\text{aq}) + \text{OH}^- \rightleftharpoons \text{UedtaOH}^-$ ,  $\log_{10}K \approx 9$ , (Table VIII-30) and other ternary complexes [\[67CAR/MAR\]](#) (Table VIII-31) reveals that the number reported by [\[59SMI\]](#) must be wrong by several orders of magnitude. The scarce experimental information given by [\[59SMI\]](#) does not allow to elucidate what has gone wrong in the experiments. The stability constant of this paper is rejected in this review.

#### [\[59TEK/VIN2\]](#)

From the concentrations of oxalate in solutions of  $\text{K}_2\text{Mg}(\text{ox})_2$  and  $\text{K}_6(\text{UO}_2)_2(\text{ox})_5$  measured by a silver oxalate electrode, the equilibrium constants of the reactions:



were determined to be  $K(\text{A.39}) = 5.7 \times 10^{-5}$  ( $I = 0.089$  M) and  $2.9 \times 10^{-2}$  ( $I = 0.049$  and  $0.031$  M),  $K(\text{A.40}) = 4.8 \times 10^{-2}$  ( $I = 0.022$  M) and  $3.0$  ( $I = 0.0008$  M),  $K(\text{A.41}) = 3.8 \times 10^{-5}$  ( $I = 0.022$  M) at 25°C. No background electrolyte has been used in these ex-

periments, and the ionic strength was calculated iteratively from the dissolved species.

In the case of magnesium oxalate three measurements are reported at 0.02, 0.01 and 0.005 M  $K_2Mg(ox)_2$ . No details are reported about the dissolution of this solid, but if we assume similar behavior as reported for  $K_2Ca(ox)_2 \cdot H_2O$  [27SCH/GAD] it rapidly decomposes in water with the effect that the solution is oversaturated with respect to  $Mg(ox) \cdot 2H_2O$ . The possible detrimental effects of incongruent dissolution of  $K_2Mg(ox)_2$  or precipitation of  $Mg(ox) \cdot 2H_2O$  were not investigated. The authors interpret their data only in terms of the complex  $Mg(ox)_2^{2-}$  but ignore the contribution of  $Mg(ox)(aq)$  to the speciation in this system. Hence, the reported results are rejected, and no attempt was made in this review to fit two stability constants to three experimental data points at three different ionic strengths.

The value of  $K(A.40)$  is drastically different from the value of  $5 \times 10^{-7}$  for the same reaction from [56GRI/PTI]. In fact, the authors pointed out that the formulae given in the right side of Reaction (A.40) is uncertain. It could be  $(UO_2)_2(ox)_4^{4-}$ . Besides, it is not clear from the paper how the protonation processes of oxalate is taken into consideration in the calculation. Therefore, the data from this work are rejected by this review. Similar dinuclear U(VI) oxalate complexes were reported in [56GRI/PTI] and later in [2002HAV/SOT]. Still, more studies are needed to confirm the presence of such complexes and obtain reliable stability constants.

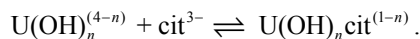
#### [59YAT/KAR]

The heat of reaction of  $Ca^{2+}$  and  $Ni^{2+}$  with edta has been measured at 25°C at ionic strengths ranging from 0.060 to 1.58 and 0.22 to 1.50, respectively. In cases of  $I > 0.6$   $NaNO_3$  was used as inert salt. Solutions of metal nitrates and  $Na_4edta$  were used. However, the poor information about the experiments actually carried out by the authors is not sufficient to judge the reliability of the reported results. Furthermore, the authors state that “experiments at the same ionic strength in presence of varying amounts of sodium nitrate showed that the possible complexing of edta with sodium ion did not have any noticeable influence on the heat effect”. This statement is in evident contrast to the findings of [76VAS/BEL2]. For these reasons the enthalpy values of [59YAT/KAR] have not been considered further in this review.

#### [60ADA/SMI]

The behavior of U(IV) in the presence of citric acid has been studied and the photochemical oxidation of U(IV) citrate by oxygen has been investigated. In the study of the complex formation of U(IV), the absorption spectra of  $5 \times 10^{-3}$  M U(IV) in 0.1 M  $HClO_4$  were measured over a pH range 1.50 – 4.50 in the presence of citric acid at room temperature. From the absorbances at 670 nm, the stability constant was calculated by assuming the formation of  $Ucit^+$  and by assuming that citrate existed as predominantly  $cit^{3-}$  in this pH range (the protonation constants in [53WAR/WEB] were used in the calculation). The calculated value of  $\log_{10}K$  for the formation of  $Ucit^+$  decreased from

9.72 at pH 1.50 to 3.93 at pH 4.50. This was attributed to the increasing hydrolysis of U(IV) with pH,



By considering the magnitude of  $\log_{10}K$ , the authors inferred that the complex was approximated to  $\text{U}(\text{OH})_2\text{cit}^-$ .

Since the change in the spectra with pH are not described, it is difficult to distinguish between the ligand species  $\text{H}_2\text{cit}^-$ ,  $\text{Hcit}^{2-}$  and  $\text{cit}^{3-}$ . The calibration of pH to  $\log_{10}[\text{H}^+]$ , the consideration of activity coefficients and quantitative consideration about the hydrolysis of U(IV) were not carried out. Since both the hydrolysis of U(IV) and the change in complex species (change in the degree of protonation in the ligand) may affect the value of  $\log_{10}K$ , this review does not accept the result of this paper.

#### [60ALE/ZHD]

It was observed in the polarographic experiments that U(VI) was first reduced to U(V) at the dropping mercury electrode, then the U(V) underwent disproportion:



The presence of anions (chloride, nitrate, sulfate, fluoride and oxalate) could facilitate the disproportionation and the effect decreased in the order:  $\text{F}^- > \text{ox}^{2-} > \text{SO}_4^{2-} > \text{NO}_3^- \sim \text{Cl}^-$ . This order was in agreement with the order of the binding strength of the anions to U(VI) and U(IV). No stability constants for U(IV, V or VI) oxalate complexes were obtained.

#### [60BAB/DUB]

The complex formation of zirconium with oxalate was investigated by spectrophotometry. The oxalate complexes of zirconium give higher absorbance at 217 to 230 nm than free oxalic acid. Thus, by measuring the absorbance at 217 nm of the solution containing  $2 \times 10^{-4}$  M  $\text{ZrOCl}_2$  and variable concentration of oxalic acid in 1 and 0.5 M  $\text{HClO}_4$ , complex formation constants were obtained for the complexes  $\text{Zr}(\text{ox})^{2+}$ ,  $\text{Zr}(\text{ox})_2(\text{aq})$ ,  $\text{Zr}(\text{ox})_3^{2-}$  and  $\text{Zr}(\text{ox})_4^{4-}$ . The species were estimated by checking their charges by electromigration experiments. The dissociation constants obtained are:  $K = 1.6 \times 10^{-10}$  for  $\text{Zr}(\text{ox})^{2+} \rightleftharpoons \text{Zr}^{4+} + \text{ox}^{2-}$ ,  $K = 4.6 \times 10^{-8}$  for  $\text{Zr}(\text{ox})_2(\text{aq}) \rightleftharpoons \text{Zr}(\text{ox})^{2+} + \text{ox}^{2-}$ ,  $K = 1.9 \times 10^{-4}$  for  $\text{Zr}(\text{ox})_3^{2-} \rightleftharpoons \text{Zr}(\text{ox})_2(\text{aq}) + \text{ox}^{2-}$  and  $K = 5.08 \times 10^{-1}$  for  $\text{Zr}(\text{ox})_4^{4-} \rightleftharpoons \text{Zr}(\text{ox})_3^{2-} + \text{ox}^{2-}$ . At lower acidities  $[\text{H}^+] = 0.001$  and  $0.5 \times 10^{-4}$ , the constants are also reported to be  $K = 2.1 \times 10^{-7}$  for  $\text{ZrO}(\text{ox}) \rightleftharpoons \text{ZrO}^{2+} + \text{ox}^{2-}$  and  $K = 4.57 \times 10^{-4}$  for  $\text{ZrO}(\text{ox})_2^{2-} \rightleftharpoons \text{ZrO}(\text{ox}) + \text{ox}^{2-}$ . The existence of  $\text{Zr}^{4+}$  in 1 and 0.5 M  $\text{HClO}_4$ , and of  $\text{ZrO}^{2+}$  in lower acidity solutions cannot be accepted. The zirconium concentration is too high to avoid hydrolytic polymerisation at these acidities. Moreover, since the difference in the absorbance at 217 nm is considered due to the difference between undissociated oxalic acid and oxalate in the complex, the proportionality of the absorbance to the concentration of the complex is not well established. The present review does not accept this pa-

per since more detailed examination such as the effect of the acidity of the solution and the metal-ion concentration is considered necessary to confirm the conclusion of this paper.

#### [\[60BOH/MAR\]](#)

In this internal progress report results are presented of potentiometric titrations of solutions containing Mg, Ca, Sr, Ba and several aminocarboxylates, including edta. The measurements were carried out in 0.1 M KNO<sub>3</sub> at 0.5, 13.4, 25.3 and 42.4°C. However, in the edta experiments a  $3.3 \times 10^{-3}$  M Na<sub>2</sub>H<sub>2</sub>edta solution was titrated with NaOH in 0.1 M KNO<sub>3</sub>. This procedure not only causes the ionic strength to increase above 0.1 M during the titration experiments, but also the effects of Na(edta)<sup>3-</sup> complexation would have to be considered in the data evaluation. Both effects were ignored by the authors. No experimental raw data are given in [\[60BOH/MAR\]](#), and hence, a re-evaluation of the results is not possible. All values reported in [\[60BOH/MAR\]](#) are discarded in this review.

#### [\[60BOU/MAR\]](#)

In connection with the composition of milk ultrafiltrates, solubility of tricalcium citrate has been determined at 21 and 95°C by dissolution in water and by precipitation from supersaturated solutions containing various proportions of calcium to citrate and at pH 4.4 to 8.8. Calcium was determined by a turbidimetric method, citrate by colorimetry, calcium ion with the ammonium purpurate method and pH with a glass electrode. Solubility products  $K_{s,0} = [\text{Ca}^{2+}]^3[\text{cit}^{3-}]^2$  were calculated with the assumptions, that is,

- at pH above 7,

$$\begin{aligned} [\text{Ca}]_{\text{T}} &= [\text{Ca}^{2+}] + [\text{Ca}(\text{cit})^-], \\ [\text{cit}]_{\text{T}} &= [\text{cit}^{3-}] + [\text{Ca}(\text{cit})^-], \end{aligned}$$

- at pH below 7,

$$\begin{aligned} [\text{Ca}]_{\text{T}} &= [\text{Ca}^{2+}] + [\text{Ca}(\text{cit})^-] + [\text{Ca}(\text{Hcit})(\text{aq})], \\ [\text{cit}]_{\text{T}} &= [\text{H}_3\text{cit}] + [\text{H}_2\text{cit}^-] + [\text{Hcit}^{2-}] + [\text{cit}^{3-}] + [\text{Ca}(\text{cit})^-] + [\text{Ca}(\text{Hcit})(\text{aq})]. \end{aligned}$$

The protonation constants of citrate used in the calculation were from [\[40ADE\]](#),  $1/K_3 = 1.19 \times 10^{-3}$ ,  $1/K_2 = 4.30 \times 10^{-5}$  and  $1/K_1 = 1.73 \times 10^{-6}$  for  $I = 0.1$  M and 18°C. For the reaction,  $\text{Ca}(\text{Hcit})(\text{aq}) \rightleftharpoons \text{Ca}(\text{cit})^- + \text{H}^+$ ,  $K = 2 \times 10^{-5}$  [\[39NOR\]](#) was used, and for the reaction,  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$ ,  $\log_{10} \beta_1 = 4.64 - 3.64\sqrt{I}$  ([\[55DAV/HOY\]](#), [\[34HAS/MCL\]](#), [\[51HEI\]](#), [\[39NOR\]](#), [\[52SCH/LIN\]](#)) was used. The ionic strength was calculated from the concentrations of dissolved species. Mainly from the relation between calcium and citrate concentrations remained in the supernatants at equilibrium at pH 7 or above at 21°C after the addition of various concentrations ( $1.0 - 7.8 \times 10^{-2}$  M) of citrate and calcium, solubility products were obtained as a function of ionic strength to be  $\text{p}K_s = (17.63 \pm 0.08) - (10.84 \pm 0.23)\sqrt{I}$  over a range of ionic strengths from 0.004 to 0.5 M. The solubility products calculated for pH < 7 and for 95°C did not show any

significant difference.

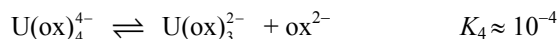
At pH 7 or above, calcium in the solution will be mainly in the form of  $\text{Ca}(\text{cit})^-$  in the presence of  $1 - 6 \times 10^{-2} \text{ M cit}^{3-}$ . Therefore main uncertainties in the calculation of the solubility product may arise from the estimation of  $[\text{Ca}^{2+}]$  with the use of the formation constant of  $\text{Ca}(\text{cit})^-$ . The sources used to estimate  $\log_{10}\beta$  in this paper are mostly not accepted (except [52SCH/LIN]) and the equation for  $\log_{10}\beta$  agrees with the NEA selected value only at the ionic strength close to  $0.1 \text{ mol} \cdot \text{kg}^{-1}$ . Moreover, in this paper, the ionic strength was not controlled and estimated from the concentrations of the dissolved species in the solution. Hence, the results of [60BOU/MAR] are not accepted in this review.

#### [60FEL/NOR]

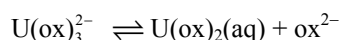
The authors have conducted potentiometric titrations of solutions containing equimolar concentrations of  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{H}_3\text{cit}$  from 0.001 to 0.01 M plus  $\text{KNO}_3$  to give total 0.136 M ionic strength. The titration curves exhibit the first and second inflection points at 3 and  $3 + 5/3$  moles of base per mole of uranyl ion. From the pH before the first inflection point, they calculated  $\log_{10}\beta$  values assuming that only one species among  $\text{UO}_2(\text{Hcit})(\text{aq})$ ,  $\text{UO}_2(\text{Hcit})(\text{OH})^-$ , and  $(\text{UO}_2)_2(\text{Hcit})_2(\text{OH})_2^{2-}$  is formed. With using  $\log_{10}K_{(\text{H})} = 4.32$  and 2.85, only  $\log_{10}\beta$  values for  $(\text{UO}_2)_2(\text{Hcit})_2(\text{OH})_2^{2-}$  showed a good constancy.  $\log_{10}^*K$  for the reaction  $2\text{UO}_2^{2+} + 2\text{Hcit}^{2-} + 2\text{H}_2\text{O} \rightleftharpoons (\text{UO}_2)_2(\text{Hcit})_2(\text{OH})_2^{2-} + 2\text{H}^+$  is reported to be  $(7.68 \pm 0.04)$ . However, the recalculation of  $\log_{10}^*K$  from the data listed in Table II of [60FEL/NOR] indicated that the reported values are constantly around 0.28  $\log_{10}$ -units smaller. The value should be 7.96. Although the authors claimed the existence of  $(\text{UO}_2)_2(\text{Hcit})_2(\text{OH})_2^{2-}$ , this species cannot be distinguished from  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  without information other than equilibrium relationship. Thus, the obtained value is considered equivalent to  $\log_{10}\beta_{2(\text{cit})} = 19.26$  for  $2\text{UO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons (\text{UO}_2)_2(\text{cit})_2^{2-}$  (assuming that the first protonation constant of citrate is  $\log_{10}K_{1,1(\text{H})} = 5.65$  at this ionic strength) and accepted in this review. Considering the possible contribution of  $\text{UO}_2(\text{cit})^-$ , the uncertainty of 0.3 is assigned to this value. From the second inflection point at  $3 + 5/3$  moles of base per mole of uranyl ion, the authors considered the reaction of  $(3/2)\text{dimer}^{2-} + 5\text{OH}^- \rightarrow \text{trimer}^{3-}$ , which corresponds to  $(\text{UO}_2)_3(\text{cit})_3(\text{OH})_5^{8-}$ . However, in this pH region,  $\text{UO}_2^{2+}$  itself hydrolyses which has to be considered in the evaluation of these reactions. Thus, this review does not accept the species as reasonable.

#### [60GRI/PET]

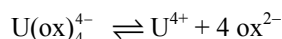
In this brief communication the authors cited the equilibrium constant of the reaction:



from a previous paper [58GRI/PET2] and reported 1) a value of  $K_3 = 4 \times 10^{-6}$  for:



obtained by solubility experiments; and 2) a value of  $K_{\text{total}} \approx 10^{-26}$  for



obtained by potentiometric titration of  $\text{K}_4[\text{U(ox)}_4] \cdot 5\text{H}_2\text{O}$  with alkali till the formation of uranium hydroxide. In calculating  $K_{\text{total}}$ , the solubility product of  $\text{U(OH)}_4$  was needed and taken as  $10^{-45}$  from [52LAT]. From the values of  $K_{\text{total}}$ ,  $K_4$  and  $K_3$ , and the assumption that  $K_1 < K_2 < K_3$ , values of  $K_1$  and  $K_2$  were estimated to be  $10^{-9}$  and  $10^{-7}$ , respectively.

The values of  $K_1$  and  $K_2$  from this reference are rejected by this review because they are not directly measured by experiments and based on another approximate value of  $K_4$  from [58GRI/PET2]. In fact, the authors pointed out in a later publication [63GRI/PET] that the data from [58GRI/PET2] were unreliable due to the partial oxidation of U(IV) in the experiments. The values of  $K_{\text{total}}$  and  $K_3$  are considered by this review (Table VI-36) but are not re-evaluated due to the lack of experimental conditions.

#### [60KON/GEL]

The solubility of Np(IV) oxalate was studied at two temperatures:

- at 19°C in (0.41 and 1.08) M HCl solutions,
- at 16°C in (1.56 and 2.09) M HCl and in 4.1 M  $\text{HClO}_4$  solutions.

After an equilibration time of 5 hours the solutions were centrifuged, and the concentration of neptunium(IV) in the solution was then determined spectrophotometrically at a wavelength of 320 nm in basic peroxide medium. The solid was not characterised, but the formula  $\text{Np(ox)}_2 \cdot 6\text{H}_2\text{O}$  is given in the paper. The authors calculated the solubility product of the solid, although they did not keep the acidity and ionic strength of the solutions constant. The following protonation constants for oxalate were used:  $\log_{10} K_1 = 4.19$  and  $\log_{10} K_2 = 1.23$ . The reported solubility constants are listed in Table A-5.

Table A-5: Solubility constants for Np(IV) oxalate in hydrochloric acid medium [60KON/GEL].

$t$ (°C)	medium	$\log_{10} K_s$
$\text{Np(ox)}_2 \cdot 6\text{H}_2\text{O}(\text{cr}) + 4 \text{ H}^+ \rightleftharpoons \text{Np}^{4+} + 2 \text{ H}_2\text{ox}(\text{aq}) + 6 \text{ H}_2\text{O}(\text{l})$		
19	0.41 and 1.08 M HCl	– (11.22 ± 0.09)
16	1.56 and 2.09 M HCl	– (11.32 ± 0.03)
$\text{Np(ox)}_2 \cdot 6\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{Np}^{4+} + 2 \text{ ox}^{2-} + 6 \text{ H}_2\text{O}(\text{l})$		
16	4.1 M $\text{HClO}_4$	– (22.30 ± 0.06)
	1.6 and 2.1 M HCl	– (22.16 ± 0.03)
19	0.4 and 1.1 M HCl	– (22.07 ± 0.09)

The authors also measured the increase in the solubility of Np(IV) oxalate with increasing oxalate concentration at  $(25 \pm 2)^\circ\text{C}$ . No information is given about the acid-



ity or ionic strength of these solutions. The results were explained by the formation of four complex species  $\text{Np}(\text{ox})_n^{4-2n}$  ( $n = 1$  to 4) with the following stability constants:  $\log_{10} \beta_1 = (8.5 \pm 0.3)$ ,  $\log_{10} \beta_2 = (17.54 \pm 0.01)$ ,  $\log_{10} \beta_3 = (23.96 \pm 0.04)$  and  $\log_{10} \beta_4 = 27.4$ . The authors claimed that the formation of  $\text{Np}(\text{ox})_4^{4-}$  was confirmed by the preparation of the solid compound  $(\text{NH}_4)_4\text{Np}(\text{ox})_4 \cdot n\text{H}_2\text{O}$ , but no solid characterisation (*e.g.*, elemental analysis) is reported in the paper. The solubility data reported in this paper was later re-analysed in [68MOS2], without changing significantly the values of the equilibrium constants.

Taking into account the scarcity of the data and that not enough experimental details are provided, the data reported in [60KON/GEL] are not included in the review process.

#### [60KOZ/KRO]

The authors report the equilibrium constants  $\log_{10} K_1 = (10.4 \pm 0.3)$  for  $\text{UO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons \text{UO}_2\text{edta}^{2-}$  and  $\log_{10} K = (15.2 \pm 0.3)$  for  $2\text{UO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons (\text{UO}_2)_2\text{edta}(\text{aq})$  in 0.1 M  $\text{NH}_4\text{Cl}$  at  $(24.0 \pm 0.1)^\circ\text{C}$ . These values were obtained from spectrophotometric measurements in solutions with a constant U(VI) concentration of  $2 \cdot 10^{-3}$  M and different edta concentrations ( $1.2 \cdot 10^{-3}$  M for measurements at pH 2 – 6, and 4 to  $50 \cdot 10^{-3}$  M for measurements at pH 4.25 – 5.25). A Beckmann “DU” quartz spectrophotometer was used for the spectrophotometric measurements. The pH was measured at the same time with an LP-5 potentiometer and a glass electrode.

However, the pH calibration and the pH scale used are not reported by the authors. The auxiliary stability constants taken from the literature are not given in the paper. The value  $\log_{10} K_1$  for  $\text{UO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons \text{UO}_2\text{edta}^{2-}$  is obtained from spectra of 1:1 U(VI) – edta solutions in the pH range 4.3 – 5.5. Under these experimental conditions the complex  $\text{UO}_2(\text{Hedta})^-$  prevails while the species  $\text{UO}_2\text{edta}^{2-}$  is practically not present (see Figure 1 and the accompanying discussion in [68SIL/SIM]). The complete neglect of  $\text{UO}_2(\text{Hedta})^-$  may be the main reason for the large discrepancy of the obtained stability constants with the reliable results of [82OVE/LUN] (Table VIII-32). For these reasons the results of this study have not been considered in this review.

#### [60LEB/PIR]

Distribution of tracer concentration of  $^{241}\text{Am}(\text{III})$  ( $\sim 10^5$  cpm  $\cdot$  mL $^{-1}$ ) between  $I = 0.2$  M  $\text{NH}_4\text{Cl}$  aqueous solution and the cation exchange resin KU-2 (140 to 200 mesh) of the  $\text{NH}_4^+$  form was studied at pH 2 ~ 4 at room temperature ( $20 - 25^\circ\text{C}$ ) in the absence and presence of oxalic acid. From the  $\alpha$ -radioactivity measurement, the concentration of Am(III) in the aqueous phase was determined. At each data point, the authors estimated the activity of  $\text{ox}^{2-}$ ,  $a_{\text{ox}^{2-}}$ , by using the protonation constants of oxalate,  $\log_{10} K_{(\text{H})}^0 = 4.27, 1.27$ , and the activity coefficients of singly and doubly charged ions taken from the literature. By analysing the distribution coefficient as a function of the activity of  $\text{ox}^{2-}$ , the overall stability constants were estimated to be  $\beta_1 = 9.8 \times 10^5$  and  $\beta_2 = 1.4 \times$

$10^{10}$  for  $\text{Am}^{3+} + n(\text{ox}^{2-}) \rightleftharpoons \text{Am}(\text{ox})^{3-2n}$ . Protonation constants used are slightly different from the values selected in this review and may have introduced some error in the concentration of  $\text{ox}^{2-}$ . The use of the calculated activity coefficients for each data point may introduce some errors. Although the authors discussed the activity coefficients of dissociated oxalates, no hints are given for the activity coefficients of  $\text{Am}^{3+}$  and its oxalate complexes used in the analysis of distribution coefficient to obtain the stability constants of oxalate complexes of Am(III). Although the values reported in this paper give very rough estimates of the stability constants of Am(III) oxalates, this paper is not accepted by this review due to the problems listed above.

#### [60LEB/PIR2]

Solubilities of  $^{241}\text{Am}_2(\text{ox})_3 \cdot 9\text{H}_2\text{O}$  in 0.05 ~ 0.3 M  $\text{HClO}_4$  and in solutions containing oxalate were obtained by determining the Am(III) concentration by  $\alpha$ -counting by equilibrating the dried americium oxalate and  $\text{HClO}_4$  for 3 ~ 5 hours at  $(25.0 \pm 0.1)^\circ\text{C}$ . The calculations of the solubility product were carried out by assuming  $[\text{ox}^{2-}]_{\text{T}}$  (total concentration of oxalate in the solution)  $= (3/2)[\text{Am}^{3+}]_{\text{T}}$  (total concentration of Am(III) in the solution) according to the formula:  $K_{s,p} = \gamma_3^2 \cdot a_{\text{ox}^{2-}}^3 \cdot [\text{Am}^{3+}]^2$ , where  $\gamma_3$  is the activity coefficient of the trivalent ion and  $a_{\text{ox}^{2-}}$  is the activity of oxalate ions calculated by using the protonation constants of oxalate,  $\log_{10} K_{(\text{H})}^{\circ} = 4.27, 1.27$ , and the activity coefficients of singly and doubly charged ions taken from the literature. From the values obtained at 0.2 and 0.3 M  $\text{HClO}_4$ , a mean value of  $\log_{10} K_{s,p}$  was obtained to be  $-30.66$ . Stability constants of Am(III) oxalates were obtained by measuring  $[\text{Am(III)}]_{\text{T}}$  as a function of  $a_{\text{ox}^{2-}}$  at  $I = 0.2$  to  $0.7$  by  $(\text{H}^+, \text{K}^+)(\text{ClO}_4^-, \text{ox}^{2-}, \text{Hox}^-)$ . For each data point, the activities of the species were calculated by using the equations for activity coefficients. Stability constants at  $I = 0$  were obtained to be  $\log_{10} \beta_1^{\circ} = (7.30 \pm 0.06)$ ,  $\log_{10} \beta_2^{\circ} = (11.46 \pm 0.10)$ , and  $\log_{10} \beta_3^{\circ} = (12.3 \pm 0.2)$  for  $\text{Am}^{3+} + n(\text{ox}^{2-}) \rightleftharpoons \text{Am}(\text{ox})_n^{3-2n}$ , respectively. The method for the separation of the solid and solution is not described. In the calculation, the use of the calculated activity coefficients for each data point may introduce some errors. Since the true equilibrium includes the hydrated water as,  $\text{Am}_2(\text{ox})_3 \cdot 9\text{H}_2\text{O} + 6\text{H}^+ \rightleftharpoons 2\text{Am}^{3+} + 3\text{H}_2\text{ox} + 9\text{H}_2\text{O}$ , the exclusion of the water activity in the equation for  $K_{s,p}$  will give some errors. Also, the protonation constants used are slightly different from the values selected by this review and may give some errors in the estimation of the concentration (activity) of oxalate ion. In Table 1 of this paper, the oxalate concentration consumed by the complex formation of Am(III) is not accounted for in the calculation of  $a_{\text{ox}^{2-}}$ . Although the solubility constants and stability constants given in this paper give rough estimates, this paper is not accepted by this review because of the problems listed above.

#### [60MAT/SAF]

The distribution of  $\text{Ca}^{2+}$  between a cation exchanger and edta was studied in the pH range 3.20 – 4.90. The  $\text{Ca}^{2+}$  concentration in the original solution amounted 0.012 M, the edta concentration was 0.01 M and the  $\text{NH}_4^+$  concentration 0.3 M. The anion of the

inert salt is not reported, and no information is provided about pH measurements and electrode calibration. In addition, there is no clue given by [60MAT/SAF] how the concentration of  $\text{edta}^{4-}$  was calculated from the total analytical edta concentration in their data evaluation. [60MAT/SAF] state that mathematical analysis of the experimental data obtained showed that with a metal:ligand ratio  $\approx 1$ , within the pH range studied, the predominant species are  $\text{Ca}(\text{edta})^{2-}$  and  $\text{Ca}_2\text{edta}(\text{aq})$ . According to these results, the dominant complex at  $\text{pH} > 5$  would be  $\text{Ca}_2\text{edta}(\text{aq})$  (Fig. 6 in [60MAT/SAF]), in obvious contradiction with all other experimental studies involving Ca, Mg : edta ratios of 1 (see discussion in Section VIII.5). The data analysis of [60MAT/SAF] might be strongly affected by using incorrect edta protonation constants and/or experimental shortcomings. All values reported in [60MAT/SAF] are discarded in this review.

#### [60MOS/KHA]

The distribution of  $^{241}\text{Am}(\text{III})$  ( $(1 \sim 2) \times 10^5 \text{ cpm} \cdot \text{mL}^{-1}$ ) between the cation exchange resin KU-2 and solutions containing oxalate or edta has been investigated. From the results obtained with edta the formation of  $\text{Am}(\text{edta})^-$  ( $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$ ,  $\log_{10} K_1 = (18.03 \pm 0.13)$ ) and  $\text{Am}(\text{Hedta})(\text{aq})$ , ( $\text{Am}(\text{edta})^- + \text{H}^+ \rightleftharpoons \text{Am}(\text{Hedta})(\text{aq})$ ,  $\log_{10} K = (1.94 \pm 0.02)$ ) is assumed. The two equilibrium constants are obtained using 4 and 5 experimental points, respectively, at pH values between 1.00 and 2.23. For oxalate, the formation of  $\text{Am}(\text{ox})_2^-$  and  $\text{Am}(\text{Hox})_4^-$  was concluded from the data obtained at 0.0005 ~ 0.005 M  $\text{H}_2\text{ox}$  total concentration at a fixed pH of 1.9 (Table 2 of this paper). From the data obtained at pH 0.70 ~ 2.80 at a fixed total  $\text{H}_2\text{ox}$  concentration of 0.005 M, the formation of  $\text{Am}(\text{Hox})_3(\text{aq})$ ,  $\text{Am}(\text{ox})_2^-$  and  $\text{Am}(\text{Hox})_4^-$  was concluded. The overall stability constants obtained are  $\log_{10} K = 9.7 \sim 10.0$  for  $\text{Am}(\text{ox})_2^-$ ,  $\log_{10} K = 9.64$  for  $\text{Am}(\text{Hox})_3(\text{aq})$  and  $\log_{10} K = 11$  for  $\text{Am}(\text{Hox})_4^-$ .

The temperature of the measurements is not given. The nominal ionic strength of the solutions is 1 M  $\text{NH}_4\text{Cl}$ , but it actually increases to 1.1 at pH 1. The pH measurements are not discussed, the actual pH scale used is left as a puzzle for the reader, the instrumentation used is not described. The edta protonation constants used by Moskvina *et al.* were taken from [59MOS/ART], they are valid for  $I = 0.1$  M. The protonation constants of oxalate,  $\log_{10} K_{(\text{H})} = 3.82, 1.85$  in 1 M  $\text{NH}_4\text{Cl}$  (taken from [58GEL/MAT]) used to estimate  $[\text{ox}^{2-}]$  are fairly different from the reliable values selected by this review. The estimation of the predominant species may have been seriously affected by these values. When the data given in Tables 2 and 3 of this paper are compared for nearly the same condition (pH 1.9 ~ 2.0,  $\text{H}_2\text{ox}$  concentration 0.005 M), the assignment and calculated concentration of the complex species are inconsistent.

Considering all these shortcomings the data obtained by Moskvina *et al.* are discarded in this review.

[\[60RAA\]](#)

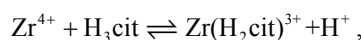
In this spectrophotometric study the complexation of magnesium with oxalate and carbonate has been studied at 20°C in 0.1 M NaCl using Eriochrom black T as colour indicator. The stability constant  $\log_{10} K_1 = (2.76 \pm 0.10)$  for the  $\text{Mg(ox)(aq)}$  complex has been derived as the mean value from four experiments, and the uncertainty is the standard deviation. The  $\log_{10} K_1$  values of the single experiments vary from 2.67 to 2.83. This review accepts  $\log_{10} K_1$  with an uncertainty of  $\pm 0.2$ .

[\[60RYA/ERM\]](#)

Distribution coefficients of  $^{95}\text{Zr}$  ( $1 \times 10^{-5}$  M with carrier) between KU-2 ion exchanger and aqueous phase containing  $0.4 - 50 \times 10^{-3}$  M citric acid were measured at 0.125, 0.5, 1 and 2 M  $\text{HClO}_4$ . Distribution coefficient can be expressed by:

$$K_d = \frac{K_d^\circ}{1 + \sum \beta_{1q(\text{H}_r\text{cit})} [\text{H}_r\text{cit}]^q},$$

where  $K_d^\circ$  is the distribution coefficient in the absence of citric acid and  $\beta_{1q(\text{H}_r\text{cit})}$  denotes the constant for the reaction  $\text{Zr}^{4+} + q\text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{Zr}(\text{H}_r\text{cit})_q^{4+q(r-3)}$ . The authors have obtained  $\beta_{1q(\text{H}_r\text{cit})}$  from plots of  $1/K_d$  against  $C_{\text{H}_3\text{cit}}$ . The plots showed nearly linear relationship indicating  $q = 1$ . By assuming the reaction,



$$^*\beta_{1q(\text{H}_2\text{cit})} = \frac{[\text{Zr}(\text{H}_2\text{cit})^{3+}][\text{H}^+]}{[\text{Zr}^{4+}][\text{H}_3\text{cit}]},$$

and using the values of  $K_d^\circ = 245$  in 2 M  $\text{HClO}_4$ , they have obtained the conditional constant as:

$$K' = \frac{^*\beta_{1(\text{H}_2\text{cit})}}{[\text{H}^+]} = (1300 \pm 216).$$

They did not give the corresponding values in 1, 0.5 and 0.125 M  $\text{HClO}_4$ , since the values of  $K_d^\circ$  were too large to be accurately determined. Even in 2 M  $\text{HClO}_4$ , the value of  $K'$  is very susceptible to the value of  $K_d^\circ$  and the selection of the fitting function. For example, the reanalysis of the experimental data given in Table 1 of this paper by a nonlinear least-squares fitting with the parameters of  $\log_{10} K'$  and  $K_d^\circ$  assuming that the percentages of Zr(IV) remaining in solution have similar precision, give  $\log_{10} K' = 2.77$  ( $K' = 587$ ) and  $\log_{10} K_d^\circ = 2.17$  ( $K_d^\circ = 148$ ), which are fairly different from the values given in the paper. Moreover, there is no argument about the selection of the species of  $\text{Zr}(\text{H}_2\text{cit})^{3+}$ . Therefore, although this paper gives qualitative information that  $\text{Zr}^{4+}$  reacts with citric acid in 2 M  $\text{HClO}_4$  solution with the conditional constants,

$$\log_{10} K' = \log_{10} \frac{^*\beta_{1(\text{H}_2\text{cit})}}{[\text{H}^+]^{3-r}} = (3 \pm 1) \quad (\text{in } 2 \text{ M } \text{HClO}_4),$$

where:

$$^*\beta_{1(\text{H}_r\text{cit})} = \frac{[\text{Zr}(\text{H}_r\text{cit})^{r+1}][\text{H}^+]^{3-r}}{[\text{Zr}^{4+}][\text{H}_3\text{cit}]},$$

this review does not accept the values as quantitative information.

### [60STA3]

The stability constants of U(VI) complexes with acetate, oxalate, tartrate and edta were determined by a solvent extraction method. The distribution of dissolved U(VI) (total metal concentration  $1.5 \cdot 10^{-4}$  M) between the two liquid phases water (0.1 M NaClO<sub>4</sub> at different pH values and in presence of the different ligands) and benzene (0.1 M benzylacetone solution) has been measured by spectrophotometry.

In the case of edta, Na<sub>2</sub>H<sub>2</sub>edta solutions were used with concentrations of 0.0005 M (pH 4 – 6), 0.001 M (pH 4 – 6), 0.002 M (pH 4.5 – 6.5), 0.005 M (pH 5 – 6.5) and 0.01 M (pH 5.5 – 6.75). In solutions of 0.1 M NaClO<sub>4</sub> the higher edta concentrations cause a variable edta excess and hence, an ionic strength  $I > 0.1$  varying with pH during the experiments. In addition, the author claims that only one complex, UO<sub>2</sub>(Hedta)<sup>−</sup> with  $\log_{10} K = (7.32 \pm 0.02)$ , is formed. It is unclear to which extent the neglect of the species UO<sub>2</sub>edta<sup>2−</sup> in the data analysis has biased the numerical results. For these reasons the results concerning edta have not been considered in this review.

The author also studied the complexation of U(VI) with oxalic acid by solvent extraction. From the effect of the ligand concentration on the distribution ratio of U(VI), the stability constant for the reaction:



$\log_{10} \beta_2$  (A.42) was calculated to be  $(11.08 \pm 0.03)$ . The ionic strength was “nominally” 0.1 M NaClO<sub>4</sub>, but could be up to 0.13 M (NaClO<sub>4</sub> + oxalate) when there was 0.01 M oxalate in the system. The temperature was not specified, but assumed to be 20°C by this review. The author used  $\log_{10} K_1 = 4.2$  and  $\log_{10}(K_1 K_2) = 5.4$  as the protonation constants of oxalic acid, but did not mention the reference. These constants coincide with those published in [61MCA/NAN] for  $\log_{10} K_1$  and [39HAR/FAL], [48PIN/BAT] for  $\log_{10} K_2$ , all valid at  $I = 0$ . Though it is not correct to use the values at  $I = 0$  for the systems in this study, the values of the protonation constants have minimal effects on the results because the pH ranged from 5.1 to 7.5 in the experiments with oxalate.

The author concluded that only the 1:2 complex, UO<sub>2</sub>(ox)<sub>2</sub><sup>2−</sup>, formed based on a slope of 2 in Figure 4 of the paper. If this is true, it appears that the concentration of free oxalate was calculated by a wrong equation in the paper:

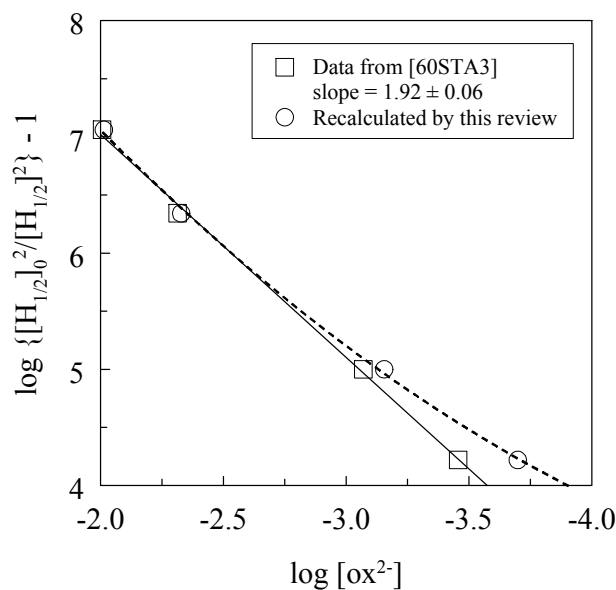
$$[\text{ox}^{2-}] + [\text{Hox}^-] + [\text{H}_2\text{ox}(\text{aq})] = C_{\text{H}_2\text{ox}} - [\text{UO}_2(\text{ox})(\text{aq})] \quad (\text{A.43})$$

The equation consistent with the exclusive formation of UO<sub>2</sub>(ox)<sub>2</sub><sup>2−</sup> should be:

$$[\text{ox}^{2-}] + [\text{Hox}^-] + [\text{H}_2\text{ox}(\text{aq})] = C_{\text{H}_2\text{ox}} - 2 [\text{UO}_2(\text{ox})_2^{2-}] \quad (\text{A.44})$$

The  $[\text{ox}^{2-}]$  is recalculated according to Eq.(A.44) by this review and Figure 4 of the original paper replotted. As Figure A-12 shows, the recalculated data show curvature that deviates from the linear fit with a slope  $\sim 2$ . This suggests that the formation of  $\text{UO}_2(\text{ox})(\text{aq})$  in the region of lower  $[\text{ox}^{2-}]$  should be considered. Since the data (only four points) are not sufficient to allow a thorough analysis, no attempts are made by this review to calculate the stability constant of  $\text{UO}_2(\text{ox})(\text{aq})$ . However, from Figure A-12, it seems that the formation of  $\text{UO}_2(\text{ox})(\text{aq})$  is insignificant and can probably be ignored when  $[\text{ox}^{2-}] > 10^{-3}$  M. Therefore, the stability constant of  $\text{UO}_2(\text{ox})_2^{2-}$  was recalculated with the lowest data point excluded. The new value of  $\log_{10} \beta_2$  (A.42) coincides with the value reported in the paper within the experimental uncertainty, indicating that the value in the paper is also obtained by ignoring the formation of  $\text{UO}_2(\text{ox})(\text{aq})$ . Thus, this value is accepted, but corrected by this review for the temperature change from 20 to 25°C based on the following method.

Figure A-12: Replot of Figure 4 from [60STA3].



Using the constant enthalpy approach [97PUI/RAR], the correction of the formation constants for temperature is expressed as:

$$\log_{10} K_{T_2} - \log_{10} K_{T_1} = \frac{\Delta_r H_m}{2.3023 R} (T_1^{-1} - T_2^{-1}) \quad (\text{A.45})$$

The enthalpy of complexation for  $\text{UO}_2(\text{ox})_2^{2-}$ ,  $\Delta_r H_m$  (A.42), is assumed to be equal to the enthalpy of complexation for the analogous U(VI) malonate complex,



as an approximation:  $\Delta_r H_m(\text{A.42}) \approx \Delta_r H_m(\text{A.46}) = (11 \pm 1) \text{ kJ} \cdot \text{mol}^{-1}$  [2002RAO/JIA]. Thus, the  $\log_{10} \beta_2(\text{A.42})$  is corrected from 20 to 25°C and the corrected value ( $\log_{10} \beta_2(\text{A.42}) = (11.11 \pm 0.11)$ ) is shown in Table VI-39.

#### [60WAT/DEW]

This paper reports a potentiometric and spectrophotometric study of the mixed complexes of Ni(II) with ethylenediamine (en) and oxalate at 25°C. The stoichiometry of the predominating complexes was obtained by spectrophotometric measurements in solutions containing 1 M  $\text{K}_2\text{ox}$ , where the oxalate to ethylenediamine ratio was varied by adding either ethylenediamine or  $\text{HNO}_3$ . Equilibrium constants were obtained from pH measurements with a glass electrode at  $9.6 > \text{pH} > 5.7$  and  $I = 1 \text{ M}$  ( $\text{KNO}_3$ ) at 25°C. Several mixed complexes were found:  $\text{Ni}(\text{ox})(\text{en})(\text{aq})$ ,  $\text{Ni}(\text{ox})(\text{en})_2(\text{aq})$ ,  $\text{Ni}(\text{ox})_2(\text{en})^{2-}$ ; in addition to the nickel-oxalate complexes:  $\text{Ni}(\text{ox})(\text{aq})$ ,  $\text{Ni}(\text{ox})_2^{2-}$ , and  $\text{Ni}(\text{ox})_3^{4-}$ .

The pH electrode was calibrated with a single buffer of pH = 10, as described in a previous paper [53WAT/AAR]. In the potentiometric titrations, solutions containing 0.02 M Ni(II), 0.06 M en, and varied concentrations of oxalate were titrated with a 2.372 M  $\text{HNO}_3$  solution. Therefore the ionic strength was not strictly constant; it varied between 1 M and  $\approx 1.1 \text{ M}$ . The titrations were not performed in the presence of a constant background electrolyte either. In the absence of oxalate the medium was  $[\text{KNO}_3] \approx 1 \text{ M}$ , but with increasing oxalate the medium changed: at the limit  $[\text{K}_2\text{ox}] = 0.25 \text{ M}$  and the background ions were  $[\text{NO}_3^-] \leq 0.3 \text{ M}$  and  $[\text{K}^+] \approx 0.7 \text{ M}$ . According to the specific ion interaction model, this affected substantially the activity coefficients of all ionic reactants and charged complexes. This was recognised by the authors only in that the protonation constants of ethylenediamine were increased slightly in the most concentrated oxalate solutions. No indication is given about how these values for the protonation constants of ethylenediamine were obtained. All other equilibrium constants were assumed to be unaffected by the change in the ionic medium. The formation of nickel-oxalate complexes, which are of interest for this review, was studied in solutions containing large amounts of ethylenediamine (the Ni(II):en ratio was kept constant at 1:3), and therefore oxalate was in most of the experimental points not able to displace to any large extent the ethylenediamine ligand from the coordination sphere of Ni(II).

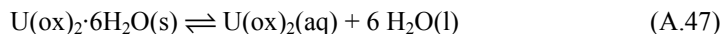
Given the limited amount of experimental data, in combination with the large number of complexes, the large variations in the ionic media, and the inadequate concentration ratios of ligands used in this study, the equilibrium constants reported for the nickel-oxalate complexes are not considered in this review.

#### [60ZAK/MOS]

The authors studied the solubility of  $\text{U}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$  in 0 – 3.0 M HCl and in 0.07 – 0.241 M  $(\text{NH}_4)_2\text{ox}$  in the presence of 0.5 M HCl by a radiometric method labelling with  $^{233}\text{U}$ .

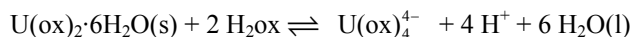
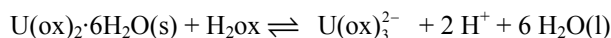
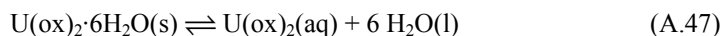
The solid was not characterised but the formula of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  was given. The temperature of the experiment was not provided.

The data of the solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in HCl were analysed with three reactions:



The equilibrium constants for the reactions were obtained by solving a system of equations. The values are listed in Table VI-30. Using the protonation constants from [58DRA/MOS2], the solubility product of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  ( $K_s = [\text{U}^{4+}] \cdot [\text{ox}^{2-}]^2$ ) was calculated (Table VI-30). From these data, the stability constants of  $\text{U(ox)}^{2+}$  and  $\text{U(ox)}_2\text{(aq)}$  were also obtained (Table VI-36).

The data of the solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in 0.07 – 0.241 M  $(\text{NH}_4)_2\text{ox}$  in the presence of 0.5 M HCl were analysed to obtain the stability constants of  $\text{U(ox)}_2\text{(aq)}$ ,  $\text{U(ox)}_3^{2-}$  and  $\text{U(ox)}_4^{4-}$ . Two methods were used in the analysis: one is the solution of a system of three equations:



The other is using the “complex formation” function, defined as  $\phi = S/[M]$  where  $S$  is the total concentration of U(IV) and  $[M]$  is the concentration of free  $\text{U}^{4+}$  in the solutions. The results obtained by the two methods are slightly different but within the uncertainties,  $\pm (0.1-0.2)$  for  $\log_{10} K'_s$  except for  $\log_{10} K$  (A.47) which was 16.85 by method 1 and 17.40 by method 2. These values are summarised in Table VI-36.

The temperature of the experiments was not given in the paper, but the solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in HCl from this paper agrees with that at 25°C from [58DOR] as shown in Figure VI-23. From this agreement, it is assumed by this review that the experiments in this reference were probably performed at  $(25 \pm 3)^\circ\text{C}$ . The values from this work are accepted in this review. However, due to the lack of information on the characterisation of the solid phase and the temperature of the experiment, the data are not re-evaluated with SIT to derive thermodynamic constants.

#### [61BAB/SHT]

By using the metal-indicator method, the stabilities of the Zr(IV) complexes were compared in 1 M HCl and at pH 3. In the experiment, the concentration of the ligand which decreases the absorbance of the xylenol orange complex of Zr(IV) half of the original absorbance (without ligand) was measured. From the result, the complexants were



shown to form more stable complexes in the order of edta > oxalate > fluoride > nta > tiron > citrate > tartrate. The dissociation constant for  $\text{Zr(ox)}^{2+} \rightleftharpoons \text{Zr}^{4+} + \text{ox}^{2-}$  was estimated to be  $K = 1.6 \times 10^{-10}$  by using  $K = 1.6 \times 10^{-9}$  of  $\text{ZrF}^{3+} \rightleftharpoons \text{Zr}^{4+} + \text{F}^-$ . Ionic strength was not controlled and the speciation of the formed complexes is not clearly established. This paper is not considered in this review.

#### [\[61BAR/BEC\]](#)

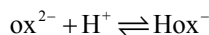
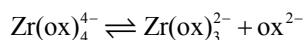
Barthel *et al.* titrated citric acid  $\approx 0.05$  M with NaOH 0.93 M in a calorimeter at  $\approx 24^\circ\text{C}$ . Under such conditions the ionic strength is expected to vary from  $\approx 0$  to 0.28 M along the titration. Similarly  $[\text{Na}^+]$  should have varied from zero to 0.14 M. Because of these large variations, the enthalpy changes for citrate protonation reported in [\[61BAR/BEC\]](#) are not considered in this review.

#### [\[61CHE/GOL\]](#)

In this study, ternary U(VI) carbonato-oxalato-compounds,  $\text{M}_2[\text{UO}_2(\text{CO}_3)(\text{ox})]$  where  $\text{M} = \text{NH}_4^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ , were prepared by dissolving  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  in solutions of corresponding carbonates ( $\text{M}_2\text{CO}_3$ ). The barium compound,  $\text{Ba}[\text{UO}_2(\text{CO}_3)(\text{ox})]$  was obtained by mixing  $(\text{NH}_4)_2[\text{UO}_2(\text{CO}_3)(\text{ox})]$  and  $\text{BaCl}_2$ . The contents of uranium, oxalate, carbonate and water in the solid precipitates were analysed and found to be close to the calculated values. Curves of potentiometric titration of  $\text{UO}_2(\text{ox}) \cdot 3\text{H}_2\text{O}$  with 1.115 M  $(\text{NH}_4)_2\text{CO}_3$  implied that carbonate first replaced water molecules to form the carbonato-oxalato-complex, then replaced oxalate and finally formed the U(VI) tricarbonato complex. No stability constants of the ternary complexes were determined.

#### [\[61GRI/AST\]](#)

To examine the composition and physical properties of zirconium complex compounds, oxalates of zirconium, such as  $\text{ZrO(ox)} \cdot n\text{H}_2\text{O}$ ,  $\text{Zr(ox)}_2 \cdot n\text{H}_2\text{O}$ ,  $\text{Zr(ox)}_2 \cdot 2\text{K}_2\text{ox} \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}_2[\text{Zr(ox)}_4]$ ,  $\text{K}_2\text{Cd}[\text{Zr(ox)}_4]$ ,  $\text{Pb}_2[\text{Zr(ox)}_4] \cdot 3\text{H}_2\text{O}$  were prepared. The compositions of the compounds were determined by the elemental analyses. To obtain the stability of the zirconium complex, 100 ml of  $2 \times 10^{-3}$  M  $\text{K}_4[\text{Zr(ox)}_4]$  solution was titrated with 0.2 – 2 ml of 0.1 M HCl. The following reactions:



were assumed to occur. For the differences between the added concentrations of HCl and the final equilibrium  $[\text{H}^+]$  calculated from the measured pH (varied from 4.5 to 3.0), the mass balance equations:

$$[\text{H}^+]_{\text{T}} = [\text{H}^+] + [\text{Hox}^-]$$

$$[\text{K}_4\text{Zr(ox)}_4]_{\text{T}} = [\text{Zr(ox)}_4^{4-}] + [\text{Zr(ox)}_3^{2-}]$$

$$[\text{Zr(ox)}_3^{2-}] = [\text{ox}^{2-}] + [\text{Hox}^-]$$

were used with the second acid dissociation constant of oxalic acid,  $K_2 = [\text{H}^+][\text{ox}^{2-}]/[\text{Hox}^-] = 6 \times 10^{-5}$ . The instability constant of the complex,  $K_{\text{instab}} = [\text{Zr}(\text{ox})_3^{2-}][\text{ox}^{2-}]/[\text{Zr}(\text{ox})_4^{4-}]$ , was obtained to be  $(0.8\text{--}1.3) \times 10^{-4}$  under the experimental condition studied.

Ionic strength was not controlled and the conversion of pH to  $-\log_{10}[\text{H}^+]$  was not carried out. This review does not accept the result of this paper.

#### [\[61ISH/YOK\]](#)

The composition of the nickel citrate complex formed by mixing the solutions of  $\text{NiCl}_2$  and  $\text{Na}_3\text{cit}$  was studied at room temperature by polarography, spectrophotometry and pH titration and found to be  $\text{Ni}(\text{cit})^-$ . In the polarographic study, the limiting current of the solution containing  $10^{-3}$  M  $\text{NiCl}_2$ , 0.1 M  $\text{NaCl}$  and 0 to  $10^{-2}$  M  $\text{Na}_3\text{cit}$  was plotted against  $[\text{Na}_3\text{cit}]$  and the dissociation constant was found to be  $0.9 \times 10^{-4}$ . In spectrophotometry, the effect of pH (2.7 to 10.5) on the absorption spectrum of solutions containing 0.1 M  $\text{NiCl}_2$  and 0.4 M  $\text{Na}_3\text{cit}$  was studied and the formation of  $\text{Ni}(\text{cit})^-$  was estimated at pH 6 ~ 9. The 1:1 composition was confirmed by the method of continuous variation, mole ratio method and slope ratio method. From the absorbance of the solution containing 0.1 M  $\text{NiCl}_2$  and 0.1 M  $\text{Na}_3\text{cit}$  at pH 7, the dissociation constant of  $\text{Ni}(\text{cit})^-$  was calculated to be  $6.3 \times 10^{-4}$  and  $2.4 \times 10^{-4}$  (the value differed depending on the way of calculation). Since the ionic strength was not maintained constant (it was mainly controlled by  $\text{NiCl}_2$  and  $\text{Na}_3\text{cit}$  themselves) and the measured values seem not enough precise (too much different from each other), this review does not accept these values.

#### [\[61KAB\]](#)

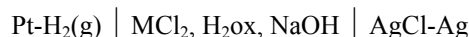
The system  $\text{Pu}(\text{V}) - \text{edta}$  has been studied by potentiometric titration of a  $\text{PuO}_2\text{ClO}_4 + \text{Na}_2\text{H}_2\text{edta}$  mixture in 0.1 M  $\text{KCl}$  versus  $\text{NaOH}$  solution. A glass electrode and an LP-4 potentiometer were used. No details about the pH measurements are given. Neither the pH scale is mentioned nor the calibration method of the pH meter is reported. Kabanova reports that absorption spectra show that at pH 11.5, in the presence of edta,  $\text{Pu}(\text{V})$  is completely stable and is not converted to the tetravalent state, at least in the course of several hours. The stability of  $\text{Pu}(\text{V})$  has obviously not been checked in the pH range 3 – 5, relevant for obtaining the reported  $\text{Pu}(\text{V})$  edta stability constant.

#### [\[61MCA/NAN\]](#)

McAuley and Nancollas reported results for the first dissociation constant of oxalic acid obtained from Harned cell measurements, cf. [\[39HAR/FAL\]](#), at five temperatures from 0 to  $45^\circ\text{C}$ . The solutions were composed of  $\text{H}_2\text{ox}$  and  $\text{HCl}$  of variable ionic strength. Solution compositions and potentials were presented only for measurements at  $25^\circ\text{C}$ , and the results are reported in [\[61MCA/NAN\]](#) as  $\log_{10}K_2$  values extrapolated to zero ionic strength by the Davies equation. The values included in Table VI-2 have not been used in the multi-linear least-squares regression analyses of this review.

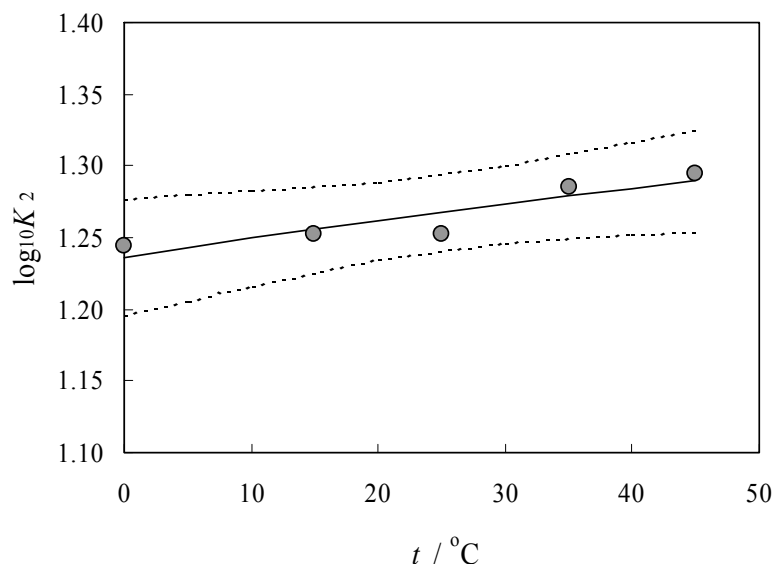
However, in order to estimate the temperature variation of  $\log_{10} K_2$  these values have been fitted in this review to a temperature function assuming  $\Delta_r C_{p,m} = 0$ . The result is  $\Delta_r H_m = (2.0 \pm 1.1) \text{ kJ}\cdot\text{mol}^{-1}$  (see Figure A-13).

McAuley and Nancollas also studied potentiometrically the complex formation between oxalate and Ni(II), Co(II) and Mn(II) using a cell without liquid junction:



at low ionic strength (millimolar concentrations) and at various temperatures: 0, 15, 25, 35, and 45°C. Even if the authors used metal ion chlorides, complexation with chloride is negligible at the experimental conditions used. The ionic strength varied slightly during the experiments but the authors extrapolated the results to  $I = 0$  using the Davies equation. For Ni(ox)(aq) the authors reported:  $\log_{10} K_1 = (5.179 \pm 0.014)$ ,  $(5.137 \pm 0.013)$ ,  $(5.158 \pm 0.009)$ ,  $(5.173 \pm 0.018)$ , and  $(5.185 \pm 0.014)$  at 0, 15, 25, 35 and 45°C, respectively. Values for  $\Delta_r H_m^\circ$ ,  $\Delta_r S_m^\circ$  and  $\Delta_r C_{p,m}^\circ$  for the reactions  $\text{M}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{M}(\text{ox})(\text{aq})$  were then determined from the temperature dependence of the stability constants. For Ni(II) the values found were:  $\Delta_r H_m^\circ(298.15 \text{ K}) = (0.6 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ ; and  $\Delta_r C_{p,m}^\circ(298.15 \text{ K}) = (146 \pm 50) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . A fitting of the  $\log_{10} K_1$  values by this review, assuming that  $\Delta_r C_{p,m}^\circ$  is constant over the temperature interval studied gives similar results:  $\Delta_r H_m^\circ(298.15 \text{ K}) = (1.4 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$ ; and  $\Delta_r C_{p,m}^\circ(298.15 \text{ K}) = (250 \pm 80) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

Figure A-13: Second protonation constant for oxalate determined and extrapolated to  $I = 0$  by [61MCA/NAN] and the constant  $\Delta_r H_m$  model with the parameters determined in this review.



**[61MOS/MAR]**

Distribution of  $^{239}\text{Np}$  at tracer concentrations between 0.05 M  $\text{NH}_4\text{ClO}_4$  and the cation exchange resin KU-2 of 50–70 mesh, in the ammonium form, was studied at  $(20 \pm 2)^\circ\text{C}$  with and without citric acid present. The initial pH of the solution was adjusted by means of  $\text{HClO}_4$  and  $\text{NH}_4\text{OH}$ , and the concentration of citric acid was varied from  $C_L = 0.1 \times 10^{-3}$  M to  $3.9 \times 10^{-3}$  M. The equilibrium pH was changed from 4.25 at  $C_L = 0.1 \times 10^{-3}$  M to 5.34 at  $C_L = 3.9 \times 10^{-3}$  M. When  $\text{NpO}_2(\text{Hcit})^-$  and  $\text{NpO}_2(\text{cit})^{2-}$  are assumed to be formed, the distribution coefficients in the presence of citric acid should follow the relation,

$$K_d = \frac{K_d^o}{1 + \beta_{1(\text{Hcit})}[\text{Hcit}^{2-}] + \beta_{1(\text{cit})}[\text{cit}^{3-}]},$$

where  $K_d^o$  is the distribution coefficient in the absence of citric acid, and  $\beta_{1(\text{Hcit})}$  and  $\beta_{1(\text{cit})}$  are the constants for  $\text{NpO}_2^+ + \text{Hcit}^{2-} \rightleftharpoons \text{NpO}_2(\text{Hcit})^-$  and  $\text{NpO}_2^+ + \text{cit}^{3-} \rightleftharpoons \text{NpO}_2(\text{cit})^{2-}$ , respectively. From the results given in Table 1 of the paper, the authors constructed the plots of  $1/K_d$  against  $[\text{cit}^{3-}]$  and  $1/K_d$  against  $[\text{Hcit}^{2-}]$  in Figs. 2 and 3 of the paper, respectively. To calculate  $[\text{cit}^{3-}]$  and  $[\text{Hcit}^{2-}]$ , protonation constants of  $\log_{10} K_{(\text{H})} = 5.95, 4.48$  and  $2.95$  were used. Both plots gave apparent straight linear relations, indicating that the contribution of the change in  $\beta_{1(\text{Hcit})} [\text{Hcit}^{2-}]$  is negligible in Fig. 2, and that of  $\beta_{1(\text{cit})} [\text{cit}^{3-}]$  is negligible in Fig. 3. In other words, the change in pH was not large enough to discriminate the formation of  $\text{NpO}_2(\text{Hcit})^-$  and  $\text{NpO}_2(\text{cit})^{2-}$ . Still, the formation of  $\text{NpO}_2(\text{Hcit})^-$  and  $\text{NpO}_2(\text{cit})^{2-}$  in the pH range of 5.25 to 5.34 is in agreement with the observation of [85SEV]. Although the authors give the values of  $\beta_{1(\text{Hcit})} = (4.9 \pm 1.4) \times 10^2$  and  $\beta_{1(\text{cit})} = (4.7 \pm 1.0) \times 10^3$  (corresponding to  $\log_{10} \beta_{1(\text{Hcit})} = 2.69$  and  $\log_{10} \beta_{1(\text{cit})} = 3.67$ ), the calculational procedure is not given and this review could not reproduce the values from the results in Table 1. Also, the ionic strength was not well controlled in this study, *i.e.*, the change in the concentration of citric acid should have changed the ionic strength. This review does not accept this paper.

**[61PAT/PAN]**

Two series of potentiometric titrations have been conducted. In one series, citric acid (0.125 M) in the absence and presence of 0.0125 M  $\text{Ca}(\text{ClO}_4)_2$  was titrated with 1 M NaOH at  $33^\circ\text{C}$ . In the other series, 0.25 M  $\text{NaClO}_4$  in the absence and presence of 0.0125 M  $\text{Ca}(\text{ClO}_4)_2$  was titrated with 0.1 M  $\text{Na}_3\text{cit}$ . By assuming the formation of  $\text{Ca}(\text{cit})^-$  only,  $\log_{10} \beta_1 = 3.42$  was obtained for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$ . However, ionic strength was not maintained constant in the titration, and there is no description about the conversion of measured pH to  $-\log_{10}[\text{H}^+]$ . Thus, this review does not accept this paper.

**[61STA/PRA]**

The composition and the stability constants of U(VI) chelates with edta and other

aminopolycarboxylic acids have been determined by means of an ion exchange method. Twenty milliliters of 0.1 M NaClO<sub>4</sub> solutions containing U(VI) (10<sup>-4</sup> M) and aminopolycarboxylic acid (5·10<sup>-4</sup> M) were shaken with 0.200g of the cation exchanger Dowex 50 for 60 min. The pH 5.3 – 7.0 was adjusted by addition of small amounts of NaOH or HClO<sub>4</sub>. The determinations of pH were made with a Radiometer PHM4b using a glass electrode with a saturated calomel electrode as a reference electrode.

A 0.1 M NaClO<sub>4</sub> solution in contact with saturated KCl solution in the calomel electrode results in precipitation of KClO<sub>4</sub> with possible emf errors. In addition, the author claims that only one complex, UO<sub>2</sub>(Hedta)<sup>-</sup> with log<sub>10</sub>*K* = (7.13 ± 0.04), is formed. It is unclear to which extent the neglect of the species UO<sub>2</sub>edta<sup>2-</sup> in the data analysis has biased the numerical results. For these reasons the results of this study have not been considered in this review.

#### [\[61WAL\]](#)

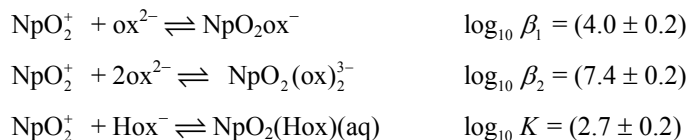
From the titration of citrate in solutions of (CH<sub>3</sub>)<sub>4</sub>NCl, NaCl and KCl at *I* = 0.16 M and 25°C, the stability constants of Na(cit)<sup>2-</sup> and K(cit)<sup>2-</sup> have been obtained to be *K*<sub>Na</sub> = 0.2 for Na<sup>+</sup> + cit<sup>3-</sup> ⇌ Na(cit)<sup>2-</sup> and *K*<sub>K</sub> = 0.37 for K<sup>+</sup> + cit<sup>3-</sup> ⇌ K(cit)<sup>2-</sup>. Then, the formation constants of Ca(cit)<sup>-</sup> and Mg(cit)<sup>-</sup> were measured spectrophotometrically in the presence and absence of sodium ions. The stability constants with the consideration of Na(cit)<sup>2-</sup> formation were log<sub>10</sub> β'<sub>1(cit)</sub> = 3.15 for Ca<sup>2+</sup> + cit<sup>3-</sup> ⇌ Ca(cit)<sup>-</sup> and 3.55 for Mg<sup>2+</sup> + cit<sup>3-</sup> ⇌ Mg(cit)<sup>-</sup>. Since the interaction of Na<sup>+</sup> or K<sup>+</sup> with cit<sup>3-</sup> is weak, the effect of liquid junction potential should be carefully considered in the pH measurement, but the calibration of pH to -log<sub>10</sub>[H<sup>+</sup>] is not described in the paper. This review does not accept these values.

#### [\[61ZOL/MAR2\]](#)

The complexation of Np(V) with oxalate and edta was studied by a cation exchange method. The distribution of trace amounts of <sup>239</sup>Np(V) was measured between 0.05 M NH<sub>4</sub>ClO<sub>4</sub> solution and the cation exchange resin KU-2 at (20 ± 2)°C. The pH was measured using an LP-5 pH meter with a glass electrode. No details are reported about the pH scale used or the calibration of the pH meter.

In edta solutions at pH 5.3 – 5.7 the authors assumed solely the formation of NpO<sub>2</sub>edta<sup>3-</sup>, with the following argument: “As the experiments were carried out at a fairly high pH, where the concentrations of hydrogen-containing edta anions are extremely low, the formation of Np(V) complexes with such anions was considered to be improbable”. As a consequence of this total ignorance of edta protonation behavior, the edta protonation constants used in their calculations are not reported by the authors, and the presence of the protonated species NpO<sub>2</sub>(Hedta)<sup>2-</sup> at the investigated pH range 5.3 – 5.7 has been ignored. The derived Np(V) edta stability constant is considered as unreliable and has been rejected in this review.

For the Np(V)-oxalate system the authors interpreted their experimental results at 0.001 M oxalic acid and at pH = 4.9 to 1.65 by the formation of  $\text{NpO}_2\text{ox}^-$ ,  $\text{NpO}_2(\text{ox})_2^{3-}$  and  $\text{NpO}_2(\text{Hox})(\text{aq})$  with the following stability constants:



Large uncertainties ( $\approx \pm 6\%$ ) are reported for the measured distribution coefficient,  $K_d$ , in Table 1 of this paper. The distribution coefficient in the absence of ligand is reported to be  $K_d^\circ = 47.8$  in the case of oxalate, but  $K_d^\circ = 37.9$  in the case of edta, but no reason is given for this disagreement. If, as the authors claim, the ionic strength was kept constant at 0.05 M, then the ionic medium changed substantially as  $\text{HClO}_4$  was added to reach pH = 1.65. Because of these experimental shortcomings the equilibrium constants were not included in the review procedure.

#### [\[62ASA/MOR\]](#)

In this work the measurement of the refractive index of reaction mixtures and “control” solutions by interferometry is described as a convenient method of studying reaction kinetics and ion binding. All measurements were carried out at room temperature (*ca.* 23°C). The stability constant  $\log_{10} K_1 = 2.61$  for  $\text{Mg}(\text{ox})(\text{aq})$  was determined in order to validate the experimental method. The only details given in this paper for the Mg oxalate experiment are that 0.1 M Tris buffer (2-amino-2(hydroxymethyl)-1,3-propanediol) was involved and 0.2 M KCl was added.

The protonated form of the Tris buffer,  $\text{H}(\text{Tris})^+$ , increases the total ionic strength above 0.2 M to a value somewhere in the range  $0.2 < I < 0.3$  M. Moreover, Tris is known to form complexes with metal ions. The  $\text{Mg}(\text{Tris})^{2+}$  formation constant has been reported as  $K_{(\text{Tris})} = 2.0$  in 1 M  $\text{KNO}_3$  at 25°C [\[82SIG/SCH\]](#). The total concentration of oxalate used in the Mg oxalate experiment is not reported, but inferring millimolar concentration in analogy with other experiments described in this paper, we have about 100-fold excess in the concentration of Tris with respect to oxalate. The  $\text{Mg}(\text{ox})(\text{aq})$  formation constant exceeds the  $\text{Mg}(\text{Tris})^{2+}$  only by a factor of about 200 and thus, the influence of Tris on magnesium complexation is in the same order of magnitude and may even exceed that of oxalate if the actual oxalate concentration used in the experiment was below millimolar. If the oxalate (and magnesium) concentration used was significantly higher than millimolar, precipitation of magnesium oxalate might have been a problem. Although the obtained value for  $\text{Mg}(\text{ox})(\text{aq})$  is not out of range compared with results reported for similar conditions [\[38CAN/KIB\]](#), this might be an artifact considering all the shortcomings discussed above, and hence the value is not credited by this review.

[\[62ISH/NAK\]](#)

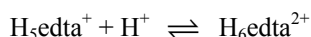
The complexation of  $^{239}\text{Np(IV)}$  with oxalate, edta and some other ligands has been studied by solvent extraction, *i.e.*, by the distribution of  $^{239}\text{Np}$  between 1% di(2-ethylhexyl)-phosphoric acid (HDEHP) - toluene and a 0.5 M aqueous HCl solution containing the ligand. Concerning the temperature of the measurements only “room temp.” is mentioned in the paper.

In the case of edta, four distribution ratios are reported for total edta concentrations of 2, 1, 0.5 and  $0.25 \cdot 10^{-2}$  M. The pH of the solutions is not reported, the authors seem to have assumed that  $[\text{H}^+] = 0.5$  M without considering the effects of adding up to 0.02 M edta. The edta protonation constants of [\[47SCH/ACK\]](#), valid for 0.1 M  $\text{KNO}_3$  at  $20^\circ\text{C}$ , have been taken for deriving a Np(IV) edta stability constant. The presence of the species  $\text{H}_5\text{edta}^+$  and  $\text{H}_6\text{edta}^{2+}$  in 0.5 M HCl solution has been neglected. The Np(IV) edta constant reported by [\[62ISH/NAK\]](#) has not been considered in this review.

According to the authors the distribution ratios obtained when studying the oxalate complexation with Np(IV) had large “fluctuations”. Therefore the authors used extraction data for Zr(IV) and Th(IV) to estimate how the distribution ratios for Np(IV) should behave under similar conditions. The limited data was interpreted by the authors assuming that complexes of stoichiometry  $\text{M}(\text{Hox})_4(\text{aq})$  were formed in their aqueous solutions ( $\text{M} = \text{Zr, Th or Np}$ ). From Figure 4 in [\[62ISH/NAK\]](#) it appears that the HCl concentration (and ionic strength) was either 0.52 M to 0.89 M but no mention is made by the authors about ionic strength effects. Given the large uncertainty in the measurements and their dubious interpretation, this review gives no credit to the Np(IV)-oxalate stability constant reported in [\[62ISH/NAK\]](#).

[\[62KRO/ERM\]](#)

The authors report values for the equilibrium constant  $K_6$  of reaction:



obtained from measurements of the solubility of  $\text{H}_4\text{edta}(\text{cr})$  in  $(\text{Na,H})\text{NO}_3$  media of  $I = 1, 2, \text{ and } 3$  M at  $25^\circ\text{C}$ . The experiments were performed with  $[\text{HNO}_3]_{\text{TOT}}$  in the range 0.2 to 1 M. Krot *et al.* analysed their data by assuming  $\log_{10} K_5 = (1.51 \pm 0.03)$  for reaction:



calculated from the data of [\[59KLY/SMI4\]](#) at  $I = 0.1$  M. Although the ionic strength dependence for this isocoulombic reaction is expected to be small ( $\Delta z^2 = 0$ ), it is quite reasonable to assume that the value of  $K_5$  would vary substantially between  $I = 0.1$  and 3 M. Therefore, the values of  $K_6$  reported in [\[62KRO/ERM\]](#) are not considered in the review procedure.

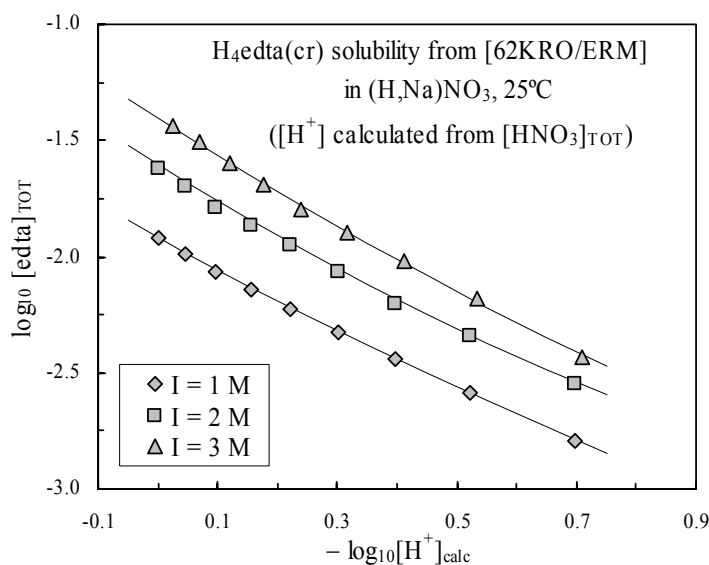
Instead, the data in [\[62KRO/ERM\]](#), (see their Table 1) in the form of

H<sub>4</sub>edta(cr) solubility *versus* [HNO<sub>3</sub>]<sub>TOT</sub> was used in this review to fit a theoretical solubility curve using a least-squares algorithm. The results of the calculations are shown in Table A-6 and Figure A-14.

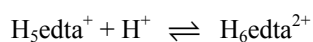
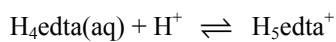
Table A-6: Solubility constants of H<sub>4</sub>edta(cr) at different ionic strengths

Reaction:	<i>I</i> = 1 M	<i>I</i> = 2 M	<i>I</i> = 3 M
(A.48) H <sub>4</sub> edta(cr) $\rightleftharpoons$ H <sub>4</sub> edta(aq)	– (4.6 ± 2.5)	– (3.4 ± 0.5)	– (4.3 ± 7)
(A.49) H <sub>4</sub> edta(cr) + H <sup>+</sup> $\rightleftharpoons$ H <sub>5</sub> edta <sup>+</sup>	– (2.15 ± 0.04)	– (2.03 ± 0.11)	– (1.85 ± 0.15)
(A.50) H <sub>4</sub> edta(cr) + 2 H <sup>+</sup> $\rightleftharpoons$ H <sub>6</sub> edta <sup>2+</sup>	– (2.30 ± 0.06)	– (1.82 ± 0.08)	– (1.60 ± 0.10)

Figure A-14: Experimental solubility of H<sub>4</sub>edta(cr) in (H<sub>3</sub>Na)NO<sub>3</sub> solutions of *I* = 1, 2 and 3 M at 25°C [62KRO/ERM] compared with calculated values using the equilibrium constants in Table A-6.



Values for  $K_5$  and  $K_6$ , corresponding to reactions:



may be calculated from the data tabulated above.  $K_5$ (A.48) is not well defined by ex-



perimental data: as seen in Table A-6 the experiments were performed at too high acidities, and  $\text{H}_4\text{edta}(\text{aq})$  is only a very minor species in the experiments. Therefore, only the values of  $K_s$  (A.48) and  $K_s$  (A.49) at  $I = 2 \text{ M}$ , and all values of  $K_s$  (A.50) were included in the evaluations described in Sections VIII.2.2 and VIII.3.2.

#### [62LEB/PIR2]

The radiolysis of  $^{241}\text{Am}_2(\text{ox})_3 \cdot 9\text{H}_2\text{O}$  under the action of  $\alpha$ -radiation was examined by measuring the volume and composition of the released gas. It was shown that on standing,  $\text{Am}(\text{III})$  oxalate decomposes under the action of  $\alpha$ -radiation to form carbonate ( $\text{Am}_2(\text{CO}_3)_3 \cdot 5\text{H}_2\text{O}$ ). The gas liberated during the decomposition consists of  $\text{CO}_2$  and  $\text{CO}$  with a predominance of  $\text{CO}_2$ , indicating some unknown mechanism. The precipitate reached a constant weight after 50 – 60 days. From the accumulation of carbonate (absorbed in 50 %  $\text{KOH}$ ) on an americium precipitate, the first-order reaction rate constant was obtained to be  $(0.22 \pm 0.04) \text{ days}^{-1}$ .

#### [62MAR/RYA2]

The sorption of  $^{95}\text{Zr}$  and  $^{181}\text{Hf}$  ( $< 5 \times 10^{-6} \text{ M}$ ) by the cation-exchange resin KU-2 in  $\text{H}^+$ -form (0.5 – 0.25 mm) from  $\text{HClO}_4$  solution (2 M and 4 M) containing chloride, nitrate or oxalate was measured. Except for the case of nitrate, the absorption of positively charged complexes by the cation-exchange resin was neglected and the distribution coefficient was considered to be in the form of  $K_d = K_d^0 / (1 + \sum \beta_j [\text{X}^-]^j)$ , where  $K_d^0$  is the distribution coefficient in the absence of any complex-forming ligand. In the case of oxalate complexes, the reaction constant was defined as:

$$K_j = \frac{[\text{M}(\text{ox})_j^{(4-2j)+}] \times [\text{H}^+]^{2j}}{[\text{M}^{4+}] [\text{H}_2\text{ox}]^j}$$

with  $\text{M} = \text{Zr}, \text{Hf}$ , and the values of  $K_j / [\text{H}^+]^{2j}$  were obtained by making Schubert plots. For zirconium oxalates, the reaction constants were obtained to be  $K_1 = (2.96 \pm 0.3) \times 10^5$ ,  $K_2 = (4.8 \pm 1.6) \times 10^9$  at 2 M  $\text{HClO}_4$  and  $K_1 = (4.0 \pm 0.5) \times 10^5$  at 4 M  $\text{HClO}_4$ .

When  $K_d$  values were re-estimated in this review using the reported reaction constants, some of them could not well reproduce the original data, especially in the case of the hafnium oxalate system. By considering the possible errors introduced in the graphical analysis of the data and the possible experimental error in the determination of  $K_d$ , this review does not accept the result of this paper.

#### [62SHV/MAS2]

By using a proposed electromigration method, the composition and stability constants of oxalate complexes of zirconium were obtained. In the solution containing  $I = 0.04 \text{ M}$  ( $\text{H}^+, \text{Na}^+, \text{Zr}^{4+}$ )( $\text{ClO}_4^-, \text{ox}^{2-}$ ) and  $[\text{H}^+] = 0.015 \text{ M}$ ,  $C_{\text{Zr}} = 4.81 \times 10^{-5} \text{ M}$ , zirconium was moved in the electric field (10 V/cm) for 21.5 min at  $(20 \pm 0.5)^\circ\text{C}$ . In one series of ex-

periments, the mobility of zirconium was measured as a function of  $R = C_{\text{ox}}/C_{\text{Zr}}$ . In another series of experiments, it was measured as a function of free oxalate ion concentration which was controlled by adding  $\text{Fe}(\text{ClO}_4)_3$  which controls  $[\text{ox}^{2-}]$  through the dissociation of  $\text{Fe}(\text{III})$ -oxalate complexes. The free oxalate ion concentration was calculated using protonation constants and stability constants of  $\text{Fe}(\text{ox})^+$ ,  $\text{Fe}(\text{ox})_2^-$  and  $\text{Fe}(\text{ox})_3^{3-}$ . In the analysis, the mobility of zirconium was expressed as:

$$u_{\text{Zr}} = \frac{u_0 + u_1\beta_1[\text{L}] + u_2\beta_2[\text{L}]^2 + u_3\beta_3[\text{L}]^3 + u_4\beta_4[\text{L}]^4}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \beta_3[\text{L}]^3 + \beta_4[\text{L}]^4}$$

where  $[\text{L}]$  stands for  $[\text{ox}^{2-}]$  and  $u_i$  is the mobility of  $\text{Zr}(\text{ox})_i^{(4-2i)}$ . For points with the same mobility in the two series of experiments, the mean number of ligands attached to one metal atom was calculated as:

$$\bar{n} = \frac{C_{\text{Zr}}R - [\text{L}]}{C_{\text{Zr}}}$$

and this was analysed in the form of:

$$\bar{n} = \frac{\beta_1[\text{L}] + 2\beta_2[\text{L}]^2 + 3\beta_3[\text{L}]^3 + 4\beta_4[\text{L}]^4}{1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \beta_3[\text{L}]^3 + \beta_4[\text{L}]^4}.$$

Probably by using the Debye-Hückel equation for the activity coefficient correction, the stepwise formation constants for  $\text{Zr}(\text{ox})_i^{(4-2i)}$  at  $I = 0$  were obtained to be  $K_1^\circ = 1.35 \times 10^{11}$ ,  $K_2^\circ = 1.50 \times 10^9$ ,  $K_3^\circ = 4.53 \times 10^6$ , and  $K_4^\circ = 1.07 \times 10^6$ .

Under the experimental condition of  $[\text{H}^+] = 0.015 \text{ M}$ , zirconium may be hydrolysed and this may cause serious effects on the experimental results. In the paper, the authors argue that the effect of this hydrolysis was neglected since zirconium had a high mobility which indicated either rapid exchange of forms with a high charge or the predominance of one form with a high ratio of charge to radius. This discussion cannot be accepted. If the former situation occurs, the constant mobility for each complex species cannot be guaranteed. If the latter situation occurs, each overall formation constant does not correspond to the reaction  $\text{Zr}^{4+} + i \text{ox}^{2-} \rightleftharpoons \text{Zr}(\text{ox})_i^{(4-2i)}$  since the starting form of zirconium is not  $\text{Zr}^{4+}$ . For the estimation of the concentration of free oxalate ion, the protonation constants of oxalate and the dissociation constants of iron oxalate complexes were used but the numbers are not reported in the paper. Considering the difficulty in the measurement of the mobility and the difficulty in estimating the zirconium species, the present review does not accept the results of this paper.

#### [\[62STA/BAL\]](#)

Although the authors report the value of  $\log_{10} \beta_{2,(\text{Hcit})} \sim 11.2$  for the reaction  $\text{UO}_2^{2+} + 2 \text{Hcit}^{2-} \rightleftharpoons \text{UO}_2(\text{Hcit})_2^{2-}$ , the reference is the unpublished work of the authors and no details are given. Since this type of complex has not been reported by any other researchers, this value is not accepted in this review.

[\[62ZAI/BOC3\]](#)

To discriminate zirconyl  $\text{ZrO}^{2+}$  and zirconium hydroxide  $\text{Zr}(\text{OH})_n^{(4-n)}$  in various zirconium compounds, they were titrated with KF at pH 8.0-8.2 where fluoride can displace hydroxide. The effectiveness of fluoride displacement of hydroxide but not oxygen in the zirconyl unit is verified by titrating  $\text{ZrO}_2$  ignited at 700 – 800°C, zirconium hydroxide dried at room temperature and freshly precipitated and aged zirconium hydroxide. The titration of precipitated zirconium hydroxide gave 2 equivalents  $\text{OH}^-$  per 1 g-atom Zr, while  $\text{ZrO}_2$  and dried hydroxide powder did not react with KF. When the salt of zirconyloxalic acid,  $\text{Ba}[\text{ZrO}(\text{ox})_2] \cdot 3\text{H}_2\text{O}$  was titrated in the presence of KF, it gave 2 equivalents  $\text{OH}^-$  per 1 g-atom Zr, indicating the real composition to be  $\text{Ba}[\text{Zr}(\text{OH})_2(\text{ox})_2] \cdot 3\text{H}_2\text{O}$ . Solutions of similar ammonium, potassium and sodium salts gave 1.4 – 1.7 equivalents  $\text{OH}^-$ . Thus, it has been shown that  $\text{ZrO}^{2+}$  exists only in solid substances and the existence of  $\text{Zr}(\text{OH})_2^{2+}$  is possible in solutions.

[\[63AND\]](#)

The enthalpy changes involved in the formation of the proton and the metal ( $\text{Me}^{x+} = \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Ba}^{2+}, \text{Sr}^{2+}, \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Cd}^{2+}, \text{Pb}^{2+}, \text{Hg}^{2+}$  and  $\text{La}^{3+}$ ) complexes of edta and an edta homologue have been determined using a direct calorimetric method. 40 mL of 0.03 M  $\text{Me}(\text{NO}_3)_x$  solution ( $I = 0.09$ ) were mixed with 10 mL of a solution containing 0.0075 M  $\text{K}_4\text{edta}$  and 0.089 M  $\text{KNO}_3$  in order to obtain 0.006 M  $\text{K}_2\text{edta}$  with  $I \approx 0.1$  M. This study is considered reliable and included in the final data evaluation of this review.

[\[63BHA/KRI\]](#)

This is a spectrophotometric study of protonated and mixed edta complexes with Cu(II), Ni(II) and Co(II). Solutions at  $I = 1$  M  $\text{NaClO}_4$  were brought to equilibrium at 25°C and the temperature in the spectrophotometer cell was in the range  $(25 \pm 1)^\circ\text{C}$ . The concentration of the complexes in the final solutions was in the range 0.005 – 0.015 M. The changes in the spectra of  $\text{Ni}(\text{edta})^{2-}$  were explained with the formation of  $\text{Ni}(\text{Hedta})^-$  from pH 0.9 to 1.4, followed by its deprotonation from pH 2.7 to 4. The complex  $\text{Ni}(\text{edta})^{2-}$  can bind  $\text{NH}_3$  (at  $\text{pH} > 8$ ) and  $\text{OH}^-$  (at  $[\text{OH}^-] > 0.1 \text{ mol} \cdot \text{dm}^{-3}$ ).

Bath and Krishnamurthy [\[63BHA/KRI\]](#) used in their calculations edta protonation constants of [\[52CAR/MAR\]](#) valid at 25°C and  $I = 1$  M KCl. There is no information in the paper whether corrections were made considering the different effects of  $\text{Na}^+$  and  $\text{K}^+$  on  $\text{edta}^{4-}$ . The pH measurements were made with a Beckman model G pH meter using glass electrodes and calomel reference electrodes. The calomel reference electrode contains saturated KCl or 1 M KCl solutions. Under such conditions the measurements are normally very difficult because of the precipitation of  $\text{KClO}_4$  occurring between the two solutions (KCl and  $\text{NaClO}_4$ ) in contact. For that reasons the values of [\[63BHA/KRI\]](#) have not been considered further in this review.

[\[63ERM/KRO\]](#)

This is a detailed study on the behaviour of U(IV) in aqueous edta solutions at different metal/ligand molar ratios using spectrophotometric, potentiometric and preparative techniques.

A considerable number of equilibrium constants has been derived by the authors from their measurements for a set of species comprising  $\text{U}_2\text{H}_2(\text{edta})_3^{2-}$ ,  $\text{U}_2\text{H}(\text{edta})_3^{3-}$ ,  $\text{U}_2(\text{edta})_3^{4-}$ ,  $\text{UedtaOH}^-$ ,  $\text{Uedta}(\text{OH})_2^{2-}$  and  $(\text{UedtaOH})_2^{2-}$ . In such investigations the accurate measurement of the pH of the solutions under study is of utmost importance in order to obtain accurate data for the derivation of equilibrium constants. However, the entire information about pH measurements given by the authors reads as follows: "The equilibrium pH was measured after each addition by a glass electrode and LP-58 valve potentiometer". These two lines on pH are not enough to ensure its rigorous use. Faced with the possibility of systematic errors of unknown size in the experimental data of [\[63ERM/KRO\]](#) this review does not accept the values reported in this paper for any quantitative use. They only may provide a qualitative idea about the complexity of the U(IV) edta system.

The authors report very interesting and detailed preparative work concerning U(IV) edta solids. According to the photomicrographs of crystals published in this paper, the analytical results could also have been verified by crystal structure determinations. Unfortunately, no such attempt seems to have been made by the authors.

[\[63FRI/VER\]](#)

This paper describes experiments and contains data on the solubility of oxalates of Ag, Cd, Pd and Y in ethylenediamine solutions. From these data the authors calculated equilibrium constants for the formation of ternary complexes of oxalate and ethylenediamine with these metals. In their Table 6 the authors list an equilibrium constant for the formation of  $\text{Ni}(\text{ox})_2^{2-}$ . It is not clear if this value is the result of some previous investigation, or if it is taken from the literature. There is no clue in the paper about the experimental method used to obtain this constant and the ionic medium in which the constant was obtained is not indicated. The value listed in [\[63FRI/VER\]](#) has been ignored in this review.

[\[63GRI/HUG\]](#)

Potentiometric investigation of alkaline earth chelates with edta and other polyamino-polycarboxylate ligands is carried out at 30°C and 0.10 M KCl. The method used involved the conversion of pH meter readings into hydrogen ion concentrations by the use of N.B.S. buffer tablets. The measurements of pH values were accurate to  $\pm 0.02$  pH units. The complexation constant for Ca-edta reported in this paper is accepted by this review.

[\[63GRI/PET\]](#)

The solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in water, dilute mineral acids ( $\text{HCl}$ ,  $\text{HClO}_4$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) and oxalic acid was studied at  $(25 \pm 0.3)^\circ\text{C}$ , by a radiometric method with  $^{233}\text{U}$ . The concentration of total uranium was determined by counting the  $\alpha$ -activity of an electroplated target or a plate on which the sample solution was directly applied and dried. The concentration of  $\text{U(IV)}$  was determined by co-precipitation with lanthanide fluoride and  $\alpha$ -activity counting.

The results indicated that, though precautions were taken to prevent the oxidation of  $\text{U(IV)}$  by saturating the solutions with hydrogen and passing nitrogen through the solutions, in the systems with dilute mineral acids except  $\text{HCl}$ , the concentration of  $\text{U(IV)}$  was much lower than the total concentration of uranium. The authors assumed that  $\text{U(IV)}$  was partially oxidised during the experiments by either oxygen or the radiolysis product of water. In 0.1 N  $\text{HCl}$ , where no oxidation was observed, the solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  was about  $7 \text{ mg} \cdot \text{L}^{-1}$ . No further calculations were performed on the data in the paper.

Because of the possible oxidation of  $\text{U(IV)}$  in some of the experiments and the minimal results from the systems of hydrochloric acid and oxalic acid, the data from this reference are not accepted in this review. Furthermore, the results from this study casts serious doubts on the earlier solubility studies [\[58GRI/PET2\]](#) and [\[60GRI/PET\]](#).

[\[63KYR/CAL\]](#)

This is a short note (letter to the editor) summarising results which have been presented in a full paper later on [\[64CAL/KYR\]](#). It is not clear how the value at  $I = 0.1 \text{ M}$  has been obtained. No clue about this value can be found in [\[64CAL/KYR\]](#).

[\[63MAT\]](#)

The distribution of  $\text{Ca(II)}$  between Amberlite IR-120 and 50 mL of aqueous solution in the absence and presence of citrate has been measured at pH 5.22, 6.19 and 7.10,  $I = 0.16 \text{ M NaCl}$  and  $25^\circ\text{C}$ . Although the calibration of pH to  $-\log_{10} [\text{H}^+]$  is not described in the paper, the protonation constants obtained by potentiometric titration in this paper,  $\log_{10} K_{(\text{H})} = 5.61, 4.31$  and  $2.94$ , are in fair agreement with those selected in this review. From the plots of  $\log_{10} (K_{\text{d}}^{\circ} / K_{\text{d}})$  against  $\log_{10} [\text{cit}^{3-}]$  at pH 7.1, where  $K_{\text{d}}^{\circ}$  and  $K_{\text{d}}$  are the distribution coefficient of  $\text{Ca(II)}$  in the absence and presence of citrate, the author obtained  $\log_{10} \beta_{1(\text{cit})} = 3.16$  for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$ . Then, from this value and the slope at pH 5.2 to 6.2, the author calculated the value of  $\log_{10} \beta_{1(\text{Hcit})}$  to be 2.67 for  $\text{Ca}^{2+} + \text{Hcit}^{2-} \rightleftharpoons \text{Ca}(\text{Hcit})(\text{aq})$ . The range of pH is too narrow to discriminate these two stability constants. Also, it is desired that the distribution of the neutral species  $\text{Ca}(\text{Hcit})(\text{aq})$  between the cation exchange resin and water should be more carefully investigated. This review does not accept these values.

[\[63STA\]](#)

The extraction of 32 metals (Be, Mg, Ca, Sr, Ba, Sc, La, Ti, Zr, Th, V, Nb, Cr, Mo, W, U, Mn, Fe, Co, Ni, Pd, Cu, Ag, Zn, Cd, Hg, Al, Ga, In, Tl, Pb and Bi,  $1 - 2 \times 10^{-4}$  M) with oxine (0.1 or 0.01 M in chloroform) solution has been studied at 20°C and  $I = 0.1$  M KClO<sub>4</sub>. The effects of pH (Radiometer pHM equipped with a glass electrode and a saturated calomel electrode as reference electrode), oxine concentration and water-soluble complexing agents (oxalic acid, tartaric acid, hydrocyanic acid, nitrilotriacetic acid, edta and trans-1,2-diaminocyclohexanetetraacetic acid, 0.01 M) have been investigated. Stability constants of the metal complexes with the various complexing agents investigated have been obtained. No information about the pH calibration and about the pH scale is given by [\[63STA\]](#).

In the case of the Mg-oxalate system the ligand is  $\text{ox}^{2-}$  in the extraction pH range 7.5 – 8.2 (six extraction points plotted in Fig. 4 of [\[63STA\]](#)). Starý assumed that the  $\text{Mg}(\text{ox})(\text{aq})$  complex predominated and reported a formation constant  $\log_{10} K_1 = (2.39 \pm 0.05)$ . However, at concentrations of about  $10^{-4}$  M total Mg and 0.01 M total oxalate the complex  $\text{Mg}(\text{ox})_2^{2-}$  cannot be neglected in the data analysis, and the reported value is not credited by this review. There are not enough experimental details reported by Starý for a re-evaluation of his measurements.

In the Ca-oxalate system Starý observed precipitation and reported a solubility product  $\log_{10} K_{s,0} = -7.9$  for the “insoluble oxalate”. No further details are given how this solubility product was obtained; it is not included in the final data analysis of this review.

In the case of the Ni-edta system the ligand is  $\text{edta}^{4-}$  in the extraction pH range ( $\approx 11$ ). It contributes significantly to the actual ionic strength, which increases from 0.1 to 0.2 M. The expected large change of the activity coefficients prevents the use of these data to obtain accurate results in this review. Furthermore, in Fig. 14 of [\[63STA\]](#) there is only a single point showing a non-zero extraction effect for Ni-edta slightly above pH 11, which is a rather shaky basis for determining a stability constant.

For the Ni-oxalate system Starý assumed that the  $\text{Ni}(\text{ox})_2^{2-}$  complex predominated. Only a single value of the total oxalate concentration was studied (0.01 M), and the free concentration of the ligand was varied by changing the pH from 4 to 5 (Fig. 14 in [\[63STA\]](#)), but the values used for the acidity constants of oxalic acid correspond approximately to those at zero ionic strength. Because of these problems, and the uncertainty in the pH measurements, the reported value of  $\log_{10} \beta_2$  is not included in the review procedure.

The U(VI)-oxalate data have been taken from [\[60STA3\]](#), see discussion in this Appendix.

[\[63TAN/TER\]](#)

The authors determined the solubility of  $\text{H}_4\text{edta}(\text{cr})$  at  $I = (0.10 \pm 0.04)$  M at 20°C, and

at  $I = 0.02$  M at both 20 and 16°C. The data were combined with literature values for the protonation constants of  $\text{edta}^{4-}$  [47SCH/ACK] to produce a value for the solubility product and enthalpy change for reaction:  $\text{H}_4\text{edta}(\text{cr}) \rightleftharpoons 4\text{H}^+ + \text{edta}^{4-}$ . The solubilities were also analysed assuming the formation of  $\text{H}_5\text{edta}^+$  and  $\text{H}_6\text{edta}^{2+}$ .

Unfortunately the values of  $[\text{H}^+]$  were calculated in this study from pH measurements and activity coefficients calculated with the Davies equation. Because of this the protonation constants and solubility constant reported by Tananaev and Tereshin are not included in this review.

### [63TOB/MIL]

The distribution of Mg(II) between 100 mg of Dowex50×12 (100 – 200 mesh,  $\text{NH}_4^+$  form) and 100 mL of aqueous solution in the absence and presence of citrate has been measured at pH 7.2,  $[\text{NH}_4^+] = 0.1$  M and 25°C. The value of  $\log_{10}\beta_{1(\text{cit})} = 3.16$  for  $\text{Mg}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Mg}(\text{cit})^-$  was obtained from the plots of  $\log_{10}((K_d^0/K_d) - 1)$  against  $\log_{10}[\text{cit}^{3-}]$ , where  $K_d^0$  and  $K_d$  are the distribution coefficient of Mg(II) in the absence and presence of citrate. Only a single series of experiments at pH 7.2 (5 points from  $[\text{cit}^{3-}] = 10^{-3}$  to  $10^{-2}$  M) has been conducted. The possibilities of unknown side reactions should be carefully excluded by checking the effect of pH,  $[\text{NH}_4^+]$ , and resin to solution ratio. In the determination procedure for magnesium in the solution, the authors have used Lewatit M2 strongly basic anion exchanger ( $\text{Cl}^-$  form) to separate  $\text{Mg}(\text{cit})^-$  from  $\text{cit}^{3-}$ . By passing through this column, they claimed that the uptake of free  $\text{cit}^{3-}$  by the resin resulted in the dissociation of the complex, thus liberating  $\text{Mg}^{2+}$  ion into the eluate. Since both  $\text{cit}^{3-}$  and  $\text{Mg}(\text{cit})^-$  are anions, this procedure must be more clearly verified. This review does not accept this paper.

### [63WAT/TRO]

The complex formation of magnesium with several ligands, including oxalate and citrate, has been studied by measuring the effect of these ligands on the fluorescence of the magnesium-8-hydroxyquinoline complex using a spectrofluorophotometer. Triethanolamine (Tea) and 2-amino-2(hydroxymethyl)-1,3-propanediol (Tris) were used as buffers and electrolyte medium at a concentration of 0.1 M at 25°C. The concentrations of magnesium, oxalate and citrate were in the range  $10^{-5}$  M. The stability constants reported are  $\log_{10} K_1 = 3.63$  (in Tris and Tea) for  $\text{Mg}(\text{cit})^-$ ,  $\log_{10} K_1 = 2.88$  (in Tris) and  $\log_{10} K_1 = 2.90$  (in Tea) for  $\text{Mg}(\text{ox})(\text{aq})$ .

Tris and Tea are known to form complexes with metal ions. The  $\text{Mg}(\text{Tris})^{2+}$  and  $\text{Mg}(\text{Tea})^{2+}$  formation constants have been reported as  $K_{(\text{Tris})} = 2.0$  and  $K_{(\text{Tea})} = 1.7$ , respectively, in 1 M  $\text{KNO}_3$  at 25°C [82SIG/SCH]. In the experimental set-up of this paper we have about 10000-fold excess in the concentration of Tris and Tea with respect to oxalate or citrate, but the  $\text{Mg}(\text{cit})^-$  and  $\text{Mg}(\text{ox})(\text{aq})$  formation constants exceed the  $\text{Mg}(\text{Tris})^{2+}$  and  $\text{Mg}(\text{Tea})^{2+}$  formation constants only by a factor of about 2000 and 400, respectively. Thus, the influence of Tris and Tea on magnesium complexation is in

the same order of magnitude and may even exceed that of oxalate and citrate. The  $\text{Mg}(\text{cit})^-$  and  $\text{Mg}(\text{ox})(\text{aq})$  formation constants reported by the authors are systematically affected (too high) by ignoring this competing complexation effect, and the good agreement of results obtained in Tris and Tea is due to very similar  $\text{Mg}(\text{Tris})^{2+}$  and  $\text{Mg}(\text{Tea})^{2+}$  formation constants. There are not enough experimental data reported in this paper for a re-evaluation, and hence the results of this study are not considered in this review.

#### [\[63ZOL/ALI\]](#)

This paper only reports results which have already been published in [\[61ZOL/MAR2\]](#). The values given in [\[61ZOL/MAR2\]](#) are rejected by this review, and no new experimental data are reported by [\[63ZOL/ALI\]](#).

#### [\[64BAN/SHA\]](#)

The oxalate complexation of  $^{237}\text{Np}(\text{IV})$  at  $I = 1 \text{ M}$  was studied by measuring the solubility of  $\text{Np}(\text{IV})$  oxalate at various oxalic acid concentrations at  $(26 \pm 2)^\circ\text{C}$  and by solvent extraction at an unknown temperature. Neptunium was initially reduced to the tetravalent state by one-hour treatment at  $80^\circ\text{C}$  with a solution of  $0.9 \text{ M}$  hydrazine and  $0.18 \text{ M}$  KI in  $5 \text{ M}$  HCl. However, it is not mentioned in the paper if the authors took precautions to avoid the oxidation of  $\text{Np}(\text{IV})$ , *e.g.*, to  $\text{Np}(\text{V})$ , during the solubility or solvent extraction experiments. The data were treated assuming the formation of  $\text{Np}(\text{ox})_n^{4-2n}$  using the protonation constants for oxalate from [\[31GAN/ING\]](#)  $\log_{10} K_1 = 3.32$  and  $\log_{10} K_2 = 0.97$ .

Solid  $\text{Np}(\text{IV})$  oxalate was obtained by mixing a neptunium(IV) chloride solution with oxalic acid, and although the authors claim that the precipitate was  $\text{Np}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$ , no solid phase characterisation is reported in the paper. The equilibration time in the solubility measurements was at least 72 hours, and the samples were then centrifuged. The ionic medium was either  $1 \text{ M}$   $\text{HClO}_4$  or a mixture of  $0.5 \text{ M}$   $\text{HClO}_4$  with  $0.5 \text{ M}$   $\text{NaClO}_4$ . The stability constants and solubility product obtained by the authors are listed in Table A-7.

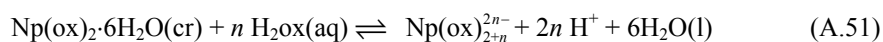
Table A-7: Equilibrium constants reported in [\[64BAN/SHA\]](#) for reactions:  $\text{Np}^{4+} + n \text{ox}^{2-} \rightleftharpoons \text{Np}(\text{ox})_n^{4-2n}$ , and  $\text{Np}(\text{ox})_2 \cdot 6\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{Np}^{4+} + 2 \text{ox}^{2-} + 6\text{H}_2\text{O}(\text{l})$ .

Stability constant	Solubility method		Solvent extraction
	1 M (Na,H)ClO <sub>4</sub> [H <sup>+</sup> ] = 0.5 M	1 M HClO <sub>4</sub>	1 M HClO <sub>4</sub>
$\log_{10} \beta_1$	$(7.40 \pm 0.05)$	$(7.47 \pm 0.01)$	$(8.19 \pm 0.06)$
$\log_{10} \beta_2$	$(13.62 \pm 0.04)$	$(13.69 \pm 0.02)$	$(16.21 \pm 0.13)$
$\log_{10} \beta_3$	$(19.45 \pm 0.09)$	$(19.37 \pm 0.07)$	--
$\log_{10} K_s$	$-(18.89 \pm 0.03)$	$-(18.89 \pm 0.03)$	



The authors also determined the first and second complex formation constant by solvent extraction of Np(IV) (the concentration of neptunium is not reported) from 1 M HClO<sub>4</sub> using a 0.05 M solution of thenoyltrifluoroacetone (TTA) in benzene. The authors state that at high oxalic acid concentrations the measurements were not reproducible, and the maximum value of [H<sub>2</sub>ox]<sub>TOT</sub> that could be used was 5×10<sup>-4</sup> M. The authors also indicated that precipitation of Np(IV) oxalate could have taken place in the experiments with the highest oxalic acid concentrations. The equilibrium constants obtained by the authors are listed in Table A-7. The formation of complex species is supported by a 10 nm shift of the characteristic absorption in visible spectra of Np(IV).

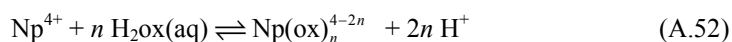
As the medium effects on the protonation constants of oxalate are not known, the data reported in [64BAN/SHA] should instead be evaluated using H<sub>2</sub>ox(aq) as the ligand. The solubilities in both ionic media (1 M HClO<sub>4</sub> and 0.5 M HClO<sub>4</sub> + 0.5 M NaClO<sub>4</sub>) were evaluated all together by this review using the SIT model, described in Appendix B, and the following equilibria:



with  $n = -2$  to  $+1$ , resulting in the following species: Np<sup>4+</sup>, Np(ox)<sup>2+</sup>, Np(ox)<sub>2</sub>(aq) and Np(ox)<sub>3</sub><sup>2-</sup>. The calculations show that the formation of Hox<sup>-</sup>, NpOH<sup>3+</sup> may not be neglected at these moderate acidities. This means that the results must be taken with some reservation, as there is quite a large uncertainty both in the hydrolysis of Np(IV) and in the first dissociation constant of oxalic acid in HClO<sub>4</sub> media. According to the SIT model the medium effects for all positively charged and neutral species are independent of the nature of the cation in the background electrolyte. The activity coefficients for both Hox<sup>-</sup> and Np(ox)<sub>3</sub><sup>2-</sup> are expected to change when the background cation changes from [H<sup>+</sup>] = 1 M to [H<sup>+</sup>] = [Na<sup>+</sup>] = 0.5 M. As a simplification [ClO<sub>4</sub><sup>-</sup>] was taken to be 1.051 molal in both media, while in the mixed background electrolyte [H<sup>+</sup>] = [Na<sup>+</sup>] = 0.5255 molal was used. According to the SIT model the equilibrium constant for reaction Np(ox)<sub>2</sub>·6H<sub>2</sub>O(cr) + H<sub>2</sub>ox(aq) ⇌ Np(ox)<sub>3</sub><sup>2-</sup> + 2 H<sup>+</sup> + 6H<sub>2</sub>O(l) is affected as follows:

$$\begin{aligned} \log_{10} K_{[\text{Na}^+]=0.5\text{M}} &= \log_{10} K_{[\text{H}^+]=1\text{M}} + \frac{\varepsilon(\text{H}^+, \text{Np(ox)}_3^{2-})}{2} I_m - \frac{\varepsilon(\text{Na}^+, \text{Np(ox)}_3^{2-})}{2} I_m \\ &= \log_{10} K_{[\text{H}^+]=1\text{M}} + 1/2 I_m \Delta\varepsilon \end{aligned}$$

where  $\Delta\varepsilon = \varepsilon(\text{H}^+, \text{Np(ox)}_3^{2-}) - \varepsilon(\text{Na}^+, \text{Np(ox)}_3^{2-})$  and  $I_m = 1.051$  molal as a good approximation. The results of the fitting depend on the value chosen for  $\varepsilon(\text{H}^+, \text{Hox}^-)$ , cf. Table A-8. It may then be concluded that the data can be reproduced using the following parameters:  $\log_{10} K_s ((\text{A.51}) n = -2) = -(10.8 \pm 1.0)$ ,  $\log_{10} K_s ((\text{A.51}) n = -1) = -(7.1 \pm 0.1)$ ,  $\log_{10} K_s ((\text{A.51}) n = 0) = -(5.3 \pm 0.1)$ ,  $\log_{10} K_s ((\text{A.51}) n = 1) = -(3.74 \pm 0.04)$ , and  $\Delta\varepsilon = \varepsilon(\text{H}^+, \text{Np(ox)}_3^{2-}) - \varepsilon(\text{Na}^+, \text{Np(ox)}_3^{2-}) = -(0.02 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ . This corresponds to the following equilibrium constants for:



$$\log_{10} {}^*\beta_1^{\circ} = (3.7 \pm 1.0), \log_{10} {}^*\beta_2^{\circ} = (5.5 \pm 1.0) \text{ and } \log_{10} {}^*\beta_3^{\circ} = (7.1 \pm 1.0).$$

It is possible to extrapolate the value of  $K_s$  (A.51),  $n = -2$  to  $I_m = 0$  using the activity of water and the  $\varepsilon$ -values listed in Appendix B,  $\log_{10} K_s^{\circ}$  (A.51),  $n = -2$  =  $-(13.1 \pm 1.0)$ .

The distribution coefficients from 1 M  $\text{HClO}_4$  solutions reported in [64BAN/SHA] were also fitted in this review using  $\text{H}_2\text{Ox}(\text{aq})$  as the ligand (Reaction (A.52), with  $n = 1$  to 3). The regression was performed with the least-squares computer program Letagrop-Distr [71LIE], [79LIE/EKE]. The formation of  $\text{NpOH}^{3+}$  can not be fully neglected in the solutions most diluted in oxalic acid. Using a model with three complexes results in the following equilibrium constants:  $\log_{10} {}^*\beta_1 = (4.1 \pm 0.2)$ ,  $\log_{10} {}^*\beta_2 = (7.4 \pm 0.4)$  and  $\log_{10} {}^*\beta_3 = (10.8 \pm 0.4)$ .

The values of  $\log_{10} {}^*\beta_1$  obtained from the two experimental techniques (solubility and solvent extraction) agree within the uncertainties. However, there is a larger discrepancy between the results from solubility and solvent extraction for the second and third complex. As a possible explanation Bansal and Sharma [64BAN/SHA] suggested that oxalic acid might have been extracted in the TTA-benzene solution. See also the discussion in Section VI.11.2.2.

Table A-8: Equilibrium constants for reactions (A.51) obtained in this review by fitting the solubility data reported in [64BAN/SHA].

$n$ (in Eqn.(A.51))	Product	$\varepsilon(\text{H}^+, \text{Hox}^-)^{\ddagger}$		
		0.5 kg·mol <sup>-1</sup>	0.0 kg·mol <sup>-1</sup>	-0.5 kg·mol <sup>-1</sup>
-2	$\text{Np}^{4+}$	$-(10.5 \pm 0.3)$	$-(10.8 \pm 0.6)$	$-(11.2 \pm 1.1)$
-1	$\text{Np}(\text{ox})^{2+}$	$-(7.06 \pm 0.07)$	$-(7.1 \pm 0.1)$	$-(7.1 \pm 0.2)$
0	$\text{Np}(\text{ox})_2(\text{aq})$	$-(5.25 \pm 0.06)$	$-(5.3 \pm 0.1)$	$-(5.5 \pm 0.3)$
1	$\text{Np}(\text{ox})_3^{2-}$	$-(3.78 \pm 0.02)$	$-(3.74 \pm 0.03)$	$-(3.63 \pm 0.06)$
$\Delta\varepsilon^{\dagger}$		$-(0.01 \pm 0.01)$	$-(0.02 \pm 0.01)$	$-(0.07 \pm 0.02)$
U <sup>§</sup>		0.012	0.025	0.112

$\ddagger$ :  $\varepsilon(\text{H}^+, \text{Hox}^-) = 0.5, 0.0$  and  $-0.5$  kg·mol<sup>-1</sup> correspond, respectively, to  $\log_{10} K = 1.66, 1.14$  and  $0.61$  (in molal units) for  $\text{Hox}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{Ox}(\text{aq})$  in 1 M  $\text{HClO}_4$  and 25°C.

$\dagger$ :  $\Delta\varepsilon = \varepsilon(\text{H}^+, \text{Np}(\text{ox})_3^{2-}) - \varepsilon(\text{Na}^+, \text{Np}(\text{ox})_3^{2-})$  obtained from fitting the data, in units of kg·mol<sup>-1</sup>.

$\S$ : U = sum of error squares:  $\sum \left( \frac{[\text{Np}^{\text{IV}}]_{\text{calc}} - [\text{Np}^{\text{IV}}]_{\text{exp}}}{[\text{Np}^{\text{IV}}]_{\text{exp}}} \right)^2$

$\P$ : Other parameters used:  $\varepsilon(\text{Na}^+, \text{Hox}^-) = -0.07$  (Appendix B); equilibrium constants for  $\text{NpOH}^{3+}$  and  $\text{Np}(\text{OH})_2^{2+}$  [2003GUI/FAN] and for  $\text{Hox}^-$  (selected in this review); for example, for reaction  $\text{Np}^{4+} + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NpOH}^{3+} + \text{H}^+$ , the value  ${}^*K = (0.32 \pm 0.18)$  mol·kg<sup>-1</sup> was evaluated for 1 M  $\text{HClO}_4$  at 25°C from the selected value at  $I = 0$  [2003GUI/FAN] and the  $\varepsilon$ -values in Appendix B and in [2001NEC/KIM].

[\[64BHA/KRI\]](#)

The U(VI) – edta system has been investigated spectrophotometrically (Beckman DU spectrophotometer with 1 cm quartz cells) in solutions of 0.15 M NaClO<sub>4</sub> at (25 ± 1)°C. All pH measurements were made with a Beckman model-G pH meter with a glass electrode and a calomel reference electrode. The concentration of H<sup>+</sup> used in the calculations was determined by calibrating the pH scale with standard perchloric acid at the same ionic strength.

The calomel reference electrode contains 1 M or saturated KCl solution. A 0.15 M NaClO<sub>4</sub> solution in contact with KCl solution results in precipitation of KClO<sub>4</sub> in the calomel electrode with possible emf errors. Furthermore, the reported equilibrium constants have been calculated neglecting the contributions of all side equilibria. Especially, the authors did not take into account the presence of UO<sub>2</sub>(Hedta)<sup>–</sup> when calculating the constant of the 2:1 complex and assumed that only this species was formed under the conditions of the measurements. This assumption is not justified as discussed by [\[68SIL/SIM\]](#). Thus, the obtained constants were not used in this review for the final data selection.

[\[64CAL\]](#)

Reported values of stability constants of oxalate complexes of zirconium are listed. All the papers listed are checked in this review.

[\[64CAL/KYR\]](#)

The sorption of 10<sup>–6</sup> M Zr<sup>4+</sup> on silica gel has been studied in static and dynamic experiments in 1–5 M HNO<sub>3</sub> in the presence of oxalic acid, edta and Arsenazo I. The distribution coefficient of zirconium was expressed by  $K_d^0 / K_d = 1 + \sum (\beta_{L,k} / a) \cdot [L]^k$ , where  $a = 1 + \sum \beta_{NO_3,i} \cdot [NO_3^-]^i + \sum \beta_{OH,j} \cdot [OH^-]^j$ . By using the reported stability constants of nitrate and hydroxide complexes as well as the protonation constants of edta and oxalate, the authors have estimated the values of  $a = [Zr^{4+}] / C_{Zr}$  and  $b = [L] / C_L$  and obtained the constants for the reactions,  $Zr^{4+} + kL \rightleftharpoons ZrL_k$  where L stands for edta<sup>4–</sup> or ox<sup>2–</sup>.

For the complexes with edta, the authors reported log<sub>10</sub> K<sub>1</sub> = 28.46, 30.58, 31.11, 30.92 and 30.63 in 1.0, 2.0, 3.0, 4.0 and 5.0 M HNO<sub>3</sub>, respectively. For each condition, the values of log<sub>10</sub>a and log<sub>10</sub>b were estimated to be (–0.67, –22.35), (–0.67, –24.18), (–0.79, –25.39), (–0.83, –26.12) and (–0.95, –26.69), respectively. To estimate b, the “stability constants of molecules H<sub>4</sub>Y (Y = edta<sup>4–</sup>) and of ions H<sub>5</sub>Y<sup>+</sup> and H<sub>6</sub>Y<sup>2+</sup>, which prevail in acid medium, were taken from [\[52CAR/MAR\]](#)”. However, [\[52CAR/MAR\]](#) do not report values for K<sub>5</sub> and K<sub>6</sub>, the fifth and sixth protonation constant of edta. Therefore, the constants reported by [\[64CAL/KYR\]](#) are discarded in this review.

For the complexes with oxalate, the authors reported log<sub>10</sub> β<sub>1</sub> = (11.07 ± 0.2), log<sub>10</sub> β<sub>2</sub> = (20.28 ± 0.3) in 1.0 M HNO<sub>3</sub>, and log<sub>10</sub> β<sub>1</sub> = (11.28 ± 0.2) in 5.0 M at HNO<sub>3</sub>.

In 1.0 and 5.0 M HNO<sub>3</sub>, the values of log<sub>10</sub>*a* and log<sub>10</sub>*b* were estimated to be (− 0.67, − 5.40) and (− 0.95, − 6.80), respectively. For the moment, this review does not accept the result of this paper since the values used to evaluate *a* and *b* are considered not well qualified. However, as all necessary analytical data can be extracted from this report, either from tables or from figures, a re-evaluation could be envisioned as soon as Zr hydrolysis and nitrate complexation data have been selected by the corresponding NEA-TDB review team.

#### [\[64CAM/OST\]](#)

Potentiometric titration has been conducted at *I* = 0.1 M NaClO<sub>4</sub> at 20°C. Using the protonation constants log<sub>10</sub> *K*<sub>(H)</sub> = 5.68, 4.35 and 2.87, Campi *et al.* obtained the constants for the reaction,  $M^{2+} + H_r\text{cit}^{r-3} \rightleftharpoons M(H_r\text{cit})^{r-1}$ , to be log<sub>10</sub> β<sub>1</sub> = 3.40 for Mg(cit)<sup>−</sup>, 1.84 for Mg(Hcit)(aq), 0.84 for Mg(H<sub>2</sub>cit)<sup>+</sup>, 3.55 for Ca(cit)<sup>−</sup>, 2.10 for Ca(Hcit)(aq) and 1.05 for Ca(H<sub>2</sub>cit)<sup>+</sup>. Experiments and data analysis have been conducted properly, except the possibility of KClO<sub>4</sub> precipitation at the junction of reference electrode and the solution. This review accepts these values with assigning the uncertainty of ± 0.15 for log<sub>10</sub> β<sub>1</sub> of M(cit)<sup>−</sup> and M(Hcit)(aq), and ± 0.2 for M(H<sub>2</sub>cit)<sup>+</sup>.

The complex formation of Ni<sup>2+</sup> with citric acid was investigated by the potentiometric method at the ionic strength 0.10 M NaClO<sub>4</sub> at 20 °C. Although the experimental details for the Ni<sup>2+</sup>-citric acid system are not given, those given for the Cu<sup>2+</sup>-citric acid system indicate that the experiments have been done carefully. The calibration of the pH meter readings to − log<sub>10</sub>[H<sup>+</sup>] values was well done. The protonation constants, log<sub>10</sub> *K*<sub>(H)</sub> = 5.68, 4.35 and 2.87, obtained by the authors and used in the calculation are close to those accepted in this review. The constants for  $Ni^{2+} + H_r\text{cit}^{r-3} \rightleftharpoons Ni(H_r\text{cit})^{r-1}$  were reported to be log<sub>10</sub> β<sub>1</sub> = 5.40 for Ni(cit)<sup>−</sup>, 3.30 for Ni(Hcit)(aq) and 1.75 for Ni(H<sub>2</sub>cit)<sup>+</sup>. Using these values and above protonation constants, the protonation constant of  $Ni(Hcit)(aq) + H^+ \rightleftharpoons Ni(H_2cit)^+$  can be estimated to be log<sub>10</sub> *K* = 1.75 − 3.30 + 4.35 = 2.8. This value means that the species Ni(H<sub>2</sub>cit)<sup>+</sup> can exist only in the very beginning of the titration (at pH lower than ~ 2.8). By considering this fact and the difference in the temperature from 25°C, this review assigns uncertainties as log<sub>10</sub> β<sub>1</sub> = (5.40 ± 0.20) for Ni(cit)<sup>−</sup>, (3.30 ± 0.20) for Ni(Hcit)(aq) and (1.75 ± 0.30) for Ni(H<sub>2</sub>cit)<sup>+</sup>.

#### [\[64INT/MAR\]](#)

In a spectrophotometric study the Zr-edta complexation has been studied in 0.1 M KCl using Fe<sup>3+</sup> as competing metal ion. The authors showed that at pH = 2 different values for the Zr-edta stability constants are obtained from solutions in which the sequence of the additions of the reacting components Zr–Fe–edta has been changed. Remarkably, during three weeks, "the solutions exhibited only negligible changes in optical density. Thus, the exchange reaction must be a very slow one". The variation of the Zr-edta constant is two orders of magnitude, and [\[64INT/MAR\]](#) give an average value log<sub>10</sub>*K*<sub>1</sub> =

( $29.0 \pm 0.9$ ). From potentiometric titration data the authors derive the formation constant of a monohydroxo chelate species and an approximate dimerisation constant of this species. The spectrophotometric data need correction for chloro and hydroxo complexing of Fe(III) and Zr(IV). In the case of Zr(IV) [64INT/MAR] assume that the tetramer is the only form of hydrolysed zirconium present in their experiments. However, a later re-evaluation of these data with proper Fe(III) and Zr(IV) chloro and hydroxo constants is not promising, because the large uncertainty in  $\log_{10}K_1$  of two orders of magnitude will remain.

#### [64KHA/BOC2]

The infrared absorption spectra of  $K_2Zr(ox)_3 \cdot 4H_2O$ ,  $(NH_4)_2Zr(ox)_3 \cdot (2.5 \text{ or } 3)H_2O$ ,  $(NH_4)_2H_2Zr(ox)_4 \cdot 4H_2O$ ,  $K_4Zr(ox)_4 \cdot 4.5H_2O$ ,  $(NH_4)_4Zr(ox)_4 \cdot 2H_2O$  (isolated from aqueous solutions and from alcoholic solutions),  $Ba_2Zr(ox)_4 \cdot 4H_2O$ ,  $(NH_4)_6Zr(ox)_5 \cdot 2H_2O$  and  $(NH_4)_3H_3Zr(ox)_5 \cdot 2.5H_2O$  were recorded. Based on the absorption bands indicating C=O double bond and antisymmetrical and symmetrical stretching vibrations of the  $-COO$  group containing two equivalent CO bonds of intermediate character, the trioxalatozirconates and tetraoxalatozirconates isolated from aqueous solutions were shown to contain only bidentate oxalate groups forming 5-membered rings with Zr atoms. The normal tetraoxalato complexes isolated from alcoholic solutions and the pentaoxalato complex were shown to contain oxalate groups with uncombined  $-COO$  groups. This paper gives useful information concerning the speciation of aqueous complexes of zirconium with oxalate.

#### [64KHA/ZAI2]

The infrared absorption spectra of the solids containing the so-called zirconyl unit,  $H_2ZrO(ox)_2 \cdot 3H_2O$ ,  $(NH_4)_2ZrO(ox)_2 \cdot 3H_2O$ ,  $BaZrO(ox)_2 \cdot 3H_2O$ ,  $ZrO(ox) \cdot 4H_2O$  and  $\{(ZrO)_2(ox) \cdot 6H_2O\}Cl_2 \cdot 7H_2O$  were obtained. All spectra indicated the absence of zirconyl groups and the presence of bidentate oxalate groups, suggesting that the anionic complex contains the tetrameric unit  $[Zr_4(OH)_8(ox)_8]^{8-}$ . Although the existence of the tetramer is not fully substantiated, this paper gives useful information about the complex species of zirconium oxalate produced at rather high pH.

#### [64PAN/VLA]

The reaction of zirconium with a number of complexones, including edta, has been studied by an ion-exchange method at pH = 2 and  $I = 2$  (the concentration scale and the inert salt used are not reported). The authors infer from their experiments that edta forms a complex which corresponds to a zirconium:edta ratio of 1:2. Neither the equilibrium nor the stoichiometry of the Zr-edta complex are defined in [64PAN/VLA], but nevertheless, the authors give an equilibrium constant of  $1.24 \times 10^{-6}$  for this undefined reaction. The poor description of the experiments does not allow any re-evaluation and hence, the data of [64PAN/VLA] have been discarded in this review.

[\[64POR\]](#)

The author studied the solubility of  $^{237}\text{Np(IV)}$  oxalate at  $23^\circ\text{C}$  in broad concentration ranges:  $[\text{H}_2\text{ox}]_{\text{TOT}} = 0.01 - 0.4 \text{ M}$ ,  $[\text{HNO}_3]_{\text{TOT}} = 0.37 - 3.76 \text{ M}$ . The purpose of these measurements was to provide data for the production of neptunium dioxide at a plant-scale, and the experimental procedure is not described unambiguously. Apparently both precipitation and solubility experiments were performed. Neptunium from a process solution was separated by anion exchange, and then reduced with ascorbic acid to the tetravalent state. It was found that the kinetics of  $\text{Np(V)}$  reduction increased with rising acidities. Hydrazine was added to inhibit subsequent oxidation of  $\text{Np(IV)}$ , but according to the author a few percent of oxidised neptunium were normally observed in freshly prepared solutions. The solubility was determined by alpha counting. The equilibration time and composition of the solid phase are not reported. The samples were filtered through “medium porosity fritted glass”. The solubility data, reported in [\[64POR\]](#) as a figure, were later analysed by [\[68MOS2\]](#) to estimate equilibrium constants for the formation of  $\text{Np(IV)}$ -oxalate complexes. Given the experimental uncertainties, the solubilities reported in [\[64POR\]](#) are not considered in this review.

[\[64RYA/MAR\]](#)

This review discusses the stabilities of the complexes of zirconium and hafnium as compared with those of other tetravalent metal ions. The values for zirconium citrate complexes are cited from [\[60RYA/ERM\]](#) and those for zirconium oxalate complexes are from [\[62MAR/RYA2\]](#).

[\[64SEK\]](#)

This paper is a short communication of an extensive experimental study, which was later published in a series full papers [\[65SEK\]](#), [\[65SEK2\]](#), [\[65SEK3\]](#), [\[65SEK4\]](#). For a discussion of the oxalate part, see [\[65SEK4\]](#) in this Appendix.

[\[64TOB/MIL\]](#)

The distribution of  $\text{Mg(II)}$  between 100 mg of Dowex50 $\times$ 12 (100 – 200 mesh,  $\text{Na}^+$  form) and 100 mL of aqueous solution in the absence and presence of citrate has been measured at pH 7.1 and  $25^\circ\text{C}$ . The effects of ionic strength (from 0.01 to 0.09 M), temperature (15, 25, 35 and  $50^\circ\text{C}$ ) and pH (7 to 9) were examined. The value of  $\log_{10} \beta_{1,0,1}^\circ = 3.96$  for  $\text{Mg}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Mg}(\text{cit})^-$  was obtained by extrapolation to infinite dilution at pH 7.1 and  $25^\circ\text{C}$ . In the analysis,  $\log_{10}(K_d^\circ / K_d)$  were plotted against  $\log_{10}[\text{cit}^{3-}]$ , where  $K_d^\circ$  and  $K_d$  are the distribution coefficients of  $\text{Mg(II)}$  in the absence and presence of citrate. Since  $[\text{Mg}(\text{Hcit})(\text{aq})]$  and  $[\text{Hcit}^{2-}]$  can be considered negligible as compared to  $[\text{Mg}(\text{cit})^-]$  and  $[\text{cit}^{3-}]$ , respectively, their analysis should have given a constant  $\log_{10} \beta_1$  at a given ionic strength. However, they obtained  $\log_{10} \beta_{1,0,1} = 3.15$  at pH 7.1 and 3.66 at pH 9.0 at  $I = 0.045$ . This implies some unknown side reaction in the distribution experiment. Also, the ionic strength given in the paper

cannot be realised from the given experimental condition. For example, in the experiment for the effect of ionic strength, the paper described that the ionic strength was varied from 0.01 to 0.09 M while the citrate concentration was kept at  $10^{-2}$  M. However,  $10^{-2}$  M of  $\text{Na}_3\text{cit}$  gives an ionic strength of 0.06 M and an ionic strength lower than this is impossible. This review does not accept this paper.

#### [\[64YEN/LIU\]](#)

In this study the cation exchange equilibrium  $\text{Hg}(\text{edta})^{2-} + \text{Me}^{2+} \rightleftharpoons \text{Me}(\text{edta})^{2-} + \text{Hg}^{2+}$ , with  $\text{Me} = \text{Ca}$  and  $\text{Mg}$ , has been investigated by means of a Hg sensitive electrode at  $(30.0 \pm 0.1)^\circ\text{C}$  in 0.1 M ( $\text{KNO}_3$ ). The Hg-edta complexation has been determined under the same conditions, but the edta protonation constants used to calculate the stability constant of  $\text{Hg}(\text{edta})^{2-}$  have been taken from [\[56SCH/REI\]](#), who in turn used the protonation constants of [\[47SCH/ACK\]](#) determined at  $20^\circ\text{C}$  in 0.1 M KCl. It is not clear whether [\[64YEN/LIU\]](#) corrected the edta protonation constants for the temperature effect. Hence, this review accepts the Ca and Mg edta constants reported by [\[64YEN/LIU\]](#) but assigns an uncertainty of  $\pm 0.3$  to account for the ambiguity concerning the used edta protonation constants.

#### [\[64ZAI2\]](#)

When aqueous solutions containing zirconium and oxalate ions are mixed, the product is a white precipitate which is sparingly soluble in water and dilute mineral acids but soluble in an excess of either of the original reagents. Its analysis indicates the formula  $\text{ZrO}(\text{ox}) \cdot n\text{H}_2\text{O}$  and the compound is called zirconyl oxalate, by analogy with zirconyl chloride  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ . A number of the derivatives of “zirconyl oxalate” have been prepared and their structures have been discussed. The results indicated that the compound called zirconyl oxalate does not contain zirconyl groups but it contains chains of Zr bridged by two OH.

#### [\[64ZAI3\]](#)

Several forms of attachment of an oxalate group to a central metal atom in complex compounds have been examined. In a pentaaxalatozirconate complex, three oxalate groups are coordinating as  $\text{COO}^-$  with equalised bonds and each of the other two groups are coordinating via one oxygen where the other oxygen is protonated or exists as  $\text{C=O}$ .

#### [\[64ZAI/BOC2\]](#)

The compound  $\text{ZrO}(\text{ox}) \cdot 4\text{H}_2\text{O}$  was prepared and contacted with solutions of perchloric, hydrochloric, nitric, acetic and sulfuric acids at  $I = 0.1$  M ( $\text{H}, \text{NH}_4$ )X,  $(25 \pm 0.2)^\circ\text{C}$ . After contacting 24-25 h, the total concentration of oxalate ( $C_{\text{ox}}$ ) in the solution was determined by permanganometric method. The authors have obtained  $C_{\text{ox}}$  to be  $(0.34 \text{ to } 1.79) \times 10^{-3}$  M in 0.01 to 0.1 M  $\text{HClO}_4$ ,  $(0.72 \text{ to } 1.94) \times 10^{-3}$  M in 0.02 to 0.1 M HCl and

$(0.59 \text{ to } 1.64) \times 10^{-3} \text{ M}$  in  $0.01 \text{ to } 0.1 \text{ M HNO}_3$ , respectively, at  $I = 0.1 \text{ M}$ . The measured values in acetic acid and sulfuric acid were not used to obtain solubility products since they seemed to be affected by the complex formation of zirconium with acetate or sulfate. The dissolution reaction was considered to be  $\text{ZrO(ox)} \cdot 4\text{H}_2\text{O} \rightleftharpoons \text{Zr(OH)}_2^{2+} + \text{ox}^{2-} + 3\text{H}_2\text{O}$ . By assuming  $C_{\text{ox}} = C_{\text{Zr}} = [\text{Zr(OH)}_2^{2+}]$ , the values of solubility product  $SP = [\text{Zr(OH)}_2^{2+}][\text{ox}^{2-}] f_{\pm}^2$  were calculated, where  $f_{\pm}$  is the activity coefficient of the doubly-charged ions ( $f_{\pm} = 0.46$  at  $I = 0.1 \text{ M}$ ).  $[\text{ox}^{2-}]$  was calculated by using the relation  $C_{\text{ox}} = [\text{ox}^{2-}](1 + K_1[\text{H}^+] + K_1K_2[\text{H}^+]^2)$  with the protonation constants of oxalate ( $\log_{10}K_{(\text{H})} = 4.193$  and  $1.229$ ), where  $[\text{H}^+]$  was calculated simply as  $[\text{H}^+] = 10^{-\text{pH}}$ . As stated by the authors, the calculated  $SP$  is arbitrary since the predominant species of zirconium is not  $\text{Zr(OH)}_2^{2+}$  but some polymerised species under this experimental condition. However, the authors claimed that since the concentrations of zirconium and oxalate in solution are found experimentally, this arbitrary  $SP$  value can be used for various types of calculations. At the acidity of  $0.01 \text{ to } 0.06 \text{ M}$  ( $I = 0.1 \text{ M}$ ), they obtained a constant value for  $SP$  to be  $0.98 \times 10^{-10}$ . At  $[\text{H}^+] \geq 0.08 \text{ M}$ , there was an increase in  $SP$ , which was considered due to the change in the chemical form of zirconium.

The absolute value of  $SP = 0.98 \times 10^{-10}$  cannot be accepted. As indicated later by the same author [67ZAI/SHU2], the solubilities are strongly affected by the change in the solid phase. Also, the value of  $SP$  includes the value of  $f_{\pm}$  of  $\text{Zr(OH)}_2^{2+}$  whose predominance is not guaranteed. In the estimation of  $[\text{ox}^{2-}]$ ,  $\log_{10}K_{(\text{H})}$  used are fairly different from those selected in this review and  $[\text{H}^+]$  is calculated simply as  $[\text{H}^+] = 10^{-\text{pH}}$  without any consideration of the difference between pH and  $-\log_{10}[\text{H}^+]$ . Moreover, the result of this paper completely depends on the assumption of  $C_{\text{ox}} = C_{\text{Zr}} = [\text{Zr(OH)}_2^{2+}]$  in the solution. There should be the complex formation of zirconium with oxalate and the relation between  $C_{\text{ox}}$  and  $C_{\text{Zr}}$  may be different. Thus, this review does not consider this paper.

#### [65BHA/RAD]

Spectrophotometric measurements of the stability constants of ternary metal edta complexes with pyridine, hydrazine, hydroxylamine, ethylenediamine and propylenediamine are reported. Also the absorption spectra of the ternary complexes are given. The solutions were brought to equilibrium at  $25^\circ\text{C}$  and ionic strength  $1 \text{ M NaClO}_4$ . The pH measurements were made with a Beckman model G pH meter using glass electrodes and calomel reference electrodes. The calomel reference electrode contains saturated KCl or  $1 \text{ M KCl}$  solutions. Under such conditions the measurements are normally very difficult because of the precipitation of  $\text{KClO}_4$  occurring between the two solutions ( $\text{KCl}$  and  $\text{NaClO}_4$ ) in contact. The ternary complexation constants of [65BHA/RAD] are listed in this review for comparison only.



[\[65FUG/CUN\]](#)

A microcalorimetric determination of the enthalpy of formation of complex ions of trivalent plutonium, americium and lanthanum with edta is reported by Fuger and Cunningham. They measured the heats of dissolution of crystalline anhydrous trichlorides in dilute solutions of edta (in 0.1 M KCl, resulting in a mean ionic strength of 0.16 M) at a carefully chosen pH value at 25°C, and compared these data with the heats of dissolution of the same chlorides in solutions of similar ionic strength, but without edta. Under their experimental conditions, the equation  $\text{MeCl}_3(\text{cr}) + 2 \text{Hedta}^{3-} \rightarrow \text{Me}(\text{edta})^- + 3 \text{Cl}^- + \text{H}_2\text{edta}^{2-}$  (Me: Pu(III), Am(III), La(III)) unambiguously describes the reaction to better than 99.8%. Combining these data with the heat of dissolution of the trichlorides in a non-complexing but otherwise identical medium  $\text{MeCl}_3(\text{cr}) \rightleftharpoons \text{Me}^{3+} + 3 \text{Cl}^-$ , and using the enthalpies of the first and second edta protonation from [\[63AND\]](#), the enthalpy of complex formation  $\text{Me}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Me}(\text{edta})^-$  is calculated as  $\Delta_r H_m = -(17.7 \pm 1.0)$ ,  $-(19.5 \pm 1.0)$  and  $-(4.8 \pm 0.8)$  for Pu(III), Am(III) and La(III), respectively. These values are considered as reliable and they are accepted in this review.

[\[65JOK/MAJ\]](#)

In this study the complexation effects of various metal cations (Ca, Mg, Ni and others) with edta and edta homologues have been studied by paper electrophoresis. The resulting stability constants are only rough estimates, in the case of Mg-edta the reported value is at variance by more than two orders of magnitude with all other reported values, e.g., [\[47SCH/ACK\]](#) and [\[56SCH/REI\]](#). Hence, the values reported in [\[65JOK/MAJ\]](#) are discarded in this review.

[\[65OGI\]](#)

The stability constants of the complexes of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  with edta and other polyaminopolycarboxylates have been determined polarographically by metal exchange and ligand exchange equilibria in acetate buffer at 25°C and  $I = 0.2$  M  $\text{KNO}_3$ . Corrections were done by [\[65OGI\]](#) for acetato complexes. The concentration of  $\text{Cu}^{2+}$  and of the uncomplexed ligand can be obtained polarographically. By the determination of the relative stability constants of complexes with different ligands the concentration of the probably protonated ligand was calculated using literature values for the respective protonation constants at  $I = 0.1$  M and 20 or 30°C. The error due to this procedure is considered negligible by [\[65OGI\]](#). The pH measurements in the  $\text{H}^+$  activity scale were corrected to proton concentrations assuming the activity coefficient of the hydrogen ion to be 0.80 at  $I = 0.2$  M.

The  $\log_{10} K_1$  value for  $\text{Ni}(\text{edta})^{2-}$  was obtained by studying the metal exchange equilibrium  $\text{Cu}^{2+}/\text{Ni}^{2+}$ . For the data evaluation  $\log_{10} K_1(\text{Cu}(\text{edta})^{2-})$  at 25°C and 0.2 M  $\text{KNO}_3$  is needed. This constant has been estimated by [\[65OGI\]](#) based on the value of [\[54SCH/GUT\]](#) at 20°C and 0.1  $\text{KNO}_3$ . However, in the study of [\[54SCH/GUT\]](#) an acetic acid/sodium acetate buffer was used for which an exact correction is very diffi-

cult. The combined effects of changes in temperature and ionic strength, and the effect of the acetate buffer on the final result are difficult to assess and thus, the value reported in [65OGI] is not considered in this review.

#### [65PAT/PAN]

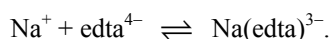
Potentiometric titration has been conducted for citric acid in the absence and presence of  $\text{MgSO}_4$  at  $32.5^\circ\text{C}$  and  $\log_{10}\beta_{1(\text{cit})} = 3.46$  for  $\text{Mg}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Mg}(\text{cit})^-$  has been reported. There is no description about the conversion of measured pH to  $-\log_{10}[\text{H}^+]$ , and ionic strength was not maintained constant in the titration. Thus, this review does not accept this paper.

#### [65PAT/PAN2]

Citrate complexation of nickel has been studied by solubility, conductometric and pH titration methods at  $35^\circ\text{C}$ . From the solubility measurements, the equilibrium constants between the solid  $\text{Ni}(\text{OH})_2(\text{s})$  and citrate complexes of  $\text{Ni}^{2+}$  were obtained to be  $\log_{10} K = 6.835$  for  $\text{Ni}(\text{OH})_2(\text{s}) + \text{H}_2\text{cit}^- \rightleftharpoons \text{Ni}(\text{cit})^- + 2 \text{H}_2\text{O}$ ,  $\log_{10} K = 3.21$  for  $\text{Ni}(\text{OH})_2(\text{s}) + \text{Hcit}^{2-} \rightleftharpoons \text{Ni}(\text{H}_1\text{cit})^{2-} + \text{H}_2\text{O}$ , and  $\log_{10} K = -7.89$  for  $\text{Ni}(\text{cit})^- \rightleftharpoons \text{Ni}(\text{H}_1\text{cit})^{2-} + \text{H}^+$ . Since ionic strength was not maintained constant and pH was not corrected to  $-\log_{10}[\text{H}^+]$ , this review does not accept these values.

#### [65PRI/SEB]

The authors describe a calorimetric instrument and methodology with applications in chemical analysis. The equipment was used to determine reaction enthalpies of metal-edta $^{4-}$  systems at  $20 - 25^\circ\text{C}$ :  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ni}^{2+}$ , *etc.* All results were based on the assumption that  $\Delta_r H_m = -5.9 \text{ kJ}\cdot\text{mol}^{-1}$  for reaction:



Because no details are given on concentration ranges, background electrolyte, ionic strength, *etc.*, the enthalpy changes reported by Priestley *et al.* are not included in this review.

#### [65RAJ/MAR]

Potentiometric titrations of the solutions containing equimolar concentrations of  $\text{UO}_2(\text{NO}_3)_2$  and  $\text{H}_3\text{cit}$  from  $7 \times 10^{-4}$  to  $1.7 \times 10^{-2} \text{ M}$  at  $I = 0.1$  and  $1.0 \text{ M}$  ( $\text{KNO}_3$ ) were conducted. From the concentration dependence of the formation constant of  $\text{UO}_2(\text{cit})^-$  calculated by:

$$\beta_1 = \frac{[\text{UO}_2(\text{cit})^-]}{[\text{UO}_2^{2+}][\text{cit}^{3-}]} = \frac{C_L - C'_L}{(C_M - C_L + C'_L)(C'_L \alpha_0)},$$

where:  $C'_L = [\text{H}_3\text{L}] + [\text{H}_2\text{L}] + [\text{HL}] + [\text{L}],$

$$\text{and } \alpha_0 = \frac{[\text{cit}^{3-}]}{[\text{H}_3\text{cit}] + [\text{H}_2\text{cit}^-] + [\text{Hcit}^{2-}] + [\text{cit}^{3-}]},$$

Rajan and Martell concluded that the dimer is formed. If both the monomer  $\text{UO}_2(\text{cit})^-$  and the dimer  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  contribute to the mass balance, the following relationship should hold:

$$\begin{aligned} C_L - C'_L &= [\text{UO}_2(\text{cit})^-] + [(\text{UO}_2)_2(\text{cit})_2^{2-}] \\ &= \beta_1 (C_M - C_L + C'_L)(C'_L \alpha_0) + \beta_{2,2} (C_M - C_L + C'_L)^2 (C'_L \alpha_0)^2 \end{aligned}$$

where  $\beta_{2,2}$  is defined for the reaction  $2\text{UO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons (\text{UO}_2)_2(\text{cit})_2^{2-}$ .

The plot of

$$\frac{C_L - C'_L}{(C_M - C_L + C'_L)(C'_L \alpha_0)} \text{ versus } (C_M - C_L + C'_L)(C'_L \alpha_0)$$

exhibited fairly good linearity, and they could estimate  $\beta_{2,2}$  and  $\beta_1$  from the slope and intercept of an unweighted regression. The results given by the authors are reported in Table A-9.

Table A-9: Citrate protonation constants and U(VI) citrate formation constants as reported in [65RAJ/MAR].

$I / \text{M}$	$\log_{10} K_{(\text{H})}$	$\log_{10} \beta_{2,2}$ for $(\text{UO}_2)_2(\text{cit})_2^{2-}$	$\log_{10} \beta_1$ for $\text{UO}_2(\text{cit})^-$
0.1	5.65, 4.30, 2.79	$(18.87 \pm 0.06)$	$(7.40 \pm 0.21)$
1	5.34, 4.11, 2.63	$(17.70 \pm 0.04)$	$(6.87 \pm 0.11)$

Since the intercepts shown in Figs. 2 and 3 in [65RAJ/MAR] are close to the origin, the uncertainties in  $\log_{10} \beta_1$  may be fairly large. Considering that the fraction of  $\text{UO}_2(\text{cit})^-$  is always very small and its contribution to the mass balance is not large enough, the values given for  $\log_{10} \beta_1$  in this paper should be regarded as the upper limits of  $\log_{10} \beta_1$ . This review accepts the following values.

Table A-10: Accepted U(VI) citrate formation constants with uncertainties estimated by this review.

	species	$I = 0.1 \text{ M (KNO}_3\text{)}$	$I = 1.0 \text{ M (KNO}_3\text{)}$
$\log_{10} \beta_{2,2}$	$(\text{UO}_2)_2(\text{cit})_2^{2-}$	$(18.87 \pm 0.10)$	$(17.70 \pm 0.10)$
$\log_{10} \beta_1$	$\text{UO}_2(\text{cit})^-$	$(7.40 \pm 0.50)$	$(6.87 \pm 0.50)$

Also, from the titration data at more than 3 moles of base per mole of uranyl ion, the authors considered the formation of  $(\text{UO}_2)_3(\text{cit})_3(\text{OH})_5^{8-}$  followed by the core-link type polymerisation. However, in this pH region,  $\text{UO}_2^{2+}$  itself changes into

hydrolysed species such as  $\text{UO}_2(\text{OH})_2(\text{aq})$  and  $(\text{UO}_2)_3(\text{OH})_5^+$ . Titration curves should be analysed with considering these reactions. Thus, this review does not accept this species as reasonable.

#### [65SEK4]

The complex formation of radioactive tracers of La(III), Eu(III), Lu(III) and Am(III) with oxalate in 1 M  $\text{Na}(\text{ClO}_4)$ ,  $-\log_{10}[\text{H}^+] = 3 \sim 4$ , at  $25^\circ\text{C}$  was studied by a distribution method using TTA and TBP or methylisobutylketone. The plots of  $\log_{10}(D_0/D)$  vs.  $\log_{10}[\text{ox}^{2-}]$  were analyzed by using the relationship,  $D_0/D = 1 + \beta_1[\text{ox}^{2-}] + \beta_2[\text{ox}^{2-}]^2 + \beta_3[\text{ox}^{2-}]^3$ , where  $\log_{10}K_{(\text{H})} = (3.54 \pm 0.01)$ , and  $\sim 1.0$  (determined at  $I = 1$  M  $\text{NaClO}_4$  by the author) were used to estimate  $[\text{ox}^{2-}]$ . Stability constants determined for Am(III) are  $\log_{10} \beta_1 = (4.63 \pm 0.08)$ ,  $\log_{10} \beta_2 = (8.35 \pm 0.09)$ ,  $\log_{10} \beta_3 = (11.15 \pm 0.07)$ . The measurement for equilibrium  $-\log_{10}[\text{H}^+]$  is not described in the paper. If the pH meter with usual glass electrode was used, the precipitation of  $\text{KClO}_4$  at the interface and the conversion of pH to  $-\log_{10}[\text{H}^+]$  may be a problem. However, since  $\log_{10}K_{(\text{H})} = (3.54 \pm 0.01)$  at  $I = 1$  M  $\text{NaClO}_4$  agrees well with the value selected in this review, this review considers the errors in  $\log_{10} \beta$  from the measurement of  $-\log_{10}[\text{H}^+]$  do not exceed 0.05. This review takes the reported values with the assigned uncertainty of 0.2 for  $\log_{10} \beta_1$  and  $\log_{10} \beta_2$  and 0.4 for  $\log_{10} \beta_3$ .

#### [65STE/MAK]

The complex formation of Am(III) with oxalate was investigated by an electromigration method at  $25^\circ\text{C}$ . The pH and the ionic strength were maintained at 1.5 and 0.1 M, respectively, by adding HCl and  $\text{NH}_4\text{Cl}$  except in the cases where the concentration of  $\text{ox}^{2-}$  is higher than  $10^{-3}$  M ( $\text{pH} = 1.8 - 3.6$  and  $I = 0.15$  and  $0.3$  M). Total mobility of Am(III),  $u_c$ , was measured as a function of  $[\text{ox}^{2-}]$ ,

$$u_c = \frac{u_k + \sum u_i \beta_i [\text{ox}^{2-}]^i}{1 + \sum \beta_i [\text{ox}^{2-}]^i}$$

where  $u_k$  is the mobility of  $\text{Am}^{3+}$ ,  $u_1$  and  $u_2$  are those of  $\text{Am}(\text{ox})^+$  and  $\text{Am}(\text{ox})_2^-$  and  $\beta_1$  and  $\beta_2$  are the overall formation constants of  $\text{Am}(\text{ox})^+$  and  $\text{Am}(\text{ox})_2^-$ . Protonation constants of oxalate,  $\log_{10}K_{1(\text{H})} = 4.27$  ([39HAR/FAL]) and  $\log_{10}K_{2(\text{H})} = 1.32$  ([39PAR/NIC], [39PAR/GIB]) used to estimate the concentration of dissociated species of oxalic acid are fairly different from those selected in this review. Neither the pH scale is mentioned nor the calibration method of the pH meter is reported. Prior to the determination of the stability constants of the complexes,  $u_k$ ,  $u_1$  and  $u_2$  were determined under the condition of the predominance of single species. By using these values, the overall formation constants were determined to be  $\log_{10} \beta_1 = (6.15 \pm 0.16)$  for  $\text{Am}^{3+} + \text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})^+$  and  $\log_{10} \beta_2 = (10.54 \pm 0.19)$  for  $\text{Am}^{3+} + 2\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_2^-$ .  $u_2$  was determined from the measured mobility at  $[\text{ox}^{2-}] > 10^{-3}$  M. However, under this condition, the ionic strength exceeds 0.1 M where  $[\text{Hox}^-]$  exceeds 0.09 M and significantly contributes to the total ionic strength. In a similar manner, the contribution of  $[\text{Hox}^-]$  and  $[\text{ox}^{2-}]$  to the

composition of the ionic medium is not negligible in the whole experiment. This change in the ionic medium may give serious effects on the mobility of each species. Because of the uncertainty in the values and in the constancy of  $u_k$ ,  $u_1$  and  $u_2$ , the results of this paper are not considered in this review.

#### [\[65STE/MAK2\]](#)

In this work, the Pu(III) edta system was investigated by an electromigration method at 25°C in the pH range 1.1 – 3.5. The complexation of Pu(III) with Na<sub>2</sub>H<sub>2</sub>edta was conducted in HCl medium in the presence of 0.01 M NH<sub>2</sub>OH·HCl. The amount of plutonium did not exceed 10<sup>-7</sup> M. The ionic strength of the solution was kept constant and equal to 0.1 by adding calculated amounts of KCl.

The edta protonation constants used in the derivation of stability constants are not given. The experimental results are given in tabular form, which in principle allows a re-evaluation of the stability constants. However, no details about the pH measurements are given. Neither the pH scale is mentioned nor the calibration method of the pH meter is reported. This precludes any reliable recalculation. The results of Stepanov and Makarova are not considered further in this review.

#### [\[65TAT/GRZ\]](#)

Potentiometric titration in the Mg citrate system has been conducted at 25°C and  $I = 0.1$  M (CH<sub>3</sub>)<sub>4</sub>NCl. By using protonation constants ( $\log_{10} K_{(H)} = 5.84, 4.36$  and  $2.88$ ) obtained in this study, the stability constants were obtained to be  $\log_{10} \beta_{1(cit)} = 3.73$  for  $Mg^{2+} + cit^{3-} \rightleftharpoons Mg(cit)^-$  and  $\log_{10} \beta_{1(Hcit)} = 1.85$  for  $Mg^{2+} + Hcit^{2-} \rightleftharpoons Mg(Hcit)(aq)$ . The pH meter was standardised with 0.05 M potassium hydrogen phthalate (pH 4.005) and 0.01 M borax (pH 9.18), and the mean activity coefficient of 0.1 M HCl was used to convert the measured pH to  $-\log_{10} [H^+]$ . This review accepts the above values with an estimated uncertainty of  $\pm 0.2$ .

#### [\[65WRI/HOL\]](#)

The heat of reaction of edta and other polyaminocarboxylate ligands with Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> has been determined calorimetrically at 25°C in a salt medium of 0.1 M KNO<sub>3</sub>. However, considering the concentrations of the used ligand solutions (0.671 M, or 0.964 M for “some of the edta solutions”) and metal solutions (0.04 M), the effective ionic strength changed during the complex formation from 0.70 to 0.32 M (or from 0.74 to 0.34 M for “some of the edta solutions”).

The formation constants for the Mg- and Ca-edta complexes listed in [\[65WRI/HOL\]](#) were all taken from the literature [\[54CHA2\]](#), [\[56CAR/STA\]](#), [\[63AND\]](#). The enthalpy value for Ni-edta complexation derived from measurements of [\[65WRI/HOL\]](#) is not accepted by this review considering the large change in effective ionic strength during the experiments.

[\[65ZAI/BOC\]](#)

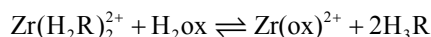
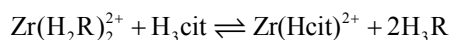
To obtain information about the polymerisation of zirconium in solution, solid compounds including various ratios of  $\text{ZrOCl}_2$  unit and oxalic acid were prepared and their structures were discussed. The solid known as  $\text{ZrOCl}_2$  actually contains the tetrameric cyclic unit  $[\text{Zr}_4(\text{OH})_8(\text{OH}_2)_{16}]^{8+}$ , where all zirconium pairs are  $\mu$ -bridged by two hydroxyl groups. Thus, in this tetrameric cyclic unit, one zirconium is coordinated by four  $\text{H}_2\text{O}$  and four OH, among which two OH are bound the neighbouring zirconium. This polymeric unit is considered to be present in the solution containing  $>10^{-4}$  M zirconium and pH above around 1. To see the effect of oxalate, the solid compounds containing various amount of oxalate were prepared and their elemental compositions were analysed. On the whole, the oxalate group is bound to the zirconium ring and does not break the tetrameric structure. The relevance to the solution species is indirect and the result cannot be used to discuss the species of zirconium at lower concentrations. No information about the stability constants is given.

[\[66ERM/MAR\]](#)

The reaction of zirconium and hafnium with edta has been studied at  $[\text{H}^+] = 2, 1$  and  $0.23$  M by an ion-exchange method. According to Table 7 in [\[66ERM/MAR\]](#)  $\text{HClO}_4$  has been used. The authors assume that under their experimental conditions,  $\text{H}_4\text{edta}(\text{aq})$  exists predominantly in the undissociated form and reacts with zirconium by displacing four hydrogen ions. This is in obvious contrast with the fact, reconfirmed in this review, that  $\text{H}_5\text{edta}^+$  and  $\text{H}_6\text{edta}^{2+}$  are mainly present in strongly acidic solutions (see Figure VIII-13). The edta protonation constants used in their data evaluation are not given in [\[66ERM/MAR\]](#). Furthermore,  $K_d^\circ$ , the distribution constant in the absence of the complexone, is not reported, and the table headings in [\[66ERM/MAR\]](#) give rise to some uncertainty concerning the  $[\text{H}^+]$  concentration. Thus, the constants reported in [\[66ERM/MAR\]](#) are discarded in this review, and there seems to be no chance to successfully re-evaluate the experimental data.

[\[66KOR/SHE2\]](#)

This paper uses the metal indicator method. The competition reactions:



in  $1$  N  $\text{HCl}$  were used to estimate the stability constant of  $\text{Zr}(\text{Hcit})^{2+}$  and  $\text{Zr}(\text{ox})^{2+}$ , where  $\text{H}_3\text{R}$  is an azo-dye (3,4-dihydroxyazobenzene-2'-carboxylic acid) which forms a colored complex  $\text{Zr}(\text{H}_2\text{R})_2^{2+}$  (absorption maximum at  $520$  nm) whose stability constant is  $1.2 \times 10^8$  (for the reaction  $\text{Zr}^{4+} + 2\text{H}_3\text{R} \rightleftharpoons \text{Zr}(\text{H}_2\text{R})_2^{2+} + 2\text{H}^+$ , where  $\text{H}_3\text{R}$  deprotonates with  $K_a = 7.5 \times 10^{-4}$ ). The formation of  $\text{Zr}(\text{Hcit})^{2+}$  and  $\text{Zr}(\text{ox})^{2+}$  was proposed from the pH independency of these reactions between pH 0 and 0.16. The absorbances of the solutions containing  $C_{\text{H}_3\text{R}} = 3 \times 10^{-4}$  M,  $C_{\text{Zr}} = 1.1 \times 10^{-5}$  M and  $C_{\text{H}_3\text{cit}} = (0.2 \sim 1.1) \times 10^{-5}$

M or  $C_{\text{ox}} = (0.55 \sim 2.2) \times 10^{-5}$  M were measured and analysed. The values of  $\beta_1 = (6.0 \pm 0.5) \times 10^{10}$  for the reaction  $\text{Zr}^{4+} + \text{Hcit}^{2-} \rightleftharpoons \text{Zr}(\text{Hcit})^{2+}$  and  $\beta_1 = (1.8 \pm 0.2) \times 10^{10}$  for the reaction  $\text{Zr}^{4+} + \text{ox}^{2-} \rightleftharpoons \text{Zr}(\text{ox})^{2+}$  are given.

For the calculations of  $[\text{Hcit}^{2-}]$  and  $[\text{ox}^{2-}]$ , the protonation constants for citrate and oxalate are necessary but not given in the paper and the results given in Table 2 of [66KOR/SHE2] could not be traced. Moreover, in this method, the stability constants of citrate and oxalate complexes estimated are dependent on the stability constant of the azo-dye complex. The paper does not discuss the reliability of the stability constant of the azo-dye complex. Since the stability is very high, this value itself may be uncertain. The reported values are not considered by the present review.

#### [66KUL/REE]

The main topic of this study was a nuclear magnetic resonance investigation of ligand exchange kinetics in the Ca-edta system. In addition, the Ca-edta system has been investigated using potentiometric techniques. The only information given concerning these potentiometric measurements is the statement, that the pH meter has been standardised with two buffer solutions. No experimental results and no further details about experimental conditions or the evaluation of the final results can be found in [66KUL/REE]. In view of all these shortcomings the stability constants reported in this study have not been considered further in this review.

#### [66LAP/PAN]

The reaction of  $\text{ZrO}(\text{ClO}_4)_2$  with nta, edta and dtpa has been studied photometrically at pH 2 in 0.01 M  $\text{HClO}_4$ . In all cases a zirconium to complexon ratio of 1:1 has been used. Nevertheless, in the case of edta [66LAP/PAN] interpret their results solely in terms of a 1:2 complex and report a stability constant of  $\log_{10}\beta_2 = (7.9 \pm 0.1)$  for  $\text{Zr}^{4+} + 2 \text{edta}^{4-} \rightleftharpoons \text{Zr}(\text{edta})_2^{4-}$ . This value is orders of magnitude at variance with all values reported for Zr-edta complexes. The results of [66LAP/PAN] have been discarded in this review.

#### [66NEB]

Complex formation of  $\text{Pu}^{4+}$  citrate was studied at pH = 0.5,  $I = 0.5$  ( $\text{NaClO}_4$ ),  $t = 25^\circ\text{C}$ . The absence of Pu(III) and Pu(VI) was confirmed by measuring the spectra of Pu(III), Pu(IV) and Pu(VI) in the absence and presence of citric acid. The species showing a spectrum with a characteristic peak at 475 nm was assigned to free  $\text{Pu}^{4+}$  ion, at 482 nm to  $\text{Pu}(\text{cit})^+$ , at 444 and 496 nm to  $\text{Pu}(\text{cit})_2^{2-}$ . Then the absorbances at 444, 490, 496 and 500 nm were analysed to obtain the stability constants. The stability constants were calculated in two different ways. The first one is to use equation (A.53):

$$\beta_{n(\text{cit})} = \frac{[\text{Pu}(\text{cit})_n]^{4-3n}}{[\text{Pu}^{4+}][\text{cit}^{3-}]^n} = \frac{E/\varepsilon_{\text{Pu}(\text{cit})_n}}{(C_{\text{Pu}} - E/\varepsilon_{\text{Pu}(\text{cit})_n})[\text{cit}^{3-}]^n}, \quad (\text{A.53})$$

where  $E$  is the absorbance and  $\varepsilon_{\text{Pu}(\text{cit})_n}$  is the molar absorption coefficient of

$\text{Pu}(\text{cit})_n^{4-3n}$  at a certain wavelength. This equation is not valid since the absorbance of free metal ion,  $\text{Pu}^{4+}$ , cannot be neglected at the measured wavelength. Another way is to use equation (A.54):

$$\Delta\bar{\varepsilon} = \frac{\Delta\varepsilon_{\text{Pu}(\text{cit})} \beta_1(\text{cit}) [\text{cit}^{3-}] + \Delta\varepsilon_{\text{Pu}(\text{cit})_2} \beta_2(\text{cit}) [\text{cit}^{3-}]^2}{1 + \beta_1(\text{cit}) [\text{cit}^{3-}] + \beta_2(\text{cit}) [\text{cit}^{3-}]^2}, \quad (\text{A.54})$$

where  $\Delta\bar{\varepsilon} = \bar{\varepsilon} - \varepsilon_{\text{Pu}}$ ,  $\Delta\varepsilon_{\text{Pu}(\text{cit})} = \varepsilon_{\text{Pu}(\text{cit})} - \varepsilon_{\text{Pu}}$  and  $\Delta\varepsilon_{\text{Pu}(\text{cit})_2} = \varepsilon_{\text{Pu}(\text{cit})_2} - \varepsilon_{\text{Pu}}$ . The extrapolations  $[\text{cit}^{3-}] \rightarrow 0$  and  $1/[\text{cit}^{3-}] \rightarrow 0$  were conducted to obtain  $\beta_{1(\text{cit})}$  and  $\beta_{2(\text{cit})}/\beta_{1(\text{cit})}$ , and the values of  $\log_{10} \beta_{1(\text{cit})} = 15.43$  and  $\log_{10} \beta_{2(\text{cit})} = 29.84$  were reported. Significant uncertainties are considered to be propagated from the estimation of  $[\text{cit}^{3-}]$ . This free ligand concentration was calculated by using the relations:

$$\begin{aligned} [\text{cit}^{3-}] &= C'_{\text{H}_3\text{cit}} \alpha_{\text{cit}} = (C_{\text{H}_3\text{cit}} - n[\text{Pu}(\text{cit})_n^{4-3n}]) \alpha_{\text{cit}}, \\ \text{and} \quad \alpha_{\text{L}} &= \frac{[\text{cit}^{3-}]}{[\text{H}_3\text{cit}] + [\text{H}_2\text{cit}^-] + [\text{Hcit}^{2-}] + [\text{cit}^{3-}]} = \frac{1}{K_{1(\text{H})} K_{2(\text{H})} K_{3(\text{H})} [\text{H}^+]^3}, \end{aligned}$$

where  $K_{1(\text{H})}$ ,  $K_{2(\text{H})}$  and  $K_{3(\text{H})}$  are the stepwise protonation constants of citrate. To avoid the errors introduced by those in  $K_{1(\text{H})}$ ,  $K_{2(\text{H})}$ , and  $K_{3(\text{H})}$  and pH, this review calculated the conditional stability constants,  $\log_{10} {}^*\beta_1'$  and  $\log_{10} {}^*\beta_2'$ , at the measured pH (= 0.5) from the reported  $\log_{10} \beta_{1(\text{cit})}$  and  $\log_{10} \beta_{2(\text{cit})}$ :

$${}^*\beta_1' = \frac{[\text{Pu}(\text{cit})_n^{4-3n}]}{[\text{Pu}^{4+}](C'_{\text{H}_3\text{cit}})^n} = \frac{\beta_n(\text{cit})}{(K_{1(\text{H})} \cdot K_{2(\text{H})} \cdot K_{3(\text{H})} \cdot [\text{H}^+]^3)^n}.$$

By using  $\log_{10} K_{1(\text{H})} = 5.49$ ,  $\log_{10} K_{2(\text{H})} = 4.39$  and  $\log_{10} K_{3(\text{H})} = 3.08$  reported in [66NEB],  $\log_{10} {}^*\beta_1'$  and  $\log_{10} {}^*\beta_2'$  were calculated to be 3.97 and 6.92, respectively at pH = 0.5. These values mean that  $(C'_{\text{H}_3\text{cit}})$  is less than  $10^{-4}$  M when  $C_{\text{H}_3\text{cit}}/C_{\text{Pu}} < 2$  ( $C_{\text{Pu}} = 5.3 \times 10^{-3}$  M). The calculation of  $C'_{\text{H}_3\text{cit}} = C_{\text{H}_3\text{cit}} - n[\text{Pu}(\text{cit})_n^{4-3n}]$  easily introduces a large error ( $|\Delta \log_{10} C'_{\text{H}_3\text{cit}}| \leq 1$ ), and it propagates to  $|\Delta \log_{10} {}^*\beta_n'| = n |\Delta \log_{10} C'_{\text{H}_3\text{cit}}| \leq n$ . Another problem in this paper is the complex speciation. Although the author claimed that the ligand species was confirmed to be  $\text{cit}^{3-}$  (not  $\text{Hcit}^{2-}$  nor  $\text{H}_2\text{cit}^-$ ) by changing pH at a constant citric acid concentration, the experimental details were not reported. Since the pH range studied is considered very limited, the possibility of  $\text{Pu}(\text{Hcit})^{2+}$  and  $\text{Pu}(\text{Hcit})_2(\text{aq})$  formation cannot be excluded according to the study [96CHO/ERT] on the citrate complexation of chemically analogous  $\text{Th}^{4+}$ .

Thus, this review does not accept the results of this paper.



[\[66NEB2\]](#)

Potentiometric titration of the mixture of 0.17 M H<sub>3</sub>cit, 0.33 M HClO<sub>4</sub> and  $2 \times 10^{-2}$  M Pu(IV) was conducted at  $I = 0.5$  M (Na,H)ClO<sub>4</sub> and 25°C. For the analysis, the author used citrate protonation constants of 6.38, 4.78 and 3.16, which are significantly different from those (5.49, 4.39 and 3.08) used in his previous paper [\[66NEB/URB\]](#), and from those (5.294, 4.148, 2.810) selected in this review. Simulation of the titration with the former protonation constants and the reported constants for  $\text{Pu}^{4+} + \text{cit}^{3-} \rightleftharpoons \text{Pu}(\text{cit})^+$  ( $\log_{10} \beta_{1(\text{cit})} = 15.8$ ) and  $\text{Pu}^{4+} + 2 \text{cit}^{3-} \rightleftharpoons \text{Pu}(\text{cit})_2^{2-}$  ( $\log_{10} \beta_{2(\text{cit})} = 29.0$ ) indicates that the predominant species changes from  $\text{Pu}(\text{cit})^+$  to  $\text{Pu}(\text{cit})_2^{2-}$  in the titration procedure. When the latter protonation constants are used with the reported stability constants,  $\text{Pu}(\text{cit})_2^{2-}$  predominates throughout the titration. In any case, free  $\text{Pu}^{4+}$  ion cannot be predominant throughout the titration procedure. This means that meaningful values of the stability constants cannot be extracted from the experimental data. The reported values are not accepted by the present review.

[\[66NEB/URB\]](#)

Potentiometric titrations of the Th(IV) and U(IV) citrate systems have been carried out and the formation curves:

$$\bar{n} = \frac{\beta_1[\text{cit}^{3-}] + 2\beta_2[\text{cit}^{3-}]^2}{1 + \beta_1[\text{cit}^{3-}] + \beta_2[\text{cit}^{3-}]^2}$$

were constructed to obtain the stability constants. For Th(IV), Th<sup>4+</sup> solution in 0.5 M HNO<sub>3</sub> with Na<sub>3</sub>cit was titrated with NaOH. In the presence of citrate, no precipitation occurred until pH 11 suggesting a strong complex formation. From the analysis of the formation curve, the stability constants were calculated to be  $\beta_1 = 1 \times 10^{13}$  and  $\beta_2 = 9.5 \times 10^{20}$ . From the similar titration of U(IV) (details are not given), the stability constants were calculated to be  $\beta_1 = 3.4 \times 10^{11}$  and  $\beta_2 = 2.9 \times 10^{19}$ .

Although this study demonstrates that U(IV)-citrate and Th(IV)-citrate complexes are formed in acidic solutions and remain stable at higher pH, the stoichiometry of the complex(es) is not well established. The formation curves for Th-citrates and U-citrates given in Figures 7 and 8 in [\[66NEB/URB\]](#) show that  $\bar{n}$  changes gradually with  $\log_{10}[\text{cit}^{3-}]$  giving no constant region of  $\bar{n}$ . These formation curves cannot be reproduced by using the reported stability constants. Therefore, this review does not accept the reported values.

[\[66STA\]](#)

The complex formation of americium and promethium with edta and oxalate has been investigated at ionic strength 0.1 M NH<sub>4</sub>Cl and 20°C by a solvent extraction method. A solution of thenoyltrifluoroacetone in benzene was used as the organic reagent forming extractable complex compounds.

For the study of edta complexation, the experimental conditions of the aqueous solutions were a pH range between 3.78 and 5.59, and the values  $\log_{10} K_1 = (16.91 \pm 0.04)$  for  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$ , and  $\log_{10} K_1 = (16.94 \pm 0.04)$  for  $\text{Pm}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Pm}(\text{edta})^-$  were obtained.

Starý reports that “we measured the equilibrium pH with a pH-meter, RNM-36 radiometer (Copenhagen)”. This is all the information about pH measurements; the meaning of “pH” in the tables [66STA] remains open (proton activity or  $-\log_{10}[\text{H}^+]$ ), as the calibration of the pH meter is not described. Because of the low total edta concentration (0.001 – 0.002 M) its contribution to  $I$  is lower than 0.007. So, although an increase of the ionic strength to  $I = 0.106$  is possible, this small effect can be neglected. In Table 3 of [66STA] the total edta concentration is given, but the edta protonation constants used to obtain the reported stability constants are not given.

A re-evaluation of Starý’s experimental data in this review gave the following results: If we assume that “pH” in the tables of [66STA] actually means  $-\log_{10}[\text{H}^+]$ , and the edta protonation constants of [47SCH/ACK] are used (valid for  $I = 0.1$  M KCl and  $20^\circ\text{C}$ ) then the results reported in [66STA] can exactly be reproduced, *i.e.*, the extraction constant for Am ( $\log_{10} K = -(7.48 \pm 0.03)$ , Table 1 in [66STA]) and  $\log_{10} K_1 = (16.91 \pm 0.04)$  for the  $\text{Am}(\text{edta})^-$  complex mentioned above. Obviously this had been the calculation scheme used by Starý.

If we use the edta protonation constants selected in this review for  $I = 0.1$  M KCl and  $20^\circ\text{C}$  (Tables VIII-8-a and VIII-8-b) then the constant  $\log_{10} K_1 = (16.75 \pm 0.06)$  for the  $\text{Am}(\text{edta})^-$  complex is obtained. If we assume that “pH” in [66STA] actually refers to proton activity, and the values are corrected to the concentration scale, pcH, with  $\text{pcH} = \text{pH} - 0.097$  using the SIT equation and parameters for  $I = 0.1$  M  $\text{NH}_4\text{Cl}$  and  $20^\circ\text{C}$ , then the Am extraction constant  $\log_{10} K = -(7.19 \pm 0.03)$  and the constant  $\log_{10} K_1 = (16.94 \pm 0.06)$  for the  $\text{Am}(\text{edta})^-$  complex are obtained.

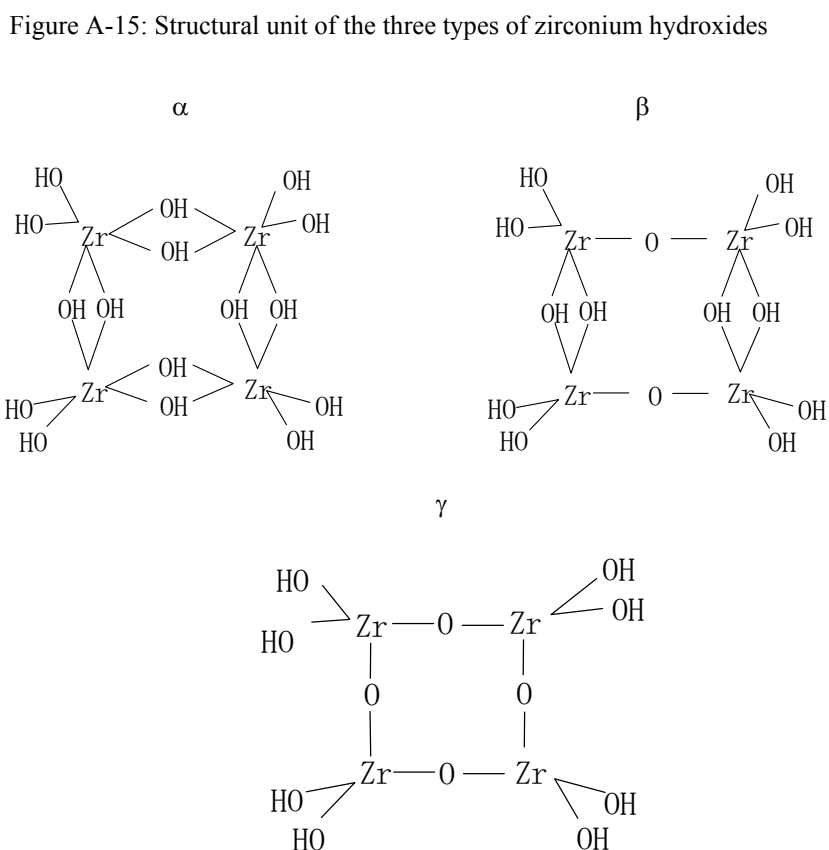
As it is not clear which variant is the correct one, but otherwise the study of Starý is reliable, this review accepts a mean value  $\log_{10} K_1 = (16.85 \pm 0.20)$  with an increased uncertainty to account for this ambiguity concerning the pH scale. Due to the use of edta protonation constants for KCl this stability constant has to be corrected for complexation effects of  $\text{Kedta}^{3-}$  (assuming that the effects of  $\text{NH}_4^+$  are comparable with  $\text{K}^+$ ). The correction term for  $I = 0.1$  M KCl and  $20^\circ\text{C}$  (Table VIII-8-a) is  $(0.285 \pm 0.170)$ . Finally, the temperature correction from 20 to  $25^\circ\text{C}$  (see Section VIII.13.3) is  $-(0.055 \pm 0.006)$ . This gives the final result accepted in this review:  $\log_{10} K_1 = (16.85 \pm 0.20) + (0.285 \pm 0.170) - (0.055 \pm 0.006) = (17.08 \pm 0.27)$ .

For oxalate complexation, the values  $\log_{10} \beta_2 = 8.3$  for  $\text{Am}^{3+} + 2\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_2^-$ , and  $\log_{10} \beta_3 = 11.8$  for  $\text{Am}^{3+} + 3\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_3^{3-}$  were obtained. However, the re-evaluation cannot be carried out since the experimental result is shown only in the form of  $\log_{10}[(D_0/D) - 1]$  against  $\log_{10}[\text{ox}^{2-}]$  and the total concentration of oxalic acid and the pH range are not given. Considering the ambiguity concerning the pH scale

and the protonation constants of oxalate, this review does not consider the values of the stability constants of oxalates reported in this paper.

**[66ZAI2]**

Three types of zirconium hydroxides have been prepared by (a) getting freshly prepared precipitate, (b) getting precipitate from concentrated “zirconyl chloride” in methanol, and (c) ageing for a long time by boiling the precipitate. By titrating the precipitate in the presence of fluoride and observing the infrared spectra, each precipitate was shown to have the structural unit as follows in Figure A-15.



Reactions with carbonate, chloride, sulphate and oxalate were examined by mixing the solution with the precipitate and checking the structure of the re-obtained precipitate from alcoholic solution by diethyl ether. The result indicated that (1) the reactivity of the hydroxide decreases in the order  $\alpha \rightarrow \beta \rightarrow \gamma$ , (2) the  $\beta$ -ring is the most stable, (3) neutral and acid salts, and small quantities of acids generally do not alter the nature of the fundamental ring of the hydroxide, and (4) reagents which are stronger complex-forming agents and give more covalent bonding with zirconium such as oxalate produce greater changes in the original hydroxide ring, leading to an increase in its stability. Thus oxalate brings about an increase in the stability of the ring converting the  $\alpha$ -ring into  $\beta$ - or  $\gamma$ -ring. At a ratio of oxalate to zirconium of 0.6 to 0.8, the reaction of zirconium hydroxides with oxalate was shown to always give the same product:  $[\text{Zr}(\text{OH})_2]_4\text{O}_2(\text{ox})_2 \cdot \text{H}_2\text{O}$ , where four peripheral hydroxides are replaced by two oxalates in the  $\beta$  structure. Increasing the oxalic acid to 1.1 - 1.5 mol alters the reaction to give the product with composition  $[\text{ZrO}(\text{ox})]_4 \cdot n\text{H}_2\text{O}$ , where eight peripheral hydroxides are replaced by four oxalates in the  $\alpha$  structure. This paper is considered to be reliable giving qualitative but good information about the chemical species of zirconium oxalates at higher pH and at higher concentrations of zirconium.

#### [\[67ABR\]](#)

The author reports the solubility of plutonium(IV) oxalate precipitated in 0.6-5.3 M  $\text{HNO}_3$ . Oxalate ions were generated homogeneously by hydrolysing dimethyl oxalate at  $60^\circ\text{C}$  for one hour. The solid Pu(IV) oxalate formed was allowed to equilibrate at room temperature for 18 hours. The author mentions that the excess oxalate ion was calculated from the amount of dimethyl oxalate, the total volume, the amount of plutonium and the acidity. In the tables the author reports the final concentrations of plutonium and of  $\text{H}^+$  as well as the excess  $[\text{ox}^{2-}]$ . However the paper does not mention which protonation constants and ionic strength corrections were used to calculate the oxalate concentration, which at these high acidities should be a minor species compared with  $\text{H}_2\text{ox}(\text{aq})$  (and  $\text{Hox}^-$ ). Because of this the solubility data reported in this paper is not considered by this review.

#### [\[67BUD/HAA\]](#)

As a by-product of this spectrophotometric study the stability constant of  $\text{Zr}(\text{edta})(\text{aq})$  has been obtained from spectra at 535 nm at  $\text{pH} = 0.5$  (Table 2 in [\[67BUD/HAA\]](#)). However, in the text [\[67BUD/HAA\]](#) report  $\log_{10}K_1 = (31.9 \pm 0.2)$  “for the ionic strength 0.8 N (hydrochloric acid)”. This last number would correspond to  $\text{pH} = 0.1$ , in contradiction to the value given in the table. Furthermore, for the calculation of  $[\text{edta}^{4-}]$  the authors used edta protonation constants determined by Beck and Görög [\[60BEC/GOR\]](#), which have been discarded in this review.

#### [\[67BUR/POR\]](#)

The solubility of Am(III) oxalate in the mixture of nitric acid (0.1 ~ 4.0 M) and oxalic

acid (0.02 ~ 0.7 M) were measured. In 0.1 and 0.25 M HNO<sub>3</sub> solutions, the solubility decreases initially (at 0.1 M HNO<sub>3</sub>, from 0.8 mg·L<sup>-1</sup> at C<sub>ox</sub> = 0.02 M to 0.7 mg·L<sup>-1</sup> at C<sub>ox</sub> = 0.02 M) and then slightly increases at higher oxalic acid concentrations (to 1.5 mg·L<sup>-1</sup> at C<sub>ox</sub> = 0.4 M) due to the formation of oxalate complexes. This effect is not noted at higher nitric acid concentrations, that is, in 1 M HNO<sub>3</sub> the solubility decreases from 300 mg·L<sup>-1</sup> at C<sub>ox</sub> = 0.03 M to 8 mg·L<sup>-1</sup> at C<sub>ox</sub> = 0.5 M. Although the solubility of Am(III) oxalate in the mixture of nitric acid and oxalic acid given in Fig. 2 of the paper gives a rough estimate of the solubility of Am(III) oxalate, the analysis of the data to obtain a solubility product was not carried out in this paper.

#### [67CAR/MAR]

Potentiometric studies are described for mixed ligand U(IV) chelate formation with edta and nta (nitrilotriacetic acid) as primary ligands. Secondary ligands studied are salicylic acid, 5-sulfosalicylic acid, disodium 1,2-dihydroxybenzene-3,5-disulfonate (tiron), pyrocatechol, 5-sulfo-8-hydroxyquinoline, disodium 1,8-dihydroxynaphthalene-3,6-disulfonate, *o*-phthalate and iminodiacetic acid. The solutions containing the needed quantity of UCl<sub>4</sub> in presence of an excess of HCl, Na<sub>2</sub>H<sub>2</sub>edta and the secondary ligand at *I* = 0.1 M KCl at 25.3°C were titrated with a standard solution of NaOH. The protonation constants used for the secondary ligands are not reported by the authors. The values are given in Table VIII-31 for comparison only; they are not further evaluated in this review.

#### [67CHR/IZA]

A thermometric titration calorimeter was used in this study to measure the very small  $\Delta_r H_m^\circ$  values associated with oxalate protonation equilibria. Solutions of the sodium salt of oxalic acid were titrated with HClO<sub>4</sub> solutions at 25°C. Four thermometric titrations were made in each of two ionic strength regions (*I* approximately 0.01 to 0.02 M and 0.05 to 0.06 M). The  $\Delta_r H_m^\circ$  values obtained showed no significant variation with ionic strength. Therefore, all values were averaged to obtain the final  $\Delta_r H_m^\circ$  values and only these final values were reported by [67CHR/IZA]. The results are given as dissociation enthalpies in Table II of [67CHR/IZA],  $-(1.50 \pm 0.05)$  kcal·mol<sup>-1</sup> corresponding to  $\Delta_r H_m^\circ(1) = +(6.3 \pm 0.4)$  kJ·mol<sup>-1</sup>, and  $-(1.02 \pm 0.05)$  kcal·mol<sup>-1</sup> corresponding to  $\Delta_r H_m^\circ(2) = +(4.3 \pm 0.4)$  kJ·mol<sup>-1</sup> for the first and second protonation of oxalate, respectively (the uncertainties have been multiplied by 1.96 to obtain error limits closer to 95% total uncertainty level). These values, measured at varying but very low ionic strength and claimed to be representative for zero ionic strength, are listed in Table VI-7 with further increased uncertainties to account for this ambiguity.

#### [67ERM/KRO2]

The disproportionation of Pu(V) into Pu(IV) and Pu(VI) in oxalate solutions was studied indirectly by measuring spectrophotometrically ( $\lambda = 676$  μm) the amount of Pu(IV) formed as a function of time. The further reduction of Pu(VI) by oxalate was assumed

to be slow and neglected. The rate of disproportionation was studied in 0.025 to 0.25 M  $(\text{NH}_4)_2\text{ox}$  solutions, pH between 0.3 and 4.15. No details are given on the calibration of the glass electrode. According to the procedure described in the paper, the initial Pu(V) concentration was 0.8 to 1.7 mM. Some experiments were performed in the temperature range 20 to 50°C. The time scale for the reaction was in the order of minutes to a few hours.

Six parameters were fitted to the experimental data: the kinetic and equilibrium constants for  $\text{PuO}_2\text{Hox}(\text{aq})$ ,  $\text{PuO}_2\text{ox}^-$  and  $\text{PuO}_2(\text{ox})_2^{3-}$ . The rates of disproportionation were determined in 0.062 and 0.123 M  $(\text{NH}_4)_2\text{ox}$  solutions (ionic strength  $\approx 0.1$  and 0.2 M, according to the authors), pH  $\approx 0$  to 4, and 25°C. The authors used the Davies equation to estimate activity coefficients, but no details are given about how these corrections were applied. The reported equilibrium constants are not credited by this review because of the uncertainties in the activity coefficients and in the assumptions concerning the speciation of the different redox states of plutonium.

#### [\[67HAS/MAK\]](#)

The complex formation of calcium and strontium with sulphate and oxalate ions has been studied in 1 M  $\text{NaClO}_4$  at  $(25.0 \pm 0.5)^\circ\text{C}$  by a liquid-liquid distribution method. Methylisobutylketone (MIBK) containing 0.1 M thenoyltrifluoroacetone (TTA) was used as the organic phase for the calcium systems, and the aqueous phase was buffered with a small amount of acetate or triethanol amine (initial concentration 0.01 M). The metal ions were used in tracer concentrations, in the case of Ca the aqueous phase was prepared to contain  $3 \times 10^{-7}$  M  $^{45}\text{Ca}$ . The distribution ratio without ligands was measured in the range  $-\log_{10}[\text{H}^+]$  5 to 7, and the distribution ratio with oxalate ( $[\text{ox}^{2-}] 1 \times 10^{-3}$  to  $4 \times 10^{-2}$  M) was measured in the range  $-\log_{10}[\text{H}^+]$  5.3 to 6.1. The experiments seem to be reliably done, and this review accepts the derived  $\log_{10} K_1 = 1.64$  and  $\log_{10} K_2 = 1.04$ . No uncertainty analysis is given by the authors but this review assumes, in analogy with a similar study [\[76MCD/KEL\]](#), see discussion in this Appendix,  $\log_{10} K_1 = (1.64 \pm 0.20)$  and  $\log_{10} K_2 = (1.04 \pm 0.25)$ .

#### [\[67JAC/MAR\]](#)

The stability constants  $K(\text{NiLX})$  for the reaction  $\text{NiL} + \text{X} \rightleftharpoons \text{NiLX}$  are determined by spectrophotometric and pH measurements at 25°C and  $I = 0.5$  M and 1.0 M for a series of ten complexes where X is a unidentate or bidentate ligand and L is a multidentate ligand. For  $\text{Ni}(\text{edta})\text{NH}_3^{2-}$  values of  $\log_{10} K(\text{NiLX}) = (1.35 \pm 0.35)$  ( $I = 0.50$  M KCl) and  $(1.39 \pm 0.01)$  ( $I = 1.00$  M  $\text{NaClO}_4$ ) are reported. However, in Table II of [\[67JAC/MAR\]](#) concentration values for  $\text{NH}_3$  are given from 0.006 to 2.6. Considering that the ratio of ammonium chloride to ammonia varied from 9 to 1.8 in the solutions prepared by [\[67JAC/MAR\]](#), this corresponds to solutions of much higher effective ionic strengths than the values inferred from the inert salts. Thus, the reported stability constants cannot be considered as reliable.

[\[67KRO/MEF2\]](#)

In this paper Krot *et al.* report a spectrophotometric study on the reduction of Np(VI) and on the disproportionation of Np(V) in oxalate media. The authors also performed a re-analysis of the experimental data on the Np(V)-oxalate system reported in [\[53GRU/KAT\]](#). This resulted in:  $\log_{10} \beta_1 = 3.29$  and  $\log_{10} \beta_2 = 5.97$  (at room temperature and  $I = 0.5$  M (NaClO<sub>4</sub>)). In order to “verify” these results, Krot *et al.* carried out a spectrophotometric titration of a  $7 \times 10^{-4}$  M solution of Np(V) with a 0.08 M solution of (NH<sub>4</sub>)<sub>2</sub>ox at pH = 3.8, 25°C and  $I = 0.1$  M (however this review calculates that for such a solution  $I \approx 0.2$  M). The stability constants  $\log_{10} \beta_1 = 3.56$  and  $\log_{10} \beta_2 = 5.89$  were obtained from this titration.

The rate of disproportionation of neptunium(V) in the presence of oxalate was studied at 57.5°C. For the interpretation of the kinetic data the concentrations of the complexes were calculated “assuming” (Table 2 in [\[67KRO/MEF2\]](#)):  $\log_{10} \beta_1 = 3.48$  and  $\log_{10} \beta_2 = 6.02$  at  $[\text{ox}]_{\text{TOT}} = 0.074$  M,  $I = 0.23$  M (HNO<sub>3</sub>?) and at 57.5°C. It is not clear however what method was used to reach such an assumption.

Because of missing details in this paper, *e.g.*, on the measurement of pH, protonation constants of oxalate, *etc.*, the reported stability constants are not considered in this review.

[\[67KUM/SER\]](#)

A value of  $\log_{10} \beta_1$  for U(ox)<sup>2+</sup> as 9.01 at 25°C and  $I = 0.1$  from this reference is cited in [\[70MER/KUM\]](#).

[\[67LEB/MAK\]](#)

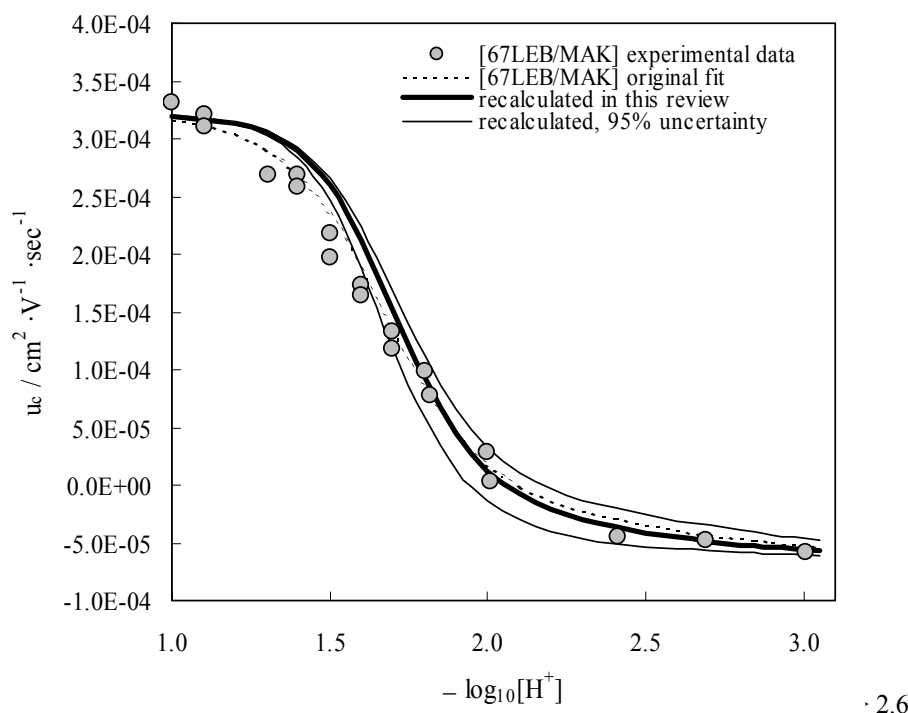
Lebedev *et al.* determined the stability constants of Am and Cm with edta by the electromigration method. The authors studied the dependence of the rate of electromigration of Am and Cm in edta solution as a function of the hydrogen ion concentration. The experiments were conducted in a somewhat modified instrument for electrophoresis on quartz powder with circulation of the electrolyte. The rate of migration was determined according to the displacement of the radioactive zone of <sup>241</sup>Am and <sup>242</sup>Cm. The required hydrogen ion concentration and the ionic strength were set with HCl and KCl. The pH measurements are not described. However, according to the consequent notation  $-\log_{10}[\text{H}^+]$  in the text and in the tables of [\[67LEB/MAK\]](#), this review assumes that proper hydrogen ion concentrations are reported in this paper. At  $(25.0 \pm 0.5)^\circ\text{C}$  in  $I = 0.1$  M KCl and total edta concentration of  $5 \cdot 10^{-4}$  M in the  $-\log_{10}[\text{H}^+]$  range 1 to 3 the authors derived  $\log_{10} K_1 = (17.00 \pm 0.05)$  for  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$  and  $\log_{10} K = (2.4 \pm 0.2)$  for  $\text{Am}(\text{edta})^- + \text{H}^+ \rightleftharpoons \text{Am}(\text{Hedta})(\text{aq})$ .

The edta protonation constants of [\[47SCH/ACK\]](#), corrected to 25°C ( $\log_{10} K_1 = 10.19$ ,  $\log_{10} K_2 = 6.11$ ,  $\log_{10} K_3 = 2.57$ ,  $\log_{10} K_4 = 1.99$ ) were used by Lebedev *et al.* in their data analysis. They ignored the species H<sub>5</sub>edta<sup>+</sup> and H<sub>6</sub>edta<sup>2+</sup> present in solutions

of  $\text{pH} < 2$ . Hence, a re-evaluation of the experimental data of [67LEB/MAK] was carried out using edta protonation constants selected in this review for  $I = 0.1 \text{ M KCl}$  and  $25^\circ\text{C}$  (Tables VIII–8–a and VIII–8–b).

This re-evaluation revealed that the experimental data [67LEB/MAK] cannot be fitted consistently over the entire pH range assuming only the two complexes  $\text{Am}(\text{edta})^-$  and  $\text{Am}(\text{Hedta})(\text{aq})$ . In the region  $-\log_{10}[\text{H}^+] > 1.7$ , where these two complexes prevail, an optimal fit gives  $\log_{10}K_1 = (17.3 \pm 0.4)$  for  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$  and  $\log_{10}K = (2.2 \pm 0.4)$  for  $\text{Am}(\text{edta})^- + \text{H}^+ \rightleftharpoons \text{Am}(\text{Hedta})(\text{aq})$  (solid lines in Figure A-16). The thick solid line in Figure A-16 represents the mean values, whereas the thin solid lines are calculated with  $\log_{10}K_1 = 17.7$  and  $\log_{10}K = 1.8$  (lower line), and with  $\log_{10}K_1 = 16.9$  and  $\log_{10}K = 2.6$  (upper line).

Figure A-16: Experimental electromigration data for the system Am – edta of Lebedev *et al.* [67LEB/MAK]. The dotted line represents the original fit of [67LEB/MAK] ignoring the species  $\text{H}_5\text{edta}^+$ . The solid lines represent recalculations using edta protonation constants selected in this review. For details see text.



would fit the experimental data, at the expense of a very bad fit of the data at  $-\log_{10}[\text{H}^+] > 1.7$ . To a certain extent this dilemma is also visible in the original fit of Lebedev *et al.* who decided for a sub-optimal fit over the entire data range (dotted line in Figure A-16). Introducing a weak complex  $\text{Am}(\text{H}_2\text{edta})^+$  would resolve this problem,



but two additional constants have to be fitted then, the stability constant and the mobility constant of the complex. Both constants are highly correlated and the numbers resulting from such a fitting exercise are almost meaningless. Hence, this review chose to fit only the data at  $-\log_{10}[\text{H}^+] > 1.7$ . Unfortunately, the experimental data in this region is scarce, especially in the most important range  $-\log_{10}[\text{H}^+] \geq 2.0$ , resulting in large uncertainties of the fitted parameters.

The stability constant  $\log_{10}K_1$  has to be corrected for complexation effects of  $\text{Kedta}^{3-}$ . The correction term for  $I = 0.1 \text{ M KCl}$  and  $25^\circ\text{C}$  (Table VIII–8–a) is  $(0.29 \pm 0.17)$ . This gives the final result accepted in this review:  $\log_{10}K_1 = (17.3 \pm 0.4) + (0.29 \pm 0.17) = (17.59 \pm 0.43)$ .

#### [\[67MAK2\]](#)

Entropy and enthalpy values for a number of equilibria, including oxalate protonation, over a wide range of temperatures have been calculated in this paper based on equilibrium values of [\[66MAK/YUS\]](#). However, the data reported by [\[66MAK/YUS\]](#) have not been considered in this review because all equilibrium constants have been determined by electric conductivity measurements in solutions of varying concentrations of reactants without using a background electrolyte. Consequently, enthalpy and entropy values calculated therefrom are not considered in this review.

#### [\[67MEF/GEL2\]](#)

This publication presents a spectrophotometric study on the complex formation between  $\text{Np(IV)}$  and oxalate at room temperature ( $\approx 20^\circ\text{C}$ ) in  $0.3 \text{ M H(ClO}_4\text{)}$  solutions. Neptunium was kept in the reduced  $\text{Np(IV)}$  state by the addition of hydrazine. The authors also synthesised and characterised the following two solids:  $\text{Na}_4\text{Np(ox)}_4 \cdot 3\text{H}_2\text{O}$  and  $\text{K}_4\text{Np(ox)}_4 \cdot 4\text{H}_2\text{O}$ .

Spectrophotometric data are presented in figures at  $\lambda = 732, 734, 736, 968$  and  $973 \text{ nm}$ , for  $[\text{Np(IV)}]_{\text{TOT}} = 2 \times 10^{-4} \text{ M}$  at oxalic acid concentrations up to  $1.5 \text{ mM}$ . Even in the presence of  $[\text{H}^+] = 0.3 \text{ M}$  oxalic acid dissociates substantially and the proton contribution from this dissociation was estimated by the authors to be  $\Delta[\text{H}^+] = [\text{Hox}^-] = K_{a_1} [\text{H}_2\text{ox}]/0.3$ . It is not clear if the same correction was applied to the oxalic acid concentrations used in the figures and in the treatment of the experimental data. The first dissociation constant of oxalic acid,  $K_{a_1}$ , used by the authors was  $0.11 \text{ M}$ , which agrees reasonably well with the value  $K_{a_1} = (0.087 \pm 0.008) \text{ M}$  obtained by this review using the SIT methodology and  $\varepsilon(\text{H}^+, \text{Hox}^-) \approx \varepsilon(\text{Li}^+, \text{Hox}^-)$ . Unfortunately, the authors did not consider that at this low acidity  $\text{Np(IV)}$  might hydrolyse. The first hydrolysis constant ( $\text{Np}^{4+} + \text{H}_2\text{O(l)} \rightleftharpoons \text{NpOH}^{3+} + \text{H}^+$ ) in  $0.3 \text{ M HClO}_4$  may be estimated using the SIT methodology and the NEA-TDB data selected in [\[2001LEM/FUG\]](#):  $\log_{10} K(\text{NpOH}^{3+}) = -(1.16 \pm 1.00)$ , i.e.,  $K(\text{NpOH}^{3+}) = (6.9 \pm 16.0) \times 10^{-2} \text{ M}$ . This indicates that the amount of  $\text{Np(IV)}$  hydrolysed in [\[67MEF/GEL2\]](#) was perhaps  $\approx 20\%$ , although there is a large uncertainty in this estimate: between  $1.5$  to  $70\%$  of the  $\text{Np(IV)}$ .

could be present as  $\text{NpOH}^{3+}$  under these conditions.

The data in Figure 3 of [67MEF/GEL2] was digitised and evaluated in this review using  $\text{H}_2\text{ox}(\text{aq})$  as the ligand with the Letagrop-Spefo software [69SIL/WAR2]. At least six parameters need to be adjusted: both an equilibrium constant and a molar absorptivity coefficient for each of:  $\text{Np}(\text{ox})^{2+}$ ,  $\text{Np}(\text{ox})_2(\text{aq})$  and  $\text{Np}(\text{ox})_3^{2-}$ . The experimental molar absorptivities shown in the figure of this publication have relatively large uncertainties, perhaps  $\pm 3\%$ , and the data becomes more inexact when reading the graphs. The complexation constants are also affected by uncertainties in the side reactions (the protonation of the ligand and the hydrolysis of  $\text{Np}(\text{IV})$ ). Nevertheless, the interpretation of the data using the reactions  $\text{Np}^{4+} + n \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Np}(\text{ox})_n^{4-2n} + 2n \text{H}^+$ , with  $n = 1$  to 3, suggest:  $\log_{10} {}^*\beta_1 = (5.5 \pm 1.5)$ ,  $\log_{10} {}^*\beta_2 = (9.5 \pm 1.0)$ , and  $\log_{10} {}^*\beta_3 = (11.7 \pm 1.0)$ , all in 0.3 M  $\text{HClO}_4$  and at room temperature. These values are considered of qualitative nature, and they are compared with other literature sources in the corresponding Section VI.11.2.2 of this review.

#### [67MIY/NUR]

The stepwise stability constants of the 1:1, 1:2 and 1:3 U(VI) oxalate complexes were determined by spectrophotometry at  $(20 \pm 0.2)^\circ\text{C}$  and  $I = 1.0 \text{ M NaClO}_4$ . The constants are:  $\log_{10} K_1 = (4.63 \pm 0.02)$ ,  $\log_{10} K_2 = (4.05 \pm 0.06)$ ,  $\log_{10} K_3 = (3.31 \pm 0.09)$ . The values from this work appear questionable because of the following reasons: 1) The protonation constants of oxalate are missing in the paper. Since the experiments were conducted in a pH range of 1.7 to 3.5, where appreciable amounts of the ligand were present as  $\text{Hox}^-$ , the protonation constants of oxalate are needed to calculate the stability constants of U(VI) oxalate complexes. It is not clear how the “effective” concentration of the anion,  $\text{ox}^{2-}$ , was calculated; 2) The concentration of oxalate seems too low to allow an accurate evaluation of three consecutive U(VI) oxalate complexes. In the experiments,  $C_{\text{U}} \sim 0.3$  and  $1.3 \text{ mM}$ , and  $C_{\text{H}_2\text{ox}} = 0.05 - 0.5 \text{ mM}$  (Table 1 of the paper). The maximum average ligand number on U(VI) was found to be  $< 1.5$  (Figure 6 of the paper). Therefore, the data from this study are not accepted by this review.

#### [67RAJ/MAR]

The protonation constants of oxalic acid and the stability constants of U(VI) complexes with carboxylates including oxalate were determined by potentiometry with a glass electrode at  $25^\circ\text{C}$  and  $I = 1.0 \text{ M KNO}_3$ . The protonation constants are:

$$\log_{10} K_1 = (3.62 \pm 0.01) \quad \text{for} \quad \text{H}^+ + \text{ox}^{2-} \rightleftharpoons \text{Hox}^-$$

$$\log_{10} K_2 = 1.1 \quad \text{for} \quad \text{H}^+ + \text{Hox}^- \rightleftharpoons \text{H}_2\text{ox}(\text{aq})$$

The stability constant of the 1:2 U(VI) oxalate complex is:

$$\log_{10} \beta_2 = (9.1 \pm 0.2) \quad \text{for} \quad \text{UO}_2^{2+} + 2 \text{ox}^{2-} \rightleftharpoons \text{UO}_2(\text{ox})_2^{2-}$$

The potentiometric titrations were conducted with U(VI) and oxalate in the cup

(molar ratio of  $\text{U/ox} = 1/2$ ) titrated with a base. The authors mentioned that separation of a solid phase was observed when the molar ratio of the base to  $\text{U(VI)}$  ( $m$ ) was higher than 2 at  $\text{pH} > 5$ . This would surely interfere with the potentiometric titrations. The authors also mentioned that, for the calculation of  $\beta_2$ , potentiometric equilibrium data in the buffer region between  $m = 1$  and  $m = 3$  of the 1:2 uranyl oxalate systems were used. It is not clear whether precipitation occurred in this region and, if it did, how the data were treated to obtain the stability constants. Lack of detailed experimental data prevents further evaluation of the results. Therefore, the stability constant from this work is not accepted by this review.

#### [\[67RIC\]](#)

The author reports the solubility of plutonium(IV) oxalate in 0 to 3.5 M  $\text{HNO}_3$  and 0 to 0.3 M oxalic acid at room temperature (20 to 22) $^\circ\text{C}$ . Also data in 3 M  $\text{HNO}_3$  and oxalic acid 0.05, 0.1 and 0.3 M were obtained at temperatures up to 95 $^\circ\text{C}$ . The solid was added to nitric acid solutions containing oxalic acid and stirred for 15 mins. Plutonium in the filtered solution was analysed radiometrically. The plutonium concentrations were found to increase with temperature. The data was obtained in order to verify the results of [\[61MAN/FRA\]](#), and the aim of this report was to obtain conditions for the separation of plutonium in a continuous process. Because of the short equilibration time the solubility data reported in this technical report is not considered by this review.

#### [\[67SHC/BEL\]](#)

The authors prepared dinuclear  $\text{U(VI)}$  oxalate compounds  $\text{M}_6[(\text{UO}_2)_2(\text{ox})_5] \cdot n\text{H}_2\text{O}$  and measured the solubility of the compounds in water where  $\text{M} = \text{K, Rb, Cs, CN}_3\text{H}_6$  and  $0.5 \text{C}_2\text{H}_4(\text{NH}_3)_2$ . The experimental conditions are very scarce. No information on the temperature (probably room temperature) or ionic strength is provided. As a result, the solubility data from this reference are rejected by this review.

#### [\[67SHC/BEL2\]](#)

The preparation of  $\text{U(VI)}$  oxalate compounds containing urea in the coordination sphere of  $\text{U(VI)}$  is reported in this reference. The solubilities of a series of such compounds,  $\text{M}_2[\text{UO}_2(\text{ox})_2\{\text{CO}(\text{NH}_2)_2\}] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{K, Rb, Cs, NH}_4$ , and  $\text{CN}_3\text{H}_6$ ) in water at 25 $^\circ\text{C}$  and the solubilities of  $\text{M}_2[\text{UO}_2(\text{ox})_2] \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Na and K}$ ) in aqueous solutions of urea were determined. Experimental details are not given in the paper. The equilibrium solid phases were not identified. In fact, it is mentioned in the paper that dissolution of the urea-containing compounds in water was accompanied by partial hydrolysis. Without confirmation of the equilibrium solid phase, the solubility data from this paper are not accepted by this review.

[\[67SKO/KUM\]](#)

Thorium citrate with the composition  $\text{Th}_3(\text{cit})_4 \cdot 7.5\text{H}_2\text{O}$  was prepared by pouring together equimolar solutions of thorium nitrate and citric acid. The salt was air-dried and its solubility in 0.1 M solutions of  $(\text{H}, \text{Na})\text{ClO}_4$  was studied at 25°C. The concentration of thorium changed from  $4.3 \times 10^{-2}$  M at pH 1.4 to  $1.0 \times 10^{-4}$  M at pH 2.7. By assuming that the solubility is controlled by the formation of  $\text{Th}(\text{cit})^+$ , the solubility product was obtained by considering the material balances for the proton. Using the values of  $\log_{10}K_{(\text{H})} = 5.816, 4.452, 2.956$ , the solubility product  $\log_{10}K_{s,0} = \log_{10}[\text{Th}^{4+}]^3[\text{cit}^{3-}]^4$  was obtained to be  $-(55.37 \pm 0.27)$  with the formation constant:

$$\log_{10} \beta_1 = \log_{10} \frac{[\text{Th}(\text{cit})^+]}{[\text{Th}^{4+}][\text{cit}^{3-}]} = 11.1.$$

The protonation constants used in the calculation are fairly different from those selected in this review. Moreover, since experimental details for the measurements of  $[\text{H}^+]$  and solubility are not described and no supporting evidence or the discussion on the speciation of the thorium citrate complex is given, this review does not accept the results.

[\[67STE/MAK2\]](#)

The stability constants of U(VI) oxalate complexes were determined at 25°C,  $I = 0.1$  N KCl and  $\text{pC}_\text{H} = 1.5$  by the electromigration method. Cerium (probably  $\text{Ce}^{3+}$ , assumed by this review) was used as an auxiliary metal ion. The rate of electromigration of uranium and cerium was determined with the aid of radioactive tracers,  $^{233}\text{U}$  and  $^{144}\text{Ce}$ . The complex formation function ( $\bar{n}$ ) was calculated from the rates of electromigration. The stability constants of the 1:1 and 1:2 U(VI) oxalate complexes were determined to be  $(5.0 \pm 1.5) \times 10^6$  and  $(6.3 \pm 3.0) \times 10^{11}$ . The values seem reasonable and agree with the majority of the data for these complexes in the literature. However, since the experiments were conducted at  $\text{pC}_\text{H} = 1.5$ , the dissociation of oxalic acid must have impact on the electromigration. The dissociation constants of oxalic acid are not given in the paper. Therefore, the data from this work are not accepted by this review.

[\[67TIK2\]](#)

The stability constants of zirconium with several polyaminopolyacetic acids, including edta, were obtained by measuring cation exchange distributions. In the case of edta four experimental points in 1.2 M HCl solutions are reported in [\[67TIK2\]](#). The coefficient  $\alpha$ , appearing in the relationship to obtain the Zr-edta stability constant, was determined experimentally by eluting columns of cation exchanger resin containing  $\text{Zr}^{4+}$  with solutions of another ligand (nta) at pH = 1.1. For this procedure the Zr-nta stability constant has to be known. The author took  $\log_{10}K_1 = 20.80$  from [\[64INT/MAR\]](#). However, [\[64INT/MAR\]](#) obtained their constant from three experimental points at pH = 2.0 and  $I = 0.1$  M KCl, where Zr mainly exists in polymeric hydroxy form. The combination of

the experimental results of [67TIK2] and auxiliary constants, all obtained at rather different conditions, introduces a systematic error whose size is difficult to estimate. In addition, the values for the edta protonation constants determined by [67TIK2] and used to calculate the Zr-edta stability constant have been rejected in this review. A successful re-evaluation of the experimental data of [67TIK2] seems to be almost impossible.

#### [67WEI/MEE]

Am(III) oxalate precipitate was prepared and the solid was analysed to be  $\text{Am}_2(\text{ox})_3 \cdot 10\text{H}_2\text{O}$  (The number of hydrated water is not very sure). X-ray powder diffraction data was obtained for this material and lattice constants,  $a = 1.119 \text{ nm}$ ,  $b = 0.963 \text{ nm}$ ,  $c = 1.024 \text{ nm}$  were obtained for monoclinic symmetry.

#### [67ZAI/SHU2]

Three types of “dizirconyl oxalate” with  $\text{Zr}:\text{ox} = 2:1$  corresponding  $\alpha$ ,  $\beta$ ,  $\gamma$  given in [66ZAI2] were prepared and confirmed by the method given in [66ZAI2]. The solubilities of these solids were determined at  $(25 \pm 0.2)^\circ\text{C}$  in aqueous  $0.02 - 1.0 \text{ M}$  perchloric acid solutions, to which ammonium perchlorate was added to reach an ionic strength  $I = 1$ . The total concentration of oxalate was determined volumetrically and  $[\text{ox}^{2-}]$  in solution was calculated by using the dissociation constants:  $K_1 = 5.90 \times 10^{-2}$  and  $K_2 = 6.40 \times 10^{-5}$ . The apparent solubility product  $SP = [\text{ZrO}^{2+}][\text{ox}^{2-}]$  was calculated to compare the properties of these three types of hydroxides. Since  $\text{ZrO}^{2+}$  does not actually exist in the solution,  $SP$  corresponds to  $SP_\alpha = [\text{ox}^{2-}] \cdot [\text{Zr}_2(\text{OH})_6^{2+}]$ ,  $SP_\beta = [\text{ox}^{2-}] \cdot [\text{Zr}_2\text{O}(\text{OH})_4^{2+}]$ , and  $SP_\gamma = [\text{ox}^{2-}] \cdot [\text{Zr}_2\text{O}_2(\text{OH})_2^{2+}]$ . The apparent equilibrium between the solid phase and  $0.02 - 1 \text{ M}$  perchloric acid solutions was established with continuous stirring in  $3 - 4 \text{ h}$ . The values of  $SP$  were calculated to be  $SP_\alpha = (5.0 \pm 1) \times 10^{-10}$ ,  $SP_\beta = (9.0 \pm 1) \times 10^{-12}$ ,  $SP_\gamma = (4.9 \pm 1) \times 10^{-11}$ . However, the prolonged stirring indicated the change in the values of  $SP$  due to the change in the solid phase (oxolation and deoxolation). The compound in which the zirconium atoms are joined only by double ol bridges ( $\alpha$ ) was shown to be unstable in more weakly acidic solutions, and at  $\text{pH } 2 - 0.7$  it undergoes oxolation with the formation of a compound containing oxo-ol bridges ( $\beta$ ). On the other hand,  $\beta$  and  $\gamma$  type solids are unstable at lower pH. Deoxolation of  $\beta$  begins at  $\text{pH } \sim 0.7$  and is completed at  $\text{pH } \sim 0.3$ , and that of  $\gamma$  begins and completed at  $\text{pH } \sim 1.3 - 0.6$ . This paper gives the useful information that the change in the solubility of certain zirconium compounds on prolonged contact with acid solutions is due to oxolation and deoxolation in the solid compound. As discussed in the paper, values of  $SP$  are only for comparing the behaviour of three types of “dizirconyl oxalate.” Although these values give some qualitative insights about the solubilities of the oxalate complexes of zirconium, they cannot be considered as thermodynamic constants.

[\[67ZAK/ORL2\]](#)

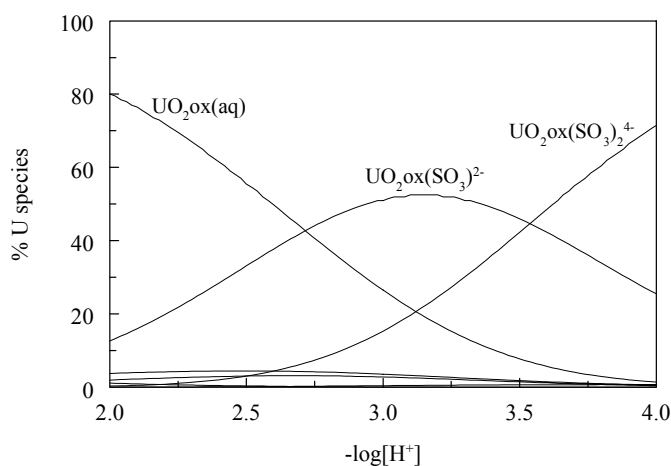
Solid U(VI) oxalates containing a sulfite anion were prepared in this study. The solubility of  $(\text{NH}_4)_2[\text{UO}_2(\text{SO}_3)\text{ox}] \cdot n\text{H}_2\text{O}$  and the stability constants of the sulfite complexes are reported. The data were obtained by dissolving  $\text{UO}_2\text{ox} \cdot 3\text{H}_2\text{O}$  in aqueous solutions of ammonium sulfite at different concentrations. When the concentration of sulfite was high, the solid was transformed into  $(\text{NH}_4)_2[\text{UO}_2(\text{SO}_3)\text{ox}] \cdot n\text{H}_2\text{O}$ . The composition of the equilibrium solid phase was confirmed by chemical analysis. The concentration of uranium in the solutions passed a minimum and then increased as the concentration of sulfite was increased, which was interpreted by the authors as the formation of a disulfite-complex,  $\text{UO}_2(\text{SO}_3)_2\text{ox}^{4-}$ . The stepwise stability constant for  $(\text{UO}_2(\text{SO}_3)\text{ox}^{2-} + \text{SO}_3^{2-} \rightleftharpoons \text{UO}_2(\text{SO}_3)_2\text{ox}^{4-})$  was calculated from the solubility data to be  $5.26 \times 10^3$  at  $t = (23 \pm 1)^\circ\text{C}$  and  $I = 2.5 \text{ mol-dm}^{-3} \text{ NH}_4\text{Cl}$ . The stability constant for the first sulfite-complex,  $\text{UO}_2(\text{SO}_3)\text{ox}^{2-}$ , was determined to be  $3.42 \times 10^4$  by spectrophotometry.

There are shortcomings associated with the solubility experiments. For example, the experiments were conducted in a mixed ionic medium  $(\text{NH}_4\text{Cl} + \text{NH}_4\text{HSO}_3)$  where the concentration of  $\text{NH}_4\text{HSO}_3$  changed from 0 to 2.65 M. Since the pH changed from 1.6 to 3.6, the degree of ionisation of  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  changed significantly, suggesting that the ionic strength could not be constant at 2.5 M as the authors claimed. Besides, in the calculation of the stability constant for  $\text{UO}_2(\text{SO}_3)_2\text{ox}^{4-}$ , the authors made two assumptions: 1)  $C_{\text{U}} = [\text{UO}_2(\text{SO}_3)\text{ox}^{2-}] + [\text{UO}_2(\text{SO}_3)_2\text{ox}^{4-}]$ , i.e., other U(VI) species such as  $\text{UO}_2\text{ox}(\text{aq})$  or  $\text{UO}_2(\text{SO}_3)(\text{aq})$  can be ignored; 2) the concentration of  $\text{UO}_2(\text{SO}_3)\text{ox}^{2-}$  remained constant and was equal to  $s_0$ , the minimum solubility, as the pH and  $[\text{HSO}_3^-]$  were changed (Table 1 of the paper). A speciation calculation using the “instability constants” of species including  $\text{UO}_2\text{ox}(\text{aq})$ ,  $\text{UO}_2(\text{ox})_2^{2-}$ ,  $\text{UO}_2(\text{SO}_3)(\text{aq})$ ,  $\text{UO}_2(\text{SO}_3)_2^{2-}$ ,  $\text{UO}_2(\text{SO}_3)\text{ox}^{2-}$  and  $\text{UO}_2(\text{SO}_3)_2\text{ox}^{4-}$ , (Table 2 of the paper) as well as the protonation constants of  $\text{H}_2\text{ox}(\text{aq})$  (from Section VI.3) and  $\text{H}_2\text{SO}_3(\text{aq})$  (from [\[2003GUI/FAN\]](#)) indicates that these assumptions are incorrect. Figure A-17 shows the percentages of major U(VI) species as a function of  $-\log_{10}[\text{H}^+]$ , in a solution where  $C_{\text{U}} = C_{\text{ox}} = 0.02 \text{ M}$  and  $C_{\text{sulfite}} = 0.2 \text{ M}$ . These conditions are close to those in the solubility experiments of this work (Table 1 of the paper). It is obvious that  $\text{UO}_2\text{ox}(\text{aq})$  cannot be ignored if  $-\log_{10}[\text{H}^+] < 3.5$  and the concentration of  $\text{UO}_2(\text{SO}_3)\text{ox}^{2-}$  cannot be considered constant as the conditions change. Besides, the authors also assumed that the  $\text{H}_2\text{SO}_3(\text{aq})$  species was not present (p.1385 of the paper). Based on estimated protonation constants of  $\text{H}_2\text{SO}_3(\text{aq})$  in 2.5 M  $\text{NH}_4\text{Cl}$  using the values at  $I = 0$  [\[2003GUI/FAN\]](#) and analogous ion interaction parameters [\[2003GUI/FAN\]](#), this assumption is found to be valid only if  $-\log_{10}[\text{H}^+] > 2.5$ . However, some of the solubility data were actually obtained at  $-\log_{10}[\text{H}^+] < 2.0$  (Table 1 of the paper) where the  $\text{H}_2\text{SO}_3(\text{aq})$  species could amount to 10 – 30 %. In summary, the stability constant of  $\text{UO}_2(\text{SO}_3)_2\text{ox}^{4-}$  was calculated based on incorrect assumptions. In fact, the calculated “instability constants” in Table 1 of the paper show a steady increase from  $1.5 \times 10^{-4}$  to  $2.5 \times 10^{-4}$ , suggesting some systematic error is associated with the calculation. Taking these shortcomings into

consideration, this review rejects the solubility data of the U(VI)-oxalato-sulfite compounds and the stability constant for  $\text{UO}_2(\text{SO}_3)_2\text{ox}^{4-}$  from this paper.

There are also shortcomings associated with the stability constant of  $\text{UO}_2(\text{SO}_3)\text{ox}^{2-}$ . The temperature for the spectrophotometric experiments is not specified. There is inconsistency about the ionic strength ( $I = 0.1 \text{ mol}\cdot\text{dm}^{-3}$  in the experimental description, but  $1 \text{ mol}\cdot\text{dm}^{-3}$  in the summary). Due to these shortcomings, the stability constant of  $\text{UO}_2(\text{SO}_3)\text{ox}^{2-}$  from this work is rejected by this review.

Figure A-17: U(VI) speciation in the U(VI)-oxalato-sulfite system ( $I = 2.5 \text{ M}$ ) using the values from [\[67ZAK/ORL2\]](#).



#### [\[68AZI/LYL\]](#)

The distribution of Am-241 between the cation exchanger (Zeo-Karb 225) and the aqueous solution of  $I = 0.5 \text{ M NaClO}_4$  was obtained in the absence ( $K_d^0$ ) and presence ( $K_d$ ) of oxalate ( $10^{-5}$  to  $2.5 \times 10^{-4} \text{ M}$ ) at pH around 3.60 at  $25^\circ\text{C}$  by measuring the  $\alpha$ -activity of Am(III) by liquid scintillation counting. The data was analysed by applying  $(K_d^0 / K_d - 1) / [\text{ox}^{2-}] = \beta_1 + \beta_2 [\text{ox}^{2-}]$ . The overall stability constants were obtained to be  $\beta_1 = (6.58 \pm 0.23) \times 10^4$  and  $\beta_2 = (4.00 \pm 0.15) \times 10^8$ . The protonation constants necessary to estimate  $[\text{ox}^{2-}]$  from total oxalate concentration at this ionic strength, and the method of adjusting and measuring pH (conversion of pH into  $-\log_{10}[\text{H}^+]$ ) are not given. Due to the insufficient description, the reliability of this paper cannot be judged and the paper is not accepted in this review.

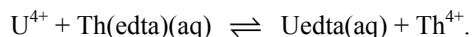
[\[68CAR/MAR\]](#)

In this paper a procedure is outlined for the preparation of pure standard U(IV) chloride solution, containing a known amount of excess acid, and potentiometric equilibrium data are reported for the formation of U(IV) chelates of edta, nta (nitrilotriacetic acid), cdta (trans-1,2-cyclohexanediaminetetraacetic acid), hedta (N-hydroxyethylethylene-diaminetriacetic acid), himda (N-hydroxyethyliminodiacetic acid), dtpa (diethylene tri-aminepentaacetic acid) and ttha (triethylenetetraminehexaacetic acid).

In the case of edta, the addition of base (NaOH) results in the formation of hydrolysed complexes, interpreted by the authors in terms of  $\text{UedtaOH}^-$  and  $(\text{UedtaOH})_2^{2-}$ . At  $\text{pH} > 7$  (or  $m \geq 5.2$ , where  $m$  represents the moles of base added per moles of metal ion) a pH drifting is observed. The authors state that it should be noted that no precipitation is observed in any of the three different solutions ( $7.5 \cdot 10^{-4}$ ,  $2.0 \cdot 10^{-3}$  and  $5.0 \cdot 10^{-3}$  M U(IV) – edta 1:1 solution) and that hydrolysis therefore produces only soluble, though perhaps very complex polynuclear chelates containing hydroxo bridges.

Also in the case of  $\text{Udtpa(aq)}$  the titrations show the formation of  $\text{UdtpaOH}^-$  and the process “most likely involves the dissociation of a coordinated water molecule to form a monohydroxo chelate”. Only the complex  $\text{Uttha}^{2-}$  shows “the fact that no hydrolysis or olation of the 1:1 chelate is noted even at the highest  $-\log_{10}[\text{H}^+]$  value attained”.

The equilibrium constant  $\log_{10}K_1 = (25.8 \pm 0.2)$  for  $\text{U}^{4+} + \text{edta}^{4-} \rightleftharpoons \text{Uedta(aq)}$  is obtained spectrophotometrically at  $-\log_{10}[\text{H}^+] = 1.40$  to  $1.50$  at  $20^\circ\text{C}$  and  $I = 0.1$  M KCl by cation exchange with Th according to the equilibrium



The absorbance of a 1:1:5 U(IV) – edta – Th(IV) solution with  $1.0 \cdot 10^{-3}$  M U(IV) has been measured. From the various species present in the competition reaction,  $\text{U}^{4+}$ ,  $\text{UOH}^{3+}$ ,  $\text{Uedta(aq)}$ ,  $\text{Th(edta)(aq)}$  and  $\text{Th}^{4+}$  only the first three absorb in the region of interest. The authors report that successive pH readings, which showed no variation over a period of 10 – 30 min, were considered as an indication that the system was at equilibrium. The order of addition of the various reagents was reversed and the same results were obtained indicating that equilibrium is reached rapidly.

The auxiliary stability constant  $\log_{10}K_1 = (23.2 \pm 0.1)$  of the Th(IV) edta 1:1 complex was taken from [\[54SCH/GUT\]](#), which is judged by this review as a reliable source. Furthermore, the U(IV) hydrolysis constant of [\[50KRA/NEL\]](#) has been used. The study of U(IV) hydrolysis by [\[50KRA/NEL\]](#) is one of the best sources of data for  $\text{UOH}^{3+}$  and has been accepted, among other studies, for the NEA selection in [\[92GRE/FUG\]](#). The possible effects of chloride complexation with U(IV) and Th(IV) have not been considered by the authors, but the effects of  $\text{UCl}^{3+}$  and  $\text{ThCl}^{3+}$  formation are small in 0.1 M KCl solutions and largely cancel in the U – Th competition reaction. However, the possible increase of the ionic strength above 0.1 M due to the large tho-



rium(IV) concentration of 0.05 M in their solutions is not considered by the investigators. Hence, the uncertainty of the derived constant is increased to  $\pm 0.3$  in order to account for this ambiguity. In addition, it has to be considered that the edta protonation constants of [47SCH/ACK] are involved in the derivation of edta stability constants by [54SCH/GUT]. The first edta protonation constant of [47SCH/ACK] needs a correction for  $K^+$  complex formation, which increases the protonation constant (and all subsequently derived constants) by 0.28 log units, according to the Tables VIII–8–a and VIII–8–b. Hence, the value accepted in this review is  $\log_{10} K_1 = (26.1 \pm 0.3)$  for  $U^{4+} + \text{edta}^{4-} \rightleftharpoons \text{Uedta}(\text{aq})$  at 20°C and  $I = 0.1$  M KCl.

#### [68FRI/VER]

This paper reports a potentiometric study of the mixed complexes of Ni(II) with glycine (gly), ethylenediamine and oxalate. Equilibrium constants were obtained from pH measurements with a glass electrode at  $I = 1$  M ( $\text{KNO}_3$ ) and 25°C. There is no mention in the paper on the calibration of the pH electrode. The Ni(II)-glycine-oxalate system was studied in solutions of pH between 10 and 6. In the potentiometric titrations, solutions containing  $[\text{Ni(II)}] = 0.02$  M,  $[\text{gly}]_{\text{TOT}} = 0.06$  M and  $[\text{ox}]_{\text{TOT}}$  between 0.06 and 0.12 M were titrated with a 2.33 M  $\text{HNO}_3$  solution. Therefore the ionic strength and the concentrations of all reactants were not strictly constant along the titration.

Assuming that Ni(II) was always coordinated by three ligands, the authors interpreted the data with two mixed complexes:  $\text{Ni(gly)}_2(\text{ox})^{2-}$ ,  $\text{Ni(gly)(ox)}_2^{3-}$ , in addition to the oxalate complex  $\text{Ni(ox)}_3^{4-}$ . The nickel-glycinate complexes:  $\text{Ni(gly)}_n^{2-n}$ , with  $n = 1$  to 3 were determined in separate titrations. The equilibrium constants were combined to obtain the overall formation constant for  $\text{Ni(ox)}_3^{4-}$ , with  $\log_{10} \beta_3 = 7.2$ . This equilibrium constant is not considered in this review because of the limited amount of experimental data, in combination with the large number of complexes, and the variations in the ionic media and reactant concentrations.

#### [68GOR/FIL]

The formation of calcium sulphate and oxalate complexes has been determined using a RMK–101 cation-exchange membrane electrode at  $(25.0 \pm 0.1)^\circ\text{C}$  in 0.05 M NaCl. In the case of oxalate,  $2 \times 10^{-3}$  M  $\text{Na}_2\text{ox}$  solutions were titrated with  $4 \times 10^{-4}$  to  $2 \times 10^{-3}$  M  $\text{CaCl}_2$  solutions, and the formation constant of the calcium oxalate complex is reported to be  $\log_{10} K_1 = 3.07$ . However, this value is subject to error since all measurements were made in solutions where the product of total calcium and oxalate was appreciably higher than the value required for spontaneous precipitation of  $\text{Ca(ox)} \cdot \text{H}_2\text{O}$ , and hence, the result of this study is rejected by this review.

#### [68KOZ]

The method of metal indicators introduced by [61BAB/SHT] was used to compare relative stability of zirconium complexes with some reagents. It was found that the stability

of respective 1:1 complexes in acid solutions (pH = 0 and 2) decreases in the series: edta > oxalate > citrate > tartrate. Since this method needs some reliable absolute stability constant at least for one complex, only qualitative information can be obtained.

#### [\[68KUE/SCH\]](#)

The main topic of this study was the determination of the rate of ligand exchange between  $\text{Cd}^{2+}$  and  $\text{Ca}(\text{edta})^{2-}$ . The authors state that in addition it was necessary to evaluate the equilibrium constants for  $\text{Ca}(\text{edta})^{2-}$  under conditions prevailing during the kinetic measurements. In their titration experiments “the hydrogen activity was monitored with a carefully standardised glass electrode”. However, no further details about these titration experiments are reported by [\[68KUE/SCH\]](#) (*i.e.*, electrode calibration, pH range investigated, results of the measurements, evaluation of the reported constants). Hence, the edta protonation constants as well as the Ca edta stability constant, given without further information in Table 1 of [\[68KUE/SCH\]](#), are not considered in this review.

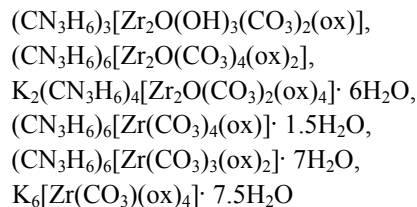
#### [\[68MAT/KRO\]](#)

The aim of this study was to determine by a solubility method the form in which Pu(IV) exists in sodium oxalate solution. The solubility of  $\text{Na}_2\text{ox}(\text{s})$  in  $\text{K}_2\text{Pu}(\text{ox})_4$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solutions (0 – 0.2 M) at 25°C has been determined. In saturated  $\text{Na}_2\text{ox}$  solution no significant difference between  $\text{K}_2\text{Pu}(\text{ox})_4$  and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  has been found and the authors conclude from these results that the predominant complex in these solutions is  $\text{Pu}(\text{ox})_4^{4-}$  and no significant tendency can be detected to form  $\text{Pu}(\text{ox})_5^{6-}$  complexes.

The solubility of  $\text{Na}_2\text{ox}(\text{s})$  in pure water at 25°C is reported to be 0.278 M ( $37.25 \text{ g} \cdot \text{dm}^{-3}$ ).

#### [\[68POS/ZAI2\]](#)

By mixing guanidinium salt of carbonate or mono-, tris, tetrakis(carbonato)zirconate and guanidinium or potassium salt of oxalate or tris, tetrakis(oxalato)zirconate, carbonato-oxalato-compounds such as:



were prepared and molar conductance and pH of solutions and infrared absorption spectra were measured. From the analysis of the infrared spectra, it was shown that, when the number of the ligands (oxalate plus carbonate) in the compound is greater than four,

oxalate denticity decreases from bidentate to monodentate, indicating that the carbonate group forms a more stable bond with zirconium than the oxalate group. This paper gives qualitative and indirect information about the stability of the aqueous complexes of zirconium oxalate but no quantitative values are given.

#### [\[68SHC/BEL\]](#)

In this study, ternary U(VI) fluoridooxalato-compounds were prepared by dissolving dioxopentafluorouranate(VI) in solutions of oxalate at 20–22°C. Replacement of fluoride by oxalate resulted in the formation of U(VI) fluoridooxalato-complexes such as  $[\text{UO}_2\text{F}_3(\text{ox})]^{3-}$  and  $[\text{UO}_2\text{F}(\text{ox})_2]^{3-}$ . Solubilities of corresponding salts of potassium and guanidinium were determined at different concentrations of oxalate. The transformation of the solid phase from dioxopentafluorouranate(VI) to ternary U(VI) fluoridooxalato-compounds was suggested by the break in the solubility curve. The contents of uranium, oxalate, fluoride and water in the solid precipitates were analysed and found to be close to the calculated values. However, the solubility experiments were not conducted at a constant ionic strength. The solubility data are rejected by this review.

#### [\[68SIL/SIM\]](#)

The uranyl complexes of edta have been studied by potentiometry under the following conditions:  $I = 0.10 \text{ M KNO}_3$  with total metal concentration of  $1 \cdot 10^{-3} \text{ M}$  and total ligand concentration of  $2 \cdot 10^{-3} \text{ M}$ , and at  $I = 1.00 \text{ M KNO}_3$  with 1:1 metal to ligand ratio at five concentrations ( $0.5, 1.0, 1.92, 2.46$  and  $4.92 \cdot 10^{-3} \text{ M}$ ) and with 2:1 metal to ligand ratio at total ligand concentration  $0.5, 1.0, 2.46$  and  $4.92 \cdot 10^{-3} \text{ M}$ . Stability constants of 1:1 and 2:1 uranyl edta chelates have been determined, as well as their hydrolysis and polymerisation constants. The authors state that “the species formed are generally quite stable, and the mathematical treatment (graphical and algebraic) of the corresponding equilibria is not too involved”.

For 1:1 molar ratio mixtures of U(VI) and edta the composition of the solutions was interpreted in terms of the formation of  $\text{UO}_2(\text{Hedta})^-$ ,  $\text{UO}_2\text{edta}^{2-}$ , (given in the paper as  $\text{UO}_2(\text{Hedta})\text{OH}^{2-}$ ),  $\text{UO}_2\text{edtaOH}^{3-}$ , and  $(\text{UO}_2\text{edta})_2^{4-}$  (given as  $[\text{UO}_2(\text{Hedta})\text{OH}]_2^{4-}$ ). In the case of 2:1 molar ratio mixtures of U(VI) and edta the composition of the solutions was interpreted by the authors in terms of a “core + links” mechanism. The complexes formed correspond to the general formula  $(\text{UO}_2)_2\text{edta}[(\text{UO}_2)_2\text{edta}(\text{OH})_2]_{n-1}^{2(n-1)-}$ , with  $n_{\min} = 1$  and  $n_{\max} = \infty$ , although the species corresponding to high values of  $n$  are unlikely. Stability constants have been derived for  $(\text{UO}_2)_2\text{edta}(\text{aq})$  ( $n = 1$ ),  $(\text{UO}_2)_4(\text{edta})_2(\text{OH})_2^{2-}$  ( $n = 2$ ), and  $(\text{UO}_2)_6(\text{edta})_3(\text{OH})_4^{4-}$  ( $n = 3$ ).

The authors emphasise that “to account for the abnormally high stability of  $\text{UO}_2\text{Hedta}^-$ , hydrogen bonding between a protonated nitrogen atom of the ligand and one oxygen atom of  $\text{UO}_2^{2+}$  is suggested”. Later on [\[83LUR/GON\]](#), this hypothesis has been rejected.

For further discussion of the results reported in this paper, see the discussion of [\[84GON/MOT\]](#) in this Appendix.

#### [\[69BOS/MAR\]](#)

Potentiometric titration of the Ca citrate system has been conducted at  $I = 0.1$  M  $\text{KNO}_3$  at  $20^\circ\text{C}$ . Using the citrate protonation constants  $\log_{10} K_{(\text{H})} = 5.78, 4.42$  and  $2.95$ , the authors obtained  $\log_{10} \beta_1 = 3.24$  for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$ . Although these values are in good agreement with the protonation constants accepted in this review and  $\log_{10} \beta_1$  reported by others, there is no description about the conversion of measured pH to  $-\log_{10} [\text{H}^+]$ . Thus, this review does not accept this paper.

#### [\[69BRU/NAN\]](#)

Gibbs energy and enthalpy changes accompanying the protonation of divalent metal – edta complexes in the reaction  $\text{Me}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Me}(\text{Hedta})^-$  have been measured potentiometrically and calorimetrically at  $25^\circ\text{C}$  and  $I = 0.10$  M  $\text{KNO}_3$ . The metals Me investigated were  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Hg}^{2+}$ .

#### [\[69DEL/BAY\]](#)

Eight aminopolycarboxylic acids, including edta, were investigated with respect to their complexation with trivalent Am. The composition of the complexes and the pH range of their stability were determined using an absorption spectrophotometer technique at  $25^\circ\text{C}$  in a constant ionic strength of  $0.1$  M  $\text{NH}_4\text{ClO}_4$ . The pH meter was standardised with Fisher Scientific Co. buffer solutions, and the reported pH values were accurate to  $\pm 0.02$  pH units.

In the case of edta, Delle Site and Baybarz [\[69DEL/BAY\]](#) assumed that the first complex formed in the pH range 1 – 2 is  $\text{Am}(\text{edta})^-$ , according to the reaction  $\text{Am}^{3+} + \text{H}_4\text{edta}(\text{aq}) \rightleftharpoons \text{Am}(\text{edta})^- + 4 \text{H}^+$  with  $\log_{10} K = -3.68$ , because their experimental data are compatible with the release of 4 protons. Using the edta protonation constants of [\[51CAB\]](#) they obtained  $\log_{10} K_1 = 18.06$  for  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$ . At higher pH values they interpreted their data in terms of complexes with Am : edta ratios 2:3 (pH 3.7 – 7.3) and 1:2 (pH 7 – 12), but “it was only possible to calculate the stability constant for the first (1:1) complex. Extensive overlapping of spectral bands made the calculations of the stability constant for the second (2:3) complex quite uncertain. The third (1:2) complex is very weakly formed and probably involves a partial hydrolysis of metal ion due to the high pH values in which the reaction takes place.”

However, the first complex forming reaction releasing 4 protons can equally well be interpreted in terms of formation of  $\text{Am}(\text{Hedta})(\text{aq})$  according to  $\text{Am}^{3+} + \text{H}_5\text{edta}^+ \rightleftharpoons \text{Am}(\text{Hedta})(\text{aq}) + 4 \text{H}^+$ , also with  $\log_{10} K = -3.68$ . According to all information evaluated in this review, the first complex formed in acidic media is  $\text{Am}(\text{Hedta})(\text{aq})$  and not  $\text{Am}(\text{edta})^-$ , and the species  $\text{H}_5\text{edta}^+$  predominates at  $\text{pH} < 1.5$  (Figure VIII–13). Using edta protonation constants for  $0.1$  M  $\text{NaClO}_4$  and  $25^\circ\text{C}$  (Table

VIII-8-a),  $\log_{10}K = (8.57 \pm 0.30)$  for  $\text{Am}^{3+} + \text{Hedta}^{3-} \rightleftharpoons \text{Am}(\text{Hedta})(\text{aq})$  is estimated by this review.

#### [69FRI/DYA]

The concentration formation constants of ternary complexes of  $\text{Ni}(\text{edta})^{2-}$  (0.05 M) with ammonia and pyridine have been investigated at ionic strength 1.5 M ( $\text{NH}_4\text{NO}_3$ ) at 25°C by pH and distribution measurements (the latter for pyridine only).

#### [69HAV]

The complexation of U(VI) with oxalate was studied by spectrophotometry at 20°C and  $I = 0.1$  and 1.0 M  $\text{NaClO}_4$ . In the data analysis, the author obtained the dissociation constants of oxalic acid by interpolation or averaging of the values in the literature:  $\text{p}K_{a1} = 1.20$  ( $I = 0.1$  M) and 1.06 ( $I = 1.0$  M),  $\text{p}K_{a2} = 3.85$  ( $I = 0.1$  M) and 3.65 ( $I = 1.0$  M). Using these values of  $\text{p}K_{a1}$  and  $\text{p}K_{a2}$ , the stability constants of  $\text{UO}_2\text{ox}(\text{aq})$  and  $\text{UO}_2(\text{ox})_2^{2-}$  at  $I = 0.1$  and 1.0 M  $\text{NaClO}_4$  and that of  $\text{UO}_2(\text{ox})_3^{4-}$  at  $I = 1.0$  M  $\text{NaClO}_4$  were reported. The stability constants of  $\text{UO}_2\text{ox}(\text{aq})$  and  $\text{UO}_2(\text{ox})_2^{2-}$  from this work are close to the values obtained by the same group in a later study [2002HAV/SOT], but the constant of  $\text{UO}_2(\text{ox})_3^{4-}$  from this work seems too low in comparison with the values from [2002HAV/SOT] and other literature (Table VI-38). Therefore, the stability constants for  $\text{UO}_2\text{ox}(\text{aq})$  and  $\text{UO}_2(\text{ox})_2^{2-}$  are accepted, but the constant for  $\text{UO}_2(\text{ox})_3^{4-}$  is rejected by this review.

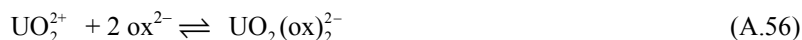
The values are corrected from molarity to molality following the method in Chapter II, and from 20 to 25°C by the following equation:

$$\log_{10} K_{T_2} - \log_{10} K_{T_1} = \frac{\Delta_r H_m}{2.3023 R} (T_1^{-1} - T_2^{-1})$$

using the enthalpy of complexation for  $\text{UO}_2\text{ox}(\text{aq})$ ,



$\Delta_r H_m(\text{A.55}) = (25.4 \pm 18.4) \text{ kJ}\cdot\text{mol}^{-1}$  (cf. Section VI.10.2.4.1), and the enthalpy of complexation for  $\text{UO}_2(\text{ox})_2^{2-}$ ,



$\Delta_r H_m(\text{A.56}) \approx \Delta_r H_m(\text{A.57}) = (11 \pm 1) \text{ kJ}\cdot\text{mol}^{-1}$  (cf. Section VI.10.2.4.1),



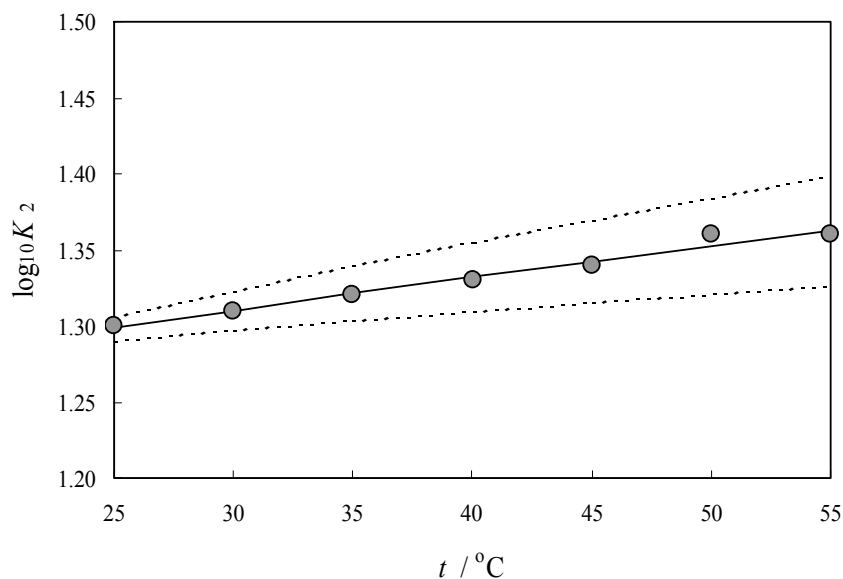
The corrections from 20 to 25°C are +0.06 for  $\log_{10} \beta_1$  and +0.03 for  $\log_{10} \beta_2$ . The corrected values, with increased uncertainties, are shown in Table VI-39.

[\[69KUR/FAR\]](#)

Kurz and Farrar reported measurements with the glass electrode of the first dissociation constant of oxalic acid. The results obtained in HCl media of varying ionic strength ( $0.04 < I < 0.15$ ) have been extrapolated by [\[69KUR/FAR\]](#) using the extended Debye-Hückel equation. The authors did not publish sufficient data to permit recalculation of the originally measured values. Hence, the  $\log_{10}K_2$  values included in Table VI-2 have not been used in the multi-linear least-squares regression analyses of this review.

However, in order to estimate the temperature variation of  $\log_{10}K_2$  these values have been fitted in this review to a temperature function assuming  $\Delta_r C_{p,m} = 0$ . The result is  $\Delta_r H_m = (4.0 \pm 0.5) \text{ kJ} \cdot \text{mol}^{-1}$ . According to the rules of error propagation discussed in Section VI.3, assuming an uncertainty of  $\pm 0.02$  in the  $\log_{10}K_2$  values, determined over the temperature range 25 to 55.0°C, the total uncertainty in  $\Delta_r H_m$  was estimated to be  $\Delta_r H_m = (4.0 \pm 1.8) \text{ kJ} \cdot \text{mol}^{-1}$ .

Figure A-18: Second protonation constant for oxalate determined and extrapolated to  $I = 0$  by [\[69KUR/FAR\]](#) and the constant  $\Delta_r H_m$  model with the parameters determined in this review.



**[69MAN/BHA]**

In this study a solvent extraction technique was used at 20°C and  $I = 0.1 \text{ M NaClO}_4$ . The extractant was oximidobenzotetronic acid in chloroform. No information about the pH calibration and about the pH scale is given. The values  $\log_{10} K_1 = (3.83 \pm 0.05)$  and  $\log_{10} \beta_2 = (7.06 \pm 0.13)$  were obtained for the complex formation between nickel(II) and oxalate. From the Fig.9 in [69MAN/BHA] it may be inferred that the pH was 3. However, no information is given on the total concentration of oxalate or on the protonation constants used in deriving the formation constants of the complexes. Because of the lack of information in the publication, the reported equilibrium constants are not included in the review process.

**[69MEF/KRO2]**

The reactions between  $^{237}\text{Np(VI)}$  and oxalate were studied using spectrophotometry and measurements of solubility. Low temperatures ( $\leq 20^\circ\text{C}$ ) and high acidities ( $[\text{H}^+] > 0.1 \text{ M}$ ) were used in order to minimise the reduction of Np(VI) to Np(V) by oxalate.

The formation of  $\text{NpO}_2\text{ox(aq)}$  and  $\text{NpO}_2(\text{ox})_2^{2-}$  was shown spectrophotometrically. The data had to be corrected for the reduction of Np(VI) by oxalate within time of the measurements. The following stability constants were estimated:  $\log_{10} K_1 = (6.0 \pm 0.8)$  in  $1 \text{ M HClO}_4$  at  $(10 \text{ to } 20)^\circ\text{C}$ ; and  $\log_{10} K_2 = (4.08 \pm 0.14)$  in  $I = 1 \text{ M (NH}_4\text{NO}_3)$  at pH 1.5 to 3.5 and at  $13^\circ\text{C}$ . The temperature effects on the formation of  $\text{NpO}_2\text{ox(aq)}$  in the range  $(10 \text{ to } 20)^\circ\text{C}$  were negligible.

Solid Np(VI)-oxalate was prepared and its analysis agreed with the composition  $\text{NpO}_2\text{ox} \cdot 3\text{H}_2\text{O}$ . Its solubility in  $0.5 \text{ M HNO}_3 + 0.023 \text{ M H}_2\text{ox}$  increased with temperature from  $\approx 1.7 \text{ mM}$  at  $\approx 1^\circ\text{C}$  to  $\approx 5.5 \text{ mM}$  at  $\approx 17^\circ\text{C}$ . The solubility of this solid in  $1 \text{ M HNO}_3$  was studied as a function of oxalic acid concentration (up to  $0.15 \text{ M}$ ). Again, the data had to be corrected for the reduction of Np(VI) by oxalate within time of the measurements. The analysis of the data gave  $\log_{10} K_1 = 6.1$  for the formation of  $\text{NpO}_2\text{ox(aq)}$  and  $\log_{10} K_s = -2.52$  for reaction,



The value used for the first protonation constant for oxalate at  $I = 1 \text{ M}$  was  $\log_{10} K_1 = 4.34$ , but the value used for the second protonation constant is not given and the temperature effects on the protonation constants, although expected to be small, is not mentioned by the authors either. The calibration method for the measurement of pH is not given either. Because of this, and because of the intrinsic instability of Np(VI) in oxalate solutions, the reported equilibrium constants can be used for qualitative purposes only.

**[69MIK]**

The solubility of Pu(IV) phenylarsonate has been measured in different acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ). The minimal solubility found in all these acids is close to  $10^{-5} \text{ M}$ . In addi-

tion, solubility has been studied in  $\text{HNO}_3 + \text{HF}$ ,  $\text{HNO}_3 + \text{H}_2\text{ox}$ , and  $\text{HNO}_3 + \text{H}_4\text{edta}$ . In the latter case, four solubility values,  $1.4 \cdot 10^{-4}$  M in 0.3 M  $\text{HNO}_3 + 2 \cdot 10^{-4}$  M  $\text{H}_4\text{edta}$ ,  $2.5 \cdot 10^{-4}$  M in 0.3 M  $\text{HNO}_3 + 4 \cdot 10^{-4}$  M  $\text{H}_4\text{edta}$ ,  $4.2 \cdot 10^{-4}$  M in 0.3 M  $\text{HNO}_3 + 6 \cdot 10^{-4}$  M  $\text{H}_4\text{edta}$ ,  $2.8 \cdot 10^{-3}$  M in 0.1 M  $\text{HNO}_3 + 6 \cdot 10^{-4}$  M  $\text{H}_4\text{edta}$ , all in 0.04 M phenylarsonic acid, have been used to calculate the equilibrium constant  $\log_{10} K_C = (3.0 \pm 0.5)$  for the complex formation  $\text{Pu}^{4+} + \text{H}_4\text{edta}(\text{aq}) \rightleftharpoons \text{Pu}(\text{edta})(\text{aq}) + 4 \text{H}^+$ . The edta protonation constants of [59KLY/SMI4] have been used to calculate the equilibrium constant  $\log_{10} K_1 = (26.0 \pm 0.5)$  for  $\text{Pu}^{4+} + \text{edta}^{4-} \rightleftharpoons \text{Pu}(\text{edta})(\text{aq})$ .

For oxalate the solubility was determined in three 0.3 M  $\text{HNO}_3$  solutions containing both phenylarsonic acid and oxalic acid.

The composition of the solid in all the experiments was not determined. The influence of Pu(IV) hydrolysis and nitrate complex formation of Pu(IV) in 0.3 and 0.1 M  $\text{HNO}_3$  on the obtained results is not considered. Furthermore, the pH of the resulting equilibrium solutions is not reported by Mikhailov, precluding any re-evaluation of the experimental solubility data. In summary, the data of Mikhailov cannot be considered in this review.

#### [69PER/KRO]

Electrolytic reduction of  $\text{UO}_2^{2+}$  to U(IV) was studied on steel, graphite and tantalum electrodes in a solution of ammonium oxalate at pH 3 - 5. It was found that the reduction goes only through disproportionation of U(V). The first stage of the reduction is  $\text{UO}_2\text{ox}(\text{aq}) + \text{e}^- \rightleftharpoons \text{UO}_2\text{ox}^-$ , which starts at potential  $-0.3$  V. Optimal conditions where almost complete reduction ( $\sim 98\%$ ) of uranyl to U(IV) could be reached were found. Effect of the temperature and the effect of several ions (nitrate,  $\text{Fe}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$ ,  $\text{Np}^{\text{VI}}$ , and  $\text{Pu}^{\text{VI}}$ ) on the reduction of uranyl were studied.

#### [69REC/HSE]

Free calcium ion concentrations in the solutions containing  $(6 - 10) \times 10^{-3}$  M  $\text{Ca}^{2+}$  and citric acid  $(0.8 - 1.0 \times C_{\text{Ca}})$  were measured with the use of Beckman 39608 calcium-selective electrode at pH 6.6 - 7.0 (adjusted by NaOH or  $\text{HClO}_4$ ),  $I = 0.1$  M ( $\text{NaClO}_4$ ) and  $25^\circ\text{C}$ . pH readings were converted to  $\log_{10} [\text{H}^+]$  using an activity coefficient of 0.76 for univalent ions at 0.1 M ionic strength. The dissociation constants of citric acid used for the calculation of the stability constant of  $\text{Ca}(\text{cit})^-$  were calculated using the extended Debye-Hückel equation and  $\log_{10} K_{(\text{H})}^\circ = 5.62, 4.34$  and  $2.91$ . Although these treatments would give some errors in the estimation of  $[\text{cit}^{3-}]$ , they are considered small since the measurements were done at the pH where almost all of citric acid is in the form of  $\text{cit}^{3-}$ . Considering the errors in the measurements of free calcium concentrations and mass balance calculations, this review accepts the reported value for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$  with assigning a large uncertainty as  $\log_{10} \beta_1 = (3.67 \pm 0.2)$ .



[\[69SHC/BEL\]](#)

The preparation of a series of  $M_2UO_2(ox)_2 \cdot nH_2O$  ( $M = Na, K, Rb, Cs, NH_4, (C_2H_5)_2NH_2$  and  $[(C_2H_5)_3(NH)]_2CN_3H_6$ ) is reported in this reference. The solubilities of some of the compounds, in water at 25–35°C were determined. Details on the solubility experiments are not given in the paper. The equilibrium solid phases were not identified. The solubility data from this paper are therefore rejected by this review.

[\[69SKO/KUM\]](#)

The solubility of Zn, Cd, Mg, Ca and Hg(I) citrates in 0.1 M (H, Na)ClO<sub>4</sub> at 25°C has been studied. Analyses of the air-dried salts indicated the composition of  $Mg_3(cit)_2 \cdot 15H_2O$  and  $Ca_3(cit)_2 \cdot 4H_2O$ . By measuring the metal ion concentration in equilibrium with these salts at  $-\log_{10} [H^+] = 4.28 - 5.30$  for Mg(II) and  $3.31 - 4.24$  for Ca(II), Skorik and Kumok have calculated the solubility products,  $K_{s,0} = [M^{2+}]^3 [cit^{3-}]^2$ . In the calculation, they have first assumed that  $I$  is equal to 0.1 M and used  $\log_{10} K_{(H)} = 5.816, 4.452$  and  $2.956$  [\[53WAR/WEB\]](#) and the values of  $\log_{10} \beta_1$  for citrate complexes of calcium and magnesium [\[64CAM/OST\]](#). By using the equilibrium concentrations thus found, they refined the ionic strength, recalculated, for the new value of  $I$ , the values of equilibrium constants using the Leden equation. Final ionic strengths were reported to be  $0.17 - 0.22$  for the case of magnesium and  $0.12 - 0.17$  for calcium. The values of  $\log_{10} K_{s,0}$  thus obtained were then recalculated to  $I = 0.1$  M. As a result, they have obtained  $\log_{10} K_{s,0} = -(11.10 \pm 0.04)$  for  $Mg_3(cit)_2 \cdot 15H_2O$  and  $\log_{10} K_{s,0} = -(14.68 \pm 0.09)$  for  $Ca_3(cit)_2 \cdot 4H_2O$ . Although it is not clear whether they have also refined the protonation constants and stability constants or not, recalculation by this review using  $\log_{10} K_{s,0}$  and  $-\log_{10} [H^+]$  given in Table 2 of [\[69SKO/KUM\]](#) did not exactly reproduce the solubility and ionic strength in the table. Since the final ionic strengths were  $0.17 - 0.22$  for Mg(II) and  $0.12 - 0.17$  for Ca(II), the ionic strength correction used in the paper is considered not enough precise. Although the information given by this paper is valuable, this review does not accept the reported values due to the too large uncertainties.

[\[69SOC/VOL\]](#)

A polarographic method for the determination of the instability constants of complexonates is proposed, which does not have limitations with respect to acidity or the ratio of the reacting metal and edta. At  $I = 3.6$  M HNO<sub>3</sub> and  $1.78$  M  $[H^+]$  ( $pH = -0.25$ ) a bismuth solution in presence of different amounts of edta gives measurable concentrations of  $Bi(edta)^-$ . From these concentration data a conditional instability constant of  $K = 7.58 \times 10^{-4} = 10^{-3.12}$  is obtained. In order to derive the concentration instability constant  $K_{inst} = 10^{-27.93}$  of the  $Bi(edta)^-$  complex [\[69SOC/VOL\]](#) used “hydrogen functions” to calculate the necessary edta protonation constants. If the Bi-edta solution in addition contains zirconium it is possible to obtain the concentration of both complexonates and to calculate the ratio of the conditional instability constants of zirconium and bismuth

edta complexes. Combining the instability constant of the  $\text{Bi}(\text{edta})^-$  complex with this ratio of 0.46 [69SOC/VOL] calculated  $K_{\text{inst}} = 10^{-28.4}$  for the  $\text{Zr}(\text{edta})(\text{aq})$  complex. However, this result strongly depends on the “hydrogen functions” used by the authors. Using the edta protonation constants evaluated in this review, a re-evaluation of the results reported in [69SOC/VOL] could be envisioned as soon as Zr hydrolysis data have been selected within the NEA TDB reviews.

#### [69STE/MAK2]

The complexation of U(VI) with edta has been studied by electromigration measurements in the pH range 1.0 – 3.5 at  $I = 0.1$  M KCl and 20°C. The authors used  $^{233}\text{U}$ , and the total concentration of uranium in the solutions did not exceed  $10^{-6}$  M. The total edta concentration in the solutions was  $6.9 \cdot 10^{-4}$  M. The authors emphasise that “the pH meter was calibrated against solutions of known concentrations and not activity of hydrogen ions”. Protonation constants for edta were taken from [47SCH/ACK], valid for  $I = 0.1$  M KCl and 20°C. The results reveal that only monomeric protonated edta complexes are formed under these experimental conditions. At  $\text{pH} < 2.5$  the species  $\text{UO}_2(\text{H}_2\text{edta})(\text{aq})$  prevails and at  $\text{pH} > 2.5$  the well known species  $\text{UO}_2(\text{Hedta})^-$  was identified.

This study is considered as reliable by this review and the stability constant reported for  $\text{UO}_2(\text{Hedta})^-$  is included in the final data evaluation. However, at  $\text{pH} < 2.5$  where the species  $\text{UO}_2(\text{H}_2\text{edta})(\text{aq})$  prevails, the presence of  $\text{H}_5\text{edta}^+$  and  $\text{H}_6\text{edta}^{2+}$  has to be considered in the calculations (see Figure VIII-13 in Section VIII.3.7), which has not been done by the authors. Hence, the stability constant reported for  $\text{UO}_2(\text{H}_2\text{edta})(\text{aq})$ , although in a reasonable range, has not been selected by this review.

#### [69SUB/COR]

In this study the kinetics of solvent extraction of Zn(II) and Ni(II) with dithizone in  $\text{CHCl}_3$  were studied at  $(25 \pm 0.1)^\circ\text{C}$  in 0.25 M  $\text{NaClO}_4$ . The pH was adjusted between 4 and 7 with buffers containing formate, phthalate and phosphate “at sufficiently low concentrations” to avoid complex formation. No information about the pH calibration and about the pH scale is given. The total concentration of oxalate is not stated and the values for the protonation constants that were used to derive the formation constants of the complexes are not given. The authors fitted their kinetic results with  $\log_{10} K_2 = (1.8 \pm 0.2)$ . Because of the lack of information in the publication, this equilibrium constant is not included in the review process.

#### [70ADI/KLO]

The extraction of U(VI) from aqueous 0.08 M citrate media into 0.10 M HTTA-benzene was studied at pH 4.00 and  $I = 0.15$  M ( $\text{NaNO}_3$ ) over the concentration range of  $5 \times 10^{-8} - 3 \times 10^{-3}$  M  $C_M$ . Since the distribution ratio of U(VI) is expressed by:

$$D = \frac{C_{M,org}}{[UO_2(cit)^-] + 2[(UO_2)_2(cit)_2^{2-}]}$$

where  $C_{M,org}$  is the concentration of U(VI) extracted into the organic phase. Values of  $\log_{10} D$  were plotted against  $\log_{10} C_{M,aq}$  where  $\log_{10} C_{M,aq} = [UO_2(cit)^-] + 2[(UO_2)_2(cit)_2^{2-}]$ . This plot should have a slope of  $-0.5$  at high concentrations increasing gradually to zero at lower concentrations as the dimer becomes more dissociated. Measured values of  $\log_{10} D$  clearly followed a straight line of slope  $-0.5$  at  $\log_{10} C_{M,aq}$  of  $-3.0$  to  $-5.0$ , indicating the predominant formation of the dimer. Since measured values of  $\log_{10} D$  at  $\log_{10} C_{M,aq}$  lower than  $-5$  showed a trend of its slope to approach zero, the authors reported the dimerisation constant to be:

$$\log_{10} K_{dim} \geq 6.0 \text{ where } K_{dim} = \frac{[(UO_2)_2(cit)_2^{2-}]}{[UO_2(cit)^-]^2}$$

However, even using purified materials, the values of  $\log_{10} D$  still showed a trend of further decrease with the decrease in  $\log_{10} C_{M,aq}$ . This presence of an unknown reaction in this solvent extraction makes us to hesitate to accept this value in this review. This review takes this result only as qualitative information.

#### [\[70BES/CHA\]](#)

Complex formation has been studied by thin-layer electrophoresis. Electrophoretic mobilities were obtained as a function of pH at  $0.7 \text{ M KNO}_3$  (with  $0.25 \text{ M}$  boric acid buffer) and explained by the formation of  $Ni(H_2cit)^+$ ,  $Ni(Hcit)(aq)$ ,  $Ni(cit)^-$  and  $Ni(H_{-1}cit)^{2-}$ . The values of  $\log_{10} K$  for the reactions  $Ni^{2+} + H_3cit \rightleftharpoons Ni(H_2cit)^+ + H^+$  and  $Ni(H_2cit)^+ \rightleftharpoons Ni(H_{-1}cit)^{2-} + 3H^+$  are reported to be  $-1.4$  and  $-12.9$ , respectively. Since the experimental data seems not quantitative enough to estimate the complex species and their stability constants, this review does not accept these values.

#### [\[70DAV/WAT\]](#)

The dissociation constants of oxalic acid were measured by titration of sodium oxalate with perchloric acid in  $3 \text{ M NaClO}_4$  at  $1.5$ ,  $25.0$ ,  $34.5$  and  $47.8^\circ\text{C}$ . The authors report the acid dissociation constants for each temperature and dissociation enthalpies and entropies calculated therefrom. In addition they mention that the errors quoted are standard deviations. The first dissociation enthalpy is reported as  $(3.4 \pm 0.8) \text{ kcal}\cdot\text{mol}^{-1}$  which corresponds to  $\Delta_r H_m = -(14.2 \pm 3.3) \text{ kJ}\cdot\text{mol}^{-1}$ , and the second dissociation enthalpy is given as  $(0.9 \pm 0.2) \text{ kcal}\cdot\text{mol}^{-1}$  which corresponds to  $\Delta_r H_m = -(3.8 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$ . Close inspection of the dissociation constants given by [\[70DAV/WAT\]](#) showed that the temperature trend is in accord with other published data. However, the signs of the reported enthalpies (Table 1 in [\[70DAV/WAT\]](#)) are in error. Furthermore, two puzzling discrepancies with other published data have to be noted here. First, the  $\log_{10} K_1$  value of  $3.50$  ( $3 \text{ M NaClO}_4$ ,  $25^\circ\text{C}$ ) reported by [\[70DAV/WAT\]](#) is in marked disagreement with all other results found under the same conditions, *i.e.*,  $3.80$  [\[66MOO/SUT\]](#),  $3.82$

[83CRU/HEY], 3.85 [94ERT/MOH], 3.81 [95MIR/SAD], 3.84 [96CHO/CHE]. Second, the temperature variation of  $\Delta \log_{10} K_2 \approx 0.35$  between 0 and 50°C reported by [70DAV/WAT] also is in significant disagreement with  $\Delta \log_{10} K_2 < 0.1$  found in all other studies [61MCA/NAN], [69KUR/FAR], [76KAL], [92ROB/STE], [98ALD/BIA], [98KET/WES]. Unfortunately, [70DAV/WAT] did not publish sufficient data to permit recalculation of the values from measured data. Hence, their results are not credited in this review.

#### [70DEY/PEN]

See comments under [75DEY/CAN].

#### [70EBE/WED]

The complex formation of Np(V) and Pu(V) with edta and other aminocarboxylates has been investigated by spectrophotometry ( $^{237}\text{Np}$ ) and by a cation-exchange method ( $^{239+240}\text{Pu}$ ,  $^{238}\text{Np}$ ). In the spectrophotometric study of Np(V) three edta complexes have been found:  $\text{NpO}_2(\text{Hedta})^{2-}$ ,  $\text{NpO}_2\text{edta}^{3-}$  and  $\text{NpO}_2\text{edtaOH}^{4-}$ . In the cation-exchange study only one species,  $\text{NpO}_2(\text{Hedta})^{2-}$  and  $\text{PuO}_2(\text{Hedta})^{2-}$  in the case of Np(V) and Pu(V), respectively, could be detected as a consequence of the large scattering of the experimental data.

All measurements were made at  $I = 0.1$  M, using  $\text{NH}_4\text{ClO}_4$  or  $\text{NaClO}_4$  as inert salts. The measured pH values were transformed to  $-\log_{10}[\text{H}^+]$  values using  $\log_{10}[\text{H}^+] = a - \text{pH}$ , with  $a = 0.085$  for  $\text{NaClO}_4$  and  $0.078$  for  $\text{NH}_4\text{ClO}_4$ .

The authors state that Table 1 of [70EBE/WED] lists the edta protonation constants used in their study. However, there are several ambiguities. First of all, the reference given in this table for the edta protonation constants is wrong. The cited paper deals with Pu(VI) acetate complexes and no edta data are reported there. The numerical values in Table 1 of [70EBE/WED] are almost identical with the data of [47SCH/ACK] valid for  $I = 0.1$  M KCl at 20°C. For some other ligands the protonation constants listed in this Table 1 refer to  $\text{NaClO}_4$  media, and also the edta protonation constants used by [71EBE/PAU] refer to  $\text{NaClO}_4$  media. In the case of  $\text{NpO}_2(\text{Hedta})^{2-}$  and  $\text{PuO}_2(\text{Hedta})^{2-}$  this ambiguity is of little importance, as the differences in  $\text{Hedta}^{3-}$  protonation at  $I = 0.1$  M in different media are small (see Table VIII–8a in Section VIII.3.7). However, in the case of  $\text{NpO}_2\text{edta}^{3-}$  the difference of apparent  $\text{edta}^{4-}$  protonation in Na and K media is substantial (see Tables VIII–8a and VIII–8b in Section VIII.3.7). If we tentatively assume that [70EBE/WED] used edta protonation constants for  $\text{NaClO}_4$  media as reported in [71EBE/PAU] and correct their  $\text{NpO}_2\text{edta}^{3-}$  value for  $\text{Na}(\text{edta})^{3-}$  complexation (see discussion of [98POK/BRO] in this Appendix), perfect agreement with the data of [98POK/BRO] is reached (Section VIII.11.2.3). However, if we assume that [70EBE/WED] used the edta protonation constants of [47SCH/ACK] and correct their  $\text{NpO}_2\text{edta}^{3-}$  value for  $\text{Kedta}^{3-}$  complexation only, a difference of 0.7 log units with the [98POK/BRO] data emerges. In the case of  $\text{NpO}_2(\text{Hedta})^{2-}$  the effects of this ambiguity

are small and good agreement with the [98POK/BRO] data is reached in any case. Nevertheless, the Np(V) edta values of [70EBE/WED] are used for comparison only in this review and the selected values are based solely on the data of [98POK/BRO].

#### [70GRZ/TAT]

Mixtures of magnesium and manganese chlorides with citric and isocitric acid have been titrated potentiometrically at the glass electrode with tetramethylammonium hydroxide at 25°C and  $I = 0.1$  M. By using the protonation constants,  $\log_{10} K_{(H)} = 5.82$ , 4.35 and 2.85, the stability constants were obtained to be  $\log_{10} \beta_{1(cit)} = 3.85$  for  $Mg^{2+} + cit^{3-} \rightleftharpoons Mg(cit)^-$  and  $\log_{10} \beta_{1(Hcit)} = 1.92$  for  $Mg^{2+} + Hcit^{2-} \rightleftharpoons Mg(cit)(aq)$  (these values do not include  $Na^+$  or  $K^+$  complexation with  $cit^{3-}$ ). The conversion of the measured pH to  $-\log_{10}[H^+]$  is done in the same way as in [65TAT/GRZ]. This review accepts the above values with assigning the uncertainty of  $\pm 0.2$ .

#### [70PET/STE2]

An anion exchange method was used to identify the charge of anionic U(IV) oxalate complexes in solution and help to analyse the data of solubility experiments. The solubility of  $U(ox)_2 \cdot 6H_2O$  was found to be  $0.9 \times 10^{-4}$  M U in 0.5 N  $KNO_3$  and  $1.9 \times 10^{-4}$  M U in 1 N  $H_2Ox$ . The charges of the anionic U(IV) oxalate complexes in these solutions were found to be 1 and 4, respectively. Accordingly, the authors assumed  $UOH(ox)_2^-$  and  $H_4U(ox)_4$  to be the dominant species in 0.5 N  $KNO_3$  and 1 N  $H_2Ox$ . No solubility constants were provided.

The solubility of  $K_2U_2(ox)_5 \cdot 8H_2O$  was studied in solutions of  $LiClO_4$ ,  $HClO_4$  and  $H_2Ox$ . The concentrations of uranium in the solution were found to be in the range of  $(0.4-1.8) \times 10^{-4}$  M. The charge on the anion in solutions was found to be 2 by ion exchange and suggested the presence of a dimeric U(IV) oxalate complex,  $[U_2(ox)_5]^{2-}$ , in solution. However, changes in the composition of the solid phase were observed and  $K_2U_2(ox)_5 \cdot 8H_2O$  underwent decomposition. As a result, the solubility data from this reference are considered to be unreliable and rejected by this review.

#### [70PRA/HAV]

The stability constants of complexes of zirconium with nta, edta, cdta, HCl,  $HNO_3$  and  $H_2SO_4$  have been determined using solutions of dinonyl naphthalene sulphonic acid as liquid ion exchanger in 2 M  $HClO_4$ . From the obtained values it appears that perchlorate is a suitable anion of the inert salt in such kind of studies. For an exact evaluation of the zirconium-edta stability constant, zirconium hydrolysis data are needed. A drawback of this study is that the total concentration of edta used in the experiments is not given. Only the calculated  $[edta^{4-}]$  concentration is reported but the edta protonation constants used for these calculations are not given by [70PRA/HAV].

[\[70SIL/SIM\]](#)

The U(VI) complexes with methyliminodiacetic acid, N-hydroxyethyliminodiacetic acid, ethylenediamine-N,N'-diacetic acid and ethyleneglycol-bis-(aminoethylether)-tetraacetic acid have been studied by potentiometry. Stability constants of the 1:1 and 2:1 metal to ligand chelates have been determined, as well as their hydrolysis and polymerisation constants. The stability for U(VI) - edta complexes, reported in Table 2 of this paper, have been taken from [\[68SIL/SIM\]](#). No new data concerning edta are reported here.

[\[70STE/PAZ\]](#)

The dissociation of  $5 \times 10^{-3}$  M oxalic acid has been determined by electromigration at 25°C and 0.05 to 1.0 M ionic strength where “the desired ionic strength and equilibrium ion concentration were produced with KNO<sub>3</sub>, HNO<sub>3</sub>, and KOH”. Except for  $I = 0.1$  and 0.5 M (data reported graphically only in Fig. 1 of the paper, the data at  $I = 0.5$  M have not been evaluated by the authors) the measured rates of electromigration are rather scarce (two or four values for each ionic strength given in Tab. 1 of the paper, the minimum to calculate the first, or the first and second dissociation constant, respectively). The first dissociation constant reported in Tabs. 2 and 3 contains a typo error (erroneous minus signs in the table headers). In addition, the authors extrapolated values to zero ionic strength using an extended Debye-Hückel equation but the reported results are grossly wrong by orders of magnitude. Besides these more formal shortcomings, the basic assumption of the authors for evaluating their data, namely that there is a pH region where the mobility of Hox<sup>-</sup> can be measured without considering the influence of H<sub>2</sub>ox(aq) or ox<sup>2-</sup>, does not hold. Simply taking the measured rate of electromigration at  $-\log_{10}[\text{H}^+] \approx 2.4$  as the mobility of the Hox<sup>-</sup> anion leads to systematic errors in the derived dissociation constants, which manifests in a systematic difference of 0.1 to 0.2 log<sub>10</sub>-units between the constants recommended by this review and the values reported in [\[70STE/PAZ\]](#). The measured data are too scarce for a re-evaluation and hence, the oxalate protonation constants reported in [\[70STE/PAZ\]](#) have not been considered in this review.

The interaction of  $1 \times 10^{-2}$  M oxalic acid with trace amounts of <sup>45</sup>Ca has been determined by electromigration at 25°C and 0.1 M ionic strength as a function of pH where “the values of  $-\log_{10}[\text{H}^+]$  were produced with the aid of KNO<sub>3</sub> and HNO<sub>3</sub>”. The above discussed erroneous values of oxalate protonation constants were used to calculate [ox<sup>2-</sup>] concentrations and  $\log_{10} K_1 = (2.30 \pm 0.07)$  was derived for Ca(ox)(aq). The electromigration experiments for the <sup>45</sup>Ca - oxalate system seem to be reliable, and the [ox<sup>2-</sup>] concentrations have been re-calculated using oxalate protonation constants selected in this review. The resulting value  $\log_{10} K_1 = (2.35 \pm 0.10)$  for Ca(ox)(aq) is included in the review process.

[\[71CHA/LIA\]](#)

The solvent extraction behavior of the system Np(IV) – HNO<sub>3</sub> – edta – thenoyl trifluoroacetate (TTA) – benzene was investigated at 25°C. The hydrogen ion activity of the aqueous phase was kept above 0.45 M and the TTA activity in the benzene phase was maintained below 0.09 M. A Toa Dempa HM-5A pH meter with external glass electrode was used for pH titration. No details are reported about the pH scale used or the calibration of the pH meter. For the reaction  $\text{Np}^{4+} + \text{H}_4\text{edta}(\text{aq}) \rightleftharpoons \text{Np}(\text{edta})(\text{aq}) + 4 \text{H}^+$  a stability constant  $K = 10^{1.80}$  is reported, but the steps for the obtainment of this result and the necessary calculations are not given. Using edta protonation constants of unknown origin, the authors report a second stability constant  $K = 10^{22.9}$  for the reaction  $\text{Np}^{4+} + \text{edta}^{4-} \rightleftharpoons \text{Np}(\text{edta})(\text{aq})$ . Obviously, the presence of the species  $\text{H}_5\text{edta}^+$  and  $\text{H}_6\text{edta}^{2+}$  has been neglected in their calculations. The constant reported by [\[71CHA/LIA\]](#) has been rejected in this review.

[\[71CHA/LIA2\]](#)

This paper reports the extension of the investigation of the Np(IV) edta system [\[71CHA/LIA\]](#) to Np(V) by solvent extraction. The same shortcomings are found as in the previous paper: no details are reported about the pH scale used or the calibration of the pH meter. In addition, the nature of the background electrolyte used to reach  $I = 1.0$  M and the temperature of the measurements are not stated. Using edta protonation constants of unknown origin, the authors report a stability constant  $K = 10^{9.05}$  for the reaction  $\text{NpO}_2^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2\text{edta}^{3-}$ , but the steps for the obtainment of this result and the necessary calculations are not given. The presence of the protonated species  $\text{NpO}_2(\text{Hedta})^{2-}$  at the investigated pH range 4 – 6 has been ignored. Hence, the constant reported by [\[71CHA/LIA2\]](#) has been rejected in this review.

[\[71EBE/PAU\]](#)

The composition and the formation constants of several Np(IV) aminopolycarboxylic acids (including edta) have been investigated by spectrophotometry. The authors describe in detail the preparation of the Np(IV) stock solution and report that the solution is stable for some hours under argon atmosphere. At longer time spans Np(IV) is oxidised to Np(V), which has been checked by spectrophotometry. All measurements have been carried out at  $I = 1.0$  M (H,Na)ClO<sub>4</sub> at  $(25.0 \pm 0.2)^\circ\text{C}$ . The molar extinction coefficient of Np(IV)(aq) at the maximum of  $\lambda = 960.4$  nm shows a dependence with the HClO<sub>4</sub> concentration at  $I = 1.0$  M (H,Na)ClO<sub>4</sub>, which probably is caused by the increasing Np(IV) hydrolysis with decreasing acidity of the solution. For pH the  $[\text{H}^+]$  concentration scale has been used and the pH calibration is described in detail in this paper. The edta protonation constants of [\[67AND\]](#), valid for  $I = 1.0$  M NaClO<sub>4</sub> at 20°C, have been used in the calculations. The reported stability constant is considered as reliable and it has been accepted in this review.



[\[71ELE/ZAI\]](#)

The complexation of americium, curium and promethium with edta is investigated by a cation exchange method using the resin KU-2. Data are reported in 0.2 M  $\alpha$ -hydroxyisobutyrate and  $1 \cdot 10^{-3}$  M edta, causing a widely varying ionic strength, and one data point in 0.1 M  $\text{NH}_4\text{ClO}_4$  and  $1 \cdot 10^{-4}$  M edta at pH 4.1. The temperature of the measurements is not reported. The pH measurements are not mentioned, neither the pH scale used nor the calibration of the pH meter. The edta protonation constants used for obtaining Am – edta stability constants are not reported and no reference is cited. The only information given is the total concentration of edta and  $[\text{edta}^{4-}]$  calculated from unknown protonation constants (Table 2 of [\[71ELE/ZAI\]](#)). Hence, although the results of [\[71ELE/ZAI\]](#) are not unreasonable, they are not further considered by this review.

[\[71GUI/BOU\]](#)

Distribution ratios of  $^{241}\text{Am}$  ( $\sim 3 \cdot 10^{-7}$  M) between TTA/benzene and aqueous phase containing 0,  $10^{-6}$ ,  $10^{-4}$ ,  $10^{-3}$ ,  $3 \cdot 10^{-3}$ , and  $10^{-2}$  M citric acid were measured at pH 2.5 – 5.5,  $I = 0.1$  M  $(\text{Li,H})\text{ClO}_4$ .

Values of  $\log_{10} {}^*\beta_1 = -5.4$  for  $\text{Am}^{3+} + \text{H}_3\text{cit} \rightleftharpoons \text{Am}(\text{cit})(\text{aq}) + 3 \text{H}^+$  and  $\log_{10} {}^*\beta_2 = -9.7$  for  $\text{Am}^{3+} + 2\text{H}_3\text{cit} \rightleftharpoons \text{Am}(\text{Hcit})(\text{cit})^{2-} + 5\text{H}^+$  were reported. These values correspond to  $\log_{10} \beta_{1(\text{cit})} = 7.7$  for  $\text{Am}^{3+} + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})(\text{aq})$  and  $\log_{10} \beta_{1(\text{cit})(\text{Hcit})} = 10.6$  for  $\text{Am}^{3+} + \text{Hcit}^{2-} + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{Hcit})(\text{cit})^{2-}$  if we use the protonation constants given in [\[71GUI/BOU\]](#) ( $\log_{10} K_{(\text{H})} = 5.84, 4.36, 2.88$ ). The simulation with these values indicates that only  $\text{Am}^{3+}$  and  $\text{Am}(\text{cit})(\text{aq})$  can be predominant under the conditions used in the experiments. Although  $\text{Am}(\text{Hcit})(\text{cit})^{2-}$  may contribute to some extent at the pH's where  $\text{Am}^{3+}$  changes to  $\text{Am}(\text{cit})(\text{aq})$ , this speciation may possibly be originated from the errors in the protonation constants used in the fitting ( $\log_{10} K_{(\text{H})} = 5.84$  seems too high as compared with that in this review). Also, in this experiment, the use of 0.1 M TTA in benzene would give significant concentration of this reagent in the aqueous solution and might affect through the complex formation with  $\text{Am}^{3+}$ . Therefore, this review accepts the value for  $\text{Am}(\text{cit})(\text{aq})$  with assigning a large uncertainty of  $\pm 0.5$  estimated from the errors in the solvent extraction technique and in the protonation constants.

[\[71MOS6\]](#)

This is not an experimental study. A value of stability constant for the U(V) oxalate complex,  $\text{UO}_2\text{ox}^-$ , was estimated from correlation, but no details were provided. Neither the temperature nor the ionic strength was specified. Therefore, this value is rejected by this review.

[\[71OHY/OHY\]](#)

Distribution coefficients ( $K_d$ ) of  $^{241}\text{Am}$  between a cation exchanger (Dowex 50 W-X8, 100 – 200 mesh) and an aqueous solution containing various compositions of citrates



and 0.1 M NaCl were measured. Series of measurements were conducted at a nearly constant  $[\text{H}_2\text{cit}^-]$  at pH 1.9–3.4 (by adding various amounts of  $C_{\text{H}_3\text{cit}}$  to 0.1 M  $C_{\text{Na}_2\text{Hcit}}$ ), at a constant pH of 3.20, and at a constant pH of 6.56.

Distribution coefficient of  $^{241}\text{Am}$  can be expressed by:

$$K_d = \frac{K_d^0}{1 + \sum \beta_i (\text{H}_2\text{cit}) [\text{H}_2\text{cit}^-]^i + \sum \beta_j (\text{Hcit}) [\text{Hcit}^{2-}]^j + \sum \beta_k (\text{cit}) [\text{cit}^{3-}]^k}$$

where  $K_d^0$  is the distribution coefficient in the absence of citrates and  $\beta_{q(\text{Hcit})}$  is defined for the reaction  $\text{Am}^{3+} + q(\text{H}_r\text{cit})^{r-3} \rightleftharpoons \text{Am}(\text{H}_r\text{cit})_q^{3+q(r-3)}$ . The plots of  $\log_{10}(K_d^0/K_d - 1)$  against  $\log_{10}[\text{Hcit}^{2-}]$  for the data obtained at pH < 3.4 lied on the same curve, indicating that only  $\text{Hcit}^{2-}$  is the possible ligand under this condition. By using the protonation constants of  $\log_{10} K_{(\text{H})} = 5.67, 4.40$  and  $2.95$  [59OKA/KOL] and plotting  $(K_d^0/K_d - 1)/[\text{Hcit}^{2-}]$  against  $[\text{Hcit}^{2-}]$ ,  $\log_{10} \beta_{1(\text{cit})} = (5.31 \pm 0.02)$  for  $\text{Am}(\text{Hcit})^+$  and  $\log_{10} \beta_{2(\text{Hcit})} = (8.23 \pm 0.02)$  for  $\text{Am}(\text{Hcit})_2^-$  were obtained. Similarly, from the plots of  $(K_d^0/K_d - 1)/[\text{cit}^{3-}]$  against  $[\text{cit}^{3-}]$  for the data obtained at pH 6.56,  $\log_{10} \beta_{1(\text{cit})} = (6.74 \pm 0.08)$  for  $\text{Am}(\text{cit})(\text{aq})$  and  $\log_{10} \beta_{2(\text{cit})} = (11.55 \pm 0.08)$  for  $\text{Am}(\text{cit})_2^{3-}$  were obtained. Although the experiments were carefully done and the fitted result in this paper seems fairly well, errors in  $K_d^0$  and  $K_d$  would seriously affect the shape of the plot. Measured  $K_d^0$  and  $K_d$  values correspond to 0.04% and 14~96%  $^{241}\text{Am}$  in the aqueous phase at the ratio of the volume of the solution to the mass of resin of 100 mL/g. Since these values were calculated by:

$$K_d = \frac{(A_i - A_s)}{A_s} \times \frac{\text{vol. of solution phase (mL)}}{\text{mass of dry resin (g)}},$$

where  $A_i$  and  $A_s$  are the initial and final activities in the aqueous phase, errors may be high when the percentages in the aqueous phase are close to 0 or 100%. The constant of  $\log_{10} \beta_1^0 = (0.24 \pm 0.03)$  for  $\text{Am}^{3+} + \text{Cl}^- \rightleftharpoons \text{AmCl}^{2+}$  selected by [2003GUI/FAN] suggests that the formation of  $\text{AmCl}^{2+}$  may not be neglected under the condition of this study. In such a case, distribution coefficient of  $^{241}\text{Am}$  should be expressed by:

$$K_d = \frac{K_d^0 (1 + \beta_{\text{Cl}} [\text{Cl}^-])}{1 + \beta_{\text{Cl}} [\text{Cl}^-] + \sum \beta_i (\text{H}_2\text{cit}) [\text{H}_2\text{cit}^-]^i + \sum \beta_j (\text{Hcit}) [\text{Hcit}^{2-}]^j + \sum \beta_k (\text{cit}) [\text{cit}^{3-}]^k}$$

and the obtained values of  $\log_{10} \beta$  should be corrected according to this relation. At  $I = 0.1$  m NaCl,  $\log_{10} \beta_{\text{Cl}}$  can be estimated to be  $-0.42$  with neglecting  $\Delta\epsilon$  term. Therefore,  $\log_{10}(1 + 10^{-0.42}[\text{Cl}^-]) = 0.02$  should be added to the reported values. Considering this effect and the possible systematic errors in the ion exchange technique, this review accepts these corrected stability constants with assigning uncertainties of 0.5.

[\[71OLI/CHO\]](#)

The kinetics of the exchange of  $\text{Ce}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Am}^{3+}$  with  $\text{La}(\text{edta})^-$  were studied using a radiotracer method. From experiments in 0.5 M  $\text{NaClO}_4$  at 24°C and pH 5.450 a stability constant  $\log_{10}K_1 = 18.0$  is reported in Table 2 of [\[71OLI/CHO\]](#) for the reaction  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$ . This constant was determined from the measured rate constants of the exchange equilibrium  $\text{Am}^{3+} + \text{La}(\text{edta})^- \rightleftharpoons \text{Am}(\text{edta})^- + \text{La}^{3+}$  using the constant  $\log_{10}K_1 = 16.34$  for  $\text{La}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{La}(\text{edta})^-$  taken from [\[65MOE/MAR\]](#). However, the latter constant is valid for  $I \rightarrow 0$  and 20°C [\[65MOE/MAR\]](#). D’Olieslager and Choppin did not correct this constant for 0.5 M  $\text{NaClO}_4$  and 24°C.

The La – edta system has not been included in this review and hence, no selected value for  $\text{La}(\text{edta})^-$  is available. However, even if this additional effort would be made in order to obtain an auxiliary constant, this would not lead to an accepted value for  $\text{Am}(\text{edta})^-$ : in contrast to the detailed reporting of Eu data, no experimental details are given for Am in [\[71OLI/CHO\]](#). Furthermore, the pH scale used and the calibration of the pH meter are not reported, and hence the meaning of “pH 5.450” is not clear. In summary, the stability constant for  $\text{Am}(\text{edta})^-$  reported in [\[71OLI/CHO\]](#) is not credited by this review, and there seems to be no promising way for a successful re-evaluation of this constant.

Remarkably, in a more recent paper of Choppin and co-workers [\[99CHE/CHO\]](#), which contains a quite complete summary of the Am - edta literature values, the results of [\[71OLI/CHO\]](#) are not mentioned.

[\[71PAZ/STE\]](#)

This paper describes the determination of the solubility of  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}$  in  $\text{HNO}_3$  solutions and also in mixed solutions of  $\text{HNO}_3$  and  $\text{H}_2\text{Ox}$ . The solubility was measured by putting  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}$  in a vessel at  $(20.0 \pm 0.1)^\circ\text{C}$  and adding the appropriate solution. After stirring vigorously with a screw stirrer for one hour, the phases were separated by filtering off the suspension on a double “blue ribbon” filter. The rate of dissolution of  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}$  in the mixed solutions is rather high. In all the solutions the concentration of calcium in the solution had reached a constant value after 40 minutes, which did not change in two days. Concentrations of 0.1, 0.5 and 1.0 M  $\text{HNO}_3$  were used, and in the mixed solutions 0.1, 0.25 and 0.5 M  $\text{H}_2\text{Ox}$  was added to these solutions. The results have been interpreted by the authors including the species  $\text{Ca}(\text{ox})(\text{aq})$  and  $\text{Ca}(\text{ox})_2^{2-}$  in their mass balance equations. Oxalate protonation constants have been taken from the literature, which can be traced back to [\[48PIN/BAT\]](#) for the first protonation constant, and to [\[41DAR\]](#) for the second one. The latter constant deviates significantly from the one selected in this review. The stability constant for  $\text{Ca}(\text{ox})(\text{aq})$ , valid for 0.1 M  $(\text{K,H})\text{NO}_3$ , has been taken from [\[70STE/PAZ\]](#) and obviously assumed to be valid at zero ionic strength. This constant has been re-evaluated in this review, see discussion in this Appendix. Activity coefficients for  $\text{H}^+$ ,  $\text{Hox}^-$ ,  $\text{ox}^{2-}$  and  $\text{Ca}^{2+}$  have been taken from

the literature or were calculated from mean activity data. The activity coefficients for  $\text{Ca(ox)(aq)}$  and  $\text{Ca(ox)}_2^{2-}$  are implicitly assumed to be unity. The authors report a solubility product for  $\text{Ca(ox)} \cdot \text{H}_2\text{O}$ ,  $\log_{10} K_{\text{Ca}}^o = -8.87$ , and a formation constant for  $\text{Ca(ox)}_2^{2-}$ ,  $\log_{10} \beta_2^o = 3.49$ . Especially the latter constant is subject to significant systematic errors because of the second oxalate protonation constant and the stability constant for  $\text{Ca(ox)(aq)}$  used in the calculations, and the inappropriate activity model applied by the authors. However, at present there is no reliable way to re-evaluate  $\text{Ca(ox)} \cdot \text{H}_2\text{O}$  solubility data in concentrated  $\text{HNO}_3 - \text{H}_2\text{ox}$  solutions because of the lack of appropriate SIT interaction parameters in such media. The results of this study are not further considered in this review.

#### [\[71PYA/KRA2\]](#)

The composition and stability constants of the oxalate complexes of zirconium and hafnium have been studied at pH 5.2 and 4.0, respectively, by measuring the solubilities of  $\text{ZrO(OH)}_2$  and  $\text{HfO(OH)}_2$  in the presence of  $(0.5 \text{ to } 2.1) \times 10^{-2}$  M oxalate. The concentrations of zirconium and hafnium were found to be  $(0.5 \text{ to } 16) \times 10^{-4}$  M. From the dependencies of the solubilities on pH and  $C_{\text{ox}}$ , it was inferred that in the pH range from 4 to 6 the reaction,  $\text{MO(OH)}_2(\text{s}) + 2\text{ox}^{2-} \rightleftharpoons \text{MO(ox)}_2^{2-} + 2\text{OH}^-$  takes place ( $\text{M} = \text{Zr, Hf}$ ). The equilibrium constant for this reaction  $K_{\text{eq}}$  was obtained and converted into the instability constant,  $1/\beta_2 = [\text{MO}^{2+}][\text{ox}^{2-}]^2 / [\text{MO(ox)}_2^{2-}]$  using the relation  $1/\beta_2 = SP/K_{\text{eq}}$  where  $SP$  is the solubility product of  $\text{MO(OH)}_2$ ,  $SP = [\text{MO}^{2+}] \cdot [\text{OH}^-]^2$ , which was estimated from the reported solubility product of  $\text{M(OH)}_4$  and first and second hydrolysis constants of  $\text{M}^{4+}$ . The instability constants were obtained to be  $1/\beta_2 = (2.1 \pm 0.2) \times 10^{-9}$  for  $\text{ZrO(ox)}_2^{2-}$ , and  $1/\beta_2 = (3.0 \pm 0.1) \times 10^{-7}$  for  $\text{HfO(ox)}_2^{2-}$ .

The values of  $K_{\text{eq}}$  in Table 1 of the paper could not be reproduced by the Equation (4) in [\[71PYA/KRA2\]](#) for some unknown reason. The difference between measured pH and  $-\log_{10}[\text{H}^+]$  may give some error in the case of hafnium. Although the logarithm of the solubility changed with  $\log_{10}[\text{H}_2\text{ox}]$  with a slope of 2, the complex species of  $[\text{MO(ox)}_2^{2-}]$  is not well-established. The existence of the  $\text{ZrO}$  and  $\text{HfO}$  unit in the solution and in the complexes cannot be accepted. Due to the uncertainty on the solubility determining reaction, this review does not accept the results of this paper.

#### [\[71RUM\]](#)

Applying the radiochemical method of Schubert, the stability constants of Ca, Sr and Ba complexes with citrate have been determined at the temperatures from 10 to 55°C. Using the ion exchanger Dowex 50 (X12, 200 – 400 mesh) at a solid to liquid ratio of 0.2 g to 50 mL, distribution coefficients  $K_d$  of  $^{45}\text{Ca}$ ,  $^{85}\text{Sr}$  and  $^{133}\text{Ba}$  were measured at pH 7.5 and 8 at 0.2 M  $\text{NH}_4\text{Cl}$  and plotted in the form of:

$$\frac{K_d^o}{K_d} = 1 + \beta_1[\text{cit}^{3-}] + \beta_2[\text{cit}^{3-}]^2.$$

For  $\text{Ca}^{2+}$ -citrates, the constants for the reactions  $\text{Ca}^{2+} + n \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})_n^{2-3n}$ , ( $n = 1, 2$ ) were obtained to be  $\log_{10}\beta_1 = 3.15$  (at 19.6°C), 3.10 (at 28.2°C), 3.04 (at 38°C), 2.97 (at 51.4°C), 2.82 (at 65.0°C) and  $\log_{10}\beta_2 = 4.33$  (at 25°C) with the uncertainties  $\pm 0.01 - 0.015$  for  $\log_{10}\beta_1$  and  $\pm 0.05$  for  $\log_{10}\beta_2$ . Also, by plotting  $\log_{10}\beta_1$  against  $1/T$ ,  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$  for the formation of  $\text{Ca}(\text{cit})^-$  were obtained to be  $-10.4 \text{ kJ} \cdot \text{mol}^{-1}$  and  $24.7 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$ , respectively.

In the cases of  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  complexes of citrate, with the increase in the temperature  $\log_{10}\beta_1$  decreased until 30°C then increased at higher temperatures. In the case of  $\text{Ca}^{2+}$ -citrate,  $\log_{10}\beta_1$  simply decreased with the temperature, although to obtain the linearity in the plots of  $\log_{10}\beta_1$  against  $1/T$ , the  $\text{Ca}^{2+}$  data at 65°C was discarded by Rumbart. By considering the similarity in the chemical nature of  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$ , this seems strange. The effects may be caused by some systematic error introduced from the experiment, where in the case of  $^{45}\text{Ca}$ , the radioactive resin was counted as a flat deposit with a GM counter of the end window type, whereas for  $^{85}\text{Sr}$  and  $^{133}\text{Ba}$  a portion of the equilibrium solution was analysed for activity by means of a single channel scintillation detector. Since small errors in  $\log_{10}\beta_1$  leads to serious errors in  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$ , this review does not accept the results of this paper.

#### [\[71SHA\]](#)

This paper only summarises stability constants published by Shalinets and co-workers in earlier papers. No new experimental data are given. In the case of Am – edta, the data shown in Table 1 of [\[71SHA\]](#) were taken from [\[67LEB/MAK\]](#).

#### [\[71SOL/IVA2\]](#)

The solvent extraction of carrier-free  $^{95}\text{Zr}$  with TTA in benzene from 2 – 4 M perchloric and nitric acid was carried out in the presence of oxalic acid at room temperature. In their previous papers ([\[66SOL/IVA1\]](#), [\[67SOL/TSV\]](#)) the authors have obtained the thermodynamic hydrolysis constants of  $\text{Zr}^{4+}$  based on the extraction data of  $^{95}\text{Zr}$  with  $5 \times 10^{-3}$  to 0.1 M TTA in the absence of any complexing agent by estimating the activity coefficients of relevant species using a method proposed by the authors. The extracted species was considered to be  $\text{ZrA}_4$  (where  $\text{A}^-$  designates deprotonated TTA). The results were also presented later in an overview paper [\[74SOL\]](#). By analysing the extraction data obtained in this study and using thermodynamic constants for the extraction and hydrolysis, it was shown that zirconium was extracted as  $\text{ZrA}_4$ ,  $\text{Zr}(\text{ClO}_4)_3$  and  $\text{Zr}(\text{NO}_3)_3$ . Based on the extraction data in the presence of oxalic acid, the thermodynamic equilibrium constant of the reaction  $\text{Zr}(\text{OH})_2^{2+} + \text{H}_2\text{ox} \rightleftharpoons \text{Zr}(\text{OH})_2(\text{ox})(\text{aq}) + 2\text{H}^+$ , was obtained to be  $4 \times 10^6$ .

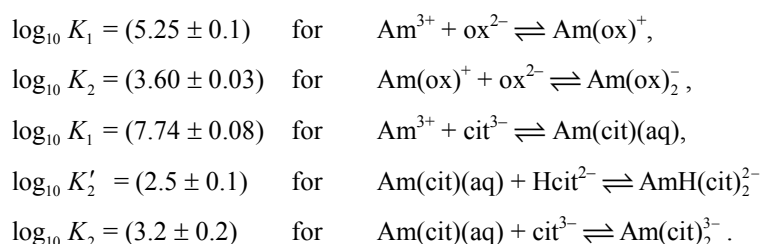
The estimation of the constants for hydrolysis and for the oxalate complex is based on the effect of acidity on the distribution ratio of Zr in the solvent extraction. Since the distribution coefficient of TTA between benzene and water ( $[\text{HA}]_{\text{org}}/[\text{HA}]_{\text{aq}}$ ) is less than  $10^2$  ([\[78STA/FRE\]](#)), the concentration of HTTA in the aqueous phase is

expected to be  $10^{-4}$  to  $10^{-2}$  M. Considering the acid dissociation constant of HTTA (around  $10^{-6.5}$  [78STA/FRE]), and given the large affinity of TTA for tetravalent ions, it is expected that TTA in the aqueous phase would give a serious effect on the speciation of Zr depending on the acidity.

The experiments were performed to model two-phase distribution of Zr(IV) for separation processes, and they were not designed to determine accurately equilibrium constants. When interpreting the data several questionable assumptions were made concerning the speciation in the organic phase ( $\text{Zr}(\text{ClO}_4)_4$  and  $\text{Zr}(\text{NO}_3)_4$ ) and about the activity coefficients in the organic and aqueous phases. The ionic activity coefficients in  $\text{HNO}_3$  solutions and the formation of  $\text{HNO}_3(\text{aq})$  used by the authors are incompatible with the specific ion interaction approach followed in this review, see also the discussion of [72SOL/IVA]. Because of this the data reported in this paper are not accepted by this review.

#### [71STE]

By determining the rate of the electromigration in the apparatus for electrophoresis on quartz sand with radioactive tracers, the stability constants of oxalate complexes and citrate complexes of La, Ce, Pm, Eu, Tb, Tm, Am, Cm, Bk, Cf and Y were obtained at  $I = 0.1$  and  $t = (25 \pm 0.5)^\circ\text{C}$ . The stability constants were determined to be:



The salt to control the ionic strength is not described. The contribution of the oxalate (up to 0.1 M) or citrate (up to  $5 \times 10^{-2}$  M) to the total ionic strength is pretty high. In the electromigration experiment, the potential given to the solution may affect the homogeneous constancy of the media. The measurement of pH or  $-\log_{10}[\text{H}^+]$  and the protonation constants used are not given in the paper. Due to the insufficiency in the description of the experimental details, this paper is not accepted in this review.

#### [71VAS/KOC2]

The enthalpy of dissociation of oxalic acid in aqueous solution was determined by three independent calorimetric methods at  $25^\circ\text{C}$ . The authors measured (1) the heat of solution of solid oxalic acid in various electrolytes at ionic strength 1.0, 1.5 and 2.0 M, (2) the heat of mixing of a 0.5 M solution of oxalic acid with sodium hydroxide solution, and (3) the heat of reaction of sodium hydrogen oxalate solution with nitric acid. The results were extrapolated to zero ionic strength in terms of an extended Debye-Hückel

type of equation discussed in [73VAS/SHE2] and [76VAS/SHE], and the result is reported as  $-(750 \pm 50) \text{ cal}\cdot\text{mol}^{-1}$ . This corresponds to  $\Delta_r H_m = + (3.1 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$  (the uncertainty has been multiplied by 1.96 to obtain error limits closer to 95% total uncertainty level).

Unfortunately, [71VAS/KOC2] is just a short summary of a complete article that has been deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No. 2958-71 Dep. From 24<sup>th</sup> May, 1971) and the deposited material was not available for this review. Hence, the value reported for zero ionic strength is listed in Table VI-7 with an increased uncertainty to account for the ambiguity introduced by the extrapolation procedure.

#### [72ARM/DUN]

The distribution of  $^{45}\text{Ca}$  between the cation-exchanger CG 120 and aqueous solutions of  $\text{NaClO}_4 - \text{Na}_2\text{ox}$  was studied at  $25^\circ\text{C}$  at an ionic strength varied from 0.02 to 0.2 M. The total calcium concentration was less than  $10^{-7}$  M. The solutions measured at a particular ionic strength (*e.g.*, 0.1 M) were made up from  $\text{NaClO}_4$  and  $\text{Na}_2\text{ox}$  solutions of the same ionic strength (*e.g.*, 0.1M  $\text{NaClO}_4$  and 0.1 M  $\text{Na}_2\text{ox}$  solutions) in such a way that the actual compositions changed from 90 vol-%  $\text{NaClO}_4 - 10$  vol-%  $\text{Na}_2\text{ox}$  to 20 vol-%  $\text{NaClO}_4 - 80$  vol-%  $\text{Na}_2\text{ox}$ . This drastic change in the ionic medium in each experimental series not only causes a large (and unknown) continuous variation in activity coefficients, but also may have a large (and unknown) influence on the properties of the cation-exchanger. The reported formation constants for  $\text{Ca}(\text{ox})(\text{aq})$  reveal no systematic variation with ionic strength between 0.02 and 0.2 M, which is in contradiction with all reliable observations (*e.g.*, [82DAN/MAR]). Regarding the above discussed ambiguities introduced by the large change in the ionic medium the results of this study are not considered in this review.

#### [72EBE/MOA]

Absorption spectra of the solutions containing *ca.*  $1.8 \times 10^{-3}$  M  $\text{Am}(\text{III})$  and variable concentrations of citric acid were measured at  $-\log_{10}[\text{H}^+] = 1$  to 10 keeping the ionic strength constant ( $I = 1$  M  $\text{NaClO}_4$ ). Absorbance readings at 504.6 nm (assigned to  $\text{Am}(\text{Hcit})^+$ ), 505.9 nm ( $\text{Am}(\text{cit})(\text{aq})$ ), 506.6 nm ( $\text{Am}(\text{cit})_2^{3-}$ ) and 509.3 nm ( $\text{Am}(\text{cit})(\text{OH})^-$ ) were analysed as a function of  $-\log_{10}[\text{H}^+]$  using the protonation constants  $\log_{10} K_{(\text{H})} = 5.43, 4.11$  and  $2.63$ . The constants were obtained to be

$$\begin{aligned}\log_{10} \beta_{1(\text{Hcit})} &= (4.53 \pm 0.04) \text{ for } \text{Am}^{3+} + \text{Hcit}^{2-} \rightleftharpoons \text{Am}(\text{Hcit})^+, \\ \log_{10} \beta_{1(\text{cit})} &= (6.96 \pm 0.06) \text{ for } \text{Am}^{3+} + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})(\text{aq}), \\ \log_{10} \beta_{2(\text{cit})} &= (10.3 \pm 0.2) \text{ for } \text{Am}^{3+} + 2\text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})_2^{3-}, \text{ and} \\ \log_{10} {}^*K &= -(5.61 \pm 0.02) \text{ for } \text{Am}(\text{cit})(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{Am}(\text{cit})(\text{OH})^- + \text{H}^+.\end{aligned}$$

The value for the last reaction implies that the alcoholic-OH in  $\text{Am}(\text{cit})(\text{aq})$  deprotonates at pH 5.6 due to the interaction with  $\text{Am}^{3+}$ . Since this value is based on the meas-

urement at higher pcH, the possibility of the formation of carbonate complexes  $\text{Am}(\text{CO}_3)_q^{3-2q}$  cannot be excluded. No description for the effect of atmospheric  $\text{CO}_2$  can be found in the paper, and if the solution is in equilibrium with the atmosphere,  $\text{Am}(\text{cit})(\text{aq})$  would be transformed into  $\text{Am}(\text{CO}_3)_q^{3-2q}$  at pH 8 ~ 10 (depending on the concentration of citrate). Considering the differences between the protonation constants used in this paper and those selected in this review ( $\log_{10} K_{1(\text{H})} = 5.43$  seems much higher), this review accepts the values with assigning large uncertainties as  $\log_{10} \beta_{1(\text{Hcit})} = (4.53 \pm 0.5)$  for  $\text{Am}(\text{Hcit})^+$ ,  $\log_{10} \beta_{1(\text{cit})} = (6.96 \pm 0.5)$  for  $\text{Am}(\text{cit})(\text{aq})$ ,  $\log_{10} \beta_{2(\text{cit})} = (10.3 \pm 0.5)$  for  $\text{Am}(\text{cit})_2^{3-}$ .

#### [72KER/CHU]

Distribution of  $\text{Ni}^{2+}$  ( $C_M = 2.98 \times 10^{-4}$  M) between 0.5 M  $\text{NaNO}_3$  ( $V = 25$  mL) and the cation exchange resin KU-2 of the  $\text{Na}^+$  form ( $m = 1000$  mg) was studied at pH 2.8 – 4.4 in the absence and presence ( $1 \times 10^{-3}$  to  $5 \times 10^{-2}$  M) of citric acid. From the colorimetric determination of  $\text{Ni}^{2+}$  in the aqueous phase, the plots of  $K_d^o/K_d - 1$  against  $C_L$  was constructed at each pH (2.80, 3.00, 3.40, 3.90, 4.40), where  $K_d^o$  and  $K_d$  are the distribution coefficients in the absence and presence of citric acid. By considering that these plots correspond to the relation:

$$\frac{K_d^o}{K_d} - 1 = \beta_{1(\text{H}_2\text{cit})}[\text{H}_2\text{cit}^-] + \beta_{1(\text{Hcit})}[\text{Hcit}^{2-}] + \beta_{1(\text{cit})}[\text{cit}^{3-}] = A C_L,$$

where  $\beta_{1(\text{H}_r\text{cit})}$  denotes the constant for the reaction  $\text{Ni}^{2+} + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{Ni}(\text{H}_r\text{cit})^{r-1}$ , the values of the slope  $A$  of these plots (five values) were analysed to give the above three  $\beta$  values. The values of  $\log_{10} \beta_1$  were calculated to be  $(1.55 \pm 0.04)$  for  $\text{Ni}(\text{H}_2\text{cit})^+$ ,  $(2.90 \pm 0.04)$  for  $\text{Ni}(\text{Hcit})(\text{aq})$  and  $(4.25 \pm 0.12)$  for  $\text{Ni}(\text{cit})^-$ . In the calculation, the values of  $\log_{10} K_{(\text{H})} = 5.135, 4.092$  and  $2.778$  were used for the protonation constants, which are smaller than those selected in this review. The hydrogen ion concentration was reported to be calculated from the measured pH using an activity coefficient estimated by the Davies equation. However, the measured pH does not give a good estimate of the hydrogen ion activity since the liquid junction potential is not negligible at this ionic strength. Under the experimental conditions used in this paper, these errors in  $[\text{H}^+]$  and in the protonation constants give serious errors in the estimation of  $[\text{H}_3\text{cit}]$ ,  $[\text{H}_2\text{cit}^-]$ ,  $[\text{Hcit}^{2-}]$  and  $[\text{cit}^{3-}]$ , which in turn give errors in  $\log_{10} \beta$  values. By this reason, the values are not accepted by this review.

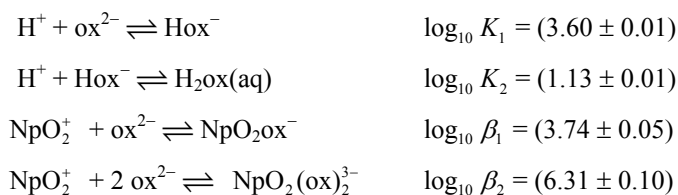
#### [72KUP]

Four different potassium oxalate compounds are known to exist at room temperature and ambient pressure:  $\text{KH}_3(\text{ox})_2 \cdot 2\text{H}_2\text{O}(\text{cr})$ ,  $\text{KHox}(\text{cr})$ ,  $\text{K}_4\text{H}_2(\text{ox})_3 \cdot 2\text{H}_2\text{O}(\text{cr})$  and  $\text{K}_2\text{ox} \cdot \text{H}_2\text{O}(\text{cr})$ . Large single crystals in the cm scale have been grown by the author from aqueous solutions. Special difficulties were encountered in growing  $\text{K}_4\text{H}_2(\text{ox})_3 \cdot 2\text{H}_2\text{O}(\text{cr})$ , which shows an incongruent solubility, and  $\text{K}_2\text{ox} \cdot \text{H}_2\text{O}(\text{cr})$ , the growth rate of which

depends strongly on the stirring rate. The solubilities of these compounds have not been measured in this study.

#### [72MAG/BIS]

The authors report a careful potentiometric determination of the complex formation between  $^{237}\text{Np(V)}$  and several organic ligands, including oxalate, at 20°C in 1 M NaClO<sub>4</sub>. For oxalate the authors report:



These equilibrium constants are included in the review process. The uncertainties in the data for oxalate protonation and complex formation are increased to  $\pm 0.02$  and  $\pm 0.10 \log_{10}$  units for  $K_1$  and  $K_2$  and to  $\pm 0.10$  and  $\pm 0.15 \log_{10}$ -units for  $\beta_1$  and  $\beta_2$ , respectively, to include possible systematic errors in the measurements.

#### [72MAN/VAR]

The complexation of U(VI) with oxalate was studied by polarography at 20°C and in the ionic medium of 0.2 M (H/Na)ClO<sub>4</sub>. The stability constants of the U(VI) oxalate complexes were calculated to be  $\beta_1 = 1.0 \times 10^5$  and  $\beta_2 = 5.6 \times 10^9$ . Serious concerns are raised during the review on the reliability of the data from this paper. First, the ionic strength was actually significantly higher than the nominal value of 0.2 M and varied from experiment to experiment due to the changing concentrations of oxalate. In one case, 0.2 M oxalic acid was used in 0.2 M NaClO<sub>4</sub> (plus some HClO<sub>4</sub>) to obtain the important parameter “*hlim*”, resulting in a mixed electrolyte system with  $I > 0.2$  M. The dissociation constants of oxalic acid ( $\log_{10} K_1 = -1.2$  and  $\log_{10} K_2 = -4.2$ ) are taken from an unknown literature, but coincide with the values published in [61MCA/NAN] for  $\log_{10} K_1$  and [39HAR/FAL], [48PIN/BAT] for  $\log_{10} K_2$ , all valid at  $I = 0$ . These values were erroneously used for the systems at  $I \approx 0.2$  M in this work. Besides, there is no information in the paper that describes how the pH/pC<sub>H</sub> conversion was accomplished in this work. It appears that the measured pH<sub>obs</sub> was incorrectly taken as pC<sub>H</sub> and the acid concentrations were accordingly calculated. Lack of details on the experiments prevents further evaluation of the data. In addition, since uranyl acetate was used in the experiment, the model should include the U(VI) acetate complex(es). The failure to do so could lead to erroneous results. Therefore, the stability constants from this work are not accepted by this review.



[\[72MAR/KLO\]](#)

As a variation of potentiometric titration, a solution containing U(VI) and citric acid was titrimetrically added to a solution of the supporting electrolyte (1 M KNO<sub>3</sub>), and the values of  $\log_{10} {}^*\beta_{2,2}$  were calculated from the measured pH's using  $\log_{10} K_{1(H)} = 5.34$ ,  $\log_{10} K_{2(H)} = 4.11$ ,  $\log_{10} K_{3(H)} = 2.63$ , where:

$${}^*\beta_{2,2} = \frac{[(\text{UO}_2)_2(\text{cit})_2^{2-}][\text{H}^+]^6}{[\text{UO}_2^{2+}]^2[\text{H}_3\text{cit}]^2} = \frac{\beta_{2,2}}{(K_{1(H)} \cdot K_{2(H)} \cdot K_{3(H)})^2},$$

( $\beta_{2,2}$  is the constant for the reaction  $2\text{UO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons (\text{UO}_2)_2(\text{cit})_2^{2-}$ ). Three titrations were performed using the titrant containing  $C_M:C_L:C_{OH} = 2:1:0$ ,  $1:1:0$ , and  $1:1:1$ , and  $C_M$  was varied from  $\sim 10^{-4}$  to  $\sim 10^{-3}$  M. Although the calculated values of  $\log_{10} {}^*\beta_{2,2}$  show some scatter at lower  $C_M$  depending on the titrant composition, they converge to a single value as  $C_M$  approaches to  $10^{-3}$  M, indicating the predominant contribution of  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  at higher  $C_M$ . The reported value of  $\log_{10} {}^*\beta_{2,2} = -6.59$  is accepted in this review as  $\log_{10} \beta_{2,2} = 17.57$  with assigning an uncertainty of  $\pm 0.2$  judged from Fig. 2 of [\[72MAR/KLO\]](#).

By using  $\log_{10} \beta_{2,2} = 17.57$  as well as the dimerisation constant  $\log_{10} K_{\text{dim}} = 6.0$  obtained at  $I = 0.1$  M by Adin *et al.* [\[70ADI/KLO\]](#), the authors also estimated  $\log_{10} \beta_{1(\text{cit})}$  to be  $(17.57 - 6.0) / 2 = 5.78$ . Since  $\log_{10} K_{\text{dim}} = 6.0$  is considered not reliable enough (see the discussion for [\[70ADI/KLO\]](#)), this review does accept this value.

[\[72MET/GUI3\]](#)

Solvent extraction of  $1 \times 10^{-7} \sim 1 \times 10^{-8}$  M Pu(IV) has been conducted with TTA/benzene at  $I = 1.0$  M LiClO<sub>4</sub>,  $C_{\text{H}_3\text{cit}} < 0.1$  M and  $0 < \text{pH} \leq 7$ . The distribution ratio of Pu(IV) has been expressed by:

$$D = \frac{[\text{PuT}_4]_o}{[\text{M}] + \sum [\text{Pu}(\text{OH})_i^{4-i}] + \sum [\text{Pu}(\text{H}_3\text{cit})_l(\text{H}^+)_{-y}]} \\ = \frac{D_0}{1 + \sum K_i^{\text{OH}}/[\text{H}]^i + \sum K_{l,y}[\text{H}_3\text{cit}]^l/[\text{H}]^y}$$

where  $D_0$  is the distribution ratio of Pu(IV) in the absence of citric acid. Using the values of stepwise hydrolysis constants of  $\text{Pu}^{4+}$ ,  $\log_{10} K_i^{\text{OH}} = -0.45, -0.75, -3.3, -6.3$ , and protonation constants,  $\log_{10} K_i^{\text{H}} = 2.70, 3.90, 5.00$ , the authors have obtained the stability constants of  $\log_{10} K_{l,y}$  for the reaction  $\text{Pu}^{4+} + l\text{H}_3\text{cit} \rightleftharpoons \text{Pu}(\text{H}_3\text{cit})_l(\text{H}^+)_{-y} + y\text{H}^+$  to be 2.85 ( $l=1, y=1$ ), 1.85(1,2), 0.1(1,3),  $-5.63(1,4)$ ,  $-9.85(1,5)$  and 4(2,1), 3.5(2,2),  $-1.53(2,4)$ ,  $-7.5(2,6)$ ,  $-16.6(2,8)$ . Numerous untenable complex species are considered to be formed, that is, all citric acid species,  $\text{H}_3\text{cit}$ ,  $\text{H}_2\text{cit}^-$ ,  $\text{Hcit}^{2-}$  and  $\text{cit}(\text{OH})^{4-}$  are considered to form complexes with  $\text{Pu}^{4+}$ . Moreover, since Pu(IV) exists mainly as hydrolysed species in this pH range, all stability constants obtained are

strongly dependent on the values of  $\log_{10} K_i^{\text{OH}}$ . The values are not accepted by the review.

#### [\[72NIK/ANT\]](#)

The dissociation constants for oxalic acid were determined potentiometrically at 25, 50, 70 and 90°C. The solutions were composed of H<sub>2</sub>ox and NaHox for the first dissociation constant, and NaHox and Na<sub>2</sub>ox for the second dissociation constant. This resulted in very low and changing ionic strengths during the experiments as no background electrolyte was used. Therefore, the results of [\[72NIK/ANT\]](#) are not credited in this review.

#### [\[72SHA\]](#)

This paper is a continuation of the work published in [\[67LEB/MAK\]](#). Shalinets determined the stability constants of Am(III), Cm(III) and Ce(III) with edta by the electromigration method.

A close inspection of Fig.1 in [\[72SHA\]](#) reveals that the experimental data for Am in the pH range 1 – 3 are identical with those given in Fig. 1 of [\[67LEB/MAK\]](#). The values given in Table 1 of [\[72SHA\]](#),  $\log_{10}K_1 = (17.00 \pm 0.09)$  for  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$  and  $\log_{10}K = (9.21 \pm 0.03)$  for  $\text{Am}^{3+} + \text{Hedta}^{3-} \rightleftharpoons \text{Am}(\text{Hedta})(\text{aq})$ , obviously have been taken from [\[67LEB/MAK\]](#) with slightly changed uncertainties.

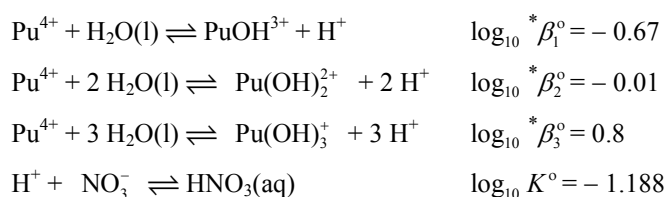
New are only the measurements from pH 9 to 13. At  $(25.0 \pm 0.1)^\circ\text{C}$  in  $I = 0.1$  M KNO<sub>3</sub> and total edta concentration of  $5 \cdot 10^{-4}$  M in the  $-\log_{10}[\text{H}^+]$  range 9 to 13 a decrease in the mobility with decreasing acidity indicates the formation of appreciable amounts of complex ions with a more negative charge than  $\text{Am}(\text{edta})^-$ . Shalinets assumed that a mixed hydroxo complex  $\text{Am}(\text{edta})\text{OH}^{2-}$  is formed and derived  $\log_{10}K = (19.98 \pm 0.07)$  for  $\text{Am}^{3+} + \text{edta}^{4-} + \text{OH}^- \rightleftharpoons \text{Am}(\text{edta})\text{OH}^{2-}$ . No discussion about the difficulties of pH measurements in alkaline solutions at  $\text{pH} > 10$  can be found in [\[72SHA\]](#), and it is not clear whether the author had been aware of these problems at all. Hence, although the data interpretation and the derived constant are not unreasonable, this review does not select a value based on this single study of uncertain accuracy in strongly alkaline solutions.

#### [\[72SMY\]](#)

The author determined the solubility of ethylenediaminetetraacetic acid in 0.1 M KNO<sub>3</sub> at 20°C by adding an excess of CuCl<sub>2</sub> to the saturated solution, and measuring the resulting pH change. Based on H<sup>+</sup>-dissociation constants from the literature, and assuming that no acid complexes are formed between H<sub>*n*</sub>edta<sup>(*n*-4)</sup> and Cu<sup>2+</sup>, the protons released by the formation of Cu(edta)<sup>2-</sup> were used to calculate the saturated concentration:  $[\text{edta}]_{\text{sat}} = 7.8 \times 10^{-5}$  M. The solubility product was then calculated using protonation constants for edta<sup>4-</sup> from the literature. This procedure required a large number of assumptions, and the results of these calculations are not considered in this review.

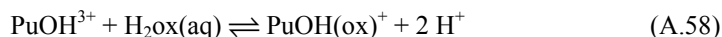
[\[72SOL/IVA\]](#)

The authors report results from solvent extraction experiments of Pu(IV) from aqueous solutions containing up to  $\approx 80$  mM  $\text{H}_2\text{Ox}$  and either: 2 M  $\text{HNO}_3$ ; 4 M  $\text{HNO}_3$ ; or a mixture of 0.1 M  $\text{HNO}_3$  and 1.9 M  $\text{HClO}_4$ . Very few experimental details are given in this paper. The organic phase contained either 0.05 M 2-thenoyltrifluoroacetone (HTTA) in benzene, or 20% (vol.) tributyl phosphate (TBP) in decane. The temperature at which the experiments were conducted is not specified here, but it is given to be 20-25°C in an overview paper published later [\[74SOL\]](#). The interpretation of the solvent extraction data involved the hydrolysis of Pu(IV) and the formation of  $\text{HNO}_3(\text{aq})$ , with the following equilibrium constants [\[74SOL\]](#):



(see also comments for [\[74SOL\]](#) in Appendix A of [\[2001LEM/FUG\]](#)), but the formation of  $\text{PuNO}_3^{3+}$  was not considered. In the organic phase the authors assumed the formation of  $\text{Pu}(\text{TTA})_4$ ,  $\text{Pu}(\text{OH})(\text{TTA})_3$  and  $\text{Pu}(\text{ClO}_4)(\text{TTA})_3$ .

The authors interpreted the solvent extraction data in media containing oxalic acid, at all ionic strengths, with the following reaction:



with  $\log_{10} K(\text{A.58}) = 7.38$ . This constant is reported as a mixed activity-concentration quotient:  $K(\text{A.58}) = [\text{PuOH}(\text{ox})^+] a_{\text{H}^+}^2 / [\text{PuOH}^{3+}] \gamma_{\text{PuOH}^{3+}} [\text{H}_2\text{Ox}(\text{aq})]$ . The authors assumed that  $\gamma_{\text{PuOH}(\text{ox})^+} / \gamma_{\text{H}_2\text{Ox}} \approx \text{constant}$ , which should add systematic errors, as one species is an electrically charged complex, and the other is not. Furthermore the paper does not contain information on the values of  $\gamma_{\text{H}^+}$  and  $\gamma_{\text{PuOH}^{3+}}$  used in the evaluation of the data, although some of the missing activity coefficients (those in  $\text{HNO}_3$  solutions) are tabulated in [\[74SOL\]](#).

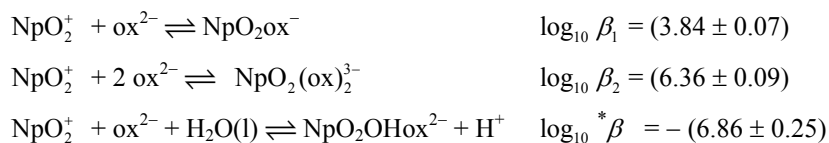
The experiments were performed to model two-phase distribution of Pu(IV) for separation processes, and they were not designed to determine accurately equilibrium constants. When interpreting the data several assumptions were made concerning the speciation in the organic phase and about the activity coefficients in the organic and aqueous phases. The ionic activity coefficients in  $\text{HNO}_3$  solutions used by the authors (which includes the formation of  $\text{HNO}_3(\text{aq})$ ) are incompatible with the SIT model implemented in the NEA-TDB reviews. Furthermore, there is the possibility of complex formation between Pu(IV) and TTA in the aqueous phase that should have been corrected for (see also the discussion of [\[71SOL/IVA2\]](#)). Because of this the equilibrium constant for reaction (A.58) reported in this paper is not accepted by this review. As not

enough experimental details are given a recalculation of the few experimental data is not feasible.

### [72STO]

The author studied the equilibria of  $^{237}\text{Np(V)}$  with different complexing agents: mono-, di- and tri-carboxylic acids, amino-acids, hydroxy- and aminopolycarboxylic acids,  $\beta$ -diketones, *etc.* Equilibrium constants were evaluated from spectrophotometric data obtained at  $I = 1.0 \text{ M}$  ( $\text{NaClO}_4$ ) and at  $(25.0 \pm 0.2)^\circ\text{C}$ . In order to determine the spectral properties of mixed species, binary systems were also studied, including  $\text{Np(V)}$ -oxalate, -citrate and -edta. The data was interpreted with the following complexes:  $\text{NpO}_2\text{ox}^-$ ,  $\text{NpO}_2(\text{ox})_2^{3-}$ ,  $\text{NpO}_2\text{cit}^{2-}$  and  $(\text{NpO}_2)_2\text{edta}^{2-}$ . Only equilibrium constants for the oxalate and citrate systems were evaluated, and only experimental data for the  $\text{Np(V)}$ -oxalate system are given in this dissertation.

For the  $\text{Np(V)}$ -oxalate system, the change in absorbance of solutions containing  $[\text{Np(V)}]_{\text{TOT}} = 2.25 \times 10^{-3} \text{ M}$  and  $[\text{ox}]_{\text{TOT}} = 0.01 \text{ M}$  was followed as a function of  $-\log_{10}[\text{H}^+]$  in the range 1.1 to 9.1. In addition a few measurements were made at  $[\text{ox}]_{\text{TOT}} = 0.02, 0.05$  and  $0.10 \text{ M}$  at  $-\log_{10}[\text{H}^+] = 8.1$  to 10.6. From these experimental data, the author calculated:  $\log_{10} \beta_1 = (4.54 \pm 0.01)$  and  $\log_{10} \beta_2 = (7.86 \pm 0.04)$ , using however incorrect protonation constants for oxalate ( $\log_{10} K_1 = 4.21$ , and  $\log_{10} K_2 = 1.19$ ). A re-analysis of the experimental data by this review indicates the formation of at least a mixed hydroxo-oxalate complex in addition to two oxalate complexes:  $\text{NpO}_2\text{ox}^-$ ,  $\text{NpO}_2(\text{ox})_2^{3-}$ . The model also included the formation of  $\text{NpO}_2\text{OH(aq)}$  [2001LEM/FUG]. The experimental data in [72STO] were fitted using the Letagrop-Spefo program [69SIL/WAR2] and with the prototaton constants for oxalate calculated with the SIT model:  $\log_{10} K_1 = (3.59 \pm 0.03)$  and  $\log_{10} K_2 = (1.07 \pm 0.04)$ . This resulted in the following equilibrium constants:



No indication was found in the data for the presence of protonated complexes such as  $\text{NpO}_2\text{Hox(aq)}$ . There are not enough measurements in the alkaline range to determine the nature of the mixed hydroxo-complex: equally good fits to the data may be obtained with either  $\text{NpO}_2\text{OHox}^{2-}$  or  $\text{NpO}_2(\text{OH})_2\text{ox}^{3-}$ . There is a substantial difference between the results obtained by this review and those listed by Stöber. The difference is due in the protonation constants used in [72STO] and not to the inclusion of  $\text{NpO}_2\text{OHox}^{2-}$ , which only is present in the data at  $\text{pH} \geq 9$ . The recalculated values of  $\beta_1$  and  $\beta_2$  are included in the review procedure with increased uncertainties of  $\pm 0.1$  and  $\pm 0.15 \log_{10}$ -units to include probable, but unknown, systematic errors.

For the  $\text{Np(V)}$ -citrate system Stöber obtained  $\log_{10} \beta_1 = (4.42 \pm 0.11)$  (Table 4

in [72STO] using the following protonation constants for citrate:  $\log_{10} K_1 = 4.91$ ,  $\log_{10} K_2 = 3.81$  and  $\log_{10} K_3 = 2.52$  (at  $I = 1$  M), while the values selected by this review are  $\log_{10} K_1 = (5.18 \pm 0.03)$ ,  $\log_{10} K_2 = (4.14 \pm 0.03)$  and  $\log_{10} K_3 = (2.84 \pm 0.03)$  (cf. Table VII-8). There are no experimental data given, neither a figure nor a table. The pH range and concentrations are not given, and no other mention is made about these measurements in the text. This equilibrium constant can not be discussed in this review because of the lack of details.

#### [73ARM/DUN]

The distribution of  $^{45}\text{Ca}$  between the cation-exchanger CG 120 and aqueous solutions of  $\text{HClO}_4 - \text{H}_2\text{ox}$  was studied at  $25^\circ\text{C}$  at a formal ionic strength of 0.1 M. The total calcium concentration was less than  $10^{-7}$  M. The solutions measured were made up from 0.1 M  $\text{HClO}_4$  and 0.3 M  $\text{H}_2\text{ox}$  solutions in such a way that the actual compositions changed from 100 vol-%  $\text{HClO}_4$  to 10 vol-%  $\text{HClO}_4 - 90$  vol-%  $\text{H}_2\text{ox}$ . The concentration of  $[\text{Hox}^-]$  was calculated by the authors always to be exactly 1/3 of the total oxalate concentration in all the mixtures, and thus a formal ionic strength of 0.1 M is maintained. The drastic change in the ionic medium in the course of the experiments not only causes a large (and unknown) continuous variation in activity coefficients, but also may have a large (and unknown) influence on the properties of the cation-exchanger. It is not surprising that the authors report difficulties in deriving formation constants for  $\text{Ca}(\text{Hox})^+$  and  $\text{Ca}(\text{Hox})_2(\text{aq})$  ("at ligand concentrations 0.020, 0.030 and 0.040 M ... the equations give  $\beta_1 \approx 24$  ... negative constants are obtained at higher concentrations"). Regarding the ambiguities introduced by the large change in the ionic medium, and the arbitrary assumption that the species  $\text{Ca}(\text{Hox})^+$  is not affected by the cation-exchanger, the results of this study are rejected by this review.

#### [73BAR/RED]

This is a short note on calorimetric measurements, which has later expanded to a full paper [75BAR/DUB]. Both papers report the same values for oxalate protonation constants. For a detailed discussion see [75BAR/DUB] in this Appendix.

#### [73CAU/GUI]

The complex formation of Pu(III) and Pu(IV) ( $\approx 1$  mM) with edta ( $\approx 1-100$  mM) has been investigated by polarography and spectrophotometry at  $(20 \pm 1)^\circ\text{C}$  in solutions with variable ionic strength (0.1 – 0.7 M  $\text{NaClO}_4$ ). The formation of the 1:1 complexes  $\text{Pu}(\text{Hedta})(\text{aq})$  and  $\text{Pu}(\text{edta})^-$  with Pu(III), and of  $\text{Pu}(\text{Hedta})^+$  and  $\text{Pu}(\text{edta})(\text{aq})$  with Pu(IV) is claimed.

The stability constants derived by Cauchetier and Guichard for the reactions  $\text{Pu}(\text{edta})(\text{aq}) + \text{H}^+ \rightleftharpoons \text{Pu}(\text{Hedta})^+$   $\log_{10} K = (2.6 \pm 0.2)$ , and  $\text{Pu}(\text{edta})^- + \text{H}^+ \rightleftharpoons \text{Pu}(\text{Hedta})(\text{aq})$   $\log_{10} K = (4.2 \pm 0.3)$  are far outside the expectation range. In the case of U(IV) only a limiting value is available  $\log_{10} K \leq 1.5$  [62KRO/ERM], and for Np(IV) no

evidence of a protonated species  $\text{Np}(\text{Hedta})^+$  is reported. For  $\text{Pu}(\text{III})$   $\log_{10}K = 1.6$  is reported by [78MER/GAT], and for  $\text{Am}(\text{III})$  we find  $\log_{10}K = 2.4$  [67LEB/MAK]. The constants derived by Cauchetier and Guichard for  $\text{Pu}(\text{edta})(\text{aq})$   $\log_{10}K_1 = (25.6 \pm 0.6)$ , and  $\text{Pu}(\text{edta})^-$   $\log_{10}K_1 = (12.2 \pm 0.7)$ , which is also in large discrepancy with all other  $\text{Pu}(\text{III})$  edta constants reported in the literature, depend on the above erratic values.

The polarograms measured at different ionic strengths are used to derive stability constants without considering the effect of widely varying ionic strength (0.1 – 0.7 M) on the numerical values of the derived constants. Furthermore, the pH scale and the calibration of the pH meter are not discussed by Cauchetier and Guichard. Because of these and other shortcomings of this study, leading to outlying stability constants, the results of [73CAU/GUI] are not credited in this review.

#### [73FIN/SMI]

Using atomic absorption spectrophotometry the authors measured at 38°C the change in optical density caused by adding oxalate solutions to solutions containing calcium and murexide with the aim of estimating the stability constant of  $\text{Ca}(\text{ox})(\text{aq})$ . The working solution contained 0.2 M NaCl,  $1 \times 10^{-4}$  M murexide, 0.028 M HCl and 0.1 M Tris (2-amino-2(hydroxymethyl)-1,3-propanediol) buffer, resulting in a final pH of 8.2. This working solution was then used as a solvent to prepare three solutions containing 0.04 M  $\text{K}_2\text{ox}$ , 0.04 M  $\text{CaCl}_2$  and 0.135 M  $\text{CaCl}_2$ . Measurements of oxalate competition were obtained by adding 1 mL of the 0.04 M  $\text{CaCl}_2$  solution to a flask containing 200 mL of the working solution, and subsequently adding 1 mL increments of the 0.04 M  $\text{K}_2\text{ox}$  solution (up to a maximum of four increments). At the end of the competition studies the 200 mL flask was charged with working solution, and 0.1 mL increments of the 0.135 M  $\text{CaCl}_2$  solution were added to calibrate the effects of Ca murexide interaction. In the mass balance equations an activity coefficient for a single divalent ion was used:  $\log_{10}\gamma = -4.808(\sqrt{I}/(1+\sqrt{I}) - 0.286 \cdot I)$ , and the value  $\log_{10}K_1^\circ = (3.37 \pm 0.01)$  is reported for  $\text{Ca}(\text{ox})(\text{aq})$  at 38°C.

The working solution at pH 8.2 contains about 500-fold excess of Tris and  $\text{H}(\text{Tris})^+$  with respect to murexide. Tris is known to form complexes with metal ions. The  $\text{Ca}(\text{Tris})^{2+}$  formation has been reported as  $K_{(\text{Tris})} = 1.8$  in 1 M  $\text{KNO}_3$  at 25°C [82SIG/SCH], whereas the  $\text{Ca}(\text{murexide})(\text{aq})$  stability is estimated as  $K_{(\text{murexide})} = 300$  to 700 in the present study. Hence, the interaction of Tris with Ca is in the same order of magnitude and may even slightly exceed the Ca - murexide interaction in the working solution, *i.e.*,  $K_{(\text{Tris})} \cdot [\text{Tris}] \geq K_{(\text{murexide})} \cdot [\text{murexide}^{2-}]$ . Thus, oxalate competes not only with murexide but also with Tris but the latter effect is not considered in the experiments and the data evaluation.

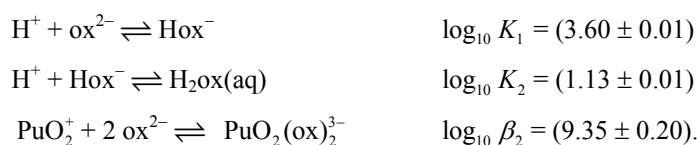
According to the above described solutions and procedures, in the competition experiments the starting solution (before adding  $\text{K}_2\text{ox}$  solution) contained about  $1 \times 10^{-4}$  M murexide and  $2 \times 10^{-4}$  M total dissolved calcium. In such a solution we have at

least  $1 \times 10^{-4}$  M  $[\text{Ca}^{2+}]$  which cannot be complexed by murexide simply because of mass considerations, and according to the Ca murexide formation constant,  $K_{(\text{murexide})} = 300$  to 700, the concentration of free  $[\text{Ca}^{2+}]$  is about  $1.9 \times 10^{-4}$  M with less than  $1 \times 10^{-5}$  M complexed calcium. The concentration of oxalate starts with  $2 \times 10^{-4}$  M and increases to  $8 \times 10^{-4}$  M at the fourth increment. Solubility measurements of  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}$  in 0.2 M NaCl at 37°C [98STR/TRA] give  $2 \times 10^{-4}$  M  $[\text{Ca}^{2+}]$ , or  $4 \times 10^{-4}$  M<sup>2</sup>  $[\text{Ca}^{2+}] \cdot [\text{ox}^{2-}]$ , and the Ca – oxalate complexation effect is in the same order of magnitude as the Ca – murexide complexation considering the results of [82DAN/MAR]. Hence, most experiments of [73FIN/SMI] involving oxalate have been carried out in the region of supersaturation and precipitation of  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}$  may systematically have influenced the obtained results.

Finally, the activity coefficient term used by [73FIN/SMI] in their mass balance equations involves a term  $-4.808$  which is very different from  $-z^2 \cdot A = -2.084$ , for  $z = 2$  and  $A = 0.521$  (38°C). This introduces a systematic error in the derived stability constant of  $\text{Ca}(\text{ox})(\text{aq})$ , but there are not enough experimental data reported in the paper in order to re-evaluate this constant. Considering all these shortcomings, the results of this study are not credited by this review.

#### [73POR/PAO]

The authors report a careful potentiometric determination of the complex formation between  $^{239}\text{Pu}(\text{VI})$  and several organic ligands, including oxalate, at 20°C in 1 M  $\text{NaClO}_4$ . For oxalate the authors report:



These equilibrium constants are included in the review process. The uncertainties in the data for complex formation are increased to  $\pm 0.50 \log_{10}$  units for  $\beta_2$  to include possible systematic errors in the measurements.

#### [73VAS/KOC]

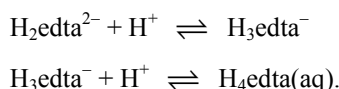
This paper reports calorimetric data for the protonation of  $\text{H}_2\text{edta}^{2-}$  at 25°C in solutions of the following background electrolytes:  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and  $\text{NaClO}_4$ . The ionic strength of the ionic media was 0.2, 0.5 and 0.75 M.

In the experiments solutions of  $\text{H}_2\text{edta}^{2-}$ , with a  $\text{pH} \approx 4$ , were mixed with either  $\text{HClO}_4$  or  $\text{HNO}_3$ . The total concentration of the ligand appears to be 0.02 M according to the caption in their Table 1.

Several shortcomings are associated with this study. The authors assumed that only  $\text{H}_2\text{edta}^{2-}$ ,  $\text{H}_3\text{edta}^-$  and  $\text{H}_4\text{edta}(\text{aq})$  were present in their solutions. However, calcu-

lations using the protonation constants of  $\text{edta}^{4-}$  and the solubility constant of  $\text{H}_4\text{edta}(\text{cr})$  recommended by this review, show that either the precipitation of the acid, or a substantial formation of  $\text{H}_5\text{edta}^+$  should have occurred at  $\text{pH} < 3$ . Furthermore, the ionic strength of the solutions should have decreased by perhaps 10% by addition of the acid.

The relative amounts of  $\text{H}_3\text{edta}^-$  and  $\text{H}_4\text{edta}(\text{aq})$  formed in the solutions were calculated using the protonation constants of  $\text{edta}$ , and this allowed to interpret the calorimetric data and to obtain heats of reaction for:



The authors extrapolated the protonation constants from [\[47SCH/ACK\]](#) to zero ionic strength, obtaining  $\log_{10} K_3^\circ = (3.11 \pm 0.05)$  and  $\log_{10} K_4^\circ = (2.21 \pm 0.05)$  which agree, within the uncertainties, with the values selected in this review. Apparently the values were then extrapolated back to the ionic strengths used in this study. It is not indicated what activity coefficient model was used to make these corrections, but probably the protonation constants obtained at each ionic strength were the same for all ionic media studied, in disparity with all available experimental evidence in the literature.

The reported enthalpy change values are included in the review process, but the uncertainties are increased to  $\pm 1 \text{ kJ}\cdot\text{mol}^{-1}$ .

#### [\[73VAS/SHE2\]](#)

Direct calorimetric measurements of (1) the heat of neutralisation of hydrogen oxalate ( $\text{Hox}^-$ ) and of (2) the heat of proton association with oxalate ( $\text{ox}^{2-}$ ) are reported by [\[73VAS/SHE2\]](#). The electrolytes used were lithium, sodium and potassium nitrate, and sodium chloride and perchlorate in concentrations of 0.5, 1.0 and 2.0 M at  $25^\circ\text{C}$ . The pH values of the starting solutions of method (1) were in the range of 2.6 – 2.9 and after the neutralisation with appropriate alkali hydroxide solution at 3.4 – 3.7. In the case of method (2), the starting pH values were 6.2 – 6.6 and after treatment with nitric acid reached 3.3 – 3.7. The error in the measurements of the thermal effects is reported as  $\pm 50 \text{ cal}\cdot\text{mol}^{-1}$ . In the present review this value has been recalculated to  $\pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$  (the uncertainty has been multiplied by 1.96 to obtain error limits closer to 95% total uncertainty level). The results of both methods show excellent agreement and are included in the present review (recalculated from calories to Joule by the factor 4.184).

#### [\[73ZAI/ALE\]](#)

The complex formation between  $\text{Pu}(\text{V})$  and oxalate was studied spectrophotometrically. Furthermore solids of composition  $\text{NH}_4\text{PuO}_2\text{ox}\cdot n\text{H}_2\text{O}$  were prepared by adding alcohol to aqueous solutions of  $\text{Pu}(\text{V})$ .

The formation of  $\text{PuO}_2\text{ox}^-$  was deduced from spectrophotometric and electro-



phoretic measurements at  $\text{pH} \approx 4.5$  in solutions of constant ionic strength  $\approx 0.15$  M ( $\text{NH}_4\text{ClO}_4$ ) and oxalate concentrations varying from 2 to 28 mM. The temperature of the experiments is not specified. According to the authors, Pu(V) is “relatively stable” towards disproportionation at the pH and oxalate concentrations used. Nevertheless the authors made the measurements “immediately after mixing the solutions”. The change in optical density at  $\lambda = 569$  nm as a function of oxalate concentration in the range 0.002 to 0.18 M was used to estimate  $\log_{10} \beta_1 = 3.7$ . Given the uncertainties related to the possible disproportionation of Pu(V), this value is not recommended by this review.

#### [74BUL]

Bulatov determined the solubility of  $\text{H}_4\text{edta}(\text{cr})$  in water and in 0.01 and 0.1 M  $\text{NaNO}_3$  at  $23^\circ\text{C}$ . The solubility product was determined from three measurements of the solubility in a narrow pH range (2.7 to 2.9) and using  $[\text{H}_n\text{edta}^{(n-4)}]$  values calculated from the pH-measurements and protonation constants from handbooks. The values of the protonation constants are not given in the text. The two experimental points in 0.01 M  $\text{NaNO}_3$  had significant changes of the ionic medium, caused by the added acid and the edta dissolved. The solubility product calculated by Bulatov can not be used in this review.

#### [74BYK/PET2]

The adsorption of Am(III) on barium oxalate was measured as a function of oxalate ion concentration at  $(25 \pm 0.1)^\circ\text{C}$ ,  $(\text{K}^+, \text{Cl}^-, \text{ox}^{2-}) = 1$  M and  $\text{pH } 5.2 - 6.3$ . The distribution coefficients were expressed as,

$$K_d^0 = \frac{[\text{Am}]_s}{[\text{Am}(\text{ox})_2^-]}$$

and

$$K_d = \frac{[\text{Am}]_s}{[\text{Am}(\text{ox})_2^-] + [\text{Am}(\text{ox})_3^{3-}] + [\text{Am}(\text{ox})_4^{5-}]}$$

And the resultant change in the distribution was discussed by:

$$\frac{K_d}{K_d^0} = \frac{1}{1 + (\beta_3/\beta_2)[\text{ox}^{2-}] + (\beta_4/\beta_2)[\text{ox}^{2-}]^2}$$

Based on the agreement of observed  $(K_d/K_d^0)$  with the calculated ratios using the reported data of  $\beta_2$ ,  $\beta_3$  and  $\beta_4$  ([60LEB/PIR], [65SEK4]), americium is considered to be transferred onto the surface of the crystals in the form of  $\text{Am}(\text{ox})_2^-$ . Since two parameter values of  $(\beta_3/\beta_2)$  and  $(\beta_4/\beta_2)$  should be obtained from a limited number of 5 data points (although each point is the mean value of 4 to 8 experimental data), no values of  $(\beta_3/\beta_2)$  and  $(\beta_4/\beta_2)$  were proposed in the paper. The result of the paper is not considered further in this review.

**[74HUB/HUS]**

Distribution ratios of  $^{241}\text{Am}$  ( $\sim 2 \times 10^{-11}$  M) between TTA/benzene and aqueous phase were measured similarly as in [71GUI/BOU] at pH 2.5 – 5.5,  $I = 0.1$  M (Li,H)ClO<sub>4</sub> but in the presence of higher concentrations of citric acid ( $3 \times 10^{-3}$ ,  $10^{-2}$ ,  $10^{-1}$  M). Values of  $\log_{10} {}^*K_{2,5} = -(9.56 \pm 0.2)$  for  $\text{Am}^{3+} + 2\text{H}_3\text{cit} \rightleftharpoons \text{Am}(\text{Hcit})(\text{cit})^{2-} + 5\text{H}^+$  and  $\log_{10} {}^*K_{2,6} = -(14.0 \pm 0.2)$  for  $\text{Am}^{3+} + 2\text{H}_3\text{cit} \rightleftharpoons \text{Am}(\text{cit})_2^{3-} + 6\text{H}^+$  were reported. They correspond to  $\log_{10} \beta_{1(\text{cit})1(\text{Hcit})} = 10.76$  for  $\text{Am}^{3+} + \text{Hcit}^{2-} + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{Hcit})(\text{cit})^{2-}$  and  $\log_{10} \beta_{2(\text{cit})} = 12.16$  for  $\text{Am}^{3+} + 2\text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})_2^{3-}$ . Distribution ratio of Am(III) can be expressed by:

$$D = \frac{[\text{AmA}_3]_0}{[\text{Am}^{3+}] + [\text{Am}(\text{Hcit})(\text{cit})^{2-}] + [\text{Am}(\text{cit})_2^{3-}]} \\ = \frac{K_{\text{ex}} [\text{HA}]_0^3 / [\text{H}^+]^3}{1 + {}^*K_{25} [\text{H}_3\text{cit}]^2 / [\text{H}^+]^5 + {}^*K_{26} [\text{H}_3\text{cit}]^2 / [\text{H}^+]^6} \approx \frac{K_{\text{ex}} [\text{HA}]_0^3 [\text{H}^+]^3}{[\text{H}_3\text{cit}]^2 ({}^*K_{25} [\text{H}^+] + {}^*K_{26})}$$

where HA is TTA and  $K_{\text{ex}}$  is the extraction constant:

$$K_{\text{ex}} = \frac{[\text{AmA}_3]_0 [\text{H}^+]^3}{[\text{Am}^{3+}] [\text{HA}]_0^3}.$$

The constants were obtained by plotting

$$\log_{10} F = \log_{10} ({}^*K_{25} [\text{H}^+] + {}^*K_{26}) \\ = \log_{10} K_{\text{ex}} + 3 \log_{10} [\text{HA}]_0 - 3\text{pH} - 2 \log_{10} [\text{H}_3\text{cit}] - \log_{10} D$$

as a function of pH. The plots of  $\log_{10} F$  versus  $\log_{10} [\text{H}^+]$  given in Fig. 5 of the paper indicate a constant part (corresponding to  $\log_{10} {}^*K_{2,6}$ ) and a gradually increasing part (corresponding to  $\log_{10} {}^*K_{2,5}$ ). However, the slope of the increase with  $\log_{10} [\text{H}^+]$  seems steeper than a slope of one. If there exists a part of slope one, the value of  $\log_{10} F$  should be  $\log_{10} 2 = 0.3$  higher than a constant part. The plots in Fig. 5 do not agree with this expectation. In this paper,  $[\text{H}_3\text{cit}]$  was calculated from  $C_{\text{H}_3\text{cit}}$  using protonation constants ( $\log_{10} K_{(\text{H})} = 5.84, 4.36, 2.88$ ) of which  $\log_{10} K_{1(\text{H})}$  is pretty different from that selected in this review. Since  $\log_{10} \beta_{1(\text{cit})1(\text{Hcit})}$  for  $\text{Am}(\text{Hcit})(\text{cit})^{2-}$  was obtained from the data at pH 4.5 ~ 5 where  $\text{Hcit}^{2-}$  is predominant, this value is susceptible to the error in  $\log_{10} K_{1(\text{H})}$ . Thus, this review accepts only the value for  $\text{Am}(\text{cit})_2^{3-}$  as  $\log_{10} \beta_{2(\text{cit})} = (12.1 \pm 0.5)$ .

**[74MEY]**

Potentiometric titrations of citric acid in the absence and presence of Ca(II) or Mg(II) ions ( $C_L/C_M = 1$  or 2) were conducted at  $I = 0.15$  M NaCl at 37°C. In the experiment, the pH was measured and converted into the concentration scale using the value of 0.755 as the activity coefficient estimated by the Davies equation at  $I = 0.15$ . This procedure may have introduced some error due to the liquid junction potential and esti-

mated activity coefficient. The obtained values of the protonation constants,  $\log_{10} K_{(H)} = 5.53, 4.21$  and  $2.75$  at  $37^\circ\text{C}$  are somewhat different from those at  $25^\circ\text{C}$  selected in this review even considering the difference in temperature. This review will take the reported values for  $M^{2+} + H_r \text{cit}^{r-3} \rightleftharpoons M(H_r \text{cit})^{r-1}$  with assigning pretty large uncertainties as  $\log_{10} \beta_1 = (3.27 \pm 0.5)$  for  $\text{Ca}(\text{cit})^-$ ,  $(1.82 \pm 0.5)$  for  $\text{Ca}(\text{Hcit})(\text{aq})$ ,  $(3.34 \pm 0.5)$  for  $\text{Mg}(\text{cit})^-$  and  $(1.62 \pm 0.5)$  for  $\text{Mg}(\text{Hcit})(\text{aq})$ .

#### [\[74NAN/GAR\]](#)

The authors investigated the association of calcium and oxalate by measuring the specific conductivity of solutions containing mixtures of  $\text{Ca}(\text{NO}_3)_2$  and  $\text{Na}_2\text{ox}$  where the total concentration of Ca varied from  $4 \times 10^{-5}$  to  $2 \times 10^{-4}$  M, and total concentration of oxalate varied from  $7 \times 10^{-5}$  to  $2 \times 10^{-4}$  M. Values for  $[\text{Ca}(\text{ox})(\text{aq})]$  were determined from the difference between measured specific conductivities and calculated ones, assuming that no ion association took place, by an iterative method involving the ionic strength. Activity coefficients of the divalent cations were assumed to be equal and were obtained from the Davies equation. At the very low ionic strengths of the salt mixtures used for conductivity measurements ( $I < 0.0013$  M) the difference between the results obtained with the Davies equation and the SIT equation is negligible. This review accepts the value  $\log_{10} K_1^\circ = 3.19$  obtained in this reliable conductivity study with an estimated uncertainty of  $\pm 0.10$ .

#### [\[74NIK/SHI\]](#)

The composition and the stability of complexes of americium(V) with edta and dtpa (diethylenetriaminepentaacetic acid) were investigated spectrophotometrically at  $25^\circ\text{C}$  and  $I = 0.1$  M  $\text{KNO}_3$  in solutions ranging from pH 2 to 7. The spectra of solutions containing  $\approx 1 \cdot 10^{-3}$  M  $\text{Am}(\text{V})$  and  $\approx 5 \cdot 10^{-3}$  M edta were measured at different pH values. The results have been interpreted by Nikolaevskii *et al.* in terms of the 1:1 complex formation of  $\text{AmO}_2^+$  with  $\text{Hedta}^{3-}$  resulting in  $\log_{10} K_1 = (4.88 \pm 0.05)$ . The edta protonation constants of [\[67AND\]](#) have been used in the data evaluation.

Because of the ligand excess a small increase of the ionic strength to 0.113 M is expected. The authors state that the pH was measured with an error not greater than  $\pm 0.01$ . However, no further information about these pH measurements is given, neither about the pH scale, nor about the calibration of the pH meter.

Nikolaevskii *et al.* report that by preliminary experiments it was established that in solutions of edta and dtpa  $\text{Am}(\text{V})$  slowly changes into the trivalent state. Under the experimental conditions, the rate of reduction of  $\text{Am}(\text{V})$  to  $\text{Am}(\text{III})$  is 2 to 3 % per hour and depends little on pH. The fall in the concentration of  $\text{Am}(\text{V})$  during the experiments was taken into account from measurements of the optical density of the solutions in the range of 500 – 510 nm, where the absorption bands of  $\text{Am}^{3+}$  and its complexes with edta and dtpa lie. This review does not select a value for the unstable species  $\text{AmO}_2(\text{Hedta})^{2-}$ .

[\[74SHA/KII\]](#)

The authors studied the complex formation between U(IV) and citric acid using spectrophotometry in solutions with  $[\text{ClO}_4^-] = 4 \text{ M}$  at  $(22 \pm 2)^\circ\text{C}$ . The absorbance was determined in equimolar solutions of uranium and citric acid ( $[\text{U(IV)}] = [\text{H}_3\text{cit}] = 0.01 \text{ M}$ ) at different acidities,  $[\text{HClO}_4] = 0.2 \text{ to } 0.7 \text{ M}$ . The data was interpreted assuming that only one complex is formed. The best fit was obtained with:



The formation of  $\text{U(H}_2\text{cit)}^{3+}$  was also considered as a possibility to explain the measurements, but it was rejected because it would require a negative equilibrium constant, which is physically impossible under the given experimental condition. The formation of a precipitate at  $[\text{HClO}_4] < 0.5 \text{ M}$  was observed in solutions with  $[\text{U(IV)}] = [\text{H}_3\text{cit}] = 0.02 \text{ M}$ . The fraction of U(IV) in the precipitate increased with decreasing acidities. Chemical analysis of the solid suggested a stoichiometry corresponding to  $\text{U}_3\text{cit}_4(\text{s})$ .

Although this study demonstrates that U(IV)-citrate complexes are formed in highly acidic solutions, the stoichiometry of the complex(es) is not well established. Variations in activity coefficients may be expected when the ionic media changes from  $[\text{Na}^+] = 0.3 \text{ to } 0.8 \text{ M}$  ( $[\text{ClO}_4^-] = 4 \text{ M}$ ), even if all species participating in the reaction are cationic or neutral. This would have a considerable effect, especially on equilibrium constants  $K \leq 10$ . Furthermore, the simultaneous formation of several complexes has not been explored, and the amount of experimental data and the concentration range are too limited to allow for a thorough speciation analysis. Taking this into consideration, the reported equilibrium constant is not accepted in this review.

[\[74SHI/NIK2\]](#)

Complex formation of Am(V) with oxalate in the pH range 1 ~ 5 was examined by spectrophotometric method at  $I = 0.25 \text{ M}$  ( $\text{K}^+$ ,  $\text{ox}^{2-}$ ,  $\text{Hox}^-$ ,  $\text{NO}_3^-$ ),  $(25.0 \pm 0.1)^\circ\text{C}$ .  $1 \times 10^{-3} \text{ M } ^{241}\text{Am(III)}$  was oxidised to Am(VI) in  $0.2 \text{ M NaHCO}_3$  with ozone, and the solution was acidified with  $1 \text{ M HNO}_3$  and then  $(4 \sim 5) \times 10^{-3} \text{ M}$  sodium nitrite was added. Dependence of the mean molar absorptivity of Am(V) on the concentration of oxalate was measured at 718, 514, 733, 522 and 726 nm. The mean values of the constants reported are  $K_1 = (1.86 \pm 0.10) \times 10^3$  for  $\text{AmO}_2^+ + \text{ox}^{2-} \rightleftharpoons \text{AmO}_2(\text{ox})^-$  and  $K_2 = (1.25 \pm 0.04) \times 10^2$  for  $\text{AmO}_2(\text{ox})^- + \text{ox}^{2-} \rightleftharpoons \text{AmO}_2(\text{ox})_2^{3-}$  ( $\log_{10} \beta = (3.27 \pm 0.02)$  and  $(5.36 \pm 0.04)$ ). The protonation constants of oxalic acid,  $\log_{10}K_{(\text{H})} = 4.27$  and  $1.27$  at  $I = 0$  were used to calculate the values for an ionic strength of  $I = 0.25$  by means of the Davies equation and were used to estimate  $[\text{ox}^{2-}]$ . Recalculation of the above values using the Davies equation for  $I = 0.25 \text{ M}$  gives 3.75 or 3.70 and 1.01 or 0.99 with a Davies coefficient 0.3 or 0.2, respectively. The exact form of the Davies equation used is not mentioned in the paper. The first protonation constant is close to the selected value  $(3.71 \pm 0.01)$  for  $I = 0.25 \text{ KNO}_3$  in this review but the second one is off by some 0.15

$\log_{10}$ -units from  $(1.15 \pm 0.04)$ . The conversion of pH to  $-\log_{10}[\text{H}^+]$  is not described. Considering these shortcomings, this review does not take the reported values.

#### [\[74SOL\]](#)

The author reports in this paper an overview of results previously published [\[72SOL/IVA\]](#) and [\[71SOL/IVA2\]](#). See comments in this Appendix for these references.

#### [\[74TER/NIK\]](#)

Terëshin and Nikiforova report the solubility product of  $\text{H}_4\text{edta}(\text{cr})$  at  $I = 0.01$  M, obtained by combining: pH measurements; the Davies equation to convert activities to concentrations; and the protonation constants by Anderegg [\[67AND\]](#) which were obtained at  $I = 0.1$  and 1 M. Although the authors reported in sections of this paper to have measured the solubility of  $\text{H}_4\text{edta}(\text{cr})$ , the data is not reported in tables or figures. Furthermore the authors also stated that the reported solubility product of  $\text{H}_4\text{edta}(\text{cr})$  was calculated from the experimental data of Anderegg [\[67AND\]](#) assuming  $[\text{H}^+] = a_{\text{H}^+}$ . Because of these uncertainties the solubility product of  $\text{H}_4\text{edta}(\text{cr})$  is not included in the review procedure.

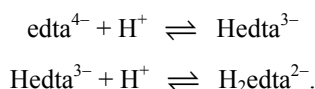
#### [\[74TER/NIK2\]](#)

The solubility of edta in presence of  $\text{NiCl}_2$  was investigated at pH 1.31 and  $I = 0.10$ , and at pH 1.64 and  $I = 0.12$  at “room temperature” ( $22 \pm 1^\circ\text{C}$ ) in order to obtain the stability constant  $K_1$  of  $\text{Ni}(\text{edta})^{2-}$  as the geometric mean of the two experimental values. For the protonation of  $\text{Ni}(\text{edta})^{2-}$  to  $\text{Ni}(\text{Hedta})^-$  a  $\log_{10}K$  value of 3.4 was obtained from 4 measurements at  $I = 0.10 - 0.15$ . Because of the limited number of measurements at scanty conditions the results of this paper are not further considered in this review.

#### [\[74VAS/KOC\]](#)

This paper reports calorimetric data for the protonation of  $\text{edta}^{4-}$  at  $25^\circ\text{C}$  in solutions of the following background electrolytes:  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{NaCl}$  and  $\text{NaClO}_4$ . The ionic strength of the ionic media was 0.2, 0.5 and 1 M.

In the experiments 0.02 M edta solutions, with an initial pH either  $\approx 5$  or  $\approx 9$ , were mixed with either  $\text{LiOH}$ ,  $\text{NaOH}$  or  $\text{KOH}$ . The relative amounts of  $\text{edta}^{4-}$ ,  $\text{Hedta}^{3-}$  and  $\text{H}_2\text{edta}^{2-}$  in the initial and final solutions were calculated using the protonation constants of edta, and this allowed to interpret the calorimetric data and to obtain heats of reaction for:



The authors extrapolated the protonation constants from [\[47SCH/ACK\]](#), [\[54CAR/MAR\]](#), [\[56CAR/STA\]](#) to zero ionic strength, obtaining  $\log_{10} K_1^\circ = (11.25 \pm 0.10)$ ,  $\log_{10} K_2^\circ = (6.94 \pm 0.11)$ ,  $\log_{10} K_3^\circ = (3.11 \pm 0.05)$  which do not differ

substantially from the values selected in this review. Based on these protonation constants Vasil'ev *et al.* assumed that  $\text{H}_2\text{edta}^{2-}$  predominates at  $\text{pH} = 5$ ,  $\text{Hedta}^{3-}$  at  $7 \leq \text{pH} \leq 9$ , and  $\text{edta}^{4-}$  at  $\text{pH} \geq 10.5$ . The calorimetric experiments were arranged so that  $\text{pH}$  changed: *a*) from 5 to 7 (according to their text), or from 5 to 8 (according to the caption in their Table 1); and *b*) from 9 to 10.4. Vasil'ev *et al.* assumed that these two types of experiments correspond to the deprotonation of  $\text{H}_2\text{edta}^{2-}$  and  $\text{Hedta}^{3-}$ , respectively.

Although this assumption may be valid at low concentrations of background alkali ions, complex formation with  $\text{K}^+$ ,  $\text{Na}^+$  and particularly  $\text{Li}^+$  at higher ionic strengths decrease the  $\text{pH}$ -range of predominance for  $\text{Hedta}^{3-}$ . Because of this, the enthalpy changes in  $\text{LiNO}_3$  are not considered in this review. Uncertainties in  $\text{Na}^+$  media are increased to  $\pm 1$  and  $\pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$  in 0.5 and 1 M, respectively.

#### [\[75BAR/DUB\]](#)

This publication describes in detail the use of a conduction micro-calorimeter. Analysis of the thermograms obtained leads to the simultaneous determination of the enthalpy change and the equilibrium constants. The treatment of the data is discussed in detail. As an example, measurements of the protonation of oxalate in 2 M  $\text{KCl}$  at  $25^\circ\text{C}$  are reported. Both, the equilibrium constants and the enthalpy values are considered in this review. The enthalpy of the first protonation constant is given as  $+(280 \pm 10) \text{ cal}\cdot\text{mol}^{-1}$ . This corresponds to  $\Delta_r H_m = +(1.2 \pm 0.4) \text{ kJ}\cdot\text{mol}^{-1}$ . The enthalpy of the second protonation constant is given as  $-(700 \pm 50) \text{ cal}\cdot\text{mol}^{-1}$ . This corresponds to  $\Delta_r H_m = -(2.9 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$ . In both cases the uncertainty has been increased to obtain error limits closer to 95% total uncertainty level.

#### [\[75CAR/SWA\]](#)

This study, mainly concerned with kinetic effects, also reports protonation and  $\text{Ca}$  complexation constants of several aminocarboxylates, including  $\text{edta}$ , measured potentiometrically in 0.5 M tetramethylammonium chloride ( $\text{Me}_4\text{NCl}$ ) at  $25^\circ\text{C}$ .

As mentioned in the text, only the protonation constants  $K_4$ ,  $K_3$  and  $K_2$  “were determined”. The source of  $K_1$  is not clear, although this value is essential for obtaining the stability constant of  $\text{Ca}(\text{edta})^{2-}$ . In Table IV of [\[75CAR/SWA\]](#)  $K_1$  values are reported for ligands having even higher first protonation constants than  $\text{edta}$ . In these cases very high  $\text{pH}$  values have to be measured, which can be obtained exactly only with special glass electrodes. No use of such electrodes is mentioned in the experimental section of the paper. Also the corresponding species  $[\text{OH}^-]$ , important at high  $\text{pH}$  values, is neglected in the mass balance equation (eq. 7 of [\[75CAR/SWA\]](#)). Nevertheless, the  $\text{edta}$  protonation constants have been considered in this review with an uncertainty of  $\pm 0.15 \log_{10}$ -units ( $K_1$ ,  $K_2$ ,  $K_3$ ) and  $\pm 0.3 \log_{10}$ -units ( $K_4$ ).

For determining  $\text{Ca}$   $\text{edta}$  stability constants the concentration of the ligand in solution was about 0.01 M with calcium ion present in a 1.5 – 3.5-fold excess. In such

solutions the ionic strength exceeds  $I = 0.5$  M  $\text{Me}_4\text{NCl}$  and may actually reach 0.6 M. This excess in calcium concentration most probably was used to keep the ligand edta in solution because of its low solubility close to 0.001 M at  $\text{pH} \approx 2$ . Although this paper contains large amounts of information and experimental observations (*e.g.*, about the kinetic inertness of the sodium edta complex) the values of the  $\text{Ca}(\text{edta})^{2-}$  and  $\text{Ca}(\text{Hedta})^-$  stability constants were not considered in this review because of the significant variations in ionic strength during the measurements and the unclear origin of the first edta protonation constant.

#### [\[75CAU/GUI\]](#)

The complex formation of Pu(V) and Pu(VI) with edta has been investigated by polarography and spectrophotometry at  $(20 \pm 1)^\circ\text{C}$  in solutions with variable ionic strength (0.01 – 0.1M  $\text{NaClO}_4$ ). The pH scale and the calibration of the pH meter are not mentioned by Cauchetier and Guichard. In addition, the edta protonation constants used in this study are not reported.

The stability constants are derived by considering the reduction kinetics of Pu(VI) to Pu(V) and finally to Pu(IV). The instability of the solutions causes large standard deviations of the obtained constants. As the authors state, the large variation of the ionic strength is neglected in their calculations because of the very approximate constancy of the obtained values for the equilibrium constants.

#### [\[75DEY/CAN\]](#)

This study and an earlier publication from the same research group [\[70DEY/PEN\]](#) reported the solubility of  $\text{M}(\text{ox}) \cdot 2\text{H}_2\text{O}$  (for  $\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{and Zn}$ ) in solutions containing  $\text{H}_2\text{SO}_4$  up to 10 mM. In [\[70DEY/PEN\]](#) the system was investigated at  $25^\circ\text{C}$ , while in [\[75DEY/CAN\]](#) results were presented for eight temperatures between 5 and  $40^\circ\text{C}$ .

Two types of solid Ni phases are formed ( $\alpha$  and  $\beta$ ). The  $\beta$ -form is meta-stable, and transforms into the  $\alpha$ -form when standing in solutions containing excess of oxalate ions. This transformation is however inhibited by sulphate ions and in solutions at  $\leq 100^\circ\text{C}$ . Only  $\beta\text{-Ni}(\text{ox}) \cdot 2\text{H}_2\text{O}$  could be synthesised in [\[70DEY/PEN\]](#), but  $\alpha\text{-Ni}(\text{ox}) \cdot 2\text{H}_2\text{O}$  was produced later by the same group [\[73DEY/BER\]](#), [\[75DEY/CAN\]](#) when longer equilibration times were allowed. The solubilities were determined by equilibrating solid oxalates in sulphuric acid solutions for 24 hours, followed by filtration through paper filters and analysis of the oxalate concentration with  $\text{KMnO}_4$ .

The authors interpreted their solubility data for  $\alpha$ - and  $\beta\text{-Ni}(\text{ox}) \cdot 2\text{H}_2\text{O}$  in  $\text{H}_2\text{SO}_4$  solutions with the formation of two aqueous complexes,  $\text{Ni}(\text{ox})(\text{aq})$  and a protonated ternary complex:  $\text{Ni}(\text{Hox})(\text{HSO}_4)(\text{aq})$ . The ionic strength of the solutions investigated was calculated by this review to be  $\leq 0.022$  M, therefore the activity coefficient calculations using the Davies equation in [\[70DEY/PEN\]](#), [\[75DEY/CAN\]](#) should give

reasonable results. Both equilibrium constants and experimental data (solubility and pH) were published in [70DEY/PEN]. However, in [75DEY/CAN] the authors calculated values of  $\Delta_r G_m^\circ$  using auxiliary thermodynamic data for  $\text{SO}_4^{2-}$ , *etc.* Neither the equilibrium constants, nor the original solubility data are listed in [75DEY/CAN], except for the solubilities in 0.005 M  $\text{H}_2\text{SO}_4$  at 25°C. The equilibrium constants at 25°C were calculated in this review (Table A-11) from the values of  $\Delta_r G_m^\circ$  and using the auxiliary data listed in [75DEY/CAN]. From the temperature variation of the equilibrium constants the authors calculated values of  $\Delta_r H_m^\circ$  assuming that the enthalpy changes did not vary within the temperature interval studied.

Table A-11: Equilibrium constants at zero ionic strength and 25°C from [70DEY/PEN], [75DEY/CAN].

Reaction	$\log_{10} K^\circ$	
	[70DEY/PEN]	[75DEY/CAN]
$\alpha\text{-Ni(ox)}\cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ni}^{2+} + \text{ox}^{2-} + 2\text{H}_2\text{O(l)}$		$-(9.68 \pm 0.10)^a$
$\beta\text{-Ni(ox)}\cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ni}^{2+} + \text{ox}^{2-} + 2\text{H}_2\text{O(l)}$	$-(9.648 \pm 0.007)$	$-(9.43 \pm 0.14)^a$
$\beta\text{-Ni(ox)}\cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ni(ox)(aq)}$	$-(4.26 \pm 0.03)$	$-(4.60 \pm 0.35)^a$
$\text{Ni}^{2+} + \text{Hox}^- + \text{HSO}_4^- \rightleftharpoons \text{Ni(Hox)(HSO}_4\text{)(aq)}$	$(6.183 \pm 0.001)$	$(6.11 \pm 0.21)^a$
$\text{Ni}^{2+} + \text{ox}^{2-} \rightleftharpoons \text{Ni(ox)(aq)}$	$(5.39 \pm 0.03)^b$	$(4.83 \pm 0.32)^a$

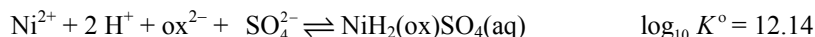
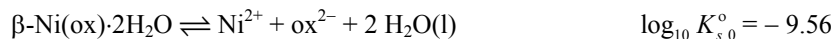
a: calculated from  $\Delta_r G_m^\circ$  data reported in [75DEY/CAN].

b: calculated by combining other equilibrium constants from [70DEY/PEN] listed in this table.

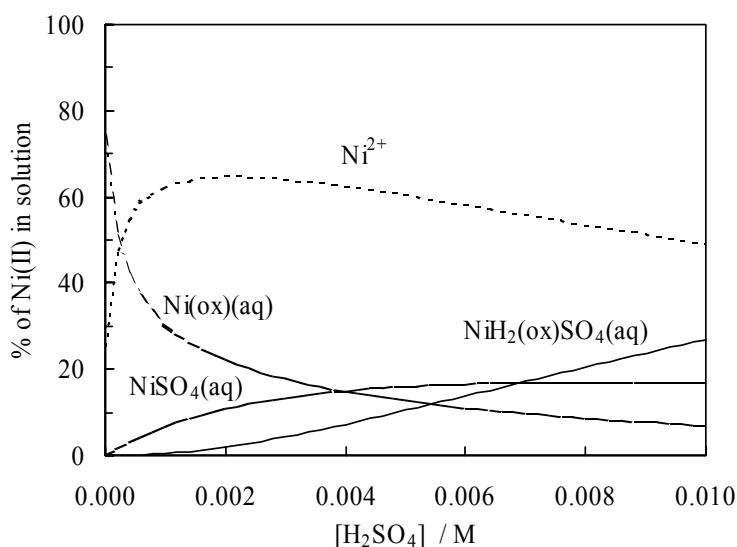
Deyrieux *et al.* rejected the formation of  $\text{NiSO}_4\text{(aq)}$  arguing that the inner sphere complex is only formed at high sulphate concentrations, and that only weak ion-pairing would occur in their solutions [70DEY/PEN]. According to literature reviews on the nickel(II)-sulphate system, *e.g.*, [99ARC], the equilibrium constant for the formation of the weak complex  $\text{NiSO}_4\text{(aq)}$  should be  $\log_{10} K_{\text{NiSO}_4}^\circ \approx (2.3 \pm 0.4)$ , indicating that  $\text{NiSO}_4\text{(aq)}$  can not be neglected, *cf.* Figure A-19. Deyrieux *et al.* fitted their data using the complex “ $\text{NiH}_2\text{(ox)SO}_4\text{(aq)}$ ” where it would be expected that both ligands are protonated. The stoichiometry of such a complex explains the increased solubility as the concentrations of  $\text{H}^+$  and  $\text{HSO}_4^-$  are increased. Other complexes that could also fulfil this task would be  $\text{NiHSO}_4^+$  and  $\text{NiH(ox)SO}_4^-$ , where probably the oxalate ligand would be protonated.



Figure A-19: Calculated species distribution in aqueous solutions of  $\text{H}_2\text{SO}_4$  equilibrated with  $\beta\text{-Ni(ox)}\cdot 2\text{H}_2\text{O}$  at  $25^\circ\text{C}$ . The curves were calculated with the following equilibrium constants fitted by this review to the experimental solubilities in [70DEY/PEN]:

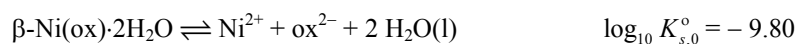


The equilibrium constant for  $\text{Ni}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{NiSO}_4(\text{aq})$  was kept fixed at  $\log_{10} K^\circ = 2.3$  during the fitting procedure.

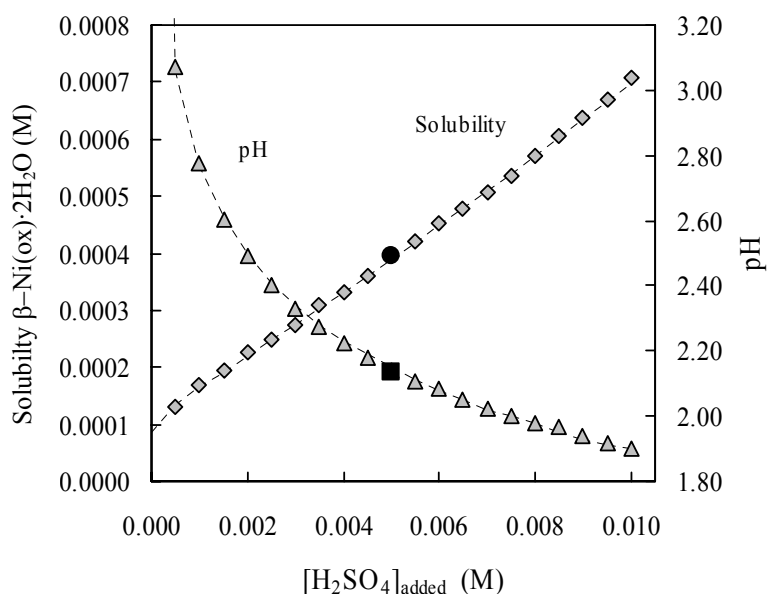


Fitting calculations by this review show that the  $\beta\text{-Ni(ox)}\cdot 2\text{H}_2\text{O}$  solubilities reported in [70DEY/PEN] can be fitted almost equally well assuming that in addition to  $\text{Ni}^{2+}$ ,  $\text{Ni(ox)(aq)}$ , and  $\text{NiSO}_4(\text{aq})$ , any one of the following complexes is formed:  $\text{NiHSO}_4^+$ ,  $\text{NiH(ox)SO}_4^-$  or  $\text{NiH}_2(\text{ox})\text{SO}_4(\text{aq})$ . Equally good fits are obtained with combinations of these three protonated complexes. The fit of the data using the “ $\text{NiHSO}_4^+$ ” model is shown in Figure A-20. Because of the low ionic strength of the solutions investigated, essentially the same results in these calculations are obtained when using either the Davies equation or a SIT model with estimated  $\varepsilon$ -values. This fitting exercise shows that the data set is not adequate to define unequivocally the stoichiometry of the protonated species formed as the concentration of added  $\text{H}_2\text{SO}_4$  is increased. Therefore the data reported in [70DEY/PEN], [75DEY/CAN] (Table A-11) are not considered reliable.

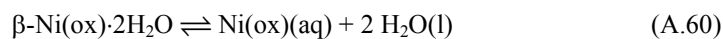
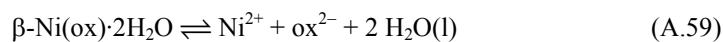
Figure A-20: Experimental data from solutions equilibrated with  $\beta$ -Ni(ox)·2H<sub>2</sub>O at 25°C: grey symbols from [70DEY/PEN]; black symbols from [75DEY/CAN]. The curves were calculated with the following equilibrium constants fitted to the experimental data:



The equilibrium constant for  $\text{Ni}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{NiSO}_4(\text{aq})$  was kept fixed at  $\log_{10} K^{\circ} = 2.3$  during the fitting procedure.



At low concentrations of H<sub>2</sub>SO<sub>4</sub> the species Ni<sup>2+</sup> and Ni(ox)(aq) dominate, but ambiguities in the overall speciation result in large uncertainties in the solubility product and in the formation constant for Ni(ox)(aq). The fitting exercise allows obtaining data for the following reactions:



The values that include all speciation alternatives are:  $\log_{10} K_{s,0}^{\circ}$  (A.59) =  $-(9.74 \pm 0.30)$  and  $\log_{10} K_{s,1}^{\circ}$  (A.60) =  $-(4.22 \pm 0.20)$ . Combining the latter constant with the selected constant for:



$\log_{10} K^\circ (\text{A.61}) = (5.19 \pm 0.04)$ , cf. Section VI.7.2, leads to  $\log_{10} K_{s,0}^\circ (\text{A.59}) = -(9.41 \pm 0.20)$ .

#### [\[75FIE/COB\]](#)

Potentiometric titrations of citric acid in the absence and presence of Mg(II) or Ca(II) ions were conducted at  $I = 0.1 \text{ M KNO}_3$  and  $25^\circ\text{C}$ . Experiments and data treatment were done properly. Using the protonation constants obtained in this study ( $\log_{10} K_{(\text{H})} = (5.70 \pm 0.02)$ ,  $(4.36 \pm 0.02)$ ,  $(2.81 \pm 0.02)$ ), the constants for  $\text{M}^{2+} + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{M(H}_r\text{cit)}^{r-1}$  were calculated to be  $\log_{10} \beta_1 = (3.38 \pm 0.07)$  for  $\text{Mg(cit)}^-$ ,  $(1.96 \pm 0.19)$  for  $\text{Mg(Hcit)(aq)}$ ,  $(3.50 \pm 0.06)$  for  $\text{Ca(cit)}^-$  and  $(2.32 \pm 0.15)$  for  $\text{Ca(Hcit)(aq)}$ . This review accepts these values but with assigning larger uncertainties as,  $\log_{10} \beta_1 = (3.38 \pm 0.3)$  for  $\text{Mg(cit)}^-$ ,  $(1.96 \pm 0.5)$  for  $\text{Mg(Hcit)(aq)}$ ,  $(3.50 \pm 0.3)$  for  $\text{Ca(cit)}^-$  and  $(2.32 \pm 0.5)$  for  $\text{Ca(Hcit)(aq)}$ .

The complex formation of  $\text{Ni}^{2+}$  with citric acid was investigated by the potentiometric method at the ionic strength  $0.10 \text{ M KNO}_3$  at  $25.0^\circ\text{C}$ . The calibration of the pH meter readings to the pcH values was well done. The protonation constants,  $\log_{10} K_{(\text{H})} = (5.70 \pm 0.02)$ ,  $(4.36 \pm 0.02)$  and  $(2.81 \pm 0.08)$ , obtained by the authors and used in the calculation are close to those evaluated by this review. The authors concluded that the contribution of  $\text{Ni(H}_2\text{cit)}^+$ , if it exists, would be too small to give a reliable stability constant under the experimental conditions. Thus, the formation constants were obtained by assuming the formation of  $\text{Ni(Hcit)(aq)}$  and  $\text{Ni(cit)}^-$ . The formation constants for the reaction  $\text{Ni}^{2+} + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{Ni(H}_r\text{cit)}^{r-1}$  are  $\log_{10} \beta_1 = (5.40 \pm 0.04)$  for  $\text{Ni(cit)}^-$  and  $(3.34 \pm 0.07)$  for  $\text{Ni(Hcit)(aq)}$ . The value for  $\text{Ni(Hcit)(aq)}$  may be affected by the assumption of the nonexistence of  $\text{Ni(H}_2\text{cit)}^+$ . Thus, this review accepts these values with assigning the uncertainties of  $\pm 0.1$  for  $\log_{10} \beta_1$  of  $\text{Ni(cit)}^-$  and  $\pm 0.2$  for  $\log_{10} \beta_1$  of  $\text{Ni(Hcit)(aq)}$ .

#### [\[75KOR/PAT\]](#)

The complexation of americium and curium with nta and edta has been determined by a solvent extraction technique using  $1 \text{ M}$  trioctylamine in toluene and  $0.05 \text{ M}$  edta in  $6 \text{ M LiNO}_3$ . No experimental details at all are given for the Am – edta system, just the final result is reported:  $\log_{10} K_1 = 17.38$  for  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am(edta)}^-$ . No discussion is found about the edta protonation constants used for evaluating experimental data measured in  $6 \text{ M LiNO}_3$ . Hence, the results of [\[75KOR/PAT\]](#) are discarded in this review.

#### [\[75NEB/AND\]](#)

Formation constants of  $\text{U}^{4+}$  and  $\text{Th}^{4+}$  complexes with acetate and  $\text{PuO}_2^{2+}$  with citrate were determined by potentiometry and spectrophotometry at  $25$ ,  $35$  and  $45^\circ\text{C}$ . For  $\text{Pu(VI)-citrate}$ s, the absorption spectra of  $9.2 \times 10^{-4} \text{ mol} \cdot \text{kg}^{-1} \text{ PuO}_2^{2+}$  in  $0.5 \text{ M HClO}_4$  were measured in the absence and presence of  $10^{-10}$  to  $4 \times 10^{-2} \text{ mol} \cdot \text{kg}^{-1}$  citric acid at  $25$ ,

35°C. The absorbances at 831, 836 and 857 nm were plotted as a function of  $\log_{10}[\text{cit}^{3-}]$  and using the value of the protonation constant of  $\log_{10}K_{1(\text{H})}K_{2(\text{H})}K_{3(\text{H})} = 12.98$ , the constants for the reactions  $\text{PuO}_2^{2+} + n\text{cit}^{3-} \rightleftharpoons \text{PuO}_2(\text{cit})_n^{2-3n}$ , ( $n = 1, 2$ ) were obtained to be  $\beta_1 = 1.0 \times 10^9$  (at 25°C),  $7.9 \times 10^8$  (at 35°C) and  $\beta_2 = 9.6 \times 10^{14}$  (at 25°C),  $7.0 \times 10^{14}$  (at 35°C).

However in the reported Figs. 4 and 5, the decrease in the absorbance at 831 nm and the simultaneous increase at 836 nm proceed in a fairly wide concentration range of citrate ( $10^{-10}$  to  $10^{-5}$  mol · kg<sup>-1</sup>), indicating that the absorption spectrum changes even with an extremely small stoichiometric amount of citrate as compared to Pu(VI) ( $9.2 \times 10^{-4}$  mol · kg<sup>-1</sup>). This cannot be explained by any complex formation equilibria. Therefore, the results of [75NEB/AND] are not credited by this review.

#### [75OHY]

This is the duplicate report of [75OHY/ODA].

#### [75OHY/ODA]

Distribution coefficients ( $K_d$ ) of  $4 \times 10^{-6} \sim 1 \times 10^{-5}$  M U(VI) between a cation exchanger (Dowex 50 W-X8, 100 – 200 mesh) and an aqueous solution containing various compositions of citrates and 0.1 M NaClO<sub>4</sub> were measured. Solutions containing various concentrations of H<sub>3</sub>cit (0.12 ~ 0.60 M) and 0.1 M NaH<sub>2</sub>cit in 0.1 M NaClO<sub>4</sub> were prepared. The pH and the concentrations of Hcit<sup>-</sup> and cit<sup>3-</sup> of each solution were controlled by the ratio of H<sub>3</sub>cit and NaH<sub>2</sub>cit. Distribution coefficients ( $K_d$ ) were calculated as:

$$K_d = \frac{([U]_t - [U]_s)}{[U]_s} \times \frac{\text{vol. of soln. phase (mL)}}{\text{mass of dry resin (g)}} \quad (\text{A.62})$$

where  $[U]_t$  and  $[U]_s$  are the concentrations of U(VI) in the supernatant solution determined spectrophotometrically with Arsenazo-III before and after the equilibration. Distribution coefficient of U(VI) can be expressed by:

$$K_d = \frac{K_d^\circ}{1 + \sum \beta_{i(\text{H}_2\text{cit})} \cdot [\text{H}_2\text{cit}^-]^i + \sum \beta_{j(\text{Hcit})} \cdot [\text{Hcit}^{2-}]^j + \sum \beta_{k(\text{cit})} \cdot [\text{cit}^{3-}]^k} \quad (\text{A.63})$$

where  $K_d^\circ$  is the distribution coefficient in the absence of citrates and  $\beta_q(\text{H}_r\text{cit})$  denotes the constant for the reaction  $\text{UO}_2^{2+} + q\text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{UO}_2(\text{H}_r\text{cit})_q^{2+q(r-3)}$ . The negligible contribution of the dimer species was confirmed by checking the dependence of  $K_d$  on the concentration of U(VI). From the dependence of  $K_d$  on  $C_L$  (total concentration of citric acid), only 1:1 complexes were confirmed to be formed ( $i, j$  and  $k = 1$ ). By using  $\log_{10} K_{(\text{H})} = 5.67, 4.39$  and  $2.96$ , the above equation was transformed into:

$$\frac{K_d^\circ}{K_d} - 1 = \beta_{1(\text{H}_2\text{cit})} \cdot [\text{H}_2\text{cit}^-] + \beta_{1(\text{Hcit})} \cdot [\text{Hcit}^{2-}] + \beta_{1(\text{cit})} \cdot \frac{K_{2(\text{H})}}{K_{1(\text{H})}} \frac{[\text{Hcit}^{2-}]^2}{[\text{H}_2\text{cit}^-]} \quad (\text{A.64})$$

or:

$$\frac{K_d^o}{K_d} - 1 = \beta_{1(\text{H}_2\text{cit})} \cdot [\text{H}_2\text{cit}^-] + \beta_{1(\text{Hcit})} \cdot \left( \frac{K_{1(\text{H})}}{K_{2(\text{H})}} [\text{H}_2\text{cit}^-][\text{cit}^{3-}] \right)^{1/2} + \beta_{1(\text{cit})} \cdot [\text{cit}^{3-}] \quad (\text{A.65})$$

$K_d^o$  was determined by a separate experiment to be  $2.3 \times 10^3$ . Eight values of  $K_d$  were measured at pH 2.19 ~ 2.88, where  $[\text{Hcit}^{2-}]$  and  $[\text{cit}^{3-}]$  were varied from  $0.65 \times 10^{-3}$  to  $3.06 \times 10^{-3}$  and from  $0.22 \times 10^{-6}$  to  $5.02 \times 10^{-6}$  M, respectively.  $K_d$  changed from 29.8 to 11.7. Since the authors prepared the solutions of  $[\text{H}_2\text{cit}^-] = 0.1$ , the first term in Eqs. (A.64) and (A.65) is constant. By plotting  $K_d^o/K_d - 1$  against  $[\text{Hcit}^{2-}]$  or  $[\text{cit}^{3-}]$  and fitting them to Eq. (A.64) or (A.65), they obtained three constants to be  $\log_{10} \beta_{1(\text{H}_2\text{cit})} = 2.79$  for  $\text{UO}_2(\text{H}_2\text{cit})^+$ ,  $\log_{10} \beta_{1(\text{Hcit})} = 4.23$  for  $\text{UO}_2(\text{Hcit})(\text{aq})$  and  $\log_{10} \beta_{1(\text{cit})} = 7.22$  for  $\text{UO}_2(\text{cit})^-$ , respectively. When  $\log_{10} \beta_{1(\text{H}_2\text{cit})} = 2.79$  is compared with those of  $\text{UO}_2^{2+}$   $\alpha$ -hydroxycarboxylate complexes, the value 2.79 seems too high. If we accept this constant, the contribution of  $\text{UO}_2(\text{H}_2\text{cit})^+$  to the potentiometric titration would be significant and seriously harm the constancy of the calculated formation constant of the dimer ( $\log_{10} \beta_{2,2}$ ). Simulated calculation by using these values indicates that the pH would be higher due to the consumption of  $\text{H}^+$  through the formation of  $\text{UO}_2(\text{H}_2\text{cit})^+$ . If we accept the results of the potentiometric titrations reported by Feldman *et al.* [60FEL/NOR], Rajan *et al.* [65RAJ/MAR] and Markovits *et al.* [72MAR/KLO],  $\log_{10} \beta_{1(\text{H}_2\text{cit})}$  should be less than 2.0.

Although the experiments were carefully done and the fitted result shown in Fig. 1 of [75OHY/ODA] seems fairly well, this does not guarantee the real contributions of the assumed species since the authors obtained three parameters from eight points. Errors in  $K_d^o$ ,  $K_d$ , pH and  $\log_{10} K_{2(\text{H})}$  would seriously affect the shape of the plot. Measured  $K_d^o$  and  $K_d$  values correspond to 4.2% and 77 ~ 90% U(VI) in the aqueous phase at the ratio of the volume of the solution to the mass of resin of  $100 \text{ ml} \cdot \text{g}^{-1}$ . Since these values were calculated by Eq.(A.62), errors may be high when the percentages in the aqueous phase are close to 0 or 100 %. To estimate the parameters in Eqs.(A.64) or (A.65) reliably,  $[\text{H}_2\text{cit}^-]$ ,  $[\text{Hcit}^{2-}]$  and  $[\text{cit}^{3-}]$  should be varied widely. Although  $[\text{Hcit}^{2-}]$  and  $[\text{cit}^{3-}]$  were varied in the experiment,  $[\text{H}_2\text{cit}^-]$  was fixed making the reliability of  $\log_{10} \beta_{1(\text{H}_2\text{cit})}$  low.

On the other hand, the authors conducted a separate experiment to obtain the formation constant  $\log_{10} \beta_{1(\text{cit})}$  for  $\text{UO}_2(\text{cit})^-$  at pH 3.9. A plot of  $(K_d^o/K_d - 1)$  versus  $[\text{cit}^{3-}]$  yielded a straight line which passes through the origin of the coordinates. Since the predominance of  $\text{UO}_2(\text{cit})^-$  is certain under this condition,  $\log_{10} \beta_{1(\text{cit})} = 7.22$  obtained from its slope is considered reliable. Moreover, this value is in fair agreement with that obtained by the above experiment,  $\log_{10} \beta_{1(\text{Hcit})} = 4.23$  recalculated for the above data using  $\log_{10} \beta_{1(\text{cit})} = 7.22$  is also considered reliable. In conclusion, this review accepts  $\log_{10} \beta_{1(\text{Hcit})} = (4.23 \pm 0.5)$  and  $\log_{10} \beta_{1(\text{cit})} = (7.22 \pm 0.3)$  at  $I = 0.1 \text{ M}$  with assigning fairly large uncertainties.

[\[75PRA/JON\]](#)

In this extensive study of derivatives of  $\beta$ -mercaptopropionic acid the stability constants for Mg and Ca with oxalate were also determined for comparison purposes. The authors report that they were “using solutions which were 0.100 M in both the chelating agent and the metal ion” in all cases of their measurements in the pH range 5 to 10. This experimental set-up exceeds the solubility of calcium oxalate by orders of magnitude, but also the solubility of magnesium oxalate is exceeded. The reported formation constants for  $\text{Mg(ox)(aq)}$  and  $\text{Ca(ox)(aq)}$ ,  $\log_{10} K_1 = 3.10$  and 3.5 respectively, are not only higher than most values reported in other studies, they are also inferring that  $\text{Ca(ox)(aq)}$  is more stable than  $\text{Mg(ox)(aq)}$ . Both effects most probably are artefacts of precipitation processes during the measurements. The results of this study are considered unreliable and they are rejected by this review.

[\[75RAM/MAN\]](#)

Although the value of  $\log_{10} \beta_1 = 3.54$  is given for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca(cit)}^-$ , this review does not accept this paper since experimental details are not given.

[\[75TER/SHE\]](#)

Spectrophotometric measurements in weakly acidic solutions ( $\text{pH} \approx 4.3$ ) and  $I = 0.5$  M (KCl) are reported where the solutions were obtained by mixing the components Zr, Nd and edta in different sequences. The formation of  $\text{Zr}_2(\text{edta})_2(\text{OH})_m^{m-}$  ( $m$  unknown),  $\text{Nd(edta)}^-$ ,  $\text{NdZr(edta)}_2^-$  and  $\text{NdZr(edta)}^{3+}$  was inferred from the molar ratio chosen for the three components, at a constant edta concentration of 0.02 M. The values of the involved equilibrium constants were obtained from the measured concentrations of the above species in the equilibrated solutions, measured two weeks after their preparation. For  $\log_{10} K(\text{Nd(edta)}^-)$  the authors used the value 15.15 in their calculations without mentioning its source. As  $\text{Zr(edta)(aq)}$  seems to be an acid with  $\text{p}K \approx 6.1$  [\[67BOT/AND\]](#), the assumption of the exclusive existence of the dimer zirconium-edta-hydroxo complex,  $\text{Zr}_2(\text{edta})_2(\text{OH})_m^{m-}$ , with unknown composition, is doubtful. Furthermore, the concentration of the non-complexed zirconium has not been corrected for hydrolysis. In summary, the “constants” obtained for equilibria involving doubtful species and strongly depending on unknown hydrolysis effects are meaningless.

[\[75ZAI/NIK\]](#)

The interaction of  $\text{Zr(IV)}$  ( $C_{\text{Zr}} = 2.9 \times 10^{-5}$  M) and citric acid has been studied by solvent extraction with TBP/decane in nitric acid solutions ( $C_{\text{HNO}_3} = 0.1 \sim 2$  M) at  $I = 2, 4$  and 6 M  $\text{LiNO}_3$  and  $25^\circ\text{C}$ . From the distribution ratios of  $\text{Zr(IV)}$  in the absence ( $D_0$ ) and presence ( $D$ ) of citric acid, the following function has been obtained:

$$K^c = \left( \frac{D_0}{D} - 1 \right) \frac{[\text{HNO}_3]^n}{[\text{H}_3\text{L}]}$$

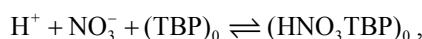
Distribution ratio was obtained as a function of nitric acid concentration at each fixed concentration of  $\text{LiNO}_3$  and citric acid, and  $K^c$  was found to be constant for  $n = 1$ . Thus, the authors proposed the formation of  $\text{Zr}(\text{H}_2\text{cit})^{2+}$ :

$$K^c = {}^*\beta_{1(\text{H}_2\text{cit})} = \frac{[\text{Zr}(\text{H}_2\text{cit})^{3+}][\text{H}^+]}{[\text{Zr}^{4+}][\text{H}_3\text{cit}]}.$$

The values of  ${}^*\beta_{1(\text{H}_2\text{cit})}$  were obtained to be  $(310 \pm 20)$  at  $I = 2$ ,  $(121 \pm 9)$  at  $I = 4$  and  $(90 \pm 6)$  at  $I = 6$  M  $\text{LiNO}_3$ , respectively. The formation of  $\text{Zr}(\text{H}_2\text{cit})^{2+}$  was confirmed by checking the constancy of the quotient:

$$K_{\text{mix}} = \frac{[\text{Zr}(\text{H}_2\text{cit})^{3+}]\{\text{H}^+\}}{[\text{Zr}^{4+}][\text{H}_3\text{cit}]},$$

where the activity coefficients of the hydrogen ion in  $\text{LiNO}_3$  was estimated (but only at 2 and 4 M  $\text{LiNO}_3$ ). However, under this experimental condition, the loss of nitric acid from aqueous phase due to the reaction:



cannot be neglected. Therefore, this review regards these values only as qualitative information.

The interaction of  $\text{Pu}^{4+}$  and citric acid has been studied by solvent extraction with TBP/decane in nitric acid solutions ( $C_{\text{HNO}_3} = 0.1 \sim 2$  M) of  $\text{LiNO}_3$  (1 ~ 6 M). From the distribution ratios of Pu(IV) in the absence ( $D_0$ ) and presence ( $D$ ) of citric acid, the following function has been obtained:

$$K^c = \left( \frac{D_0}{D} - 1 \right) \frac{[\text{HNO}_3]^n}{[\text{H}_3\text{L}]}.$$

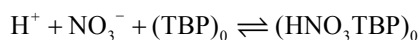
Since  $K^c$  was found to be practically constant at each fixed concentration of the nitrate ion ( $[\text{HNO}_3]$  varied for various fixed concentrations of nitrate ion and citric acid) for  $n = 2$ , the authors proposed the formation of  $\text{Pu}(\text{Hcit})^{2+}$ :

$$K^c = \frac{[\text{Pu}(\text{Hcit})^{2+}][\text{H}^+]^2}{[\text{Pu}^{4+}][\text{H}_3\text{cit}]}.$$

The values of  $\log K^c$  were obtained to be 1.63 at  $I = 1$ , 1.04 at  $I = 2$ , 0.46 at  $I = 4$  and  $-0.07$  at  $I = 6$  M  $\text{LiNO}_3$ , respectively. The formation of  $\text{Pu}(\text{Hcit})^{2+}$  was confirmed by checking the constancy of the quotient:

$$K_{\text{mix}} = \frac{[\text{Pu}(\text{Hcit})^{2+}]\{\text{H}^+\}^2}{[\text{Pu}^{4+}][\text{H}_3\text{cit}]},$$

where the activity coefficients of the hydrogen ion in  $\text{LiNO}_3$  was estimated. This review accepts the speciation of the complex. However, under this experimental condition, the loss of nitric acid from aqueous phase due to the reaction:



cannot be neglected. The reported values are not considered in the present review.

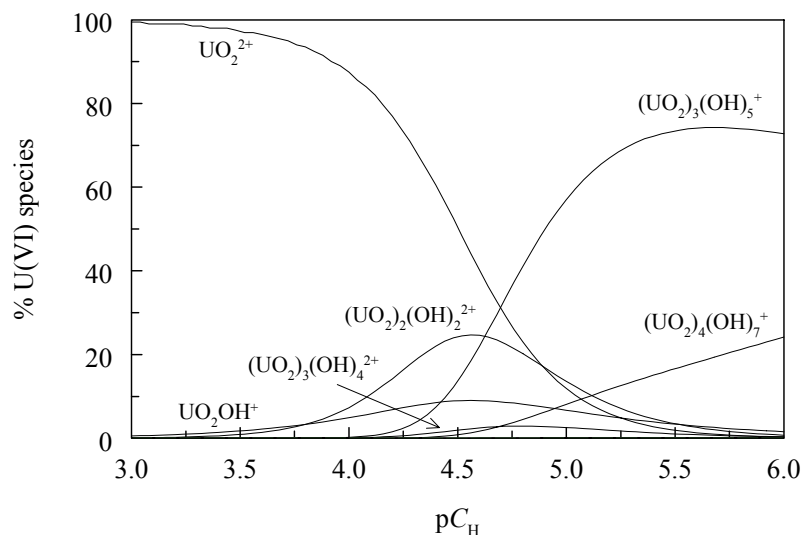
[\[76BAG/RAM3\]](#)

See comments under [\[77RAM/RAM2\]](#).

[\[76BRI/ELD\]](#)

The complexation of U(VI) with oxalate was studied by spectrophotometry and polarography at 25°C and  $I = 0.5$  M (H/K)NO<sub>3</sub>. The dissociation constants of H<sub>2</sub>ox(aq) and Hox<sup>−</sup> used in this paper are  $6 \times 10^{-2}$  and  $3 \times 10^{-4}$ , respectively. The authors assumed the formation of UO<sub>2</sub>(Hox)<sub>2</sub>(aq) at pH = 1.7 ( $\log_{10} K = (6.00 \pm 0.08)$ ) and the formation of UO<sub>2</sub><sup>2+</sup> at pH = 4.5 ( $\log_{10} \beta_2 = (9.36 \pm 0.25)$ ). The constants appear reasonable and fairly consistent with some other data from the literature. However, the calculation seems to be based on the assumption that (UO<sub>2</sub>)<sub>3</sub>O<sub>2</sub><sup>2+</sup>, equivalent to (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup>, is the dominant U(VI) species (if not the only species) at pH = 4.5. This assumption is very likely to be false. With the hydrolysis constants of U(VI) selected by [\[2003GUI/FAN\]](#) and the  $C_U = 0.004$  M in the paper, speciation calculation shows that the (UO<sub>2</sub>)<sub>3</sub>(OH)<sub>4</sub><sup>2+</sup> species is minor (Figure A-21). This raises serious concerns on the calculation of  $\log_{10} \beta_2$ . Besides, it remains questionable whether the protonated U(VI) oxalate complex, UO<sub>2</sub>(Hox)<sub>2</sub>(aq), forms at pH 1.7 and, if it forms, what is the percentage at this pH. The experimental details in the paper are not sufficient to allow recalculation of the data. Therefore, the data from this work are not accepted by this review.

Figure A-21: U(VI) speciation ( $C_U = 0.004$ M)





[\[76DAN/OST\]](#)

In order to study the formation of mixed complexes of  $\text{Ni}^{2+}$  and citrate with L-histidine or histamine, the stability constants of the  $\text{Ni}^{2+}$  complexes with citrate have been re-determined by potentiometric titrations of solutions containing  $C_{\text{Ni}} = C_{\text{L}}$  (as  $\text{H}_3\text{cit}$ ) =  $3 \times 10^{-3}$  M and  $C_{\text{Ni}} = C_{\text{L}} = 6 \times 10^{-3}$  M at 0.1 M  $\text{KNO}_3$  and  $(25 \pm 0.2)^\circ\text{C}$ . The calibration of the pH meter readings to the pcH values was well done. The constants for the reaction  $\text{Ni}^{2+} + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{Ni}(\text{H}_r\text{cit})^{r-1}$  were obtained to be  $(5.30 \pm 0.02)$  for  $\text{Ni}(\text{cit})^-$  and  $(3.23 \pm 0.03)$  for  $\text{Ni}(\text{Hcit})(\text{aq})$ . These values are taken by this review but with larger uncertainties of  $\pm 0.1$  since the protonation constants obtained in this paper,  $\log_{10} K_{(\text{H})} = 5.61, 4.30$  and  $2.87$ , are a little smaller than those evaluated by this review. Also,  $\log_{10} K = -(4.71 \pm 0.03)$  was estimated for the reaction  $2\text{Ni}^{2+} + 2\text{cit}^{3-} + 2\text{H}_2\text{O} \rightleftharpoons (\text{Ni})_2(\text{cit})_2(\text{OH})_2^{4-} + 2\text{H}^+$  from the titration data at higher pH. Although the authors claimed that the inclusion of the hydrolysis of  $\text{Ni}^{2+}$  in the calculation did not affect the result, rough estimation with the solubility product of around  $\log_{10} K_{s,0} = -13$  to  $-15$  for  $\text{Ni}(\text{OH})_2(\text{s})$  indicates the occurrence of the precipitation at around pH 9 to 10 even in the presence of citric acid under the experimental condition in this paper. Taking these considerations into account, this review accepts the values with assigning fairly large uncertainties as  $\log_{10} \beta_1 = (5.30 \pm 0.20)$  for  $\text{Ni}(\text{cit})^-$  and  $\log_{10} \beta_1 = (3.23 \pm 0.20)$  for  $\text{Ni}(\text{Hcit})(\text{aq})$ .

[\[76HUB/HUS\]](#)

The stability constants of citrate complexes of  $\text{Pu}^{3+}$ ,  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ,  $\text{Bk}^{3+}$ ,  $\text{Cf}^{3+}$ ,  $\text{Es}^{3+}$  and  $\text{Fm}^{3+}$  have been obtained at  $I = 0.1$  M  $(\text{Li,H})\text{ClO}_4$  at  $25^\circ\text{C}$  by using the solvent extraction with TTA/benzene in a similar manner as described in [\[74HUB/HUS\]](#). For  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ ,  $\text{Cf}^{3+}$  and  $\text{Es}^{3+}$ , the measurements have also been conducted at temperatures between 10 and  $50^\circ\text{C}$ , and  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$  for the reactions,  $\text{Am}^{3+} + 2\text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})_2^{3-}$  and  $\text{Am}^{3+} + \text{Hcit}^{2-} + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{Hcit})(\text{cit})^{2-}$  were estimated. For  $\text{Pu}^{3+}$  and  $\text{Bk}^{3+}$ , the measurements failed due to the disturbance of the formation of  $\text{Pu}^{4+}$  and  $\text{Bk}^{4+}$ . For the  $\text{Am}^{3+}$  citrate complexes, the speciation and the stability constants at  $25^\circ\text{C}$  are the same as in [\[74HUB/HUS\]](#) (see the discussion in [\[74HUB/HUS\]](#)). By assuming that pH and  $\log_{10} K_{(\text{H})}$  are constant in the temperature range of 10– $50^\circ\text{C}$ ,  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$  were estimated to be  $\Delta_r H_m^\circ = 2.93 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_r S_m^\circ = 243 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  for  $\text{Am}^{3+} + 2\text{cit}^{3-} \rightleftharpoons \text{Am}(\text{cit})_2^{3-}$ . Considering the uncertainties derived from experimental errors and the assumptions in the calculation, this review does not accept these values.

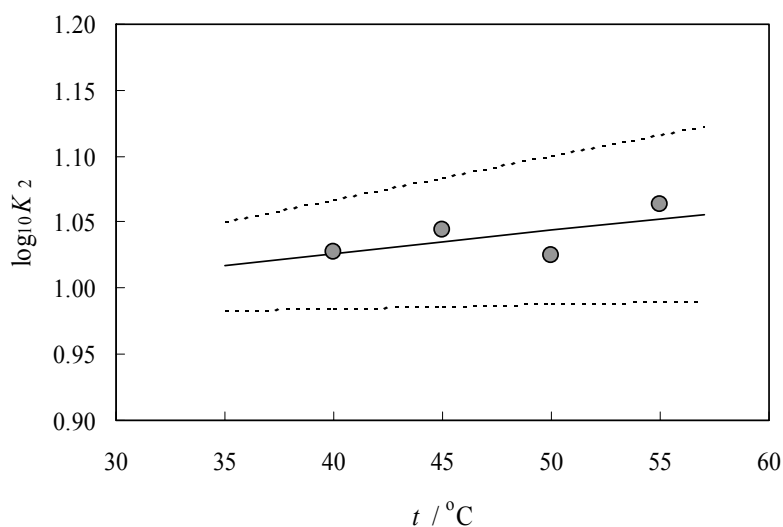
[\[76KAL\]](#)

The first dissociation constant of oxalic acid has been determined potentiometrically in 1 M  $\text{NaClO}_4$  and 1 M  $\text{KNO}_3$  at 35, 40, 45, 50 and  $55^\circ\text{C}$ . The acidity constants were found to be virtually invariant, despite medium and temperature changes, and [\[76KAL\]](#) calculated an average  $\text{p}K_a$  value from all data.

However, in order to estimate the temperature variation of  $\log_{10} K_2$  the values

reported by [76KAL] have been fitted in this review to a temperature function assuming  $\Delta_r C_{p,m} = 0$ . The results are:  $\Delta_r H_m = (3.5 \pm 2.9) \text{ kJ}\cdot\text{mol}^{-1}$  in 1 M NaClO<sub>4</sub> and  $\Delta_r H_m = (2.3 \pm 3.0) \text{ kJ}\cdot\text{mol}^{-1}$  in 1 M KNO<sub>3</sub>.

Figure A-22: Second protonation constant for oxalate determined in 1 M NaClO<sub>4</sub> by [76KAL] and the constant  $\Delta_r H_m$  model with the parameters determined in this review.

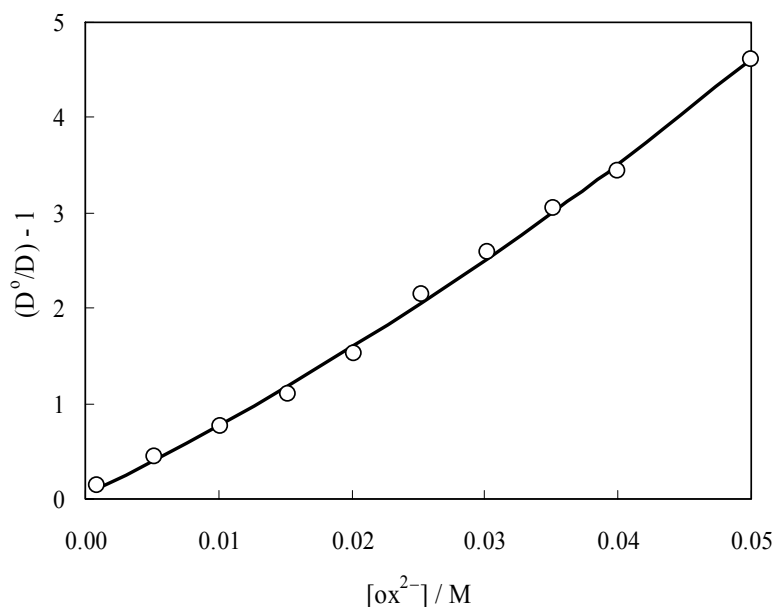


#### [76MCD/KEL]

The tendency of divalent nobelium to form complexes with citrate, oxalate and acetate has been examined by solvent extraction techniques and compared with the complex forming ability of calcium and strontium under the same conditions. Solvent extraction studies were carried out using 0.005 M di(2-ethylhexyl)phosphoric acid (HDEHP) in n-octane as the organic phase and 0.5 M NH<sub>4</sub>NO<sub>3</sub> as the aqueous phase. The choice of the salt and its concentration for the background electrolyte was dictated by the need for a sufficient concentration of salt to minimise medium changes as ligand was added and the need for a volatile salt in small enough quantity to vaporise quickly from the counting plates. Trace studies involving elements for comparison used <sup>45</sup>Ca, <sup>47</sup>Ca, <sup>85</sup>Sr, and <sup>87</sup>Sr. The <sup>85</sup>Sr and <sup>47</sup>Ca tracers were of high specific activity so that the solutions were approximately  $2 \times 10^{-9}$  M in strontium and  $3 \times 10^{-11}$  M in calcium. In the case of Ca oxalate the authors evaluated their data in terms of a single Ca(ox)(aq) complex and derive  $\log_{10} K_1 = (1.95 \pm 0.01)$ . However, in a solvent extraction study using similar concentration ranges [67HAS/MAK] not only Ca(ox)(aq) but also Ca(ox)<sub>2</sub><sup>2-</sup> has been detected, see discussion in this Appendix. Inspection of Fig. 5 in [76MCD/KEL] reveals that the experimental Ca oxalate data significantly deviate from linearity indicating the presence of Ca(ox)<sub>2</sub><sup>2-</sup>. The raw experimental data given in Fig. 2 of [76MCD/KEL] have been digitised and re-fitted in this review assuming two complexes, Ca(ox)(aq)

and  $\text{Ca(ox)}_2^{2-}$ . The result of this fit is shown in Figure A-23, and the fitted parameters are  $\log_{10} K_1 = (1.83 \pm 0.08)$  and  $\log_{10} K_2 = (0.86 \pm 0.22)$ .

Figure A-23: Experimental solvent extraction data from [76MCD/KEL] (open circles) re-fitted in this review assuming two complexes,  $\text{Ca(ox)(aq)}$  and  $\text{Ca(ox)}_2^{2-}$  with  $\log_{10} K_1 = (1.83 \pm 0.08)$  and  $\log_{10} K_2 = (0.86 \pm 0.22)$ , respectively (line).



#### [76TRI/SCH]

The stability constants of the complexes of zirconium and hafnium with chloride, thiocyanate, sulphate, oxalate and phosphate have been investigated by solvent extraction of  $^{95}\text{Zr}$  and  $^{181}\text{Hf}$  with  $\beta$ -isopropyltropolone. The stability constant of zirconium oxalate was determined at 2, 3 and 4 M  $[\text{H}^+]$  in  $I = 4 \text{ M}$  ( $\text{HClO}_4 + \text{NaClO}_4$ ) to be  $K = (2 \pm 0.2) \times 10^4$  for  $\text{ZrOH}^{3+} + \text{H}_2\text{ox} \rightleftharpoons \text{Zr(ox)}_2^{2+} + \text{H}^+ + \text{H}_2\text{O}$ . The authors assumed the predominant existence of  $\text{ZrOH}^{3+}$  in the examined acidity range without giving any basis for this assumption. On the contrary, Connick and McVey [49CON/MCV] have shown the predominance of  $\text{Zr}^{4+}$  at lower concentration and the acidity higher than 2 M. Although the hydrolytic behaviour of zirconium in this acidity range is not well known, the predominance of  $\text{Zr}^{4+}$  in 3 and 4 M acid solution is considered more probable. Since the assumption of the predominance of  $\text{ZrOH}^{3+}$  affects the following analysis, this review does not consider the result of this paper.

#### [76VAS/KOC]

This paper was performed using the same experimental techniques and data interpreta-

tion procedures as in a previous paper discussed in this Appendix [73VAS/KOC]. Vasil'ev *et al.* report experimental calorimetric data at 15 and 35°C in their Table 1. Enthalpy changes for reaction:  $\text{H}_2\text{edta}^{2-} + \text{H}^+ \rightleftharpoons \text{H}_3\text{edta}^-$ , are reported in their Table 2 also at 25°C, but these values seem to be those already published in [73VAS/KOC].

#### [76VAS/SHE]

The enthalpy of the first ionisation of oxalic acid has been determined by calorimetric measurements of the heat of reaction of oxalic acid with NaOH in 0.15 M sodium nitrate at 8, 10, 15, 25 and 30°C. The enthalpy of the second ionisation step has been determined by method (1) as described in [73VAS/SHE2]. The electrolyte used was sodium nitrate in concentrations of 0.5, 1.0 and 2.0 M at 5, 15, 25 and 35°C. The error in the determination of thermal effects is given by [76VAS/SHE] as the mean square deviation from the mean value based on 3 – 4 measurements. In the present review the uncertainties reported in [76VAS/SHE] have been multiplied by 1.96 to obtain error limits closer to 95% total uncertainty level, and the results have been recalculated from calories to Joules by the factor 4.184.

Treatment of the experimental data by [76VAS/SHE] showed that the enthalpy of the second ionisation of oxalic acid depends linearly on temperature. Hence, in order to estimate the temperature variation of  $\Delta_r H_m$ , the experimental results of [76VAS/SHE] have been fitted in this review to a temperature function assuming  $\Delta_r C_{p,m} = \text{const.}$  The results are included in Table VI-7 and shown graphically in Figure A-24 and Figure A-25.

Figure A-24: Enthalpy of the first protonation constant for oxalate determined in the indicated media by [76VAS/SHE] and the constant  $\Delta_r C_{p,m}$  model with the parameters determined in this review.

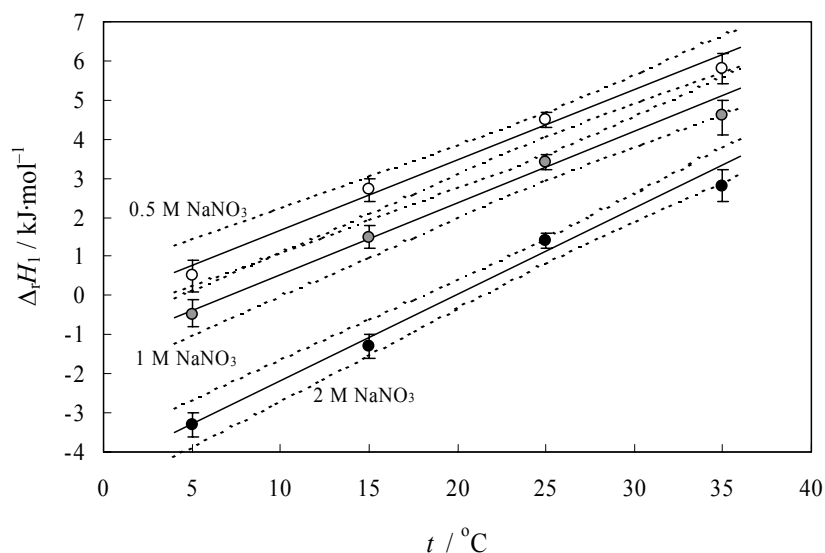
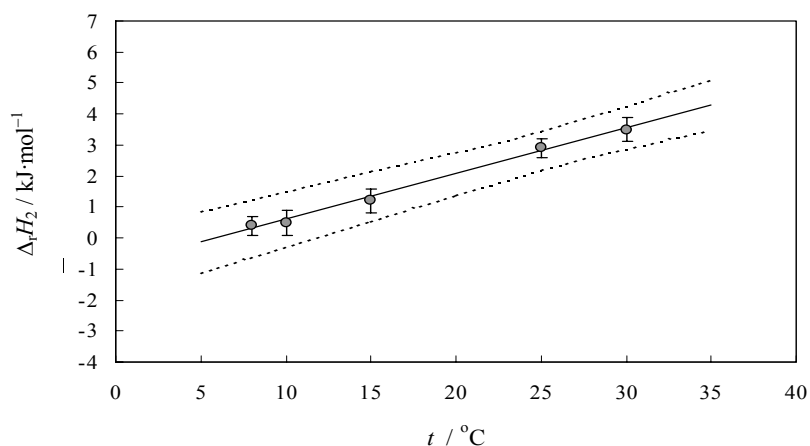
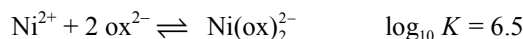
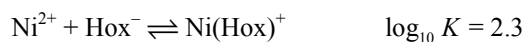


Figure A-25: Enthalpy of the second protonation constant for oxalate determined in 0.15 M NaNO<sub>3</sub> by [76VAS/SHE] and the constant  $\Delta_r C_{p,m}$  model with the parameters determined in this review.



#### [76YAD/GHO]

This study on the complex formation between oxalate and Cu<sup>2+</sup> and Ni<sup>2+</sup> was performed at 30°C by paper electrophoresis. The authors state that the solutions had initially 0.005 M H<sub>2</sub>ox and 0.1 M HClO<sub>4</sub> and that the pH was varied between 1 and 6.5 by the addition of aqueous NaOH. This suggests that the ionic strength and total oxalate concentration were perhaps not kept constant. No information about the pH calibration and about the pH scale is given. From two plateaus of the mobility curve *versus* pH, the authors assumed the formation of two complexes, a cation and an anion, and the following equilibrium constants were reported:



However, calculations by this review using these equilibrium constants show that the mobilities given in [76YAD/GHO] can not be reproduced in the pH interval 1 to 3, where the Ni(Hox)<sup>+</sup> complex should have its highest concentration. The electrophoresis method is of limited accuracy and the experimental conditions were not well defined, and therefore the reported equilibrium constants are not considered in this review.

#### [77CHO/GOE]

The authors reported in this and in a companion paper [77GRI/GOE] protonation constants for a series of ligands, including edta. The protonation constants are not credited by this review, see comments for [77GRI/GOE] in this appendix.

In [77CHO/GOE] the authors report the first two heats of protonation for edta in 0.5 M KNO<sub>3</sub> at 25°C. The reported value of  $\Delta_r H_m$  for  $\text{edta}^{4-} + \text{H}^+ \rightleftharpoons \text{Hedta}^{3-}$  is lower than all other calorimetric values in the literature at 25°C, and it is clearly an outlier. It is not possible to explain this discrepancy due to the scarcity of experimental details given in [77CHO/GOE], such as the concentration of edta and acid used, *etc.* Because of this, the reported  $\Delta_r H_m$  values are not included in this review.

#### [77FED/KHO]

The solubility of magnesium oxalate was studied at 25°C in *I* M Na(ClO<sub>4</sub>,L) solutions, where L was formiate, acetate, proprionate and butyrate, and *I* took the values 0.5, 1.0, 2.0, 3.0, 4.0, 6.0 and 8.0 M. The magnesium concentration of the saturated solutions was determined complexometrically. The pH in the test solutions was varied from 5.5 to 7.0. The solubility of magnesium oxalate in pure water is reported to be  $9.24 \times 10^{-3}$  M.

The results of the mixed ligand systems are outside the scope of the present review, but the reported solubility products and Mg(ox)(aq) formation constants as a function of NaClO<sub>4</sub> concentration would be of interest. However, no description is given by the authors how the solubility experiments were carried out: From oversaturation or from undersaturation? The equilibration time is not mentioned and no clue is provided if and how the status “saturated solution” was checked. The solubility of magnesium oxalate in pure water reported in this paper is three times higher than any other value ever published in the literature (see Section VI.5.1). This leads to the suspicion that the solubility experiments were carried out as precipitation experiments, and that the authors were not aware of the fact that magnesium oxalate exhibits very slow precipitation kinetics, and that strongly oversaturated solutions might be stable for days [08KOH]. The suspicion that solutions with a variable degree of oversaturation have been measured in this study is also corroborated by the observation that the Mg(ox)(aq) formation constants are significantly lower than values reported in similar NaCl solutions [2001CHO/BON], and they exhibit a strong non-linear behaviour in a SIT plot, in contrast to the data of [2001CHO/BON]. Considering all these ambiguities the results are rejected by this review.

#### [77GRI/GOE]

The authors determined the protonation constants of edta<sup>4-</sup> at 25°C and *I* = 0.5 M, in both KNO<sub>3</sub> and NaClO<sub>4</sub> solutions. The authors report that “no detectable differences between KNO<sub>3</sub> and NaClO<sub>4</sub> were observed in the  $pK_a$ ” and that the acid-base constants in these two media “were used interchangeably.” This observation is in disagreement with all other experimental determinations reported in the literature, and therefore the protonation constants reported by Gritmon *et al.* are not included in the present review.

[\[77HOS/UEN\]](#)

A 0.04 – 0.06 M thorium, uranium(VI) or plutonium(IV) solution in 0.5 M HCl was mixed with 0.05 or 0.2 M citric acid. To these mixtures, 0.2 M  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  was added and precipitates were obtained. The precipitates were analysed to be  $[\text{Co}(\text{NH}_3)_6]_2[\text{Th}(\text{cit})_2]_3 \cdot 10\text{H}_2\text{O}$ ,  $[\text{Co}(\text{NH}_3)_6]_2[\text{UO}_2(\text{Hcit})_2]_3 \cdot 4\text{H}_2\text{O}$ , and  $[\text{Co}(\text{NH}_3)_6]_2[\text{Pu}(\text{cit})_2]_3 \cdot 12\text{H}_2\text{O}$  and their solubilities in water at  $(25 \pm 2)^\circ\text{C}$  were measured.

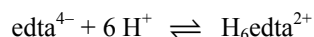
Although this work gives us qualitative information about the stabilities of citrate complexes, *i.e.*, that a protonated complex forms in the case of uranyl ion whose dioxo structure forces the ligand to coordinate only from its equatorial plane, no attempts have been made to derive quantitative thermodynamic information.

[\[77KOS/SHE\]](#)

Complex formation of zirconium and hafnium with edta has been studied by  $^1\text{H}$  NMR. The authors report that “the Zr(Hf)-edta systems were prepared in the following manner: Zirconium (or hafnium) oxide chloride in the chosen ratio was added to edta with vigorous stirring, and the pH adjusted by dropwise addition of alkali with even more vigorous stirring to prevent precipitation at the point of the alkali”. No absolute concentrations are given in [\[77KOS/SHE\]](#). The authors interpret their NMR results by assuming the following complexes: (A) In 1:1 Zr:L (L = edta) mixtures a complex  $\text{ZrL}_\text{I}$  forms at pH 1–3 (*i.e.*, the 1:1 complex with coordination of six edta donor-atoms bound to Zr), at pH 3.5–6 a complex  $\text{ZrL}_\text{II}$  forms and at pH > 7 zirconium hydrolysis predominates. The complex  $\text{ZrL}_\text{II}$  “can be either a hydrolysed form of the complex  $\text{ZrL}_\text{I}$ , or the dimer  $\text{ZrL}_\text{II}$ , in which each zirconium ion is connected with two iminodiacetate groupings of two ligands” [\[75TER/SHE\]](#). (B) In 1:2 Zr:L mixtures the complexes  $\text{ZrL}_\text{I}$  and  $\text{ZrL}_\text{II}$  are found at pH < 6, but at pH > 6 the formation of  $\text{ZrL}_2$  is proposed according to the equilibrium  $\text{ZrL}_\text{II} + \text{L} \rightleftharpoons \text{ZrL}_2$  with  $\log_{10}K_2 = (1.8 \pm 0.2)$  at  $I = 1.0$  M. This is the only quantitative result reported in [\[77KOS/SHE\]](#) but considering the ambiguity of the postulated complex  $\text{ZrL}_\text{II}$ , this number has not been considered in this review.

[\[77LYM/VAS\]](#)

The authors determined calorimetrically the heats of protonation of ethylenediaminetetraacetate at 15, 25, and  $35^\circ\text{C}$ . The experiments involved mixing solutions of  $\text{Na}_4\text{edta}$  or  $\text{K}_4\text{edta}$  (pH = 12) with 2 M solutions of  $\text{HClO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$ . The data was extrapolated to zero ionic strength by correcting for the heats of dilution of  $\text{Na}_4\text{edta}$  or  $\text{K}_4\text{edta}$  solutions. The final solutions (in  $[\text{H}^+] \approx 2$  M) were assumed to contain only  $\text{H}_6\text{edta}^{2+}$ . For the reaction:



the authors obtained from the experiments with  $\text{K}_4\text{edta}$  solutions:  $\Delta_\text{r}H_\text{m} = -(36.2 \pm 0.6)$ ,  $-(32.0 \pm 0.6)$ , and  $-(27.0 \pm 0.6)$   $\text{kJ}\cdot\text{mol}^{-1}$ , at 15, 25, and  $35^\circ\text{C}$  respec-

tively. Our calculations show however that the fraction of  $\text{H}_5\text{edta}^+$  under these conditions is not negligible ( $\approx 30\%$ ). Because of this, and taking into account that the protonation enthalpy of  $\text{H}_5\text{edta}^+$  is expected to be only a few  $\text{kJ}\cdot\text{mol}^{-1}$ , the uncertainties in the values of  $\Delta_r H_m$  reported in [77LYM/VAS] are increased in this review to  $\pm 2 \text{ kJ}\cdot\text{mol}^{-1}$ . More detailed studies on the same reaction were reported by the same authors in [77VAS/LYM], [77VAS/LYM2] which are discussed in this Appendix.

#### [77MOY/FRI]

The authors describe the performance of a new cation exchange resin. The procedure to determine the Ca-edta stability is described by [77MOY/FRI] as follows: 0.05 to 0.20 mmol of edta and 0.05 to 0.15 mmol of metal ion were mixed with 0.20 g of resin. The pH was adjusted to 10.0; the mixtures were equilibrated for 2.0 hours in a  $60^\circ\text{C}$  water bath and for a further 2.0 hours at room temperature. The samples were filtered and washed thoroughly with deionised water. The quantity of metal remaining in the effluent was determined by atomic absorption. Hence, the ionic strength of the solutions varied considerably, the nature of the metal salt used is not reported, and no experimental data are given. In view of all these shortcomings the value reported by [77MOY/FRI] has not been considered further in this review.

#### [77MUN/GRO]

1:1 or excess amount of  $\text{K}_3\text{Cit}$  (Cit is the notation in the paper, the meaning of this notation will be discussed below) were added to the solution of  $10^{-3} \text{ M}$   $\text{K}_2\text{TcBr}_6$  (at pH 7), and for this mixture, potentiometric titration, thin layer chromatography, absorption spectrophotometry and electric conductivity measurements have been carried out. The equivalent weights were also obtained for the solid compounds. When the ratio of citrate to Tc(IV) is around 1, the polymeric form of Tc(IV) complex forms and this changes to low molecular weight complex with the increase in citrate amount. From the potentiometric titration between pH 4 to 7, the equivalent weight analyses on the solid compounds, as well as the measurements as noted above, the authors assigned the formulas to these species as  $[\text{Tc}(\text{OH})_3\text{Cit}]_n^{2n-}$  (I) and  $[\text{Tc}(\text{OH})_2(\text{Cit})_2]^{6-}$  (II), respectively. Also the formation of  $[\text{Tc}(\text{OH})_2(\text{CitH})_2]_n^{4n-}$  (III) is claimed but without detailed discussion.

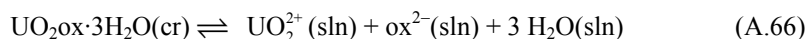
In this paper, the reviewer has faced the problem of the meaning of Cit. Since the authors denote the addition of  $\text{K}_3\text{Cit}$ , Cit means the same as cit (giving the charge  $-3$ ) or according to the notation in this review,  $(^-\text{OOC}-\text{CH}_2-\text{C}(\text{OH})(\text{COO}^-)-\text{CH}_2-\text{COO}^-)$ . However, in Fig. 2 of [77MUN/GRO] showing the proposed structure of the complexes, the citrate ligand coordinates to Tc(IV) through the deprotonated alcoholic oxygen in citrate for (I) or the deprotonated alcoholic oxygen and one dissociated carboxylate in citrate for (II). In this context, Cit seems to mean  $\text{H}_4\text{cit}$  (giving the charge  $-4$ ) according to the notation in this review. The reviewer cannot assign the same charge to Cit in the species (I), (II) and (III). Moreover, the existence of such a highly charged mono-



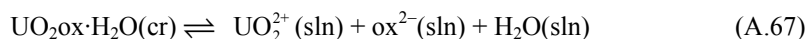
meric species as (II) as a stable predominant species in the solution is doubtful. Although Münze and Grossmann report the formation of certain complex species of Tc(IV) with citrate, this review does not accept the speciation proposed in this paper.

### [77OHA]

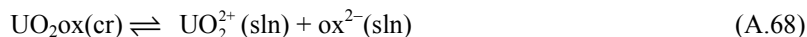
Solution calorimetric studies were conducted to determine the enthalpies of dissolution of  $\text{H}_2\text{Ox} \cdot 2\text{H}_2\text{O}(\text{cr})$ ,  $\text{UO}_2\text{Ox} \cdot 3\text{H}_2\text{O}(\text{cr})$ ,  $\text{UO}_2\text{Ox} \cdot \text{H}_2\text{O}(\text{cr})$  and  $\text{UO}_2\text{Ox}(\text{cr})$  in a solution of  $2.8 \text{ mol} \cdot \text{kg}^{-1}$  nitric acid:



$$\Delta_r H_m(\text{A.66}) = (25.1 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

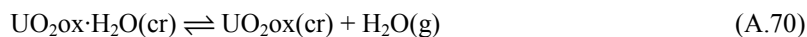
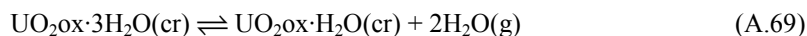


$$\Delta_r H_m(\text{A.67}) = -(6.6 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$$



$$\Delta_r H_m(\text{A.68}) = -(35.8 \pm 0.4) \text{ kJ} \cdot \text{mol}^{-1}$$

Using a thermochemical cycle upon which  $\Delta_r H_m^\circ(\text{UO}_2\text{Ox} \cdot 3\text{H}_2\text{O})$  is based and relevant auxiliary data, the standard enthalpies of formation of  $\text{UO}_2\text{Ox} \cdot 3\text{H}_2\text{O}(\text{cr})$ ,  $\text{UO}_2\text{Ox} \cdot \text{H}_2\text{O}(\text{cr})$  and  $\text{UO}_2\text{Ox}(\text{cr})$  at 298.15 K were calculated to be  $-(2715.3 \pm 2.4)$ ,  $-(2711.8 \pm 2.4)$ , and  $-(1796.7 \pm 2.5) \text{ kJ} \cdot \text{mol}^{-1}$ , respectively. The standard enthalpy of the dehydration reactions (A.69) and (A.70) are calculated to be  $\Delta_r H_m^\circ(\text{A.69}) = (119.9 \pm 3.4) \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta_r H_m^\circ(\text{A.70}) = (73.3 \pm 3.5) \text{ kJ} \cdot \text{mol}^{-1}$  at 298.15 K:



The standard enthalpy of formation of  $\text{UO}_2\text{Ox} \cdot 3\text{H}_2\text{O}(\text{cr})$  from this work is considered by this review. Combined with the value from the heat of combustion obtained by bomb calorimetry [92THA/KUM], a value of  $\Delta_r H_m^\circ(\text{UO}_2\text{Ox} \cdot 3\text{H}_2\text{O}, \text{cr})$  is selected by this review. More discussions are given under [92THA/KUM].

### [77OYA/MAT]

Oyama *et al.* determined the protonation constants of  $\text{edta}^{4-}$  in 1 M  $\text{NaClO}_4$  at  $25^\circ\text{C}$  using data from a titration with  $[\text{edta}]_{\text{TOT}} = 13.5 \text{ mM}$  (*cf.* their Figs. 1 and 2). It is known however that the solubility of  $\text{H}_4\text{edta}(\text{cr})$  in the pH range of  $\approx 1$  to  $\approx 2$  is  $\approx 1 \text{ mM}$  [67AND], [83KRA/DEC]. It is therefore quite possible that precipitates were formed during the acid ranges of their titrations. Because of this, the reported values of  $K_4$ ,  $K_5$  and  $K_6$  (their  $\beta_{041}$ ,  $\beta_{051}$  and  $\beta_{061}$ ) are disregarded in this review.

### [77RAM/RAM]

See comments under [77RAM/RAM2].

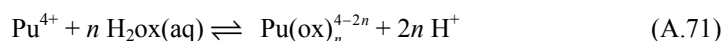
### [\[77RAM/RAM2\]](#)

Results from solvent extraction studies on the complexation of tetravalent actinides with oxalate were presented in a series of papers from the same research group [\[76BAG/RAM3\]](#), [\[77RAM/RAM2\]](#), [\[77RAM/RAM\]](#), [\[79KUS/GAN\]](#). All these studies are discussed here.

The radionuclides,  $^{232}\text{Th}$ ,  $^{237}\text{Np}$  and  $^{238}\text{Pu}$  were analysed using scintillation counting. Thorium and neptunium were spiked with  $^{234}\text{Th}$  and  $^{238}\text{Np}$ . The extractant was either thenoyltrifluoroacetone (TTA) in benzene [\[76BAG/RAM3\]](#), [\[77RAM/RAM\]](#) or dinonylnaphthalene sulphonic acid (DNNS) also in benzene [\[77RAM/RAM2\]](#). All Np and Pu experiments were performed at  $I = 1.0$  ( $\text{HClO}_4$ ) and  $(25.0 \pm 0.1)^\circ\text{C}$ . Data at 10 and  $40^\circ\text{C}$  were also reported in [\[77RAM/RAM\]](#). No reductant was needed for Np(IV) in solutions containing oxalic acid, but Fe(II) sulphamate was used as a reductant in the absence of  $\text{H}_2\text{ox}$ . In the case of Pu(IV),  $\text{NH}_4\text{VO}_3$  was added to avoid the reduction to Pu(III) in all solutions when the extractant was DNNS [\[77RAM/RAM2\]](#), or only in the oxalic-free solutions when TTA was used [\[76BAG/RAM3\]](#). The oxidation state of Np and Pu in the DNNS experiments was checked afterwards by TTA extraction. The oxalate protonation constants from [\[66MOO/SUT\]](#) were used for the interpretation of the data:  $\log_{10} K_1 = 3.55$  and  $\log_{10} K_2 = 1.08$ .

The equilibrium constants reported by the authors are listed in Table VI-47 (Section VI.11.2.2) and in Table VI-58 (Section VI.12.2.2) for Np(IV) and Pu(IV), respectively. Because of TTA complexing in the aqueous phase the authors estimated that the reported equilibrium constants should be increased by 0.3  $\log_{10}$ -units [\[76BAG/RAM3\]](#), [\[77RAM/RAM2\]](#). The hydrolysis on Pu(IV) was estimated to require an additional increase of 0.3  $\log_{10}$ -units.

While the distribution coefficients reported in [\[76BAG/RAM3\]](#), [\[77RAM/RAM2\]](#) for Np(IV) agree well, those of Pu(IV) show larger discrepancies. The authors did not make any comments about this or about the resulting discrepancies in the equilibrium constants for Pu(IV). A re-evaluation of the data was performed by this review using  $\text{H}_2\text{ox}(\text{aq})$  as the ligand



with  $n = 1$  to 3; with the least-squares software Letagrop-Distr [\[71LIE\]](#), [\[79LIE/EKE\]](#). The formation of  $\text{PuOH}^{3+}$  was included in the calculations with  $\log_{10} {}^*\beta_1 = -(0.48 \pm 0.24)$ , while the first dissociation constant for  $\text{H}_2\text{ox}(\text{aq})$  was taken to be  $10^{-(1.16 \pm 0.11)}$  M (all at 1 M  $\text{HClO}_4$ , in molar units). The DNNS data from [\[77RAM/RAM2\]](#) results in:  $\log_{10} {}^*\beta_1 = (4.92 \pm 0.03)$ ,  $\log_{10} {}^*\beta_2 = (7.3 \pm 0.3)$ , and  $\log_{10} {}^*\beta_3 = (10.4 \pm 0.3)$  for reaction (A.71), all in 1 M  $\text{HClO}_4$  and at  $25^\circ\text{C}$ . The TTA data from [\[76BAG/RAM3\]](#) results in:  $\log_{10} {}^*\beta_1 = (5.26 \pm 0.07)$ ,  $\log_{10} {}^*\beta_2 = (8.0 \pm 0.4)$ , and  $\log_{10} {}^*\beta_3 = (10.8 \pm 0.5)$ , also for reaction (A.71). The TTA values are larger than those obtained with DNNS, even though complex formation by TTA in the aqueous

phase is expected to result in lower values in the case of TTA. This indicates some systematic errors in one or both sets of data. Because the TTA extractant is better established than DNNS, the TTA values are considered more reliable, but the uncertainties are increased to 0.3, 0.6 and 0.7  $\log_{10}$ -units for  $\text{Pu}(\text{ox})^{2+}$ ,  $\text{Pu}(\text{ox})_2(\text{aq})$  and  $\text{Pu}(\text{ox})_3^{2-}$ , respectively. Conversion to molal units gives:  $\log_{10}^* \beta_1 = (5.28 \pm 0.30)$ ,  $\log_{10}^* \beta_2 = (8.04 \pm 0.60)$ , and  $\log_{10}^* \beta_3 = (10.90 \pm 0.70)$ , including the uncertainty in the formation of  $\text{PuOH}^{3+}$ .

The original Np(IV) data from [76BAG/RAM3], [77RAM/RAM2] are fitted jointly by this review using  $\text{H}_2\text{ox}(\text{aq})$  as the ligand:  $\text{Np}^{4+} + n \text{H}_2\text{ox}(\text{aq}) \rightleftharpoons \text{Np}(\text{ox})_n^{4-2n} + 2n \text{H}^+$ , with  $n = 1$  to 3. The least-squares fit using the Letagrop-Distr software [71LIE], [79LIE/EKE] results in:  $\log_{10}^* \beta_1 = (4.6 \pm 0.1)$ ,  $\log_{10}^* \beta_2 = (6.9 \pm 1.0)$ , and  $\log_{10}^* \beta_3 = (9.9 \pm 0.7)$ , all in 1 M  $\text{HClO}_4$  and at 25°C.

#### [77VAS/LYM]

The authors reported calorimetric measurements for the reaction:

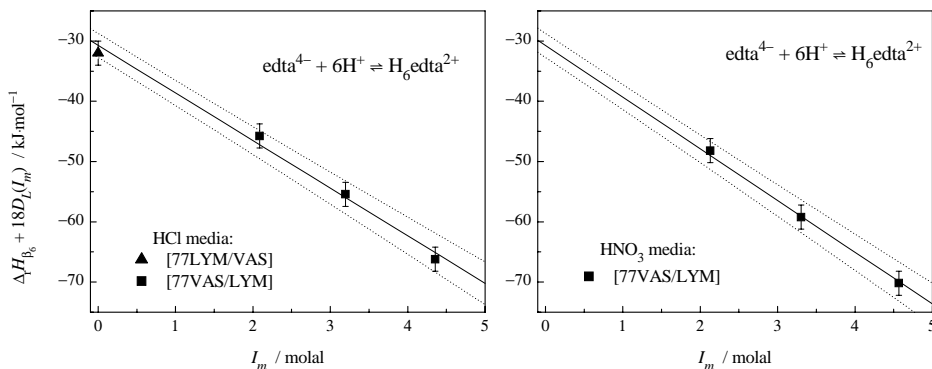


The experiments involved mixing solutions of  $\text{Na}_4\text{edta}$  or  $\text{K}_4\text{edta}$  ( $\text{pH} = 12$ ) with concentrated solutions of  $\text{HClO}_4$ ,  $\text{HCl}$  and  $\text{HNO}_3$  ( $\geq 2 \text{ M}$ ). The data was extrapolated to zero ionic strength by correcting for the heats of dilution of  $\text{Na}_4\text{edta}$  or  $\text{K}_4\text{edta}$  solutions. The final solutions (in  $[\text{H}^+] \geq 2 \text{ M}$ ) were assumed to contain only  $\text{H}_6\text{edta}^{2+}$ . Our calculations show however that the fraction of  $\text{H}_5\text{edta}^+$  under these conditions is not negligible ( $\approx 30\%$  at  $[\text{H}^+] \approx 2 \text{ M}$ ). Because of this, and taking into account that the protonation enthalpy of  $\text{H}_5\text{edta}^+$  is expected to be only a few  $\text{kJ}\cdot\text{mol}^{-1}$ , the uncertainties in the values of  $\Delta_r H_m^\circ$  reported in [77VAS/LYM] are increased in this review to  $\pm 2 \text{ kJ}\cdot\text{mol}^{-1}$ . The data obtained with solutions of  $\text{K}_4\text{edta}$  are plotted in Figure A-26 as a function of the ionic strength according to the SIT model. The result reported by the same authors in [77LYM/VAS] is also given in the figure for comparison. The weighted multi-linear least-squares fits gave:  $\Delta_r H_m^\circ (\text{A.72}) = -(30.7 \pm 2.0) \text{ kJ}\cdot\text{mol}^{-1}$ . The slopes of the lines in the figure correspond to the values of  $\Delta \epsilon_L(\text{HCl}) = (10.6 \pm 0.5) \times 10^{-3} \text{ kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $\Delta \epsilon_L(\text{HNO}_3) = (11.6 \pm 0.5) \times 10^{-3} \text{ kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

By comparing the data involving solutions of  $\text{Na}_4\text{edta}$  and  $\text{K}_4\text{edta}$  the authors reported:

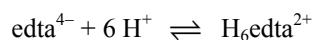


Figure A-26: Enthalpy changes for the reaction:  $\text{edta}^{4-} + 6\text{H}^+ \rightleftharpoons \text{H}_6\text{edta}^{2+}$  plotted according to the SIT methodology. Starting solutions:  $\text{K}_4\text{edta}$  at pH = 12.



#### [\[77VAS/LYM2\]](#)

In this paper the authors reported data at 15 and 35°C for the reaction:



investigated at 25°C by the same authors in reference [\[77VAS/LYM\]](#) which is discussed in this Appendix.

#### [\[77ZAK/KOR\]](#)

A weighed sample of freshly prepared  $^{241}\text{Am}$  oxalate was introduced into solutions of various concentrations of nitric acid (0, 0.1–1.0 M) in the absence or presence of oxalic acid (0–0.4 M) at 14, 30, 45 and 60°C and the americium concentration in the solution was determined by  $\gamma$ -counting. In the absence of an excess of oxalate, the solubility of americium increased linearly with nitric acid concentration (36.4  $\text{mg}\cdot\text{L}^{-1}$  at  $[\text{HNO}_3] = 0$  M to 992  $\text{mg}\cdot\text{L}^{-1}$  at  $[\text{HNO}_3] = 1.0$  M at 14°C). The introduction of an excess of oxalate sharply decreased the solubility of americium and the solubility increased with nitric acid concentration but not linearly. Dependence of the solubility at 14°C on  $C_{\text{ox}}$  in 0.1 to 1.0 M  $\text{HNO}_3$  (shown in Figure 3 of the paper) is on the whole similar to that reported for 25°C in [\[60LEB/PIR2\]](#). By assuming that  $C_{\text{ox}} = (3/2)[\text{Am}^{3+}]$  in the solution without an excess of oxalate and by using the calculated activity coefficients of the charged ions and the protonation constants of oxalate  $\log_{10} K_{(\text{H})}^{\circ} = 4.25$  and 1.27, the solubility product  $K_{\text{sp}} = \gamma_3^2 \cdot a_{\text{ox}}^3 \cdot [\text{Am}^{3+}]^2$  was calculated to be  $10^{-29} \sim 10^{-31}$  in nitric acid and  $6.4 \times 10^{-20}$  in water. The experiments were conducted without maintaining constant ionic strength. The use of the calculated activity coefficients in each condition may introduce errors. No analysis was conducted considering the complex formation (and hydrolysis) of americium in the aqueous solution, and the constancy of the solubility products was

not confirmed. The difference between the constants in nitric acid and in water indicates the incorrectness of the analysis. This paper is not accepted in this review.

#### [\[78ARE/MUS\]](#)

The authors determined the stability constants for the complexes between Cu(II) and  $\text{edta}^{4-}$ , and with some amino acids. The stability of ternary complexes was also determined. The acid-base constants for  $\text{edta}^{4-}$  (and for the amino acids) were determined at 37°C and  $I = 0.15 \text{ M}$  ( $\text{NaClO}_4$ ) potentiometrically using a glass electrode. The reported value of  $\log_{10} K_1$  for the first protonation of  $\text{edta}^{4-}$  equal to  $(9.74 \pm 0.03)$  may be converted to  $(9.91 \pm 0.03)$  at 25°C using  $\Delta_r H_m^\circ$  selected in this review. This value is  $> 0.4$   $\log_{10}$ -units larger than the other reported values under similar conditions. No apparent reason for this large discrepancy can be found in the publication. This outlier value has not been included in the selection procedure for  $\log_{10} K_1^\circ$  of  $\text{edta}^{4-}$ .

#### [\[78JAW\]](#)

This review is discussed with [\[80JAW\]](#).

#### [\[78KER/CHU\]](#)

The potentiometric study was carried out by titrating the solution containing citric acid (0.01 M) and nickel perchlorate (0.1 M) in 1 M  $\text{NaClO}_4$  at 25.0°C and the constants for the reaction  $\text{Ni}^{2+} + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{Ni}(\text{H}_r\text{cit})^{r-1}$  were obtained to be  $\log_{10} \beta_1 = 4.30$  for  $\text{Ni}(\text{cit})^-$ , 2.90 for  $\text{Ni}(\text{Hcit})(\text{aq})$  and 1.45 for  $\text{Ni}(\text{H}_2\text{cit})^+$ . The pH calibration was well done. However, due to the larger uncertainties in the protonation constants in high ionic media, the protonation constants  $\log_{10} K_{(\text{H})} = 5.05, 4.05$  and  $2.71$  used in the calculation are fairly different from those selected in this review. Thus, this review accepts these values but with assigning large uncertainties of  $\pm 0.4$ .

#### [\[78KOR/VAL\]](#)

This very short paper reports spectrophotometric measurements of Ni(II) edta and nitrilotriacetate complexes at  $(20 \pm 2)^\circ\text{C}$ . No details on the pH measurements are given. Because of this shortcoming and the overall poor information in this short report, the values reported by [\[78KOR/VAL\]](#) are not considered in this review.

#### [\[78MER/GAT\]](#)

In this study Merciny *et al.* report to have titrated coulometrically 5 mM solutions of ethylenediaminetetraacetic acid in KCl solutions of  $I = 1 \text{ M}$ . However, it is known that the solubility of  $\text{H}_4\text{edta}(\text{cr})$  in the pH range of  $\approx 1$  to  $\approx 2.2$  is lower than 1 mM [\[67MES/VIN\]](#). It is therefore quite possible that precipitates were formed during the most acid ranges of their titrations. Therefore the values of  $K_4$ ,  $K_5$  and  $K_6$  for edta reported in this paper (*i.e.*,  $\text{p}K_{-1}$ ,  $\text{p}K_0$  and  $\text{p}K_1$  in their Table 1) are not included in this review.

[\[78MOS/POZ\]](#)

See comments under [\[79MOS/POZ\]](#).

[\[78STR/KAR\]](#)

Solutions containing 0.1 M zirconium oxychloride ( $\text{ZrOCl}_2$ ) and 0.1M citric acid ( $\text{H}_3\text{cit}$ ) in 1:1 and 1:2 ratios were studied by proton NMR and by potentiometric titration. The mixtures of zirconium with citric acid at molar ratio 1:1 showed several characteristic signals with the change in pH.

- 1)  $0.4 < \text{pH} < 2.5$ : Zirconium precipitated.
- 2)  $2.5 < \text{pH} < 7$ : Zirconium dissolved suggesting the strong complex formation of zirconium with citrate. The authors observed two NMR signals (*a* and *b*) different from the signal of the free  $\text{H}_3\text{cit}$ . The signal *a*, situated at weaker field, was assigned to a complex where zirconium was bound with 2 carboxylic groups and to non-dissociated OH groups of citrate. The signal *b*, situated at stronger field was assigned to a complex where only carboxylic groups were taking part in the complexation.
- 3)  $7 < \text{pH}$ : A new signal *c* appeared at pH 7, which was situated to the right of the citrate anion signal. The signal shift to strong field was considered due to the dissociation of the alcoholic group. Although the signals *h* of free citrate, not bound with zirconium, appeared at pH 9 – 10, formation of zirconium hydroxide precipitate did not occur up to 12.5, suggesting a possible formation of polymeric complexes.

The other series of NMR experiments was done at the ratio of 1:2.

- 1)  $0.03 < \text{pH} < 0.4$ : Only signal of free citric acid was observed indicating insignificant bonding of the ligand in a complex.
- 2)  $1.2 < \text{pH} < 2.8$ : The signal of free citric acid disappeared and one signal *d* was observed, which was assigned to 1:2 complex (protonated complex).
- 3)  $2.5 < \text{pH}$ : Splitting of the signal *d* occurred and two new signals appeared, coinciding with the position of the free acid and 1:1 complex (*b*), which dominated up to pH 4.
- 4)  $7 < \text{pH}$ : Same as the case of the mixture at molar ratio of 1:1.

NMR experiments were complemented by a potentiometric titration. For molar ratio 1:1, the precipitate was observed at the pH range 0.4-2.5, which then dissolved at higher pH. At pH 6.8 an inflection point was observed which was assigned to the dissociation of alcoholic OH in the ligand. Considering that peak area of NMR signals are proportional to concentrations of individual complexes, the stability constants have been calculated using the formula,

$$\beta_n = \frac{\bar{c}_k}{\bar{c}_{\text{Zr}} \cdot \bar{c}_{\text{cit}}^n}, \quad n = 1, 2.$$

The values of  $\beta_1$  for  $\text{Zr}(\text{cit})^+$  were reported to be  $0.7 \times 10^8$  (at pH 3.0),  $1 \times 10^8$  (at pH 3.1),  $0.4 \times 10^8$  (at pH 3.2) and  $1 \times 10^8$  (at pH 3.4), and those of  $\beta_2$  for  $\text{Zr}(\text{cit})_2^{2-}$  were  $1 \times 10^{14}$  (at pH 3.0),  $6 \times 10^{14}$  (at pH 3.1),  $1 \times 10^{14}$  (at pH 3.2) and  $1 \times 10^{14}$  (at pH 3.4).

Experimental and calculational details such as the temperature, pH calibration, ionic strength and protonation constants of citrate are not given. In the calculation, hydrolysis of Zr(IV) was not taken into account. Moreover, the assignment of the NMR signals to the complex species is considered unclear. Although the signal *c* was considered due to the dissociation of the alcoholic OH in the complex, this signal is always accompanied with the signal *h*, which corresponds to free citrate anion. This makes us to suspect the formation of zirconium hydroxides at pH >7, though the precipitation was not observed until at higher pH. The degree of protonation of the free citrate and that in the complex was not well discriminated. Therefore, although this study demonstrates that Zr(IV)-citrate complexes are formed in acidic solutions, the stoichiometry of the complex(es) is not well established and the results should be considered as qualitative and the values are not accepted in this review.

#### [\[78VAS/KOC\]](#)

This paper reports calorimetric data for the protonation of  $\text{edta}^{4-}$  at (15, 25 and 35)°C in  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and  $\text{NaClO}_4$ . The concentration of the ionic media was kept constant at values between 0.2 and 1 M.

Two experimental procedures were used. In the first procedure 0.02 M edta solutions, with an initial pH either 11 or 6.5, were mixed with  $\text{HNO}_3$  or  $\text{HClO}_4$  using as background electrolytes  $\text{KNO}_3$  or  $\text{NaClO}_4$ , respectively. The pH changed in the experiments from 11 to 9.5 and from 6.5 to 5.5.

The second procedure was similar to the technique used in [\[74VAS/KOC\]](#): 0.02 M edta solutions, with an initial pH of either 5.5 or 9, were mixed with either  $\text{LiOH}$ ,  $\text{NaOH}$  or  $\text{KOH}$ . The pH changed from 5.5 to 6.5 and from 9 to 10.5. The heats of reaction in this case were corrected for  $\text{Na}^+$  complexation. It is not clear what procedure was used in the case of *e.g.*,  $\text{LiNO}_3$  media. Because of this the reported values from this procedure are not included in this review.

Both experimental procedures were based on the assumption that  $\text{H}_2\text{edta}^{2-}$  predominates at pH = 5,  $\text{Hedta}^{3-}$  at  $7 \leq \text{pH} \leq 9$ , and  $\text{edta}^{4-}$  at pH  $\geq 10.5$ . Although this assumption may be valid at low concentrations of background alkali ions, complex formation with  $\text{K}^+$ ,  $\text{Na}^+$  and particularly  $\text{Li}^+$  at higher ionic strengths decrease the pH-range of predominance for  $\text{Hedta}^{3-}$ . Therefore the enthalpy changes in  $\text{LiNO}_3$  are not considered in this review. Uncertainties in  $\text{Na}^+$  media are increased to  $\pm 1$  and  $\pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$  in 0.5 and 1 M, respectively.

[\[78VAS/LYM\]](#)

The heat of reaction of zirconium(IV) with edta at 25°C and ionic strengths equal to 2, 3, 3.7 and 4 M HClO<sub>4</sub> have been determined by direct calorimetric methods. The results obtained show good agreement. The subsequent calculations of other thermodynamic parameters were carried out using the value  $\log_{10}K(\text{Zr(edta)(aq)}) = 29.4$  at 25°C and  $I = 0.1$  M [\[64INT/MAR\]](#) and 33.79 at  $I = 0$  using the Davies equation. Only the enthalpy values are considered in this review, but not the parameters derived from these values.

[\[79BAU\]](#)

One of the standard buffer solutions of the US National Bureau of Standards (NBS, now NIST) is 0.05 m potassium tetr(a)oxalate solution, KH<sub>3</sub>(ox)<sub>2</sub>·2H<sub>2</sub>O. Conductivity and solubility measurements, however, have revealed that the 0.05 m buffer represents a saturated solution at 5°C. The author determined the solubility of KH<sub>3</sub>(ox)<sub>2</sub>·2H<sub>2</sub>O between 0 and 20°C. The results were fitted with the equation:

$$\log_{10}m_s = -1440 T^{-1} + 3.884$$

(solubility  $m_s$  in mol·kg<sup>-1</sup>,  $T$  in K) which yielded the formal enthalpy of dissolution  $\Delta_{\text{sol}}H_m = 27.6$  kJ·mol<sup>-1</sup>, and the saturation temperatures of the buffer solutions of interest, *i.e.*,  $m_s = 0.05$  mol·kg<sup>-1</sup> at  $(4.8 \pm 0.1)^\circ\text{C}$  and  $m_s = 0.10$  mol·kg<sup>-1</sup> at  $(22.0 \pm 0.2)^\circ\text{C}$ . The solubility of KH<sub>3</sub>(ox)<sub>2</sub>·2H<sub>2</sub>O at 25°C is  $m_s = 0.11$  mol·kg<sup>-1</sup>.

[\[79BUL/SAC\]](#)

This paper gives the method of calculation of free Ca<sup>2+</sup> in a solution containing calcium, magnesium (or manganese) and up to five complexing reagents. The relevant protonation constants and stability constants are listed in Table 1 of [\[79BUL/SAC\]](#), where  $\log_{10} \beta_1 = 2.95$  for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca(cit)}^-$  is reported. Since ionic strength, method of determination and other conditions are not given, this review does not accept this value.

[\[79CRA/MOO\]](#)

In this study  $5 \times 10^{-4}$  to  $5 \times 10^{-3}$  M calcium chloride solutions were titrated with Na<sub>3</sub>cit at 25 °C,  $I = 0.10$  M NaCl and pH between 6 and 7. Free concentrations of Ca<sup>2+</sup> were determined with poly(vinyl chloride) matrix membrane calcium ion-selective electrode based on calcium bis[di(4-octylphenyl)phosphate] sensor. pH readings were converted to  $\log_{10}[\text{H}^+]$  using an activity coefficient of 0.76 at 0.1 M ionic strength. The dissociation constants of citric acid used for the calculation of the stability constant of Ca(cit)<sup>-</sup> were  $\log_{10}K_{(\text{H})} = 5.74, 4.42$  and  $2.95$ . The value of the constant for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca(cit)}^-$  has been determined to be  $\log_{10} \beta_1 = (3.42 \pm 0.06)$ . Considering the uncertainties derived from the conversion of pH to  $\log_{10}[\text{H}^+]$  and from slightly different values of  $\log_{10}K_{(\text{H})}$ , this review accepts this result with assigning a larger uncertainty as  $\log_{10} \beta_1 = (3.42 \pm 0.20)$ .



This study also reports the stability of  $\text{Ca}(\text{edta})^{2-}$ , determined with the Ca sensitive electrode in the pH range 5 to 6 in 0.1 M NaCl. The authors actually measured the equilibrium  $\text{Ca}^{2+} + \text{H}_2\text{edta}^{2-} \rightleftharpoons \text{Ca}(\text{edta})^{2-} + 2 \text{H}^+$  and used tabulated edta protonation constants in their data evaluation without mentioning for which conditions these tabulated values should be valid. As it happens, the sum of the first and second edta protonation constant,  $\log_{10} K_1 + \log_{10} K_2 = 16.58$ , used by [79CRA/MOO] differs only by 0.03  $\log_{10}$ -units from the value recommended in this review for 0.1 M NaCl solutions at 25°C considering  $\text{Na}(\text{edta})^{3-}$  complexation (16.61, see Table VIII-8-a). Hence, this review corrects the value of [79CRA/MOO] only by 0.03 and assigns an uncertainty of  $\pm 0.05 \log_{10}$ -units.

Furthermore, the stability of  $\text{Ca}(\text{ox})(\text{aq})$  has been determined at  $I = 0.05, 0.10$  and 0.15 M NaCl and the pH adjusted to approximately 9 with NaOH. The authors report that “for example, a solution of  $10^{-3}$  M sodium oxalate at  $I = 0.05$  M was titrated with calcium chloride solution, such that the total calcium-ion concentration varied between  $2 \times 10^{-5}$  and  $5 \times 10^{-5}$  M. Slightly different concentrations were used for titrations at  $I = 0.10$  and 0.15 M. Although the reported solubility product was exceeded, no precipitation was observed in the reaction vessel and the final electrode potentials were steady (to about 0.1 mV over several days”. The only further information provided concerning  $\text{Ca}(\text{ox})(\text{aq})$  complexation are the stability constants  $\log_{10} K_1 = (2.70 \pm 0.03)$ ,  $(2.54 \pm 0.09)$ , and  $(1.99 \pm 0.04)$  for at  $I = 0.05, 0.10$  and 0.15 M, respectively. The difference in the reported stability constants between  $I = 0.05$  and 0.10 M, 0.16  $\log_{10}$ -units, is in accordance with the expected ionic strength behaviour, but the difference between  $I = 0.10$  and 0.15 M, 0.55  $\log_{10}$ -units, is out of order, indicating some irregularities in the experiments. Despite the statement of the authors, precipitation effects, or perhaps other experimental difficulties may have affected the titrations. However, no further experimental data are given in the paper which would allow to examine the results in some detail, and hence, the reported stability constants are not included in the final data analysis of this review.

#### [79KUM/CHA]

The stability constants of the 1:1, 1:2 and 1:3 U(VI) oxalates and the stability constants of a few mixed ligand U(VI)/oxalate/ $L_1$  complexes (where  $L_1$  stands for malonate or iminoacetate), and U(VI)/oxalate/ $L_1/L_2$  complex (where  $L_1$  and  $L_2$  stand for malonate and iminoacetate) were determined by potentiometry ( $t = (25 \pm 1)^\circ\text{C}$ ,  $I = 0.1$  M  $\text{KNO}_3$ ). The  $\text{p}K_{a1}$  and  $\text{p}K_{a2}$  of oxalic acid were determined to be 1.66 and 3.90 in this work. The overall stability constants of  $\text{UO}_2\text{ox}(\text{aq})$ ,  $\text{UO}_2(\text{ox})_2^{2-}$ ,  $\text{UO}_2(\text{ox})_3^{4-}$  were  $(3.97 \pm 0.27)$ ,  $(9.08 \pm 0.25)$ ,  $(16.40 \pm 0.12)$ . From these, the stepwise stability constants of the 1:1, 1:2 and 1:3 U(VI) oxalates are:  $\log_{10} K_1 = 3.97$ ,  $\log_{10} K_2 = 5.11$  and  $\log_{10} K_3 = 7.32$ . These appear obviously erroneous. Details of the potentiometric titrations were not provided in the paper. It is not clear whether the  $\text{pH}_{\text{obs}}$  or  $\text{pC}_\text{H}$  was determined in the experiments. The stability constants for the binary and ternary complexes from this paper

are rejected by this review. The discussion of the quaternary complexes is beyond the scope of this review.

#### [\[79KUS/GAN\]](#)

This appears to be a short progress report, giving no details. The equilibrium constants and the thermodynamic data for the oxalate complexation of actinides are the same as in previous publications [\[76BAG/RAM3\]](#), [\[77RAM/RAM2\]](#), [\[77RAM/RAM\]](#).

#### [\[79MOS/POZ\]](#)

The comments in this entry refer to three papers by Moskvina and Poznyakov [\[78MOS/POZ\]](#), [\[79MOS/POZ\]](#) and [\[79MOS/POZ4\]](#). These papers present the application of the co-precipitation technique to the study of complex equilibria between several inorganic and organic ligands with pentavalent actinides (Np, Pu and Am). Most of the experimental details are given in [\[78MOS/POZ\]](#).

The co-precipitation technique is equivalent to sorption of radionuclides on fresh  $\text{Fe}(\text{OH})_3$  precipitate [\[78MOS/POZ\]](#). The sorption process is performed at  $\text{pH} \approx 8.5$  where the actinide(V) hydrolysis may be neglected. Np(V) is stabilised in the experiments by the presence of 0.05 M  $\text{NaNO}_2$ . The radionuclides were analysed by  $\alpha$ -scintillation, and the uncertainty was 4 to 10% (at a confidence level of 95%).

Distribution coefficients are treated in the same manner as data from two phase solvent extraction, or from cation exchange. This methodology has only been used by Soviet researchers and the whole process depends on many parameters which have to be optimised. The sorbent, fresh  $\text{Fe}(\text{OH})_3$  precipitate,  $[\text{Fe}(\text{III})]_{\text{Tot}} = 0.05 \text{ M}$ , is not in thermodynamic equilibrium. Therefore the measurements have to be performed quickly, but at reproducible time periods: stirring for the first 1–2 minutes, followed by an equilibration time of 30 minutes. The separation of the solution from the solid phase is not described in the papers available to this review.

There are several factors to mistrust the results from this technique: a) the scarcity of experimental details given in [\[78MOS/POZ\]](#), [\[79MOS/POZ\]](#) and [\[79MOS/POZ4\]](#); b) the natural thermodynamic instability of the sorbent; c) it is not clear if increasing ligand concentrations affect the sorption properties of the amorphous precipitate; d) the unknown mechanism and stoichiometry behind the sorption process.

The sorption mechanism for cations and anions on hydrous ferric oxide has been extensively described in the literature, for example in the monograph by Dzombak and Morel [\[90DZO/MOR\]](#). Sorption depends largely on the charge of the ions and on the surface. For the experiments performed by Moskvina and Poznyakov the charge on the surface is constant, as the experiments were performed at constant pH and constant ionic strength. At  $\text{pH} \approx 8.5$  the sorption of anions with charge  $-1$  and  $-2$  is limited, but anions of charge  $-3$  may be significantly sorbed, cf. Chapter 7 in [\[90DZO/MOR\]](#). Another important factor is the structure for organic ligands [\[98EVA/DZO\]](#). Both, an in-

crease or a decrease of metal sorption may occur in the presence of ligands, depending on their concentration [\[78DAV/LEC\]](#), [\[98BUR/FAH\]](#), [\[2002NOW\]](#).

Moskvin and Poznyakov [\[78MOS/POZ\]](#), [\[79MOS/POZ\]](#), [\[79MOS/POZ4\]](#) studied the co-precipitation of Np(V), Pu(V) and Am(V) with iron hydroxide,  $\text{Fe}(\text{OH})_3$ , in presence of different complexing agents (among others oxalate and ethylenediamine-tetraacetate). For oxalate the following stability constants were obtained at  $\text{pH} \approx 8.5$ ,  $(20 \pm 2)^\circ\text{C}$  and  $I = 0.5 \text{ M NH}_4\text{Cl}$ :

$$\begin{aligned}\text{Np}^{\text{V}} : \log_{10} \beta_1 &= (3.38 \pm 0.11) & \log_{10} \beta_2 &= (5.65 \pm 0.12) \\ \text{Pu}^{\text{V}} : \log_{10} \beta_1 &= (3.95 \pm 0.12) & \log_{10} \beta_2 &= (6.43 \pm 0.25) \\ \text{Am}^{\text{V}} : \log_{10} \beta_1 &= (3.08 \pm 0.08)\end{aligned}$$

The equilibrium constants for the formation of oxalate complexes of Am(V) and Pu(V) are not accepted because these oxidation states are unstable towards reduction by the oxalate ligand. In the case of Np(V), because of the limitations discussed above of the experimental method the equilibrium constant reported for  $\text{NpO}_2(\text{ox})_2^{3-}$  is considered unreliable. Although the value for  $\text{NpO}_2\text{ox}^-$  might be acceptable with an increased uncertainty, it is not included in the review process because the ionic medium effects on oxalate in ammonium solutions are unknown (*cf.* Section VI.11.2.3).

Stability constants for the reaction  $\text{AmO}_2^+ + \text{Hedta}^{3-} \rightleftharpoons \text{AmO}_2(\text{Hedta})^{2-}$  were reported at  $I = 0.1 \text{ M NH}_4\text{Cl}$  and  $\text{pH} \approx 8.5$ :  $\log_{10} \beta_1 = (4.73 \pm 0.11)$  [\[78MOS/POZ\]](#), [\[79MOS/POZ\]](#) and  $\log_{10} \beta_1 = (4.83 \pm 0.10)$  [\[79MOS/POZ4\]](#), and at “ $\text{pH} \neq \text{const}$ ”:  $\log_{10} \beta_1 = (4.81 \pm 0.10)$  [\[79MOS/POZ4\]](#). In contrast to oxalate, where the  $[\text{ox}^{2-}]$  concentration can be assumed to be equal to the total oxalate concentration at  $\text{pH} \approx 8.5$ , the  $[\text{Hedta}^{3-}]$  concentration has to be calculated from the total edta concentration using appropriate edta protonation constants at an exactly determined  $[\text{H}^+]$  concentration. In the papers of Moskvin and Poznyakov, the pH scale has not been defined and the calibration of the pH meter is not described, and no other information is provided than “ $\text{pH} \approx 8.5$ ” and “ $\text{pH} \neq \text{const}$ ”. In addition, the actual edta protonation constants used are not reported, only the references [\[47SCH/ACK\]](#), [\[67LEB/MAK\]](#) and [\[68EBE/SCH\]](#) are given in [\[78MOS/POZ\]](#) and [\[79MOS/POZ4\]](#). The reference [\[68EBE/SCH\]](#) deals with Pu(VI) acetate complexes and no edta data are reported there. In [\[67LEB/MAK\]](#) the edta protonation constants of [\[47SCH/ACK\]](#), valid at  $I = 0.1 \text{ M KCl}$  and  $20^\circ\text{C}$ , have been used “with corrections to  $t = 25^\circ\text{C}$ ”. Furthermore, Moskvin and Poznyakov did not consider that Am(V) slowly changes into the trivalent state in the presence of edta [\[74NIK/SHI\]](#), and there is no reasoning why the authors assume that  $\text{AmO}_2(\text{Hedta})^{2-}$  is formed at pH 8.5 but not, *e.g.*,  $\text{AmO}_2\text{edta}^{3-}$ . In view of all these shortcomings, the equilibrium constants reported for the Am(V) edta system by Moskvin and Poznyakov are not credited in this review.

[\[79MOS/POZ4\]](#)

See comments under [\[79MOS/POZ\]](#).

[\[79NIK\]](#)

The solubility of  $\text{U(ox)}_2 \cdot 6\text{H}_2\text{O}$  in solutions of 0.1005 m and 0.735 m  $\text{HClO}_4$  and solutions of  $10^{-9}$ – $10^{-2}$  m oxalate was determined at 25–90°C ( $\pm 0.04^\circ\text{C}$ ). The equilibrium constants and thermodynamic functions of three reactions were obtained:



The ionic strength was not kept constant in the experiments ( $I = 0.2$ – $1.0$  M). The author assumed an uncertainty of the values of  $\log_{10} K$  to be  $\pm 0.1$ . The equilibrium constants were found to increase as the temperature was increased as shown in Table A-12.

The following functions were obtained by fitting the data and the enthalpy of the three reactions were accordingly obtained:

$$\log_{10} K (\text{A.73}) = 1.619 - 4.935 \times 10^{-2} T + 9.303 \times 10^{-5} T^2$$

$$\log_{10} K (\text{A.74}) = 16.38 - 5.628 \times 10^{-2} T + 9.714 \times 10^{-5} T^2$$

$$\log_{10} K (\text{A.75}) = 21.97 - 11.73 \times 10^{-2} T + 20.32 \times 10^{-5} T^2.$$

These data were later discussed by the same author in [\[82NIK\]](#) and [\[82NIK2\]](#). The results from [\[79NIK\]](#) are accepted in this review. Discussions are given in Sections VI.10.1.1 and VI.10.2.2.

Table A-12: Calculated solubility products for U(IV)/oxalate defined by reactions (A.73), (A.74) and (A.75)

$\log_{10} K$	Temperature, °C							$I$ , m
	25	40	50	60	70	80	90	
$\log_{10} K(\text{A.73})$	– 4.82	– 4.73	– 4.61	– 4.48	– 4.35	– 4.24	– 4.02	$\leq 0.1$
$\log_{10} K(\text{A.74})$	8.27	8.32	8.35	8.40	8.48	8.54	8.78	$0.2 < I < 0.8$
$\log_{10} K(\text{A.75})$	5.06	5.15	5.27	5.40	5.55	5.84	6.22	$\leq 0.1$

[\[79VAS/KOC\]](#)

The authors determined the heats of dissolution of  $\text{H}_4\text{edta}(\text{cr})$  at 25°C in  $\text{HNO}_3$ ,  $\text{HClO}_4$ ,  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and  $\text{NaClO}_4$ , at concentrations from 1 to 3 M. The experimental

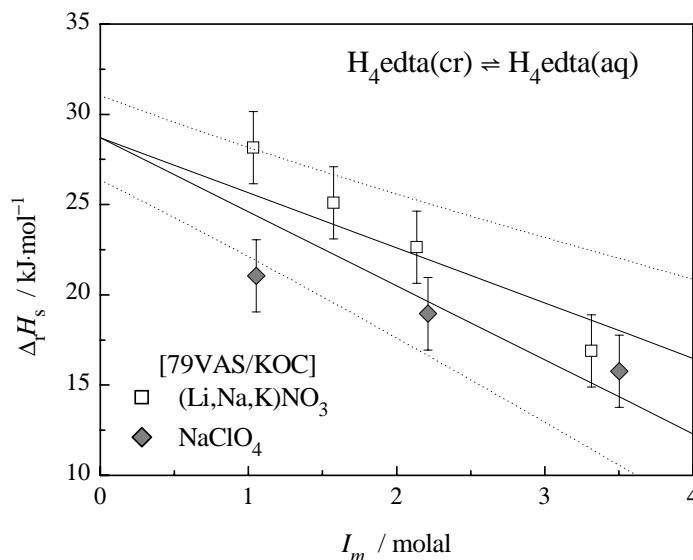
data was combined with protonation constants and enthalpies from their previous studies [73VAS/KOC].

Their tabulated values for reaction:

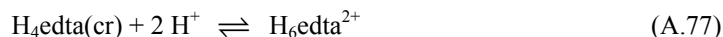


in all alkali metal nitrate media are linearly dependent on the molality of the salt, and give  $\Delta_r H_m^\circ = (33.9 \pm 0.7) \text{ kJ}\cdot\text{mol}^{-1}$  at zero ionic strength. In  $\text{NaClO}_4$  solutions the data are instead extrapolated to  $\Delta_r H_m^\circ = (23.5 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$ . Both sets of data may be seen in Figure A-27. Although no reason is given for this discrepancy, it might be due to the calculation of the fractions of  $\text{H}_3\text{edta}^-$ ,  $\text{H}_2\text{edta}^{2-}$ , and  $\text{Hedta}^{3-}$ , which was based on pH determinations. The data may be also modelled by setting a common value for  $\Delta_r H_m^\circ$  (A.76) for all ionic media studied by Vasil'ev *et al.*, resulting in  $\Delta_r H_m^\circ$  (A.76) =  $(29 \pm 3) \text{ kJ}\cdot\text{mol}^{-1}$ , *cf.* Figure A-27.

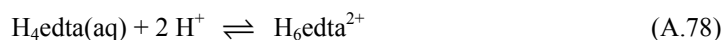
Figure A-27: Enthalpy changes for the reaction:  $\text{H}_4\text{edta}(\text{cr}) \rightleftharpoons \text{H}_4\text{edta}(\text{aq})$  plotted according to the SIT methodology.



The values of  $\Delta_r H_m^\circ$  for reaction:

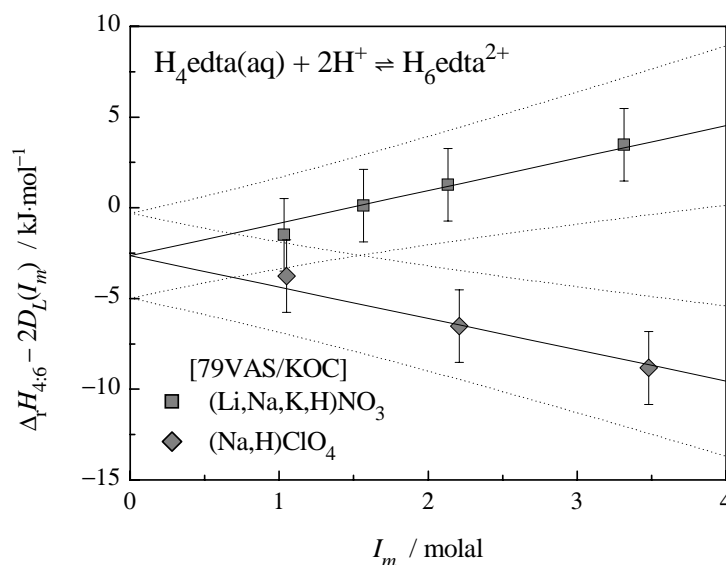


determined by the authors in  $\text{HNO}_3$  and  $\text{HClO}_4$ , were combined with the data for (A.76), giving the enthalpy change for reaction:



When treated according to the SIT model, the data give  $\Delta_r H_m^\circ$  (A.78) =  $-(2.6 \pm 2.3) \text{ kJ}\cdot\text{mol}^{-1}$ , *cf.* Figure A-28. The slopes of the lines in the figure correspond to  $\Delta \varepsilon_L((\text{Li,Na,K,H})\text{NO}_3) = -(2.4 \pm 1.3) \times 10^{-3} \text{ kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $\Delta \varepsilon_L((\text{Na,H})\text{ClO}_4) = (2.3 \pm 1.2) \times 10^{-3} \text{ kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

Figure A-28: Enthalpy changes for the reaction:  $\text{H}_4\text{edta}(\text{aq}) + 2\text{H}^+ \rightleftharpoons \text{H}_6\text{edta}^{2+}$  plotted according to the SIT methodology.



#### [79ZHI/KOL]

The aim of this investigation was to obtain information about the solubility of  $\text{Na}_2\text{ox}(\text{s})$  in  $\text{NaNO}_3$  solutions. The solubility isotherm in the  $\text{Na}_2\text{ox}$ – $\text{NaNO}_3$ – $\text{H}_2\text{O}$  system at  $20^\circ\text{C}$  has been determined, from pure  $\text{Na}_2\text{ox}$  to pure  $\text{NaNO}_3$ , and the composition of the solids has been checked crystal-optically by polarisation microscopy. The solution of  $\text{Na}_2\text{ox}(\text{s})$  in pure water at  $20^\circ\text{C}$  is reported to be 3.27 mass-% ( $= 0.252 \text{ mol}\cdot\text{kg}^{-1}$ ).

#### [80ARE/CAL]

The authors determined the protonation and  $\text{Na}^+$  complexation equilibrium constants for citrate (among other ligands) at  $25$  and  $37^\circ\text{C}$ . Equilibrium constants for sodium complex formation were determined by comparing their protonation constants in  $\text{NaClO}_4$  media with literature values obtained in tetraalkylammonium media. The protonation constants reported by Arena *et al.* were corrected for  $\text{Na}^+$  complex formation, and are therefore not included in the review procedure.

Enthalpy changes for the protonation reactions were determined from calo-

rimetric titrations of the sodium salts with  $\text{HClO}_4$ . For citrate the ionic strength range was 0.004 to 0.175 M. Apparently the ionic strength was not kept constant during the calorimetric titrations. It is not indicated if the  $\Delta_r H_m$  values for protonation are corrected for  $\text{Na}^+$  complex formation, although the protonation constants obtained by combining  $\Delta_r H_m$  and  $\Delta_r S_m$  correspond to their tabulated  $\log_{10} K$  values corrected for  $\text{Na}^+$  complex formation. Because of these uncertainties the reported enthalpy changes are not considered in the review procedure.

Arena *et al.* also report in this paper enthalpy changes for  $\text{Na}^+$  complexation by citrate determined calorimetrically. However, details on the experimental methodology for the corresponding calorimetric titrations are not given in the paper. Owing to this, the reported values for  $\Delta_r H_m (\text{NaH}_n(\text{cit})^{n-2})$  are not considered in this review.

#### [\[80DAN/RIG\]](#)

The authors reported a potentiometric study at 37°C on the protonation of citrate in different media and on the complex formation between citrate and  $\text{K}^+$  ions.

Complex formation between  $\text{K}^+$  and citrate was studied by comparing protonation constants for citrate obtained in a medium where no complex formation occurs ( $\text{Et}_4\text{NBr}$ , tetraethylammonium bromide) with the same constants obtained in a potassium electrolyte ( $\text{KNO}_3$ ). Nevertheless, the authors used  $\text{KOH}$  as titrant in both cases, introducing a systematic error on the ionic medium concept. Furthermore large variations in the ionic media also occurred in the titrations performed with  $\text{Et}_4\text{NBr}$  because of the large concentration of citrate. The difference between the first protonation constant obtained in  $\text{KNO}_3$  and  $\text{Et}_4\text{NBr}$  media ( $\approx 0.09 \log_{10}$ -units) could well be ascribed to these systematic errors. Therefore, the protonation constants for citrate in  $\text{Et}_4\text{NBr}$  and the formation constants for  $\text{Kcit}^{2-}$  and  $\text{KHcit}^-$  reported in [\[80DAN/RIG\]](#) are not considered in this review.

Daniele *et al.* combined their results at 37°C with the data reported by Bates and Pinching [\[49BAT/PIN\]](#) at 0 to 50°C to derive enthalpy changes for the first protonation constant of citrate and for the formation of  $\text{Kcit}^{2-}$ , without giving details on the calculation procedure. These enthalpy values are not considered in this review.

#### [\[80HED/LID\]](#)

The complex formation of  $\text{Ni}^{2+}$  with citric acid was investigated by the potentiometric method at the ionic strength 0.10 M  $\text{KCl}$  at 25.0 °C. The calibration of the pH meter readings to the pcH values and the analysis of the data were well done. The protonation constants,  $\log_{10} K_{(H)} = (5.72 \pm 0.02)$ ,  $(4.37 \pm 0.02)$  and  $(2.94 \pm 0.01)$ , obtained by the authors and used in the calculation agree well with those accepted in this review. From the analysis of the sum of the squares of weighted residuals in the least-squares method on the titration data with the ratio of  $C_L/C_{\text{Ni}} \approx 1$ , the authors concluded the existence of  $\text{Ni}(\text{H}_2\text{cit})^+$  as well as  $\text{Ni}(\text{Hcit})(\text{aq})$  and  $\text{Ni}(\text{cit})^-$ . Similarly, the formation of  $\text{Ni}(\text{cit})_2^{4-}$

was confirmed from the analysis on the titration data with  $C_L/C_{Ni} \approx 2$  to 3 (pH range 3 – 6). The speciation was also confirmed from the absorbance spectra of nickel-citric acid solutions of various  $C_L/C_{Ni}$  at various pH. The constants for the reaction  $Ni^{2+} + qH_r cit^{r-3} \rightleftharpoons Ni(H_r cit)_q^{2+q(r-3)}$  were reported to be  $\log_{10} \beta = (5.49 \pm 0.04)$  for  $Ni(cit)^-$ ,  $(7.82 \pm 0.20)$  for  $Ni(cit)_2^{4-}$ ,  $(3.35 \pm 0.06)$  for  $Ni(Hcit)(aq)$ , and  $(1.50 \pm 0.16)$  for  $Ni(H_2cit)^+$ . This review accepts these values with the uncertainties doubled.

#### [80JAW]

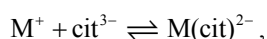
Jawaid [78JAW], [80JAW] determined the protonation constants of  $edta^{4-}$  in 1 M  $NaNO_3$  at 25°C. In the least squares procedure, however, he took into account the formation of  $Na(edta)^{3-}$ . In this review “conditional” protonation constants have been examined and therefore the equilibrium constants reported by Jawaid have not been included.

#### [80KOL/ZHI]

This study is a continuation of the investigation reported in [79ZHI/KOL]. Solubility isotherms in the  $Na_2Ox-NaNO_3-H_2O$  system at 50 and 75°C are reported. The solution of  $Na_2Ox(s)$  in pure water at 50 and 75°C is 4.35 mass-% ( $= 0.339 \text{ mol}\cdot\text{kg}^{-1}$ ) and 5.22 mass-% ( $= 0.411 \text{ mol}\cdot\text{kg}^{-1}$ ), respectively.

#### [80PEA]

Potentiometric titrations of citric acid in the absence and presence of  $Mg(II)$  or  $Ca(II)$  ions were conducted at  $I = 0.1 \text{ M } KNO_3$  and 25°C. Experiments and data treatment were done in a qualified manner. The authors considered the formation of  $Na(cit)^-$  ( $K_{(Na)} = 5.7$ ) and  $K(cit)^-$  ( $K_{(K)} = 3.7$ ) for:



and used the protonation constants  $\log_{10} K_{(H)} = 5.83, 4.34$  and  $2.89$  [75PEA/CRE] which are in good agreement with those accepted in this review. The values of  $M^{2+} + H_r cit^{r-3} \rightleftharpoons M(H_r cit)^{r-1}$  reported are  $\log_{10} \beta'_1 = 3.63$  for  $Mg(cit)^-$ ,  $3.64$  for  $Ca(cit)^-$ , and  $\log_{10} \beta_1 = 1.78$  for  $Mg(Hcit)$ ,  $0.60$  for  $Mg(H_2cit)$ ,  $2.03$  for  $Ca(Hcit)$ ,  $1.04$  for  $Ca(H_2cit)^+$ . Since this review treats the values of  $\log_{10} \beta_1$  for  $Mg(cit)^-$  and  $Ca(cit)^-$  without considering the complex formation of  $Na^+$  or  $K^+$  with  $cit^{3-}$ , the values are converted into  $\log_{10} \beta_1 = 3.50$  for  $Ca(cit)^-$  and  $3.49$  for  $Mg(cit)^-$ , where for example  $\beta_1 = [Ca(cit)^-] / ([K(cit)^{2-}] + [cit^{3-}]) \cdot [Ca^{2+}] = \beta'_1 / (K_{(K)} + 1)$ . By considering the deviations of the data given in the paper, this review assigns the uncertainties as  $\log_{10} \beta_1 = (3.49 \pm 0.10)$  for  $Mg(cit)^-$ ,  $(1.78 \pm 0.20)$  for  $Mg(Hcit)(aq)$ ,  $(0.60 \pm 0.4)$  for  $Mg(H_2cit)$ ,  $(3.50 \pm 0.10)$  for  $Ca(cit)^-$ ,  $(2.03 \pm 0.20)$  for  $Ca(Hcit)(aq)$  and  $(1.04 \pm 0.4)$  for  $Ca(H_2cit)^+$ . Pearce also has obtained the stability constants of  $Ca(cit)^-$  and  $Ca(Hcit)(aq)$  at  $I = 0$  by plotting the values of  $\log_{10} \beta_1$  obtained in the range of  $0.035 - 0.15 \text{ M}$  against  $0.512 \times (\sqrt{I} / (1 + \sqrt{I}) - 0.2I)$ . The plots gave fairly good linear relationship and the extrapolated values are  $\log_{10} \beta_1^o = 4.87$  for  $Ca(cit)^-$  and  $3.03$  for  $Ca(Hcit)(aq)$ .



These extrapolated values are not considered in this review, since the analysis based on the SIT approach as the method of choice.

#### [80STI/WIK]

The complex formation of  $\text{Ni}^{2+}$  with citric acid was investigated by the potentiometric method and spectrophotometric method at the ionic strength 0.10 M  $\text{KNO}_3$  at 25.0°C. From the absorbance measurement at 390 nm of 50 mL of a solution containing 4.2 mmol of  $\text{Ni(II)}$  as a function of citrate concentration,  $\log_{10} K$  for the reaction  $\text{Ni(cit)}^- + \text{cit}^{3-} \rightleftharpoons \text{Ni(cit)}_2^{4-}$  was obtained to be  $(2.85 \pm 0.02)$ . From the potentiometric titration,  $\log_{10} K$  for the reaction  $\text{Ni}^{2+} + \text{H}^+ + \text{cit}^{3-} \rightleftharpoons \text{Ni(Hcit)}(\text{aq})$  was obtained to be  $(8.75 \pm 0.01)$ . Moreover, the potentiostatic titration at pH 10.0 and 10.5 showed that 1 mol of  $\text{OH}^-$  was consumed per mol of nickel added ( $C_{\text{Ni}}$ ) until  $C_{\text{Ni}}$  reached  $4/3C_L$ . After this point, around 1.6 mol of  $\text{OH}^-$  was consumed per mol of nickel added. Based on this observation and some other information, the authors claimed the formation of  $\text{Ni}_4\text{OH}(\text{H}_- \text{cit})_3^{5-}$  and obtained the value of  $\log_{10} K$  for the reaction  $4\text{Ni}^{2+} + 3\text{cit}^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{Ni}_4\text{OH}(\text{H}_- \text{cit})_3^{5-} + 4\text{H}^+$  to be  $-7.1$ . However, the relationship between this speciation and the potentiostatic data is not clear enough. The effect of the hydrolysis of  $\text{Ni}^{2+}$  itself and its precipitation should be more clearly discussed. Although the calibration of the pH meter readings to the pcH values were done with the relationship of  $\text{pcH} = \text{pH} - 0.11$ , no reason for this relationship is given. By this reason, this review does not accept the reported values.

#### [80VAN/KUC]

Five series of 1 M-(H, Na,  $(\text{UO}_2)_{0.5}$ )cit solutions containing  $C_M = 0.001, 0.004, 0.01, 0.04$  and  $0.1$  M,  $C_L = 1$  M, and different concentrations of hydrogen ions were prepared, and the pH values (1.4 ~ 4.0) and the absorption spectra were measured. By assuming the formation of some set of complexes and using  $\log_{10} K_{(\text{H})} = 5.26, 4.11$  and  $2.76$  obtained by themselves [76VAN/KUC], least-squares fitting was conducted for the absorbances at the wavelength 444, 436, 428, 424, 385, and 370 nm to obtain the best set of the formation constants and molar absorptivities ( $\epsilon$ ) for each complex. The number of parameters adjusted were  $7 \times (\text{the number of complexes})$ , where 7 means one  $\log_{10} \beta_{q,p}$  + six molar absorptivities at the above wavelengths. The best fit (smallest sum of squares of the deviations) was obtained with the combination of complexes  $\text{UO}_2(\text{cit})^-$  ( $\log_{10} \beta_1 = 6.20$ ),  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  ( $\log_{10} \beta_{2,2} = 15.25$ ),  $\text{UO}_2(\text{Hcit})(\text{aq})$  ( $\log_{10} \beta_1 = 3.82$ ),  $(\text{UO}_2)_2(\text{Hcit})_2$  ( $\log_{10} \beta_{2,2} = 8.89$ ) and  $\text{UO}_2(\text{H}_2\text{cit})^+$  ( $\log_{10} \beta_1 = 1.53$ ), where  $\log_{10} \beta$  is defined for the reaction  $p\text{UO}_2^{2+} + q\text{H}_r\text{cit}^{r-3} \rightleftharpoons (\text{UO}_2)_p(\text{H}_r\text{cit})_q^{2p+q(r-3)}$ . A close value of the sum of squares of deviations was obtained also with the combination of  $\text{UO}_2(\text{cit})^-$  ( $\log_{10} \beta_1 = 7.17$ ),  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  ( $\log_{10} \beta_{2,2} = 17.00$ ), and  $\text{UO}_2(\text{Hcit})(\text{aq})$  ( $\log_{10} \beta_1 = 4.56$ ). As discussed by the authors themselves, uncertainties of the speciation and their constants come from the way of processing the spectrophotometric data. Since the parameters  $\beta_{q,p}$  and  $\epsilon$  contribute to the absorbance as their product ( $\beta_{q,p} \epsilon$ ), the error in one parameter can be partly compensated by the change in the other parameter. Also,

the complexes having similar molar absorptivities, such as  $\text{UO}_2(\text{H}_2\text{cit})^+$  and  $\text{UO}_2(\text{Hcit})(\text{aq})$ , are poorly discriminated. This means that, although the formation of  $(\text{UO}_2)_2(\text{Hcit})_2(\text{aq})$  and  $\text{UO}_2(\text{H}_2\text{cit})^+$  may be possible, their constants are difficult to be defined. Considering the effect of the values of  $\log_{10} \beta_{2,2}$  for  $(\text{UO}_2)_2(\text{Hcit})_2(\text{aq})$  and  $\log_{10} \beta_1$  for  $\text{UO}_2(\text{H}_2\text{cit})^+$  on the other constants, we will accept the latter set of constants with assigning rather large uncertainties:  $\text{UO}_2(\text{cit})^-$  ( $\log_{10} \beta_1 = (7.17 \pm 1.0)$ ),  $(\text{UO}_2)_2(\text{cit})_2^{2-}$  ( $\log_{10} \beta_{2,2} = (17.00 \pm 1.0)$ ), and  $\text{UO}_2(\text{Hcit})(\text{aq})$  ( $\log_{10} \beta_1 = (4.56 \pm 1.0)$ ).

#### [\[81CER/CAS\]](#)

This study reports calorimetric data obtained by thermometric titrimetry. The authors were mainly interested in the effects of water – methanol media. In the experiments with pure water no background electrolyte has been used and thus, the ionic strength varied considerably during the titration of oxalic acid in the calorimeter. This effect is not mentioned in the paper, and the results (neutralisation enthalpies only, no dissociation enthalpies) are given as pure numbers without any estimate of their uncertainty. The values given by [\[81CER/CAS\]](#) are not credited in this review.

#### [\[81CUC/DAN\]](#)

The authors determined the protonation constants of citrate at 37°C in  $\text{LiNO}_3$ ,  $\text{RbI}$ , and  $\text{CsCl}$  media at different ionic strengths (0.04 to  $\approx 1$  M). They used however 1 M  $\text{KOH}$  as titrant in all cases. The authors state to have calibrated the glass electrode in pH units. Because of these experimental problems the reported protonation constants are disregarded by this review.

Cucinotta *et al.* calculated the equilibrium constants for the formation of alkali metal complexes with citrate by comparing their protonation constants with those obtained in tetraethylammonium media [\[80DAN/RIG\]](#) (see however the discussion of [\[80DAN/RIG\]](#) in this Appendix). Equilibrium constants for the formation of  $\text{Na}(\text{cit})^{2-}$  and  $\text{NaHcit}^-$  were also reported by Cucinotta *et al.* from a re-analysis of data from previous studies (their Table II, footnote *b*). This methodology to obtain formation constants for alkali metal complexes with citrate is nevertheless not credited in this review, *cf.* Section VII.4.

#### [\[81DAN/RIG\]](#)

The second dissociation constant of oxalic acid was determined potentiometrically by alkalimetric titration at 37°C in different media,  $\text{NaNO}_3$ ,  $\text{KNO}_3$  and  $\text{Et}_4\text{NI}$  (tetraethylammonium iodide) at ionic strengths ranging from 0.03 to 0.3  $\text{mol}\cdot\text{dm}^{-3}$ . Complex formation between  $\text{Na}^+$ ,  $\text{K}^+$  and oxalate was studied by comparing protonation constants for oxalate obtained in a medium where no complex formation is supposed to occur ( $\text{Et}_4\text{NI}$ ) with the same constants obtained in sodium and potassium nitrate. No details about the titrant and analytical concentrations are given in [\[81DAN/RIG\]](#) but only a reference to [\[80DAN/RIG\]](#). From this reference we infer that the authors used  $\text{KOH}$  as

titrant in all cases, introducing a systematic error on the ionic medium concept. Furthermore, some variations in the ionic media may have happened due to (large?) concentrations of citrate.

In the present review the constants reported in [81DAN/RIG] have been extrapolated to 25°C using enthalpy data evaluated and recommended in this review. Because of possible systematic errors due to the KOH titrant and the unknown oxalate concentrations data at  $I < 0.1$  M were rejected and the uncertainties of the remaining constants were increased to  $\pm 0.05 \log_{10}$ -units.

#### [81MUE]

200 mg  $K_2TcBr_6$  and 1 g citric acid were mixed in 25 mL water and then neutralised by 0.5 M NaOH to pH 6-7. After heating 2 h at 358 K, the solvent was removed under reduced pressure. After purification, violet amorphous material was obtained. By carrying out polarography, IR, osmometric measurements, Faraday measurements and NMR, the solid was concluded to be  $Na_9Tc_3O_3(cit)_5 \cdot 10H_2O$ .

This study does not give any information about the technetium complexes at lower concentrations since the formation of such polymers should be very unlikely at lower concentrations. No attempt has been made to derive quantitative thermodynamic information.

#### [81SIN/GHO]

Sinha *et al.* [81SIN/GHO] used a cell without a liquid junction to determine the first dissociation constant of oxalic acid, basically the same method as described in [39PAR/NIC]. For determining the first dissociation constant at 10 to 50°C in steps of 5°C mixtures of NaHox,  $Na_2ox$  and NaCl, and KHox (?),  $Na_2ox$  and NaCl were studied at very low ionic strength ( $I < 0.1$  M). The protonation constants have been evaluated by using an extended Debye-Hückel formalism, and only values at zero ionic strength are reported in [81SIN/GHO]. These values already extrapolated to zero ionic strength have not been considered in this review.

#### [81URB/BIE2]

This is a polarographic study of the nickel(II)-oxalate system performed at  $(20 \pm 0.1)^\circ C$  and at  $I = 0.1$  M ( $NaClO_4$ ). In this paper and in a companion publication [81URB/BIE] the authors used as a reference a saturated calomel electrode connected by a salt bridge with saturated  $NaClO_4$ , possibly introducing systematic errors: precipitation of  $KClO_4$ , junction potential variations, *etc.* Sodium oxalate was varied in the range  $5 \times 10^{-5}$  to 0.005 M but the pH is not reported. The irreversible polarographic Ni(II) signal has to be interpreted kinetically, and in this case the first complex was found to be labile and the second complex inert. The authors reported the values  $\log_{10} \beta_1 = 4.255$  and  $\log_{10} \beta_2 = 7.544$ , which agree with other results from selected references for this system. Nevertheless, the reported values are not included in the review procedure because of

the problems with the salt bridge for the reference electrode, and the fact that this system requires so many kinetic and equilibrium parameters for the interpretation of the data.

#### [81VAS/VAS]

The heat of reaction of the Ni-edta-ethylenediamine (en) system has been measured calorimetrically at 25°C and 35°C at an ionic strength of 1.5 M (KNO<sub>3</sub>). The equilibrium constant and the values of  $\Delta_r G_m$ ,  $\Delta_r H_m$ ,  $\Delta_r S_m$  and  $\Delta_r C_{p,m}$  for the reaction  $\text{Ni(edta)}^{2-} + \text{en} \rightleftharpoons \text{Ni(edta)en}^{2-}$  have been calculated from these and spectrophotometric and pH titration data.

#### [82AMI/DAN]

Potentiometric titrations of citric acid in the absence and presence of Ca(II) or Mg(II) ions were conducted at  $I = 0.03, 0.1$  and  $0.3$  M KNO<sub>3</sub> at 37°C. Experiments and data treatment were done in a qualified manner. The authors treated the data with and without considering the complex formation of  $\text{cit}^{3-}$  or  $\text{Hcit}^{2-}$  with  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{NH}_4^+$ . The protonation constants and the formation of alkali metal ion with citrate were expressed as a function of ionic strength:

$$\log_{10} \beta = \log_{10} \beta^\circ + \frac{\Delta z^2 A \sqrt{I}}{1 + B \sqrt{I}} + C I$$

where  $A$  is the Debye-Hückel constant,  $\log_{10} \beta^\circ$ ,  $B$  and  $C$  were given in Table 3 in the paper. The values of protonation constants at 0.03, 0.1 and 0.3 M KNO<sub>3</sub> calculated are in good agreement with those evaluated for 25°C in this review. The constants for  $\text{M}^{2+} + \text{H}_r \text{cit}^{r-3} \rightleftharpoons \text{M}(\text{H}_r \text{cit})^{r-1}$  without considering  $\text{K}(\text{cit})^{2-}$  formation were calculated at each ionic strength to be  $\log_{10} \beta_{1(\text{cit})} = (3.909 \pm 0.003)$  ( $I = 0.03$  M KNO<sub>3</sub>),  $(3.485 \pm 0.006)$  (0.1),  $(2.936 \pm 0.007)$  (0.3) for  $\text{Ca}(\text{cit})^-$ ,  $\log_{10} \beta_{1(\text{Hcit})} = (2.23 \pm 0.02)$  (0.03),  $(2.09 \pm 0.02)$  (0.1),  $(1.65 \pm 0.05)$  (0.3) for  $\text{Ca}(\text{Hcit}(\text{aq}))$ ,  $\log_{10} \beta_{1(\text{cit})} = (3.940 \pm 0.005)$  (0.03),  $(3.451 \pm 0.005)$  (0.1),  $(3.068 \pm 0.005)$  (0.3) for  $\text{Mg}(\text{cit})^-$ ,  $\log_{10} \beta_{1(\text{Hcit})} = (1.79 \pm 0.05)$  (0.03),  $(1.51 \pm 0.07)$  (0.1) and  $(1.60 \pm 0.03)$  (0.3) for  $\text{Mg}(\text{Hcit}(\text{aq}))$ . The authors have also analysed the data by considering that  $\log_{10} \beta$  follows the above equation and obtained  $\log_{10} \beta$  (at  $I = 0.1$ ),  $B$  and  $C$ . Since the results were essentially the same, this review accepts the above values with uncertainties of  $\pm 0.1$  for  $\text{Mg}(\text{cit})^-$  and  $\text{Ca}(\text{cit})^-$  and  $\pm 0.2$  for  $\text{Mg}(\text{Hcit}(\text{aq}))$  and  $\text{Ca}(\text{Hcit}(\text{aq}))$ . Since the discussion on the extrapolation to  $I = 0$  depends on the activity correction equation and the obtained parameters ( $B$  and  $C$ ), the results in this paper can be applied only in the range of  $0 < I \leq 0.3$ . Therefore, the values of  $\log_{10} \beta^\circ$  estimated in this paper, are not accepted and the data at each ionic strength will be analysed by SIT together with the other data in this review.

#### [82DAN/MAR]

This paper reports the stability constants of the Ca and Mg complexes with oxalate and

sulphate, studied with respect to their ionic strength dependence at 37°C by means of potentiometric measurements with glass and calcium ion-selective electrodes. The calibration of the glass electrode in  $-\log_{10}[\text{H}^+]$  units was achieved by titrating nitric acid with standard, carbonate free KOH; the calcium ion-selective electrode was standardised in  $-\log_{10}[\text{Ca}^{2+}]$  units by adding known amounts of  $\text{Ca}(\text{NO}_3)_2$ . The background salt in the pH-metric measurements was tetraethylammonium iodide,  $(\text{Et})_4\text{NI}$ , or  $\text{KNO}_3$ , while only the latter was employed with the calcium-selective electrode. Data measured in  $\text{KNO}_3$  were corrected for  $\text{Kox}^-$  complexation. One example of such a procedure is given in Tab. 1 of [82DAN/MAR] for  $\text{Ca}(\text{ox})(\text{aq})$  at  $I = 0.03 \text{ M}$ , which shows that the agreement between the data obtained by the two different background salts is good. Mean values of the stability constants at the different ionic strengths are listed in Tab. 2 of [82DAN/MAR]. As the present review does not include  $\text{Kox}^-$  complexation (see Section VI.4) the results of this study are accepted with twice the given uncertainties (with a minimum uncertainty of  $\pm 0.10$ ) in order to account for a possible bias of the mean values by averaging  $\text{Kox}^-$  “corrected” values and values derived in  $(\text{Et})_4\text{NI}$  media.

#### [82HIR/KIS]

In this isotachopheresis study, the sample solution containing the objective ion (0.01 M citric acid) was sandwiched between the leading solution containing the ion ( $\text{Cl}^-$ ) having a higher mobility and the terminating solution containing the ion (N-tris(hydroxymethyl)-methyl-3-aminopropanesulphonic acid for pH 8 or  $\epsilon$ -aminocaproic acid for pH 4.4) having a lower mobility, and electrophoretically migrated. The chloride of  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  (1–3 mM) was added to the leading solution. Then the ratio of the potential gradient of the sample zone to that of leading zone was measured at 25°C, which can be estimated for the sample zone with a steady-state of complex-forming equilibria, when the absolute mobilities, thermodynamic acid dissociation constants and the relevant stability constants are known. Since the ionic strength of the sample solution changed with the experimental conditions (the degree of acid dissociation and the degree of complex formation), the thermodynamic stability constants were used as the objective parameters with the correction of the activity coefficients estimated from Debye-Hückel equation. The protonation constants used were  $\log_{10} K^\circ(\text{H}) = 6.396, 4.671 \text{ and } 3.128$  [64SIL/MAR]. The values reported for  $\text{M}^{2+} + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{M}(\text{H}_r\text{cit})^{r-1}$  are  $\log_{10} \beta_1^\circ = (1.672 \pm 1.20)$  for  $\text{Mg}(\text{Hcit})(\text{aq})$ ,  $(4.917 \pm 0.044)$  for  $\text{Mg}(\text{cit})^-$ ,  $(2.786 \pm 0.132)$  for  $\text{Ca}(\text{Hcit})(\text{aq})$ , and  $(4.850 \pm 0.046)$  for  $\text{Ca}(\text{cit})^-$  at 25°C. The experiments were conducted under conditions where the estimation of ionic strength of the sample solution and the activity coefficient correction for that solution seriously affects the results. Also, the large difference between the values of  $\log_{10} \beta_1^\circ$  for  $\text{Mg}(\text{Hcit})(\text{aq})$  and  $\text{Ca}(\text{Hcit})(\text{aq})$  arises some doubts about the determination procedures. Thus, this review does not accept these values.

#### [82INO/TOC]

The synergistic solvent system, neptunyl(V)-thenoyltrifluoroacetone (TTA)-

methyl-n-octylammonium chloride (Capriquat, Q) was used for determination of stability constants of  $^{239}\text{Np(V)}$  complexes with 14 carboxylic acids at  $(25 \pm 2)^\circ\text{C}$ . The distribution of neptunyl(V) ion between two phases was studied at two different experimental conditions: *a*) pH 5.5 (buffer 0.05 M acetic acid/ammonium acetate); and *b*) pH 8.4 (buffer: 0.05 M sodium borate and 0.2 M boric acid). The pH was measured but no experimental details are given about this. The ionic strength was not kept constant, but it is not clear if for example the values for the protonation constants were corrected for ionic strength effects. In the case of oxalate the experiments at pH = 5.5 were also performed with solutions where 1 M NaCl had been added, but the concentration of oxalate in the experiments varied up to 0.05 M, which would by itself affect the ionic media.

The experimental data on Np(V)-oxalate were fitted by the authors assuming the formation of two complexes:  $\text{NpO}_2\text{ox}^-$  and  $\text{NpO}_2(\text{ox})_2^{3-}$ . At pH = 5.5 and in the presence of 1 M NaCl the authors reported  $\log_{10} \beta_1 = (3.42 \pm 0.05)$  and  $\log_{10} \beta_2 = (5.64 \pm 0.05)$ . Because of the shortcomings in the experimental procedure and in the interpretation of the data these values are not considered in this review.

#### [\[82NIK\]](#)

Previously reported experimental data [\[79NIK\]](#) are discussed in this reference. Since this reference does not present new original data, it is not considered in this review.

#### [\[82NIK2\]](#)

Previously reported experimental data [\[79NIK\]](#) are discussed in this reference. Since this reference does not present new original data, it is not considered in this review.

#### [\[82OVE/LUN\]](#)

Overvoll and Lund determined the protonation constants of  $\text{edta}^{4-}$  in 0.1 M  $\text{KNO}_3$  and  $25^\circ\text{C}$ . However, the authors used NaOH as titrant (in 0.1 M  $\text{KNO}_3$ ). Other sources of  $\text{Na}^+$  where the  $\text{Na}_2\text{H}_2\text{edta}$  salt used to prepare the ligand solutions. At pH = 11 and at the ligand concentration used,  $[\text{edta}]_{\text{TOT}} = 0.5 \text{ mM}$ , it is expected that  $[\text{Na}^+]_{\text{TOT}} \approx 3 \times 10^{-3} \text{ M}$ . Because of the differences in complex formation between  $\text{Na}^+$  and  $\text{K}^+$  with  $\text{edta}^{4-}$  a systematic error is introduced. The magnitude of this error in the protonation constant  $K_1$  is expected to be  $\leq 0.095 \log_{10}$ -units (*cf.* Section V.3.3, Eq.(V.52), with  $K_M \approx 80 \text{ M}^{-1}$ ,  $[\text{Na}^+] \approx 0.003 \text{ M}$ ,  $I = 0.1$ ). Therefore, the reported value of  $\log_{10} K_1$  was increased by 0.095 units, and its uncertainty set to  $\pm 0.15$  in the review procedure.

The complex formation of U(VI) with edta, dtpa (diethylenetriaminepentaacetic acid) and ttha (triethylenetetraminehexaacetic acid) has been studied by pH titrations at  $(25.0 \pm 0.1)^\circ\text{C}$  in argon atmosphere with subsequent computer evaluation of the titration data. All solutions were made 0.1 M in  $\text{KNO}_3$ . The acidic solutions were titrated with 0.1 M NaOH. A Beckman Research pH meter was used with Orion glass and reference electrodes. The pH meter was standardised against 0.05 m potassium hydrogenphthalate and 0.01 m borax buffers. The activity coefficient of the hydrogen ion ( $f_{\text{H}}$ ) was deter-

mined by measuring pH in nitric acid solutions of known strength and using the equation  $f_{\text{H}} = 10^{-\text{pH}} / [\text{H}^+]$ . The parameter  $f_{\text{H}}$  was found to be  $(0.83 \pm 0.02)$  in 0.1 M  $\text{KNO}_3$  at 25.0°C. The edta protonation constants obtained in this work agree well with [\[47SCH/ACK\]](#), valid for  $I = 0.1$  M KCl and 20°C.

This study is considered as reliable by this review and the stability constants have been included in the final data evaluation. However, the edta protonation constants obtained in this study are systematically lower by about 0.1  $\log_{10}$ -units than the protonation constants selected in this review for  $I = 0.1$  M  $\text{KNO}_3$  and 25°C. This systematic shift has been considered in the final data evaluation of this review.

#### [\[82RAO/AGA\]](#)

This short paper reports a study about the association constant of calcium oxalate at 37°C using a calcium ion-sensitive electrode. In a typical “titration” experiment, a solution of  $4.0 \times 10^{-3}$  M sodium oxalate was added to  $3.45 \times 10^{-4}$  M calcium chloride solution. No background electrolyte has been used and thus, the added salts caused a very low ionic strength, which varied considerably during the experiments. Only one “typical set of data” is given in the paper, and a “thermodynamic equilibrium constant” derived from these numbers using the Davies equation, but no experimental data are reported. Hence, the stability constant reported by [\[82RAO/AGA\]](#) has been rejected by this review.

#### [\[82TER/IVA\]](#)

The authors determined the solubility of ethylenediaminetetraacetic acid in  $(\text{H,K})\text{NO}_3$  solutions.

The solubility of  $\text{H}_4\text{edta}(\text{cr})$  at  $I = 0.1$  M ( $\text{KNO}_3$ ) at 20 and 25°C were combined with protonation constants for  $\text{edta}^{4-}$  from the literature [\[47SCH/ACK\]](#), [\[55MAC/KRI\]](#), to produce values for the solubility constant and for the enthalpy change for reaction:  $\text{H}_4\text{edta}(\text{cr}) \rightleftharpoons 4 \text{H}^+ + \text{edta}^{4-}$ . The corresponding experimental data is not reported in tables or in figures. Values of  $[\text{H}^+]$  were calculated in this study from pH measurements and activity coefficients calculated with the Davies equation. As the value of  $\log_{10} K_{\text{s},4}$ , for Reaction (A.79):  $\text{H}_4\text{edta}(\text{cr}) \rightleftharpoons \text{H}_4\text{edta}(\text{aq})$ , is not very sensitive to the method used to calibrate the  $\text{H}^+$ -electrode, the data at  $I = 0.1$  M ( $\text{KNO}_3$ ) at both 20 and 25°C are included in this review with an assigned uncertainty of  $\pm 0.2 \log_{10}$ -units. The reported enthalpy change, evaluated from the solubility difference in a very narrow temperature range,  $\Delta t = 5^\circ\text{C}$ , is not considered in this review. Other solubility constants and enthalpies for reactions  $\text{H}_4\text{edta}(\text{cr}) \rightleftharpoons (4-n) \text{H}^+ + \text{H}_n\text{edta}^{(n-4)}$  are reported in [\[82TER/IVA\]](#), but they are necessarily the result of combining the experimental  $\log_{10} K_{\text{s},4}$  with the literature values for the protonation constants and their temperature dependence. These values are not taken into account.

The solubility of edta was also measured at  $I = 2$  M  $(\text{H,K})\text{NO}_3$  at 20°C. The minimum solubility for  $\text{H}_4\text{edta}(\text{cr})$  under such conditions was found to be  $3.8 \times 10^{-4}$  M. The solubility data were analysed in terms of the formation of  $\text{H}_n\text{edta}^{(n-4)}$ , with  $n = 2$  to



6. The authors report the following stepwise protonation constants ( $\log_{10} K_n$ ): 2.63, 2.35, 1.36 and 0.33 for  $n = 3$  to 6; and the solubility constants:  $\log_{10} K_{s,4}$  (A.79) =  $-(3.43 \pm 0.02)$ , and  $\log_{10} K_s = -0.99$  for  $\text{H}_6\text{edta}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}(\text{cr}) \rightleftharpoons \text{H}_6\text{edta}^{2+} + 2\text{NO}_3^- + 3\text{H}_2\text{O}(\text{l})$ . The experimental data is reported in a table and in a graph.

As mentioned above the values of  $[\text{H}^+]$  were calculated from pH measurements and activity coefficients calculated with the Davies equation, which can give erroneous results at  $I = 2$  M. Because of this the equilibrium constants from [82TER/IVA] at  $I = 2$  M are disregarded. Instead the data in Table 1 of [82TER/IVA], in the form of  $\text{H}_4\text{edta}(\text{cr})$  solubility *versus*  $[\text{HNO}_3]_{\text{TOT}}$  at  $I = 2$  M ((H,K)NO<sub>3</sub>) and  $(20 \pm 1)^\circ\text{C}$  was re-evaluated in this review by fitting it to a theoretical solubility curve using a least-squares technique. The calculations gave the following equilibrium constants:



$$\log_{10} K_{s,4} (\text{A.79}) = -(3.7 \pm 0.5),$$



$$\log_{10} K (\text{A.80}) = (1.7 \pm 0.5),$$



$$\log_{10} K (\text{A.81}) = (0.1 \pm 0.2).$$

The values of  $K_3$  and  $K_4$ , corresponding to reactions:  $\text{H}_3\text{edta}^- + \text{H}^+ \rightleftharpoons \text{H}_4\text{edta}(\text{aq})$  and  $\text{H}_2\text{edta}^{2-} + \text{H}^+ \rightleftharpoons \text{H}_3\text{edta}^-$  were ill defined by the data. The values listed above were converted to  $25^\circ\text{C}$  and included in the evaluations described in Sections VIII.2.2 and VIII.3.

#### [82VAS/BEL]

The thermal effects for the interaction of  $\text{Ni}(\text{edta})^{2-}$  (0.0004 – 0.015 M) with glycine (0.05 – 0.5 M, pH = 11.5 obtained with KOH) at  $25^\circ\text{C}$  and ionic strength 1.5 M ( $\text{KNO}_3$ ) have been measured calorimetrically.

#### [82VAS/VAS]

This study reports a combined spectrophotometric and pH-metric determination of the formation constants of ternary complexes of  $\text{Ni}(\text{edta})^{2-}$  with ammonia, oxalate and pyrophosphate at ionic strength 1.0, 1.5 and 2.0 M maintained with  $\text{KNO}_3$  at room temperature (?). Spectra (360 – 700 nm) and the pH were measured for solutions containing 0.05 M  $\text{K}_2\text{Ni}(\text{edta})$  and

- (a) variable ammonia concentrations (0 – 1.58 M),
- (b) in the presence of 0.2 M  $\text{ox}^{2-}$  and variable ammonia concentrations (0 – 0.474 M), and
- (c) in the presence of 0.1 M  $\text{P}_2\text{O}_7^{4-}$  and variable ammonia concentrations (0 – 0.474 M).



Neither the modus of the pH calibration in the three different pH ranges is mentioned nor the components of the used cell reported. In the cases (b) and (c) the large total ligand concentrations give constant contributions to the ionic strength of 0.4 and 1 M, respectively. Hence, the activities of the investigated species are changed by unknown amounts due to these large total ligand concentrations. Therefore, only the results obtained in case (a) (*i.e.*, ammonia) can be considered reasonable. However, in this case “the dissociation constant of  $\text{NH}_4\text{OH}$ ” was taken from the literature without any guarantee of its reliability, in addition to the uncertainty concerning the ionic product of  $\text{H}_2\text{O}$ , as both quantities are not mentioned in [\[82VAS/VAS\]](#).

#### [\[82ZUB/KRO\]](#)

By using  $^{243}\text{Am}$ ,  $\text{KAmO}_2(\text{ox}) \cdot x\text{H}_2\text{O}$  and  $\text{CsAmO}_2(\text{ox}) \cdot x\text{H}_2\text{O}$  were prepared. These salts were found not to be isomorphous with similar salts of  $\text{Np(V)}$ . The compound  $\text{CsAmO}_2(\text{ox}) \cdot x\text{H}_2\text{O}$  was identified as in the cubic system with the lattice constant  $a = 1.25$  nm. By spectrophotometry, it was found that in solutions with a high oxalate-ion concentration (0.166 M  $\text{K}_2\text{ox}$ ) the stability of americium in the +5 oxidation state depends on the solution pH. At  $64.8^\circ\text{C}$ ,  $\text{Am(V)}$  is stable for 240 min at pH 5.90, 3.5 % of  $\text{Am(III)}$  formed in 260 min at pH 3.62, and 7%  $\text{Am(III)}$  formed in 120 min at pH 3.29. No thermodynamic values are reported.

#### [\[83ARE/MUS\]](#)

The stability constants of the edta complexes with calcium and magnesium have been determined pH-metrically in aqueous solution over wide range of ionic strength (0.17 – 0.77 M) and temperature (10 –  $45^\circ\text{C}$ ). The authors used tetramethylammonium chloride ( $\text{Me}_4\text{NCl}$ ) as inert salt, added 0.25 M NaOH as titrant, and corrected the ionic strength and the stability constants for the effects of edta species and  $\text{Na(edta)}^{3-}$  complexes in solution. The authors also report equilibrium constants for protonation and  $\text{Na}^+$  complexation, citing [\[83DAN/RIG\]](#) and [\[85DAN/RIG\]](#).

Daniele *et al.* [\[83DAN/RIG\]](#), [\[85DAN/RIG\]](#) report protonation constants for several tetraalkylammonium salts, but not for  $\text{Me}_4\text{NCl}$ . The most similar salt is  $\text{Me}_4\text{NBr}$  [\[85DAN/RIG\]](#). Furthermore, the authors used 1 M KOH as titrant in all cases, which introduced a systematic error because of the complex formation between  $\text{edta}^{4-}$  and  $\text{K}^+$ . Because of these ambiguities in the protonation constants, which were considered in this review with an uncertainty of  $\pm 0.10 \log_{10}$ -units, this review assigns an uncertainty of  $\pm 0.15 \log_{10}$ -units to the Mg and Ca edta constants reported by [\[83ARE/MUS\]](#). Only the data at  $25^\circ\text{C}$  have been considered in this review for the evaluation of stability constants. The enthalpy values derived by [\[83ARE/MUS\]](#) from the temperature variation of stability constants are rejected as the differences in stability constants are well within the assigned uncertainties.

**[83CAC/CHO]**

The stability of the initial step of the hydrolysis reaction of Eu(III) and Am(III) has been calculated from measurements of the apparent stability constant of the complexes with oxalate in the pH range 6 to 8 by solvent extraction using dibenzoylmethane and TBP in benzene. In this procedure, the stability constants of Am(III) oxalates were obtained to be  $\log_{10} \beta_1 = (4.58 \pm 0.05)$  for  $\text{Am}^{3+} + \text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})^+$  and  $\log_{10} \beta_2 = (7.91 \pm 0.10)$  for  $\text{Am}^{3+} + 2\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_2^-$  at  $I = 0.7 \text{ M NaCl}$  at  $21^\circ\text{C}$ . The solvent extraction was conducted at pH 6.0 where all the oxalate exists as  $\text{ox}^{2-}$ . The experiment and analysis were conducted properly. No correction was made for  $\text{Cl}^-$  complexation. The correction of the formation of  $\text{AmCl}^{2+}$  and  $\text{AmCl}_2^+$  can be estimated as described in Section V.4. This results in a correction of the  $\log_{10} \beta$  values (expressed in molality scale) by  $+0.03 \log_{10}$  units. By considering the temperature difference from  $25^\circ\text{C}$  and the possible systematic error in the solvent extraction, this review selects the values as  $\log_{10} \beta_1 = (4.61 \pm 0.10)$  and  $\log_{10} \beta_2 = (7.93 \pm 0.15)$  at  $I_m = 0.71 \text{ m NaCl}$  at  $25^\circ\text{C}$ .

**[83CHO/BOK]**

Solvent extraction experiments with TBP were conducted to determine the stability constants of U(VI) and Pu(IV) oxalate complexes at  $I = 4.0 \text{ M}$  and  $25^\circ\text{C}$ . Both tracer ( $^{233}\text{U}$  and  $^{239}\text{Pu}$ ) and macroamount ( $^{238}\text{U}$ ) experiments were conducted. The concentration of  $\text{HNO}_3$  was varied from 1 to 4 M (keeping  $[\text{NO}_3^-]_{\text{TOT}} = 4 \text{ M}$  by adding  $\text{NaNO}_3$ ) and the concentration of oxalic acid was varied up to 0.4 M. Data analysis indicates that the complexed species are  $\text{UO}_2\text{ox}(\text{aq})$  and  $\text{Pu}(\text{ox})^{2+}$ , not  $\text{UO}_2\text{Hox}^+$  or  $\text{Pu}(\text{Hox})^{3+}$ . No second complex of U(VI) oxalate was observed, although  $\text{Pu}(\text{ox})_2(\text{aq})$  could be inferred from the distribution data. The authors observed that, in the absence of oxalic acid, the distribution ratios of U(VI) and Pu(IV) varied with the ratio of  $[\text{HNO}_3]/[\text{NaNO}_3]$ , which was assumed by the authors to reflect the formation of  $\text{TBP} \cdot n\text{HNO}_3$  complexes in the organic phase. However, this could also indicate the medium effect on the activity coefficients of the species in solution. In fact, the stability constants for  $\text{UO}_2\text{ox}(\text{aq})$  ( $\log_{10} \beta_1$ ) were found to change (from  $(6.20 \pm 0.06)$  to  $(6.38 \pm 0.08)$ ) when the ionic medium was varied from 1 M  $\text{HNO}_3/3 \text{ M NaNO}_3$  to 4 M  $\text{HNO}_3$ . Similar, but less regular changes could be observed in the Pu(IV) oxalate constants. The protonation constant of oxalic acid in 4 M  $\text{NaNO}_3$  determined by potentiometry ( $\log_{10} K = (5.00 \pm 0.03)$  for  $2\text{H}^+ + \text{ox}^{2-} \rightleftharpoons \text{H}_2\text{ox}(\text{aq})$ ) was used in the calculations.

The stability constant of  $\text{UO}_2\text{ox}(\text{aq})$  in 4.0 M  $\text{HNO}_3$  from this work ( $\log_{10} \beta_1 = (6.36 \pm 0.06)$ , the average of two values from tracer and macro studies) is accepted by this review, converted from molarity to molality units by the method in Chapter II, and corrected for the complexation of U(VI) by nitrate as follows:

$$\log_{10} \beta_{\text{corr.}} = \log_{10} \beta_{\text{exp.}} + \log_{10} (1 + K_{\text{NO}_3^-} [\text{NO}_3^-]) \quad (\text{A.82})$$

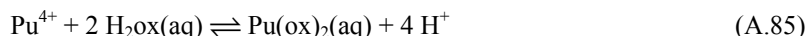
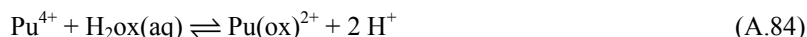
where  $K_{\text{NO}_3^-}$  is the formation constant of  $\text{UO}_2\text{NO}_3^+$  and is calculated to be

$(1.50 \pm 1.08) \text{ kg}\cdot\text{mol}^{-1}$  at  $I = 4.56 \text{ m}$  ( $\text{HNO}_3$ ), from the thermodynamic parameters for the complexation:



$\log_{10} K_{\text{NO}_3}^\circ = (0.30 \pm 0.15)$ ,  $\Delta\epsilon(\text{A.83}) = \epsilon(\text{UO}_2\text{NO}_3^+, \text{ClO}_4^-) - \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - \epsilon(\text{H}^+, \text{NO}_3^-) = (0.33 \pm 0.04) - (0.46 \pm 0.03) - (0.07 \pm 0.01) = -(0.20 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  [2003GUI/FAN]. Therefore, the corrected value of  $\log_{10} \beta_1$  is  $(7.25 \pm 0.30)$ , as shown in Table VI-39.

The equilibrium constants for the formation of  $\text{Pu}(\text{ox})^{2+}$  and  $\text{Pu}(\text{ox})_2(\text{aq})$  are also considered reliable. The hydrolysis of Pu(IV) has a large effect in the experiments in  $[\text{HNO}_3] = 0.1 \text{ M}$  and  $[\text{NaNO}_3] = 3.9 \text{ M}$ , and only the values at  $[\text{H}^+] \geq 1 \text{ M}$  are considered by this review. As all other Pu(IV) studies in the literature are performed in strong acid media to avoid hydrolysis, the constants listed in [83CHO/BOK] using  $\text{ox}^{2-}$  as a ligand are converted into:



with the protonation constant determined by the authors. The values in Table 2 of [83CHO/BOK] ( $\log_{10} \beta_1 = (8.30 \pm 0.30)$  and  $\log_{10} \beta_2 = (14.87 \pm 0.40)$ , the unweighed averages with uncertainties assigned by this review) become  $\log_{10} \beta_1$  (A.84) =  $(3.30 \pm 0.30)$  and  $\log_{10} \beta_2$  (A.85) =  $(4.87 \pm 0.40)$ . Conversion from molarity to molality gives  $\log_{10} \beta_1$  (A.84) =  $(3.36 \pm 0.30)$  and  $\log_{10} \beta_2$  (A.85) =  $(4.98 \pm 0.40)$ . The correction for nitrate complexation is performed using  $\log_{10} K_{\text{NO}_3}^\circ = (1.95 \pm 0.15)$  [2001LEM/FUG], [2003GUI/FAN] and  $\epsilon(\text{PuNO}_3^{3+}, \text{NO}_3^-) \approx \epsilon(\text{PuNO}_3^{3+}, \text{ClO}_4^-) = (0.70 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$  (from the value of  $\Delta\epsilon$  selected in [2001LEM/FUG] for  $\text{HClO}_4$  media), giving  $\log_{10} K_{\text{NO}_3}^\circ = (0.75 \pm 0.51)$ , *i.e.*,  $K_{\text{NO}_3}^\circ = (5.6 \pm 6) \text{ kg}\cdot\text{mol}^{-1}$  at  $I = 4.56 \text{ m}$  ( $\text{HNO}_3$ ), and use of Eq.(A.82) results finally in  $\log_{10} \beta_1$  (A.84) =  $(4.78 \pm 0.64)$  and  $\log_{10} \beta_2$  (A.85) =  $(6.41 \pm 0.75)$ , both equilibrium constants in molal units.

### [83DAN/RIG]

The authors report a potentiometric study at  $37^\circ\text{C}$  on the protonation of oxalate, citrate and  $\text{edta}^{4-}$  (among others). Protonation constants were reported at several ionic strengths. The ionic strength varied along the titrations, and Daniele *et al.* took this into account in their data analysis. The protonation constants at  $I \leq 0.1 \text{ M}$  should be disregarded because of the relatively large concentration of organic ligands used in the titrations, and in the case of  $\text{edta}^{4-}$ , only the data at  $I \geq 0.3 \text{ M}$  has been considered.

The ionic media ( $\text{Et}_4\text{NI}$ , tetraethylammonium iodide) was chosen to avoid complex formation with alkali cations. However, the authors used  $1 \text{ M KOH}$  as titrant in all cases. Because of the possibility of complex formation between  $\text{edta}^{4-}$  and  $\text{K}^+$  added with the titrant, systematic errors were introduced in the corresponding protonation constants. The magnitude of this error in the first protonation constant of  $\text{edta}^{4-}$  is

expected to be  $\leq 0.02 \log_{10}$ -units (*cf.* Section V.3.3, Eq.(V.52), with  $K_M \approx 3 \text{ M}^{-1}$ ,  $[K^+] \approx 0.02 \text{ M}$ ,  $I = 0.3$ ). The uncertainties of the reported values were increased accordingly in the review procedure.

Because of possible systematic errors due to the KOH titrant the uncertainties of the oxalate constants obtained in  $\text{LiNO}_3$  and  $\text{NaNO}_3$  were increased to  $\pm 0.05 \log_{10}$ -units.

#### [\[83INO/TOC\]](#)

The complex formation of  $^{239}\text{Np(V)}$  with 22 organic ligands (including oxalate and edta) has been determined in 1 M  $\text{NaClO}_4$  at  $25^\circ\text{C}$  by using the solvent extraction method with TTA (thenoyl trifluoroacetone) and 1,10-phenantroline. Ligand protonation constants have been taken from [\[77MAR/SMI\]](#). In the case of edta these are: 10.17, 6.11, 2.68 and 2.0, as reported in Table 2 of [\[83INO/TOC\]](#). The pH was adjusted by the addition of buffers, and it was measured with a pH meter Toa Dempa HM-5BS equipped with a glass electrode. Unfortunately, no details are reported about the pH scale used or the calibration of the pH meter. For this reason, the reported Np(V) edta stability constant is not further considered in this review.

For the system Np(V)-oxalate the protonation constants of the ligand were 3.55 and 1.04, which agree with the values selected by this review for 1 M  $\text{NaClO}_4$  within the uncertainties. The ligand concentration varied between 4 and 60 mM, and the pH was 7.5, 6.7 and 5.8. The weighted average of the three values listed in Table 2 of [\[83INO/TOC\]](#) are:  $\log_{10} \beta_1 = 3.62$  and  $\log_{10} \beta_2 = 6.20$ . These values are included in this review with the uncertainty increased to  $\pm 0.2$  because insufficient details describing the pH-measurements and to take into consideration the problems associated with the solvent extraction technique described in [\[92TOC/INO\]](#).

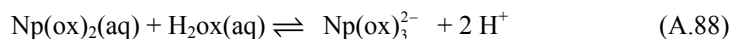
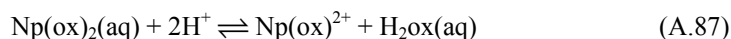
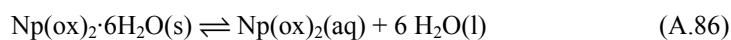
#### [\[83KOR/PRO\]](#)

The formation of ternary complexes of the Cu(II) and Ni(II) chelates of edta and edta with cyanide and ethylenediamine (en) has been investigated by spectrophotometry. The stability constant for  $\text{Ni(edta)CN}^{3-}$  listed in [\[83KOR/PRO\]](#) has been taken from the literature [\[70COO/MAR\]](#). In the case of  $\text{Ni(edta)en}^{2-}$  Korsse *et al.* report a stability constant of  $\log_{10} K = (2.74 \pm 0.34)$  for the reaction:  $\text{Ni(edta)}^{2-} + \text{en} \rightleftharpoons \text{Ni(edta)en}^{2-}$  (pH = 11.1,  $c_{\text{Ni(edta)}} = 5 \text{ mM}$ ,  $c_{\text{en}} = 0 - 15 \text{ mM}$ ). The authors state that the measurements on this system were not performed at constant ionic strength (*i.e.*, no inert salt was added), but nevertheless the  $K$ -value should be reasonably accurate because the neutral ligand ethylenediamine is involved (*i.e.*, an isocoulombic reaction was investigated). As ethylenediamine hydrochloride was added the ionic strength increased by its addition and the obtained values are considered by this review as approximate only.

#### [\[83LUE\]](#)

The author studied the solubility of  $^{237}\text{Np(IV)}$  oxalate at three temperatures, 22, 45 and

60°C in broad concentration ranges:  $[\text{H}_2\text{ox}]_{\text{TOT}} = 0.014 - 0.8 \text{ M}$ ,  $[\text{HNO}_3]_{\text{TOT}} = 0.4 - 10 \text{ M}$ . The neptunium(IV) oxalate was not characterised, although the formula  $\text{Np}(\text{ox})_2 \cdot 6\text{H}_2\text{O}$  is given. The equilibration time was 24 hours, after this period samples were taken through a  $0.25\mu\text{m}$  filter and the neptunium concentrations were determined by radio-metric measurements. Hydrazine was added to keep neptunium in the tetravalent oxidation state. Both precipitation and solubility experiments were performed at room temperature, but the data at 45 and 60°C were obtained from precipitation experiments only. The author interpreted the solubility data by the formation of three complexes,  $\text{Np}(\text{ox})_n^{4-2n}$  ( $n = 1$  to 3). The parameters listed in this report correspond to the reactions:



with the following equilibrium constants at 22, 45 and 60°C:

$$\log_{10} K_s (\text{A.86}) = -(4.75 \pm 0.07), \quad -(4.2 \pm 0.2) \quad -(3.75 \pm 0.05)$$

$$\log_{10} K (\text{A.87}) = -(2.15 \pm 0.08), \quad -(1.6 \pm 0.2) \quad -(2.09 \pm 0.06)$$

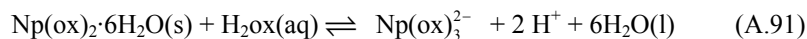
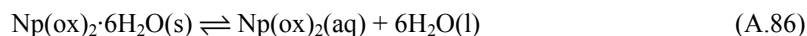
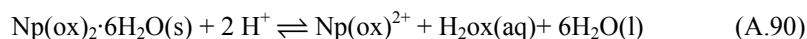
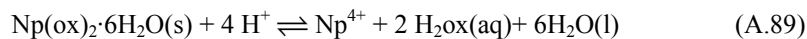
$$\log_{10} K (\text{A.88}) = (0.29 \pm 0.08), \quad (0.6 \pm 0.2) \quad (0.02 \pm 0.07)$$

Given the large variations in the ionic strength, these equilibrium constants cannot be accepted in this review.

There is no data available on the activity coefficients of  $\text{Np}^{4+}$  in  $\text{NO}_3^-$  media, which would be necessary to make a correct interpretation of the solubility data listed in [83LUE]. An attempt is made by this review to re-analyse the data at 22°C using the SIT model for activity coefficients described in Appendix B, being aware that the results are only of qualitative nature. The following assumptions are used:

- a) the solid phase in all these experiments is indeed  $\text{Np}(\text{ox})_2 \cdot 6\text{H}_2\text{O}(\text{s})$ ;
- b) the SIT model for activity coefficients described in Appendix B may be used up to 4 M  $\text{HNO}_3$ ;
- c)  $\epsilon(\text{Np}^{4+}, \text{NO}_3^-) \approx \epsilon(\text{Np}^{4+}, \text{ClO}_4^-)$ .

The data were interpreted using the following equilibria:



The formation of  $\text{NpOH}^{3+}$  and of  $\text{NpNO}_3^{3+}$  [2001LEM/FUG] is considered as

well. The following specific ion interaction coefficients were used:  $\varepsilon(\text{NpOH}^{3+}, \text{NO}_3^-) \approx \varepsilon(\text{NpOH}^{3+}, \text{ClO}_4^-) = (0.5 \pm 0.1) \text{ kg}\cdot\text{mol}^{-1}$  [2001NEC/KIM] and  $\varepsilon(\text{NpNO}_3^{3+}, \text{NO}_3^-) \approx \varepsilon(\text{NpNO}_3^{3+}, \text{ClO}_4^-) = (0.82 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ , which results in  $\Delta\varepsilon = - (0.09 \pm 0.08) \text{ kg}\cdot\text{mol}^{-1}$  for  $\text{Np}^{4+} + \text{NO}_3^- \rightleftharpoons \text{NpNO}_3^{3+}$ , cf. [2001LEM/FUG]. The activity of water at 25°C listed in Table B-1 is used. As the experiments were performed at relatively high concentrations of oxalic acid, the value of the solubility constants for the formation of  $\text{Np}^{4+}$  and  $\text{Np}(\text{ox})^{2+}$ , eqns. (A.89) and (A.90), have high uncertainty. An additional uncertainty in these concentrated  $\text{HNO}_3$  solutions is the possible existence of other nitrate complexes not considered here, such as  $\text{Np}(\text{NO}_3)_2^{2+}$ . The analysis results in the following values:

$$\begin{aligned}\log_{10} K_s^o(\text{A.89}) &= - (12.2 \pm 0.2), \\ \log_{10} K_s^o(\text{A.90}) &= - (5.7 \pm 0.5), \\ \log_{10} K_s^o(\text{A.86}) &= - (5.1 \pm 0.1), \\ \log_{10} K_s^o(\text{A.91}) &= - (5.2 \pm 0.1), \\ \varepsilon(\text{Np}(\text{ox})^{2+}, \text{NO}_3^-) &= (1.6 \pm 0.6) \text{ kg}\cdot\text{mol}^{-1}, \\ \varepsilon(\text{H}^+, \text{Np}(\text{ox})_3^{2-}) &= (0.0 \pm 0.2) \text{ kg}\cdot\text{mol}^{-1}.\end{aligned}$$

#### [83LUR/GON]

The nature of the edta complex of U(VI) is discussed, and it is concluded that there is no need to postulate stabilisation of the complex by hydrogen-bonding between a protonated nitrogen atom and the uranyl ion, as it has been inferred in [68SIL/SIM], [70SIL/SIM] and [70SIL/SIM2]. No new data concerning U(VI) edta complexation are reported here.

#### [83PER/MIS]

In this study involving derivative spectrophotometry it was found that in acidic media U(IV) and edta form a complex with a 1:1 U : edta ratio. In weakly acidic media, a 2:3 complex was found by the method of molar ratios, while with edta and oxalate a ternary complex is formed with a ratio 1:1:1. However, the experimental information given by the authors is very scarce. It is not clear whether a background electrolyte has been used, and there is no discussion at all concerning the constancy of the ionic strength during the experiments. Furthermore, the temperature is not mentioned, and the pH scale and the pH calibration are not given. Hence, the values reported by the authors are not credited in this review.

#### [83ZUB/KRO]

Double oxalates of Am(III) and potassium with general composition  $\text{KAm}(\text{ox})_2 \cdot n\text{H}_2\text{O}$  were synthesised. Depending on the conditions such as temperature and the concentration of  $\text{K}_2\text{ox}$ , three phases, phase I ( $n = 5$ ), phase II ( $n = 3.5$ ) and phase III ( $n = 2.5$ ), were isolated and analysed by XRD, TGA and IR. As compared with the

$\text{KLn}(\text{ox})_2 \cdot n\text{H}_2\text{O}$  ( $\text{Ln} = \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}$ ) with the same composition, phase I is more stable and phase III is more unstable for  $\text{Am}(\text{III})$ . In the case of long contact with water, double oxalates of  $\text{Am}(\text{III})$  and potassium are reported to be gradually converted to  $\text{Am}_2(\text{ox})_3 \cdot 10\text{H}_2\text{O}$ .

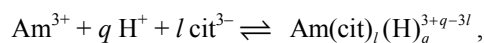
#### [\[83ZUB/KRO2\]](#)

Double oxalates of  $\text{Am}(\text{III})$  and potassium with general composition  $\text{MAm}(\text{ox})_2 \cdot n\text{H}_2\text{O}$  ( $\text{M} = \text{Na}, \text{NH}_4$  or  $\text{Cs}$ ) were synthesised and the stabilities of the compounds were examined. In contact with the solution of  $\text{M}_2\text{ox}$ , only one phase,  $\text{NaAm}(\text{ox})_2 \cdot 5\text{H}_2\text{O}$ ,  $(\text{NH}_4)\text{Am}(\text{ox})_2 \cdot 5\text{H}_2\text{O}$  or  $\text{CsAm}(\text{ox})_2 \cdot 0.5\text{H}_2\text{O}$  was obtained.

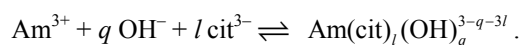
#### [\[84BOU/GUI\]](#)

Solvent extraction and potentiometric methods were used to obtain stability constants of citrate complexes of americium. Although the numerical values for the complex formation given in Tableau 1 of the paper are somewhat different, the data of the solvent extraction experiment seem the same as in [\[71GUI/BOU\]](#) and [\[74HUB/HUS\]](#). Using the citrate protonation constants of  $\log_{10} K_{(\text{H})} = 5.53, 4.36$  and  $2.97$ , the stability constants are reported to be  $\log_{10} K = 10.1$  for  $\text{Am}^{3+} + \text{H}^+ + \text{cit}^{3-} \rightleftharpoons \text{Am}(\text{Hcit})^+$  and  $\log_{10} K = 20$  for  $\text{Am}^{3+} + 2\text{H}^+ + 2\text{cit}^{3-} \rightleftharpoons \text{Am}(\text{Hcit})_2^-$  (corresponding to  $\log_{10} \beta_{1(\text{Hcit})} = 4.57$  and  $\log_{10} \beta_{2(\text{Hcit})} = 8.94$ ),  $\log_{10} \beta_{1(\text{cit})} = 8.0$  for  $\text{Am}(\text{cit})(\text{aq})$ ,  $\log_{10} \beta_{2(\text{cit})} = 12.1$ ,  $\log_{10} K = 16.3$  for  $\text{Am}^{3+} + \text{H}^+ + 2\text{cit}^{3-} \rightleftharpoons \text{Am}(\text{Hcit})(\text{cit})^{2-}$  (corresponding to  $\log_{10} \beta_{1(\text{Hcit})(\text{cit})} = 10.77$ ). However, the simulation with the reported values showed that only  $\text{Am}(\text{cit})(\text{aq})$  and  $\text{Am}(\text{cit})_2^{3-}$  can contribute as predominant species. The uncertainties are considered to be the same ( $\pm 0.5$ ) as in [\[71GUI/BOU\]](#) and [\[74HUB/HUS\]](#).

Potentiometric titrations were also conducted for the solutions of  $c_{\text{H}_3\text{cit}}/c_{\text{Am}} = 1 \sim 5$ , where  $C_{\text{H}_3\text{cit}} = 1.6 \times 10^{-3} \sim 10^{-2}$  and  $c_{\text{Am}} = 1.4 \times 10^{-3} \sim 2.4 \times 10^{-3}$  at  $I = 0.1 \text{ M}$   $\text{LiClO}_4$ . The stability constants are reported to be  $\log_{10} {}^*K = 11.36$  for  $\text{AmHcit}^+$ ,  $8.69$  for  $\text{Am}(\text{cit})(\text{aq})$ ,  $18.97$  for  $\text{Am}(\text{Hcit})(\text{cit})^{2-}$ ,  $14.29$  for  $\text{Am}(\text{cit})_2^{3-}$ ,  $10.53$  for  $\text{Am}(\text{OH})(\text{cit})^-$  and  $22.80$  for the reactions:



or



However, since mass balance calculation for the data at the pH near the equivalence point introduces large errors (pH changes drastically for the small change of added amount of alkali), the results for the speciation at  $\text{pH} > 3$  are doubtful. Therefore, this review does not accept the values obtained by potentiometry.

#### [\[84BRI/LAG\]](#)

Complexation of the uranyl ion ( $\text{UO}_2^{2+}$ ) with some polyaminocarboxylate ligands (including edta) has been investigated in  $3 \text{ M}$   $\text{NaClO}_4$  solutions at  $25^\circ\text{C}$ . Spectrophotometric measurements at  $\lambda = 250 - 300 \text{ nm}$  were performed for solutions with pH values



between 1 and 3, containing U(VI) ( $5 \cdot 10^{-4} - 5 \cdot 10^{-3}$  M) and edta ( $10^{-3} - 10^{-2}$  M). The molar absorption coefficients of  $\text{UO}_2^{2+}$ ,  $\text{UO}_2(\text{Hedta})^-$  and  $(\text{UO}_2)_2\text{edta}(\text{aq})$  are reported to be very close to each other in the entire range of wavelengths investigated.

The literature concerning this topic is cited by the authors but not considered in the discussion of their results. From these papers it is apparent that the investigation of the U(VI) – edta system can be extended to much higher pH values than 3 without interfering  $\text{UO}_2^{2+}$  hydrolysis effects [82OVE/LUN]. The molar absorption coefficients of the edta complexes differ strongly from those reported by [64BHA/KRI]. At 290 nm the molar absorption coefficient of  $\text{UO}_2^{2+}$  reported in the latter paper is much lower than those of the edta complexes, in contrast to the findings of [84BRI/LAG]. The equilibrium constant obtained by [84BRI/LAG] for  $\text{UO}_2\text{edta}^{2-} + \text{H}^+ \rightleftharpoons \text{UO}_2(\text{Hedta})^-$ ,  $\log_{10}K = 2.94$ , differs strongly from other literature values: 5.63 at  $I = 0.1$  M  $\text{NaClO}_4$  [64BHA/KRI], 5.76 at  $I = 0.1$  M  $\text{KNO}_3$  [82OVE/LUN] and 5.09 at  $I = 0.3$  m  $\text{NaCl}$  [98POK/BRO]. A plausibility check by alkalimetric titrations, as done in [68SIL/SIM], would have shown that in 1:1 U(VI) – edta mixtures  $\text{UO}_2\text{edta}^{2-}$  has a protonation constant larger than 5 and not 3, in agreement with [69STE/MAK2]. The question why [84BRI/LAG] did not use alkalimetric titrations to verify their spectrophotometric results remains open. The results reported in this paper have not been considered in this review.

#### [84DAN/OST]

The authors reported a potentiometric study performed at temperatures between 10 and  $45^\circ\text{C}$  from which they determined the protonation of citrate and the complex formation between citrate and  $\text{K}^+$ ,  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$ . Enthalpy changes were calculated from the temperature dependence of equilibrium constants. Several ionic media were used ( $\text{KNO}_3$ ,  $\text{KCl}$ , and  $\text{Et}_4\text{NBr}$ , tetraethylammonium bromide). When a potassium electrolyte was used as the background, it was not stated whether the anion was nitrate or chloride. It is not clearly indicated if the ionic strength varied or was kept constant during the titrations. The authors used 1 M  $\text{KOH}$  as titrant in all cases, even when  $\text{Et}_4\text{NBr}$  was used as ionic media, introducing a systematic error because of differences in ionic activity coefficients.

Because of these shortcomings in the experimental procedure, the reported protonation constants in  $\text{K}^+$  media are not accepted in this review, while the reported data for 0.25 M  $\text{Et}_4\text{NBr}$  media is included with an assigned uncertainty of  $\pm 0.06$   $\log_{10}$ -units.

The reported enthalpy and entropy changes for the protonation of citrate correspond to the equilibrium constants determined in  $\text{Et}_4\text{NBr}$ , except for the amount of  $\text{K}^+$  introduced with the titrant (up to 35 mM). Because the systematic errors introduced in the  $\log_{10}K$  values by the potassium ions in the titrant, although small, are of the same order of magnitude as the small temperature effects involved, the reported enthalpy changes for the protonation of citrate are not accepted in this review.



Daniele *et al.* calculated  $K^+$ -citrate complexation constants by comparing the protonation constants obtained in  $\text{Et}_4\text{N}^+$  and potassium media. This methodology is however not credited in this review, *cf.* Section VII.4. The values of  $\Delta_r H_m$  for  $K^+$  complexation obtained from the temperature variation of the corresponding formation constants are therefore not considered in this review.

The equilibrium constants and  $\Delta_r H_m$  for  $\text{Ni}^{2+}$ -citrate complexation were also obtained and reported in this paper. However, since they were obtained using the protonation constants and  $K^+$ -citrate complexation constants determined by the authors, they are not considered in this review.

#### [\[84DUF/MAY\]](#)

Stability constants of edta and dtpa complexes of  $\text{Ca(II)}$ ,  $\text{Mg(II)}$ ,  $\text{Mn(II)}$ ,  $\text{Zn(II)}$  and  $\text{Cd(II)}$  have been measured under biological conditions ( $I = 0.15 \text{ M NaCl}$  and  $37^\circ\text{C}$ ). An improved electrode calibration technique was utilised. The values reported by [\[84DUF/MAY\]](#) represent the only determination of  $\text{Ca(edta)}^{2-}$  and  $\text{Mg(edta)}^{2-}$  stability at  $37^\circ\text{C}$  and  $0.15 \text{ M NaCl}$ . They have not been included in the final data evaluation.

#### [\[84GON/MOT\]](#)

Uranyl complexes of *n*-alkanediaminotetraacetic acids have been studied by potentiometry. A range of ligand and metal concentrations between  $5 \cdot 10^{-4}$  and  $5 \cdot 10^{-3} \text{ M}$  was used to allow the study of polymeric species. At concentrations below  $5 \cdot 10^{-4} \text{ M}$  no polymeric species are formed, and at concentrations above  $5 \cdot 10^{-3} \text{ M}$  the polymeric species precipitate as soon as they are formed.

However, no new experimental data concerning the  $\text{U(VI)}$  edta system are reported in this paper. Instead, the experimental data of [\[68SIL/SIM\]](#) are newly refined using the program MINQUAD. The obtained stability constants are compared with those obtained by [\[68SIL/SIM\]](#) using graphical and algebraic methods (Table 4 in [\[84GON/MOT\]](#)).

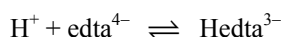
First of all, we notice that the data in Table 4 of [\[84GON/MOT\]](#), claimed to be taken from [\[68SIL/SIM\]](#) for comparison, are not consistent with those reported in the original paper (Table V in [\[68SIL/SIM\]](#)). For example, combining  $\log_{10} K = 7.35$  (Table V in [\[68SIL/SIM\]](#)) for the reaction:



with  $\log_{10} K = 17.55$  (Table 4 in [\[84GON/MOT\]](#)) for the reaction:

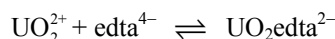


results, for the reaction,

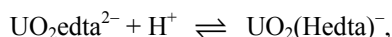


in  $\log_{10} K = 10.22$  instead of 9.93, as reported in Table 1 of [\[84GON/MOT\]](#). Likewise,

combining  $\log_{10}K = 10.88$  for the equilibrium:



with  $\log_{10}K(\text{A.93}) = 17.55$  (both values from Table 4 in [84GON/MOT]) results, for the reaction:



in  $\log_{10}K = 6.67$  instead of 5.62, as reported in Table V of [68SIL/SIM].

Besides these inconsistencies, the differences between the new refinement and the original one are more serious. The species  $\text{UO}_2\text{edta}^{2-}$  and  $\text{UO}_2\text{edtaOH}^{3-}$ , reported by [68SIL/SIM], disappear in the new refinement, whereas the stability constants of  $\text{UO}_2(\text{Hedta})^-$  and  $(\text{UO}_2)_2\text{edta}(\text{aq})$  decrease in the new refinement by 1.27 and 1.63  $\log_{10}$  units, respectively. Considering the alkalimetric titration curves, reported in [68SIL/SIM] for  $I = 0.1 \text{ M KNO}_3$ , it can be concluded that always the formation of  $\text{UO}_2(\text{Hedta})^-$  and  $(\text{UO}_2)_2\text{edta}(\text{aq})$  is observed in the beginning of the titration at low pH, and, after a clear point of inflection, all their hydrolytic products with more or less uncertain compositions are formed by strong base addition. Because of this behaviour, the calculation of the formation constants of the two species  $\text{UO}_2(\text{Hedta})^-$  and  $(\text{UO}_2)_2\text{edta}(\text{aq})$  can be done separately, by algebraic or by more complex methods of calculation, and the other experimental data are then used to obtain the remaining equilibrium constants, as shown in [70SIL/SIM]. Hence, it can be expected that for the two species  $\text{UO}_2(\text{Hedta})^-$  and  $(\text{UO}_2)_2\text{edta}(\text{aq})$  the same stability constants should be obtained from a given set of experimental data, irrespective of the method used for their calculation.

The effective experimental titration data for  $I = 1.0 \text{ M KNO}_3$  have not been reported in [68SIL/SIM], [70SIL/SIM] or [84GON/MOT], but it is expected that the titrations began near pH 1 because of the large concentrations of the components. Under these conditions, the presence of  $\text{H}_5\text{edta}^+$  and  $\text{H}_6\text{edta}^{2+}$  has to be considered in the calculations, which has not been done neither by [68SIL/SIM] nor by [84GON/MOT]. Furthermore, for refining the stability constants of U(VI) edta hydrolysis and polymeric species only data for  $(\text{UO}_2)_2(\text{OH})_2^{2+}$ ,  $(\text{UO}_2)_3(\text{OH})_4^{2+}$  and  $(\text{UO}_2)_3(\text{OH})_5^+$ , have been included in the calculations, but the monomeric species  $\text{UO}_2\text{OH}^+$  and  $\text{UO}_2(\text{OH})_2(\text{aq})$  were ignored.

Considering all these ambiguities and shortcomings, neither the original data of [68SIL/SIM] nor the new refinement of these data by [84GON/MOT] has been further considered in this review.

#### [84RAO/CHO]

The formation constants for  $\text{NpO}_2\text{ox}(\text{aq})$  and  $\text{NpO}_2(\text{ox})_2^{2-}$  were required for the interpretation of kinetic data on the reduction of Np(VI) by dicarboxylic acids. Although it is not written in this publication how the tabulated values were obtained, they were in fact

estimated using the model by Münze [72MUN], [76CHO/UNR], and they are not considered in this review.

#### [84REE/DAN]

Distribution of  $^{237}\text{Np}$  ( $3 \times 10^{-7}$  M) between 0.1 M  $\text{NaClO}_4$  solution and the cation exchange resin AG50WX8 of 100 – 200 mesh, in the sodium form, was studied at 10, 25 and  $35^\circ\text{C}$  with and without citric acid present. The pH of the solution was adjusted to be 7.5 by means of  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  (total phosphate concentrations between  $10^{-3}$  and  $10^{-2}$  M), and the concentration of citric acid was varied from  $c_L = 2 \times 10^{-6}$  M to  $10^{-4}$  M. The relation,

$$\log \left( \frac{K_d^o}{K_d} - 1 - \sum_i \beta_i [L_i] \right) = \log_{10} \beta_1 (\text{cit}) + \log_{10} [\text{cit}^{3-}],$$

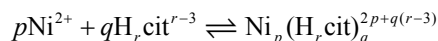
was used to obtain the constant ( $\log_{10} \beta_1$ ) for  $\text{NpO}_2^+ + \text{cit}^{3-} \rightleftharpoons \text{NpO}_2(\text{cit})^{2-}$ , where  $\sum_i \beta_i [L_i]$  expresses the effect of hydroxide and phosphate complexes. The stability constants of  $\text{NpO}_2(\text{cit})^{2-}$  were obtained to be  $\log_{10} \beta_1 = (4.70 \pm 0.53)$ ,  $(4.84 \pm 0.72)$  and  $(4.93 \pm 0.11)$  at 10, 22 and  $35^\circ\text{C}$ , respectively. These values and those also reported for phthalate complexes in this report seem too high as compared with other carboxylate complexes of Np(V) [92TOC/INO], [89STO/CAC], though the reason is not clear. These values are not accepted in this review.

#### [84REK/GAL]

This paper reports calorimetric data on the heats of neutralisation of pH-buffer solutions containing citrate. No enthalpies of reaction are reported.

#### [84SAL/DEV]

The nuclear magnetic relaxation efficiency of  $\text{Ni}^{2+}$  in the presence of citric acid (0.1 ~ 1.0 M) was obtained as a function of pH. The citrate protonation constants,  $\log_{10} K_{(H)} = 11.6$  ( $\log_{10} K_{0(H)} = 5.40 \pm 0.10$ ),  $(4.15 \pm 0.08)$  and  $(2.86 \pm 0.06)$  at  $0.5 < I < 3$  obtained by the authors were used in the calculation. The constants for the reaction:



were obtained to be  $\log_{10} \beta (\text{Ni}(\text{Hcit}), \text{aq}) = 2.6$ ,  $\log_{10} \beta (\text{Ni}(\text{cit})^-) = 4.6$ ,  $\log_{10} \beta (\text{Ni}_2(\text{cit})(\text{H}_{-1}\text{cit})^{3-}) = 14.8$ ,  $\log_{10} \beta (\text{Ni}_2(\text{H}_{-1}\text{cit})_2^{4-}) = 17.7$ ,  $\log_{10} \beta (\text{Ni}(\text{H}_2\text{cit})_2, \text{aq}) = 1.8$ ,  $\log_{10} \beta (\text{Ni}(\text{Hcit})_2^{2-}) = 4.3$ ,  $\log_{10} \beta (\text{Ni}(\text{cit})_2^{4-}) = 8.0$ , and  $\log_{10} \beta (\text{Ni}(\text{cit})_3^{7-}) = 8.8$ . Experimental conditions such as ionic strength, temperature, pH to p<sub>c</sub>H correction are not given in the paper. Also, many improbable species are included. Thus, this review does not accept these values.

#### [84SIR]

The stability constants of ternary U(VI)-oxalate-nitriloacetate complexes and the binary U(VI) oxalate complexes were determined by electrophoresis at  $40^\circ\text{C}$  and  $I = 0.1$  M

NaClO<sub>4</sub>. The stability constant for  $\text{UO}_2(\text{ox})_2^{2-}$  was calculated to be  $10^{6.47}$ . This value, as well as the constants for the ternary complexes, is questionable, because the experiments were conducted at pH = 10 and it appears that the hydrolysis of U(VI) was not taken into consideration. Therefore, the stability constants from this study are not accepted by this review.

#### [\[85DAN/RIG\]](#)

The authors reported a potentiometric study on the protonation and alkali metal complexation of some ligands, including  $\text{edta}^{4-}$ , at temperatures between 10 and 45°C. Several ionic media were used: LiNO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub>, tetramethylammonium bromide (Me<sub>4</sub>NBr), tetraethylammonium bromide and iodide (Et<sub>4</sub>NBr and Et<sub>4</sub>NI), and tetrapropylammonium bromide (Pr<sub>4</sub>NBr).

Daniele *et al.* reported the first protonation constant of  $\text{edta}^{4-}$  in all the ionic media studied by them, as well as the second protonation constant in Li, Na and K nitrates and in Pr<sub>4</sub>NBr. As an alternative data interpretation, Daniele *et al.* assumed that activity coefficients depend only on ionic strength and temperature, which is in disagreement with the SIT model adopted by this review, *cf.* Appendix B. Using this assumption and comparing the protonation constants obtained in Pr<sub>4</sub>N<sup>+</sup> media with those determined in other background salts, Daniele *et al.* obtained complexation constants of  $\text{edta}^{4-}$  with not only alkali metals (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>), but also with Me<sub>4</sub>N<sup>+</sup> and Et<sub>4</sub>N<sup>+</sup>. Overall protonation constants,  $\log_{10}\beta_r(\text{edta}^{4-} + r \text{H}^+ \rightleftharpoons \text{H}_r\text{edta}^{(r-4)})$  corrected for complexation with background cations were also reported (*supplementary material to [85DAN/RIG]*). The former type of protonation constants, that may be referred to as “conditional”, were included in the review procedure (Section VIII.3). The protonation constants “corrected for complexation” are identical to the “conditional” constants in Pr<sub>4</sub>NBr and were included as such in this review (*cf.* Table VIII-2).

Unfortunately, the authors used 1 M KOH as titrant for all potentiometric titrations, even when Li, Na, or tetraalkylammonium salts were used as ionic media. This introduced a systematic error because of the complex formation between  $\text{edta}^{4-}$  and K<sup>+</sup>. The magnitude of this error in the first protonation constant is expected to be  $\leq 0.06$  log<sub>10</sub>-units (*cf.* Section V.3.3, Eq.(V.52), with  $K_M \approx 8 \text{ M}^{-1}$ ,  $[\text{K}^+] \approx 0.02 \text{ M}$ ,  $I = 0.1 \text{ M}$ ). Because of this, in the review procedure the reported values of  $\log_{10}K_1$  in Me<sub>4</sub>NBr, Et<sub>4</sub>NBr and Pr<sub>4</sub>NBr media are corrected for these small effects, and all values of  $\log_{10}K_1$  in ionic media without K<sup>+</sup> are assigned an uncertainty of  $\pm 0.1$ .

Due to the large electrical charge of  $\text{edta}^{4-}$ , this ligand may have a large contribution to the ionic strength, and therefore equilibrium constants at  $I < 0.1 \text{ M}$  in [\[85DAN/RIG\]](#) were not considered in this review.

The enthalpy and entropy changes reported by Daniele *et al.* for the protonation of  $\text{edta}^{4-}$  correspond to the equilibrium constants determined in Pr<sub>4</sub>NBr, except for the amount of K<sup>+</sup> introduced with the titrant (1 to 16 mM). The original “conditional”

protonation constants were fitted in this review to the constant heat capacity function, and the results are listed in Table VIII-9 (Section VIII.3.8). The data in  $\text{LiNO}_3$ , which are discrepant with the results reported in [74VAS/KOC] were not included in the review procedure, see further the discussion of [74VAS/KOC] in this Appendix and Section VIII.3.8.

As mentioned above, Daniele *et al.* calculated complexation constants between  $\text{edta}^{4-}$  and  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Me}_4\text{N}^+$ , and  $\text{Et}_4\text{N}^+$  by comparing the protonation constants obtained in  $\text{Pr}_4\text{N}^+$  media with those determined with the other background salts. However, large uncertainties are associated with this method, because these formation constants also include differences in activity factors between the different ionic media. Because of the systematic errors due to the use of KOH as titrant, and the uncertainty in the method of analysis, these complex-formation constants are not considered in this review. Similarly, the  $\Delta_r H_m$  values for alkali-metal complexation obtained from the temperature variation of the corresponding alkali metal formation constants are also discarded.

#### [85DAN/ROB]

The authors reported a potentiometric study on the complex formation at 25°C between lanthanum(III) and the ligands acetate, malonate and citrate. Protonation constants were obtained in  $\text{NaNO}_3$  and in an unspecified tetraethylammonium “salt”. However, the authors used 0.5 M NaOH as titrant in all cases. Equilibrium constants for  $\text{Na}^+$  complex formation were obtained by comparing the protonation constants in the two ionic media. The reported protonation constants were corrected for  $\text{Na}^+$  complex formation and are therefore not considered in this review.

#### [85MAR/EVA]

This paper is discussed with [86MAR/EVA].

#### [85RED/RAO]

The authors report a potentiometric study at 35°C on the protonation of oxalate (among other ligands). The main topic of this study was the investigation of ternary metal-cytidine complexes. Protonation constants were determined in 0.1 M  $\text{KNO}_3$  but the authors used standard NaOH as titrant and hence, systematic errors were introduced in the corresponding protonation constants due to a varying ionic medium. In addition to this ambiguity concerning the ionic medium some other experimental or computational errors seem to have affected the results, as the reported oxalate protonation constants are significantly discrepant to the results of all other similar studies. Especially the second protonation constant reported in [85RED/RAO] is one order of magnitude higher than the ones determined in other studies [69CON/MAR], [80GRA/MUS], [84JOH/JON]. No experimental data are provided in [85RED/RAO] which would allow to check and to re-evaluate their results. The results of this study are not credited in this review.

In addition to the equilibrium constants for ternary metal ion complexes, the stability constants of some binary complexes were also determined, including Mg(ox)(aq), Ca(ox)(aq) and Ni(ox)(aq). In the case of Ca(ox)(aq) the solubility of calcium oxalate certainly was exceeded in the experiments, as the authors report that  $10^{-3}$  M solutions were used for both, metal and ligand. The reported constants infer that Ca(ox)(aq) is more stable than Mg(ox)(aq), which most probably is an artefact of calcium oxalate precipitation processes during the measurements. No experimental data are provided in [85RED/RAO] which would allow to check and to re-evaluate their results. Hence, the results of this study are not credited in this review.

#### [85RIZ/ANT]

ESCA core line spectra was obtained for citrate, dipicolinate and tripolyphosphate salts. In their study, Rizkalla *et al.* obtained protonation constants of citric acid and stability constants of the complexes of calcium and magnesium with citrate by potentiometric titration at  $I = 0.10$  M NaCl and 298 K. The values reported are,  $\log_{10} K_{(H)} = 5.48, 4.31, 3.02$  for protonation and  $\log_{10} \beta_1 (M^{2+} + H_r \text{cit}^{r-3} \rightleftharpoons M(H_r \text{cit})^{r-1}) = (3.46 \pm 0.06)$  for Mg(cit)<sup>-</sup>,  $(2.13 \pm 0.10)$  for Mg(Hcit)(aq),  $(3.43 \pm 0.04)$  for Ca(cit)<sup>-</sup>, and  $(2.80 \pm 0.20)$  for Ca(Hcit)(aq). In the experiment, the pH was measured with a combined glass-calomel electrode. Rizkalla *et al.* considered this value gave hydrogen ion activity and converted it into the concentration scale using the value of 0.782 as the activity coefficient. This procedure may have introduced some error due to the liquid junction potential. The value of  $\log_{10} K_{(H)}$  seems smaller as compared with the selected value in this review. Since the value of  $\log_{10} K_{(H)}$  seriously affects the calculated values of stability constants, this review does not accept these values.

#### [85ROB/STE]

Protonation constants and the formation of ammonium complexes for different dicarboxylic acids at 25°C and  $0.02 < I < 0.95$  are reported in [85ROB/STE]. However, the nature of the ammonium salt used as background electrolyte, *i.e.*, the anion X, is not revealed in the short paper of [85ROB/STE]. For that reason, the data measured in NH<sub>4</sub>X were not considered in this review. In addition, a few data measured in tetraethylammonium iodide are reported in [85ROB/STE] which are included in this review.

#### [85SEV]

The spectra of  $2.532 \times 10^{-4}$  M Np(V) in the presence of a 100-fold excess of citric acid were measured using a 5.0 cm cell over the pH range of 1 – 12 keeping the ionic strength constant ( $I \cong 0.05$ ). This paper gives useful information on the complex species. Speciation was conducted by plotting:

$$\log_{10} b_{986} = \log_{10} \frac{[\text{NpO}_2\text{H}_i\text{cit}^{i-2}]}{[\text{NpO}_2^+][\text{Hcit}^{2-}]} + (i-1)\text{pH} = \log_{10} \frac{(\bar{\varepsilon} - \varepsilon_M)}{(\varepsilon'_i - \bar{\varepsilon})[\text{Hcit}^{2-}]}$$

against pH, where  $\bar{\varepsilon}$  is the average molar absorption coefficient at 986 nm,  $\varepsilon_M$  is the molar absorption coefficient of  $\text{NpO}_2^+$  at 986 nm,  $\varepsilon'_i$  is the molar absorption coefficient equal to the average value of  $\bar{\varepsilon}$  over the pH range  $\cong 4.7 - 8.5$  at 986 nm ( $\varepsilon'_i = 221.2 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ ). From the slopes (0 at pH 3 – 5 and 1 at pH > 5), the predominant complex species were assigned to be  $\text{NpO}_2(\text{Hcit})^-$  at pH 3 – 5 and  $\text{NpO}_2(\text{cit})^{2-}$  at pH > 5. By using the equation,

$$\bar{\varepsilon} = \frac{\varepsilon_M + \varepsilon_{\text{MHcit}} \beta_{1(\text{Hcit})} \cdot [\text{Hcit}^{2-}] + \varepsilon_{\text{Mcit}} \beta_{1(\text{cit})} \cdot [\text{cit}^{3-}]}{1 + \beta_{1(\text{Hcit})} \cdot [\text{Hcit}^{2-}] + \beta_{1(\text{cit})} \cdot [\text{cit}^{3-}]},$$

the constants for  $\text{NpO}_2^+ + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{NpO}_2(\text{H}_r\text{cit})^{r-2}$  were calculated by the method of successive approximation, for which the graphically averaged values of  $\bar{\varepsilon}$  for the wavelengths 981 and 986 nm were used. The values are  $\log_{10} \beta_{1(\text{Hcit})} = (3.08 \pm 0.33) \times 10^2$  for  $\text{NpO}_2(\text{Hcit})^-$  and  $\log_{10} \beta_{1(\text{cit})} = (7.41 \pm 0.89) \times 10^2$  for  $\text{NpO}_2(\text{cit})^{2-}$  (corresponding to  $\log_{10} \beta_{1(\text{Hcit})} = 2.49$  and  $\log_{10} \beta_{1(\text{cit})} = 2.87$ ), with  $\varepsilon_{\text{MHcit}} = 188.4$  and  $\varepsilon_{\text{Mcit}} = 128.0$  at 981 nm and  $\varepsilon_{\text{MHcit}} = 210.1$  and  $\varepsilon_{\text{Mcit}} = 227.2 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  at 986 nm. The difference from the value of  $\varepsilon_{\text{Mcit}} = 205 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  at 985.5 nm reported by [90RIZ/NEC] may originate from the poor resolution of the spectrophotometer since the paper gives  $\varepsilon_M = 223.5 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  at 981 nm with FWHM = 9.1 nm as compared with  $\varepsilon_M = 398 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  at 980.4 nm with FWHM = 7.1 nm reported by [90RIZ/NEC]. Unfortunately, the author used the protonation constants of  $\log_{10} K_{(\text{H})} = 5.40, 4.74$  and  $3.06$ , among which  $\log_{10} K_{2(\text{H})}$  is too large as compared to the value selected in this review (4.48). Since this will seriously affect the estimated  $\log_{10} \beta_{1(\text{Hcit})}$  and  $\log_{10} \beta_{1(\text{cit})}$ , this review does not accept these values. Although the author claimed the formation of  $\text{NpO}_2(\text{OH})(\text{cit})^{3-}$  at pH > 9 (for the absorption band with a maximum at 1007 nm), this review does not accept the formation constant of  $\text{NpO}_2(\text{OH})(\text{cit})^{3-}$  reported, since the hydrolysis of  $\text{NpO}_2^+$  itself (*i.e.*, the formation of  $\text{NpO}_2(\text{OH})_i^{1-i}$ ) must have seriously affected the result at pH > 9.

#### [85SHI]

The reaction of Am(VI) with 0.16 ~ 32 mM  $\text{H}_2\text{Ox}$  in 0.03 ~ 1.0 M perchloric acid was investigated. In solutions with excess  $\text{H}_2\text{Ox}$ , Am(VI) was found to be reduced by oxalate and mainly to disproportionate into Am(V) and Am(III).

#### [85VAS/KOZ]

The heat of reaction of aqueous millimolar ( $3 - 5 \times 10^{-3} \text{ M}$ ) solutions of  $\text{Me}(\text{II})(\text{edta})^{2-}$  (Me = Ni, Cu, Zn, Cd) with KOH solutions (0, 0.1, 0.2 and 0.3 M) in a background of  $\text{KNO}_3$  (0.75 – 1.5 M) has been measured calorimetrically. In the case of Ni only measurements at  $I = 1.5 \text{ M}$  and  $25^\circ\text{C}$  were carried out. The results could allow the obtainment of the thermodynamic characteristics of the reaction  $\text{Ni}(\text{edta})^{2-} + \text{OH}^- \rightleftharpoons \text{Ni}(\text{edta})\text{OH}^{3-}$  under these conditions. However, the large change in the KOH concentration during the experiments is considered as outside the range of a constant back-

ground medium needed for a reliable determination of an equilibrium constant.

#### [\[85VEN/SWA\]](#)

The authors studied the ternary complexes of U(VI) containing phthalic acid and other ligands including oxalic acid at 25°C and  $I = 0.1$  M KNO<sub>3</sub>. The binary complexes of U(VI) with oxalate were studied by potentiometry. No details of the experiments were given in the paper. The dissociation constants of oxalic acid were calculated but not provided. The stability constants of UO<sub>2</sub>ox(aq) and UO<sub>2</sub>(ox)<sub>2</sub><sup>2-</sup>, as well as the constants for the ternary complexes, from this study are not accepted by this review.

#### [\[86CRU/WAT\]](#)

The authors reported the equilibrium constants and enthalpy changes for the protonation of citrate in 1 M [Cl<sup>-</sup>] at 25°C. Potentiometric titrations were performed with [cit<sup>3-</sup>]<sub>TOT</sub> = 0.02 M (Fig. 1 in [\[86CRU/WAT\]](#)).

In the calorimetric measurements a much larger concentration of citrate was used: a solution containing 0.1 M Na<sub>3</sub>cit in 1 M (Na)Cl was titrated with 1 M HCl. Therefore, along the calorimetric titration [Na<sup>+</sup>]<sub>TOT</sub> was held constant to 1.3 M, while the stoichiometric ionic strength varied from 1.6 to 1.3 M. These disparities in the ionic media introduced systematic errors of unknown magnitude in the protonation enthalpies reported in [\[86CRU/WAT\]](#). These errors are of two types:

- the corrections made for the heats of dilution (in this case mixing) were slightly inadequate, and
- the dependence of  $\Delta_r H_m$  with ionic strength contributed to the measured heat evolution. A later study by Bénézeth *et al.* [\[97BEN/PAL\]](#) indicates for example that for the first protonation constant in  $\approx 1$  M NaCl solutions,  $(\partial \Delta_r H_m / \partial I) \approx (1.4 \pm 0.9) \text{ kJ} \cdot \text{dm}^3 \cdot \text{mol}^{-2}$ .

The uncertainties in the values of  $\Delta_r H_m$  reported in [\[86CRU/WAT\]](#) are therefore assigned to be  $\pm 2 \text{ kJ} \cdot \text{mol}^{-1}$ .

#### [\[86MAR/EVA\]](#)

In this, and in a previous paper [\[85MAR/EVA\]](#), Marini *et al.* described a twin-cell differential titration calorimeter. The experimental set-up was applied to the determination of the protonation constants of edta<sup>4-</sup> and the stability of its Ca<sup>2+</sup> complex.

In both papers 2 cm<sup>3</sup> of a 10 mM edta<sup>4-</sup>, 0.2 M KCl solution was titrated at 25°C with either 1 M KOH, 1 M HCl or 1 M CaCl<sub>2</sub>. Volume increments of 10% were common according to the authors, indicating that the ionic strength changed during the titrations from 0.2 to at least 0.3 M, potentially introducing systematic errors in the reported values. Because of this, the data reported in [\[85MAR/EVA\]](#), [\[86MAR/EVA\]](#) are not considered by this review.



[\[86MAT/PAS\]](#)

The results of research of the effect of oxalate ions on Zr(IV) species in aqueous solutions (pH = 0 to 3) are reported. No constants are given.

[\[86RED/RAO\]](#)

The same data already published in [\[85RED/RAO\]](#) are presented again in this paper. See discussion of [\[85RED/RAO\]](#).

[\[86VAS/KOZ\]](#)

The reactions of Ni(II), Cu(II), Zn(II), and Cd(II) – edta ( $5 \times 10^{-3}$  M) with glycine solution (0 – 0.4 M) have been studied calorimetrically at 25°C and ionic strength 1.5 M (KNO<sub>3</sub>) in the pH range 10.5 – 12.0.

[\[87BER/VAS\]](#)

This paper describes a calorimetric methodology to determine equilibrium constants and enthalpy changes for complex formation. In the last paragraph, the authors mention that the methodology has been tested with systems previously studied in the literature, giving as a single example the system  $\text{edta}^{4-}\text{-Na}^+$ .

At ionic strengths 0.6 to 1, Bera *et al.* found  $\log_{10} K \approx 1$  and an enthalpy change of 84 kJ·mol<sup>-1</sup> for the formation of  $\text{Na}(\text{edta})^{3-}$ . Because of the lack of details on concentration ranges, background electrolyte, temperature, *etc.*, and because the authors indicate that the precision of the method is limited, these values are not considered in this review.

[\[87BLA/BER\]](#)

Formation constants of the magnesium and calcium complexes with glutamate, aspartate, glycinate, lactate, pyroglutamate, pyridoxine and citrate were determined by potentiometric titrations at  $I = 0.15$  M NaClO<sub>4</sub> and 37°C. Blaquière and Berthon used the reported protonation constants of  $\log_{10} K_{(\text{H})} = 5.539, 4.236, 2.869$  [\[78BER/MAY\]](#) to obtain their stability constants. The values of  $\log_{10} \beta'_{(i,j,k)}$  obtained for the complex  $\text{M}_i(\text{cit})_j(\text{H})_k$  where  $\beta'_{(i,j,k)} = [\text{M}_i(\text{cit})_j(\text{H})_k] / ([\text{M}^{2+}]^i [\text{cit}^{3-}]^j [\text{H}^+]^k)$  are:  $\log_{10} \beta'_{(1,1,2)} = (11.008 \pm 0.063)$ ,  $\log_{10} \beta'_{(1,1,1)} = (7.483 \pm 0.024)$ ,  $\log_{10} \beta'_{(1,1,0)} = (3.333 \pm 0.009)$ ,  $\log_{10} \beta'_{(1,2,1)} = (10.411 \pm 0.069)$ ,  $\log_{10} \beta'_{(1,2,0)} = (5.126 \pm 0.041)$ ,  $\log_{10} \beta'_{(2,2,-2)} = -(12.638 \pm 0.033)$  and  $\log_{10} \beta'_{(1,1,-2)} = -(18.468 \pm 0.015)$  for  $\text{Mg}^{2+}$ , and  $\log_{10} \beta'_{(1,1,2)} = (11.005 \pm 0.034)$ ,  $\log_{10} \beta'_{(1,1,1)} = (7.614 \pm 0.015)$ ,  $\log_{10} \beta'_{(1,1,0)} = (3.364 \pm 0.006)$ ,  $\log_{10} \beta'_{(1,2,0)} = (4.965 \pm 0.044)$ ,  $\log_{10} \beta'_{(1,1,-1)} = -(8.935 \pm 0.026)$  and  $\log_{10} \beta'_{(1,2,-2)} = -(16.808 \pm 0.023)$  for  $\text{Ca}^{2+}$ . For the monomeric species, these values correspond to  $\log_{10} \beta_1$  of the reaction,  $\text{M}^{2+} + \text{H}_r\text{cit}^{r-3} \rightleftharpoons \text{M}(\text{H}_r\text{cit})^{r-1}$ , as 1.233 for  $\text{Mg}(\text{H}_2\text{cit})^+$ , 1.944 for  $\text{Mg}(\text{Hcit})(\text{aq})$ , 3.333 for  $\text{Mg}(\text{cit})^-$ , 1.230 for  $\text{Ca}(\text{H}_2\text{cit})^+$ , 2.075 for  $\text{Ca}(\text{Hcit})(\text{aq})$  and 3.364 for  $\text{Ca}(\text{cit})^-$ . The disagreement in the speciation and stability constants of the

dimeric species between magnesium and calcium, and their very small contribution to the overall data fit raise some doubts about the existence of these species. In the pH measurement, although the authors described the calibration of the pH meter reading to  $-\log_{10} [\text{H}^+]$ , the possibility of  $\text{KClO}_4$  precipitation which may have occurred at the liquid junction of the reference electrode and the 0.15 M  $\text{NaClO}_4$  solution was not considered. Thus, considering the possible errors in the measurement and calculation, this review accepts the values for  $\text{M}(\text{H}_2\text{cit})^+$ ,  $\text{M}(\text{Hcit})\text{(aq)}$  and  $\text{M}(\text{cit})^-$  with assigning larger uncertainties as  $\log_{10} \beta_1 = (1.23 \pm 0.4)$  for  $\text{Mg}(\text{H}_2\text{cit})^+$ ,  $(1.94 \pm 0.20)$  for  $\text{Mg}(\text{Hcit})\text{(aq)}$ ,  $(3.33 \pm 0.10)$  for  $\text{Mg}(\text{cit})^-$ ,  $(1.23 \pm 0.4)$  for  $\text{Ca}(\text{H}_2\text{cit})^+$ ,  $(2.08 \pm 0.20)$  for  $\text{Ca}(\text{Hcit})\text{(aq)}$  and  $(3.36 \pm 0.10)$  for  $\text{Ca}(\text{cit})^-$ .

#### [\[87CAC/NEC\]](#)

This is a short communication where several experimental details are missing. The authors studied the interaction of neptunyl(V) with simple aliphatic di-carboxylic acids using VIS-NIR spectroscopy. Experimental conditions were: ionic strength 1.0 M ( $\text{NaClO}_4$ ), pH = 6.0 and  $(23 \pm 2)^\circ\text{C}$ . The results for oxalate complexes of  $\text{Np(V)}$  were:  $\log_{10} \beta_1 = (3.52 \pm 0.06)$  and  $\log_{10} \beta_2 = (6.09 \pm 0.06)$ . Similar results were published later by the same authors on the same system in a somewhat more detailed publication [\[89STO/CAC\]](#). The data reported in this publication is abandoned in favour of the later publication.

#### [\[87JOA/BIG\]](#)

A solvent extraction method is used to determine the complexation of zirconium and hafnium with carbonate and edta at ionic strength 1.0 and 2.5 M  $\text{NH}_4\text{NO}_3$ . The temperature is not reported. The experiments in the zirconium edta system have been carried out at pH 9.9 and the authors assume that  $\text{Zr}(\text{OH})^{2+}$  is the only hydrolytic species of zirconium under these conditions. This arbitrary assumption is at variance with all knowledge of higher zirconium hydrolysis products under alkaline conditions. The experimental results are reported as plots of distribution coefficients *versus* the concentration of the completely dissociated ligand  $[\text{edta}^{4-}]$ . The edta protonation constants used to calculate  $[\text{edta}^{4-}]$  from the analytical edta concentrations are not given in [\[87JOA/BIG\]](#). Hence, the data of [\[87JOA/BIG\]](#) are discarded because there is no way to re-evaluate the experimental data using edta protonation constants selected in this review and proper Zr hydrolysis constants.

#### [\[87LIN/GU\]](#)

The heat of the stepwise protonation of oxalate:



has been measured in 1 M  $\text{KNO}_3$  at  $25^\circ\text{C}$  by a conduction calorimeter. According to

Table 2 in [87LIN/GU] the initial pH of the solutions ranged between 6.2 and 6.4, and the final pH was found in the range 2.3 to 2.7. The results are reported as  $\Delta_r H_m$  (A.94) =  $(2.71 \pm 0.02)$  kJ·mol<sup>-1</sup> and  $\Delta_r H_m$  (A.95) =  $(7.80 \pm 1.47)$  kJ·mol<sup>-1</sup>. Within the pH range explored in the experiments of [87LIN/GU] the second protonation step of oxalate is a very minor effect and thus, the value  $\Delta_r H_m$  (A.95) derived for the second protonation enthalpy is a mere error absorber in the data fitting routine than a thermodynamic quantity. This latter value is not credited in this review. Considering other reliable calorimetric measurements discussed in this review, and the ambiguity due fitting an additional error absorber ( $\Delta_r H_m$  (A.95)) to the experimental data, an uncertainty of  $\Delta_r H_m$  (A.94) =  $(2.7 \pm 0.8)$  kJ·mol<sup>-1</sup> seems appropriate.

Note that the enthalpy values given in this paper refer to the stepwise protonation of oxalate, as indicated above, although the corresponding equilibrium constant  $K_1$  and  $K_2$  are defined by the authors as the stepwise dissociation constants of oxalic acid.

#### [87PAZ/KRI]

Solubility of  $\text{Am}_2(\text{ox})_3 \cdot 7\text{H}_2\text{O}$  (composition was determined by chemical analysis) was determined at  $(25 \pm 0.2)^\circ\text{C}$  as a function of oxalate concentration. The ionic strength was not maintained constant but calculated from the estimated concentrations of various species of americium and oxalate. The solubility product was recalculated using the data in [60LEB/PIR2] and the authors obtained a relationship between the solubility product and the ionic strength as  $\log_{10} K_{sp} = 13.8 I - 29.38$ . For each data point,  $[\text{H}^+]$  was calculated from the measured pH using the equation:

$$-\log_{10} \gamma_{\text{H}^+} = \frac{0.5063 \sqrt{I}}{1 + 1.5100\sqrt{I}} - 0.2395 I.$$

By using this value and the concentrations of other species, “concentration constants” were obtained to be:

$$\begin{aligned} \beta_1 &= 7.8 \times 10^6 & \text{for} & \quad \text{Am}^{3+} + \text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})^+, \\ \beta_2 &= 5.4 \times 10^9 & \text{for} & \quad \text{Am}^{3+} + 2\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_2^-, \\ \beta_3 &= 3.8 \times 10^{11} & \text{for} & \quad \text{Am}^{3+} + 3\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_3^{3-}, \text{ and} \\ \beta_{1(\text{Hox})} &= 4.4 \times 10^4 & \text{for} & \quad \text{Am}^{3+} + \text{Hox}^- \rightleftharpoons \text{Am}(\text{Hox})^{2+}. \end{aligned}$$

In Figure 1 of the paper which shows the obtained relation between  $\log_{10}[\text{Am}^{3+}]_{\text{total}}$  and  $\log_{10}[\text{ox}^{2-}]$ ,  $[\text{ox}^{2-}]$  in the x-axis is somewhat unclear whether this indicates the added concentration of oxalate,  $[\text{ox}^{2-}]_{\text{added}}$ , or the calculated equilibrium concentration of free  $\text{ox}^{2-}$ ,  $[\text{ox}^{2-}]$ , or the total concentration of oxalate in the solution,  $[\text{ox}^{2-}]_{\text{total}}$ . The mass balance,  $[\text{ox}^{2-}]_{\text{total}} = [\text{ox}^{2-}]_{\text{added}} + (3/2)[\text{Am}^{3+}]_{\text{T}}$  should be more clearly treated. The ionic strength was not maintained constant and the calculation of “concentration constants” which are constant at variable ionic strength cannot be accepted. This paper is not accepted in this review.

[\[87RAY/DUF\]](#)

To estimate the behaviour of plutonium in the environment, Th(IV) was selected as a chemical analogue of Pu(IV) and the complex formation with citrate was investigated by potentiometric titration. Solutions containing 2.2 – 3.5 mM  $\text{Th}^{4+}$  and 2.3 – 10.1 mM citric acid in 0.1 M NaCl were titrated at 25°C. Measured pH was converted to  $-\log_{10} [\text{H}^+]$ , and the analysis of the formation curve (the average number of protons bound per ligand against  $-\log_{10} [\text{H}^+]$ ) gave the values of protonation constants of citrate as  $\log_{10} K_{(\text{H})} = 5.650, 4.323$  and  $2.910$ . Similarly, the formation curve (the average number of ligand bound per metal against  $-\log_{10} [\text{cit}^{3-}]$ ) was analysed. The hydrolysis data for  $\text{ThOH}^{3+}$  and  $\text{Th}(\text{OH})_2^{2+}$  from [\[86AHR\]](#) for 1 M  $\text{ClO}_4^-$ , and for  $\text{Th}_2(\text{OH})_2^{6+}$  and  $\text{Th}_2(\text{OH})_3^{5+}$  from [\[76BAE/MES\]](#) for 0.5 M  $\text{Cl}^-$  were included in the analysis. The formation constants  $\log_{10} \beta_{p,q,r}$  for the reaction  $p\text{Th}^{4+} + q\text{cit}^{3-} + r\text{H}^+ \rightleftharpoons \text{Th}_p(\text{cit})_q\text{H}_r^{(4p-3q+r)}$  were obtained to be:  $\log_{10} \beta_{1,1,0} = (11.611 \pm 0.039)$ ,  $\log_{10} \beta_{1,2,0} = (21.139 \pm 0.057)$ ,  $\log_{10} \beta_{1,2,1} = (23.637 \pm 0.035)$ ,  $\log_{10} \beta_{1,2,-2} = (12.572 \pm 0.077)$ ,  $\log_{10} \beta_{1,3,0} = (26.113 \pm 0.075)$  and  $\log_{10} \beta_{1,3,1} = (30.374 \pm 0.069)$ . Among these species, the species (1, 2, 1) and (1, 3, 1) seem chemically unreasonable because one citrate in the complex is in the protonated form (Hcit) while other citrates are in the deprotonated form (cit). This may happen only when the electronic states of two or three citrates in the complex are very closely conjugated via the bonds between thorium and citrates. These species may be an artefact of the use of improper values of hydrolysis data since they are the values at different ionic strengths. Moreover, data for the complex formation of  $\text{Th}^{4+}$  with chloride are considered necessary for the analysis. This review does not accept the reported values in this paper.

[\[87SUE/HU\]](#)

The authors determined the solubility of Pu(III) oxalate at  $(21 \pm 0.5)$  and  $(50 \pm 0.5)^\circ\text{C}$  in nitrate media. In the reaction vessel oxalic acid was added to a Pu(III) solution containing  $(\text{Na,H})\text{NO}_3$  as ionic medium as well as 0.1 M hydrazine ( $\text{N}_2\text{H}_4$ ) and 0.2 M hydroxylamine nitrate ( $\text{NH}_3\text{OHNO}_3$ ) as reductants under  $\text{N}_2$  bubbling. The authors checked that no significant Pu(IV) was present in the solutions with solvent extraction using TTA in xylene. For the experiments at  $[\text{H}^+]_{\text{TOT}} \leq 2$  M the ionic strength was kept constant to  $I = 2.3$  M by the addition of  $\text{NaNO}_3$ . The experiments in 3 M  $\text{HNO}_3$  had  $I = 3.3$  M.

The solid that precipitated was aged for 50 hours, and Pu was analysed radiometrically in the equilibrium solution after centrifugation. The solid phase was not characterised. The data was reported as solubility of Pu(III) oxalate in  $\text{mg}\cdot\text{L}^{-1}$ , but as the chemical formula is not given in the paper, it is uncertain if the authors converted the analysed Pu-concentrations into solubility of  $\text{Pu}_2(\text{ox})_3$  or of  $\text{Pu}_2(\text{ox})_3\cdot 10\text{H}_2\text{O}$ . As a consequence there is an uncertainty of 0.1  $\log_{10}$ -units in the data.

[\[88CRO\]](#)

The interactions between Cd(II) and benzimidazole and between Ni(II) and oxalate were characterised by polarography. For Ni(II)-oxalate the values  $\log_{10} \beta_1 = 4.16$  and  $\log_{10} \beta_2 = 7.58$  were obtained using diffusion coefficients from the literature [\[81URB/BIE2\]](#), see also the corresponding discussion in this Appendix. Although some experimental details for the Cd(II) experiments are stated, *e.g.*, that a 50% v/v methanol-water solvent was used, for the Ni(II)-oxalate system it is implied that the same experimental conditions as in [\[81URB/BIE2\]](#) were used. No mention is made of the polarographic equipment, and the measurement of pH is not mentioned by the author. Because of the scarcity of details given for experimental conditions, the data presented by Crow [\[88CRO\]](#) is not included in the review process.

[\[88DAN/OST\]](#)

The equilibrium constants and  $\Delta_r H_m$  for  $\text{Ni}^{2+}$ -citrate complexation were listed in Table 2 in this paper. These values were calculated by re-analysing the experimental data reported in [\[84DAN/OST\]](#). Because of the shortcomings in the experimental procedures in [\[84DAN/OST\]](#), these values are not considered in this review.

[\[88EVS/SMI\]](#)

In this study of the complex formation of edta with Cu(II) and Ni(II), solutions of copper sulphate (0.02 – 0.04 M) and nickel chloride (0.024 – 0.048 M), acidified with concentrated HCl, and  $\text{Na}_2\text{H}_2\text{edta}$  (0.02 – 0.04 M) were used. These solutions were titrated with 0.5 M NaOH and the resulting pH changes measured with a glass electrode. No background electrolyte was used and hence, the ionic strength varied considerably during the titrations. The temperature of the measurements is not mentioned and no hint is given by [\[88EVS/SMI\]](#) about the calibration of the glass electrode. Auxiliary data (*i.e.*, for  $\text{Ni}(\text{edta})^{2-}$  and for the edta protonation constants) in their data analysis were taken from the literature without any concern about the validity for their experimental conditions. This review considers the measurements and reported results of [\[88EVS/SMI\]](#) as unreliable.

[\[88GHA/MAN\]](#)

In this study of the mixed complexes MAL, where M = Mg(II), Ca(II), Sr(II) and Cd(II), A = oxalic or citric acid, L = pyruvic acid, also the protonation constants of oxalate and citrate, and the stability constants of binary oxalate and citrate complexes were determined by potentiometric titration at  $I = 1.0$  M  $\text{NaClO}_4$  and 30°C (at least this temperature is given in the text, whereas in Table 1 of [\[88GHA/MAN\]](#) one finds “Temp. = 25°C”). The constants for  $\text{M} + \text{A} \rightleftharpoons \text{MA}$  were reported as  $\log_{10} \beta_1 = 2.65$  for  $\text{Mg}(\text{ox})(\text{aq})$ , 3.62 for  $\text{Mg}(\text{cit})^-$ , and 3.02 for  $\text{Ca}(\text{cit})^-$ . If and how the conversion of pH meter readings to  $-\log_{10}[\text{H}^+]$  was done is not described by [\[88GHA/MAN\]](#). In addition, the used background electrolyte can cause precipitation of  $\text{KClO}_4$  at the junction of the

KCl saturated reference electrode and the 1.0 M NaClO<sub>4</sub> solution. The protonation constants obtained in this study,  $\log_{10} K_1 = 3.45$  for oxalate, and  $\log_{10} K_n = 5.0, 3.70$  and  $2.25$  for citrate, are fairly different from those evaluated in this review. In summary, this review rejects all values reported by [\[88GHA/MAN\]](#).

#### [\[88NIK/DZY\]](#)

The authors studied the rate of oxidation of oxalic acid by Pu(IV) at 80-98°C in HNO<sub>3</sub> solutions. Spectrophotometric measurements showed that Pu(III) was not accumulated in the solutions. The rate of oxidation was determined by taking samples, separating Pu by hydroxide precipitation at pH = 10 – 11, acidification of the solution with H<sub>2</sub>SO<sub>4</sub> and titrating the oxalic acid with potassium permanganate at 60-70°C. The experiments were performed with solutions containing  $[H_2ox]_0 = 0.04$  M and  $[Pu(IV)]_{TOT} = 0.06$  M at  $I = 5$  M (H,Na)NO<sub>3</sub> and 98°C. From the  $[H^+]$ -dependence of the reaction rate the authors estimated  $\log_{10} K = (2.34 \pm 0.09)$  for  $Pu(IV) + H_2ox(aq) \rightleftharpoons Pu(ox)^{2+} + 2 H^+$ . In hydrochloric acid solutions the authors report  $\log_{10} K = (2.0 \pm 0.2)$ . These data have only qualitative value: the hydrolysis and nitrate complex formation of Pu(IV) at  $\approx 100^\circ C$  are not known. Furthermore, as the original data is not given in the paper, it is difficult to estimate the uncertainties in the reported equilibrium constants.

#### [\[89ABD/ALI\]](#)

The stability constants of U(VI) complexes with oxalate, citrate, phosphate and tartrate were determined in this study by an indirect spectroscopic method using ascorbic acid as the “indicator”. By monitoring the difference of absorbance at 410 nm between the solutions with and without the ligand(s), the stability constant was calculated. For oxalate,  $\log_{10} K = 3.22$  at  $t = (20 \pm 1)^\circ C$  and  $I = 0.05$  M. The data from this paper are rejected by this review because 1) the acidity of the solutions is not known; 2) it appears that only the 1:1 complex was considered; 3) no information on the protonation constants of oxalic acid was given in the paper; and 4) there might be systematic errors associated with the constant since it appears too low in comparison with the majority of the data for the same complex or the data of relevant systems such as lanthanide oxalate complexes or U(VI) complexes with other dicarboxylates in the literature.

#### [\[89ISH/ENO\]](#)

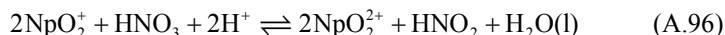
Ni(II)-citrate complexation equilibrium was studied in relation to the nickel plating. Changes in absorption spectra and pH buffer capacity were shown to be consistent with the formation of  $Ni(Hcit)(aq)$ ,  $Ni(cit)^-$ ,  $Ni(cit)_2^{4-}$  and  $Ni(H_2cit)^{2-}$  and the relevant equilibrium data [\[45BOB/JOR\]](#), [\[57PAT/PAN2\]](#), [\[59LI/LIN\]](#), [\[61ISH/YOK\]](#), [\[64CAM/OST\]](#), [\[75FIE/COB\]](#), [\[80HED/LID\]](#), [\[80STI/WIK\]](#). No new data are reported in the paper.

**[89MAN/APE]**

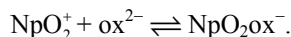
Formation constants of mixed metal complexes of citrate, malate and tartrate were obtained by potentiometric titration, where one metal is U(VI) and the other is Fe(III), Al(III), In(III) or Cu(II). For the citrate system, potentiometric titrations were conducted for (a) citric acid, (b) citric acid and uranyl 1:1 mixture, (c) citric acid and Fe(III) 1:1 mixture and (d) citric acid, uranyl and Fe(III) 2:1:1 mixture in 0.5 M KNO<sub>3</sub> at 298.1 K. From (a), protonation constants of citrate were obtained to be  $\log_{10} K_{(H)} = 6.30, 4.70$  and 3.13. The constants for the reaction,  $UO_2^{2+} + M^{z+} + 2H_3cit \rightleftharpoons UO_2M(H_{-1}cit)_2^{z-6} + 8H^+$  where  $M^{z+}$  is  $Fe^{3+}$ ,  $Al^{3+}$ ,  $In^{3+}$  or  $Cu^{2+}$  are reported to be 2.45 for Fe(III), 8.21 for Al(III), 11.30 for In(III) and  $-1.41$  for Cu(II). The pH electrodes were calibrated only by using potassium hydrogen phthalate and sodium borate buffers and the conversion of pH into  $-\log_{10} [H^+]$  was not conducted. The obtained protonation constants of citrate are considerably different from those selected in this review. Thus, the reported values are not accepted by this review.

**[89NIK/ION2]**

The equilibria and kinetics of isotope exchange ( $^{237}\text{Np}$  and  $^{239}\text{Np}$ ) in both oxidation states  $\text{Np}^V$  and  $\text{Np}^{VI}$  were studied in the presence of oxalic acid. The authors claimed to have studied the equilibrium:



spectrophotometrically at a wavelength of 980 nm, where only Np(V) adsorbs. The adsorbance data (eight experimental points in the absence of HNO<sub>2</sub>) were evaluated by the authors to give  $\log_{10} \beta_1 = 4.39$  for:



The experimental conditions were: 25°C,  $I = 1$  M (H,K)NO<sub>3</sub>,  $[H^+] = 0.1$  M,  $[\text{Np}^V] = 2.3 \times 10^{-4}$  M,  $[\text{H}_2\text{ox}]_{\text{Tot}} \leq 0.15$  M. However, the protonation constants for oxalate are not reported. Because of this, and given the scarcity of measurements, the reported equilibrium constant for the formation of  $\text{NpO}_2(\text{ox})^-$  is not considered by this review.

**[89POC]**

A computer method has been used for direct analysis of potentiometric (pH) curves of solutions containing equimolar amounts of the metal ion  $\text{Me}^{z+}$  and the protonated ligand  $\text{H}_n\text{L}$  titrated with strong base. The composition and stability constants of complexes of Pu(III), Nd(III) and Ca with citrate, edta, and other organic acids have been determined. The pH measurements have been performed at room temperature (20–22°C) by addition of 0.05 M KOH to solutions with the following initial compositions:  $10^{-3}$  M ligand acid,  $10^{-3}$  M metal chloride, and 0.1 M KCl. In the case of Pu(III),  $10^{-2}$  M NH<sub>3</sub>OHCl was also added to maintain plutonium in the trivalent state. For each system, *i.e.*, Pu(III)-citrate, Pu(III)-edta, Nd(III)-edta, Ca-edta, only one experiment has been conducted comprising ten pH measurements. In the case of edta this results in an average of

2.5 points for each of the four deprotonation steps.

The stability of the Ca-edta complex actually is determined by four pH measurements in a single experiment. The reported value  $\log_{10}\beta_1 = (10.73 \pm 0.10)$  for  $\text{Ca}(\text{edta})^{2-}$  agrees with other literature data obtained under similar conditions.

The results for the systems Pu(III)-edta and Nd(III)-edta are interpreted in terms of the complexes  $\text{Me}(\text{edta})^-$  and  $\text{Me}(\text{Hedta})(\text{aq})$ . The  $\log_{10} K$  values of the reaction  $\text{Me}(\text{edta})^- + \text{H}^+ \rightleftharpoons \text{Me}(\text{Hedta})(\text{aq})$  differ by more than one order of magnitude from other literature values. The same is true for  $\log_{10} \beta_1$  of the  $\text{Nd}(\text{edta})^-$  complex. The pH values measured in the presence of Pu(III) are lower than those measured in the presence of Nd(III) at the same degree of neutralisation (Table 1, columns 3 and 4 in [89POC]). This would indicate a larger stability of the  $\text{Pu}(\text{edta})^-$  complex. However, the reported stability constants (Table 2 in [89POC]) reveal the opposite behaviour:  $\log_{10} \beta_1 = (16.14 \pm 0.56)$  for  $\text{Pu}(\text{edta})^-$ , and  $\log_{10} \beta_1 = (17.89 \pm 1.08)$  for  $\text{Nd}(\text{edta})^-$ . No attempt was made in this review to resolve this inconsistency.

In the case of citrate the pH values measured in the presence of Pu(III) also are lower than those measured in the presence of Nd(III) at the same degree of neutralisation (Table 1, columns 1 and 2 in [89POC]). But in this case the reported stability constants reveal the expected relation with slightly stronger Pu(III) citrate complexes (Table 2 in [89POC]), even if the difference is only 0.2  $\log_{10}$ -units. The formation constants of Pu(III) citrate were obtained to be  $\log_{10} \beta_1 = (4.82 \pm 0.27)$  for  $\text{Pu}(\text{Hcit})^+$ ,  $\log_{10} \beta_1 = (6.71 \pm 0.25)$  for  $\text{Pu}(\text{cit})(\text{aq})$ , and  $\log_{10} \beta_1 = (15.33 \pm 0.30)$  for  $\text{Pu}(\text{H}_3\text{cit})^-$  using the following protonation constants of citrate:  $\log_{10} K_n$  ( $n = 3, 2, 1, 0$ ) = 3.0, 4.4, 6.1 and 16. The values of these protonation constants are somewhat different from those recommended in this review. Furthermore, the conversion of measured pH to  $-\log_{10}[\text{H}^+]$  was not conducted by [89POC].

In view of all these shortcomings the values reported by [89POC] have not been considered further in this review.

#### [89RIZ/SUL]

This calorimetric study of americium(III) complexation by amino carboxylates reports numbers of dubious quality: The enthalpy of  $\text{Am}(\text{edta})^-$  complex formation is reported in Table II of [89RIZ/SUL] as  $\Delta_r H_m = -22.9$  to  $-25.0$   $\text{kJ mol}^{-1}$ . However, in Table III and in the abstract of [89RIZ/SUL] a value of  $\Delta_r H_m = (23.9 \pm 1.0)$   $\text{kJ mol}^{-1}$  is found. An inspection of the original experimental data does not resolve this conflicting signs: A plot of observed heats (Fig. 1 of [89RIZ/SUL]) shows positive values for edta, whereas the same quantities are given as negative quantities in Table II of [89RIZ/SUL]. Also in the text no clue can be found whether the enthalpy should be positive or negative.

Other shortcomings are in the same line: An earlier calorimetric study of the Am – edta system [65FUG/CUN] is not mentioned in this paper. The stability constant



for  $\text{Am}(\text{edta})^-$  given in Table III of [89RIZ/SUL] is taken from the literature, according to footnote d of Table III. However, an inspection of the corresponding paper revealed that the cited reference does not report a stability constant for  $\text{Am}(\text{edta})^-$ . Remarkably, in a later publication of the same group [99CHE/CHO], which contains quite a complete summary of the literature values concerning the Am – edta system, the paper of [89RIZ/SUL] is not mentioned. This review does not credit the results of [89RIZ/SUL].

#### [89ROS/DIT]

This paper describes a study of complex equilibria between  $^{239}\text{Np}(\text{V})$  with a few ligands (oxalate, tartrate, sulphate) using a modified electromigration technique at  $(25.0 \pm 0.1)^\circ\text{C}$ . For oxalate the experiments were performed at pH 5.5 to 8.9, at  $I = 0.05$ , 0.1 or 0.3 M. The ionic media varied from pure  $\text{Na}_2\text{Ox}$  to  $\text{NaClO}_4$ . The effect of the “background” electrolyte was checked at  $I = 0.1$  M by adding  $\text{NaNO}_3$  instead of sodium perchlorate. The overall ionic mobilities were interpreted in terms of individual ionic mobilities and stability constants for complex formation.

The data showed that the first oxalate complex (which should be  $\text{NpO}_2\text{Ox}^-$ ) had an ionic mobility corresponding to a cation. Similarly, in the case of  $\text{SO}_4^{2-}$  the data indicate that no anionic complexes were formed. In order to explain this inconsistency the authors proposed that  $\text{Np}(\text{V})$  forms the species  $\text{NpO}^{3+}$ , which would then give cationic 1:1 complexes with both sulphate and oxalate. This is in contradiction with all other available evidence that  $\text{Np}(\text{V})$  exists as  $\text{NpO}_2^+$  in solution. This review is unable to explain, or accept, the results presented in [89ROS/DIT].

#### [89STO/CAC]

The study seems to be an enlarged report of experiments and results described in [87CAC/NEC] because the same experimental conditions were used ( $-\log_{10}[\text{H}^+] = 6.0$ ,  $(23 \pm 2)^\circ\text{C}$ ,  $I = 1.0$  M ( $\text{NaClO}_4$ )). The authors studied the interaction of neptunyl(V) with simple aliphatic di-carboxylic acids. A Vis-NIR spectrophotometer was used in order to determine properties of absorption bands of complex species in comparison with  $\text{NpO}_2^+$ . The free concentration of  $\text{H}^+$  was measured with a glass electrode.

For oxalate the protonation constants were 3.55 and 1.04, which agree with the values selected in this review (at 1 M  $\text{NaClO}_4$ ) within the uncertainties. The following stability constants were found:  $\log_{10} \beta_1 = (3.53 \pm 0.04)$  and  $\log_{10} \beta_2 = (6.12 \pm 0.05)$ . The molar absorptivities at band maximum are in a good agreement with the values calculated from the data in [72STO]. The  $\text{Np}(\text{V})$ -oxalate constants are included in the review procedure with increased uncertainties of  $\pm 0.1 \log_{10}$ -units to include possible systematic errors.

#### [89VAS/KAL]

The behaviour of hydrated oxalates of  $\text{Am}(\text{III})$  at temperatures up to  $800^\circ\text{C}$  in helium or oxygen atmosphere was studied by DTA and X-ray phase analysis. The results agreed

with those reported in [58MAR2] and [67WEI/MEE] showing that the oxalate dehydration process completes at 280°C regardless of the atmosphere and that the decomposition of anhydrous americium oxalate completes at 415°C.

#### [90DAN/ROB]

This is a short paper summarising a study fully described in [90DAN/ROB2], which is discussed below in this Appendix.

#### [90DAN/ROB2]

The authors determined the protonation constants of citrate at different ionic strengths (0.04 to 1 M) and temperatures (10 to 50°C). The total citrate concentration was 5 to 20 mM, largely affecting the ionic media for experiments at  $I = 0.04$  M. Therefore, the protonation constants reported at  $I = 0.04$  M are not considered in this review.

Several background electrolytes were used: LiCl, NaCl, KCl, RbCl, and CsCl. However, the titrant was 0.3 M NaOH in all cases, and unknown systematic errors are expected in the protonation constants due to small specific ion interaction effects in the ionic activity coefficients.

Ionic strengths were corrected for alkali metal - chloride ion association. Reported values of  $I$  in [90DAN/ROB], [90DAN/ROB2] are therefore lower than the concentration of background electrolyte. Apparently the ionic strength was varied during the titrations, and this was also taken into account during the data analysis performed by Daniele *et al.*

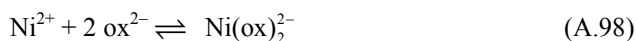
Because of these shortcomings, the uncertainty for the reported protonation constants is assigned in this review to be  $\pm 0.1 \log_{10}$ -units, except for the data obtained in NaCl media, where the assigned uncertainty is set to  $\pm 0.05 \log_{10}$ -units.

Because NaOH was used as titrant in all cases, systematic errors were introduced in the  $\log_{10} K$  values obtained in media other than NaCl. These errors are expected to be small but of the same order of magnitude as the small temperature effects in the protonation constants. Therefore the reported enthalpy changes for the protonation of citrate are not credited in this review, with the exception of the  $\Delta_r H_m$  data obtained in NaCl media.

Alkali cation complexation constants were calculated by comparison with protonation constants obtained in Et<sub>4</sub>NI (tetraethylammonium iodide) media. However, neither the source nor the values in Et<sub>4</sub>NI media are given in the paper. This methodology is nevertheless not credited in this review, *cf.* Section VII.4. The values of  $\Delta_r H_m$  for alkali metal complexation obtained from the temperature variation of the corresponding formation constants are therefore not considered either in this review.

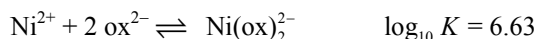
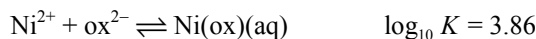
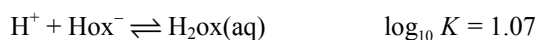
[\[90LIN/GU\]](#)

The authors carried out a calorimetric determination of the heats of stepwise complexation in the binary Ni(II)-oxalate system:



as well as in the ternary Ni(II)-oxalate-ethylenediamine system. The experimental conditions were the same as those in [\[60WAT/DEW\]](#):  $(25.0 \pm 0.2)^\circ\text{C}$ ,  $I = 1 \text{ M}$  ( $\text{KNO}_3$ ) and the authors also used the stability constants from [\[60WAT/DEW\]](#) in their calculations, which resulted in the following values:  $\Delta_r H_m(\text{A.97}) = -(5.40 \pm 0.20) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_r H_m(\text{A.98}) = -(11.02 \pm 0.25) \text{ kJ}\cdot\text{mol}^{-1}$ , and  $\Delta_r H_m(\text{A.99}) = -(17.05 \pm 0.54) \text{ kJ}\cdot\text{mol}^{-1}$ .

This review re-evaluates the three measurements performed in [\[90LIN/GU\]](#), using the calorimeter reaction volumes reported previously [\[88LIN/GU\]](#), and the selected protonation and formation constants in the Ni(II)-oxalate system extrapolated to 1 M  $\text{KNO}_3$  using the SIT model:



and  $\log_{10} \gamma_{\text{H}^+} = -0.132$ . These values were obtained using the specific ion interaction coefficients listed in Tables B-4 and B-5, while  $\varepsilon(\text{Ni}^{2+}, \text{ClO}_4^-)$  and  $\varepsilon(\text{Ni}^{2+}, \text{NO}_3^-)$  were estimated to be  $(0.33 \pm 0.03)$  and  $(0.125 \pm 0.020) \text{ kg}\cdot\text{mol}^{-1}$ , respectively. The re-evaluation of the three calorimetric measurements in [\[90LIN/GU\]](#) using the equilibrium constants listed above results in  $\Delta_r H_m(\text{A.97}) = -(5.0 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r H_m(\text{A.98}) = -(12.6 \pm 0.3) \text{ kJ}\cdot\text{mol}^{-1}$ .

[\[90RED/SAT\]](#)

The authors report a potentiometric study at  $35^\circ\text{C}$  on the ternary complex formation between thiodiacetic acid and several ligands, including oxalate. The metals studied were Cu(II), Ni(II), Co(II) and Zn(II). Protonation constants were determined in 0.1 M  $\text{KNO}_3$  but the authors used standard NaOH as titrant and hence, systematic errors were introduced in the corresponding protonation constants due to a varying ionic medium. In addition to this ambiguity concerning the ionic medium some other experimental or computational errors seem to have affected the results, as the expected protonation constants at  $35^\circ\text{C}$  would be  $\log_{10} K_1 = (3.86 \pm 0.01)$  and  $\log_{10} K_2 = (1.21 \pm 0.03)$  at  $I = 0.1$  ( $\text{KNO}_3$ ) which are appreciably smaller than the reported values of  $(4.09 \pm 0.05)$  and

( $1.41 \pm 0.05$ ), respectively. Based on these protonation constants the complexes of the binary systems were determined, including Ni(ox)(aq). The results of this study are not credited in this review.

#### [\[90RIZ/NEC\]](#)

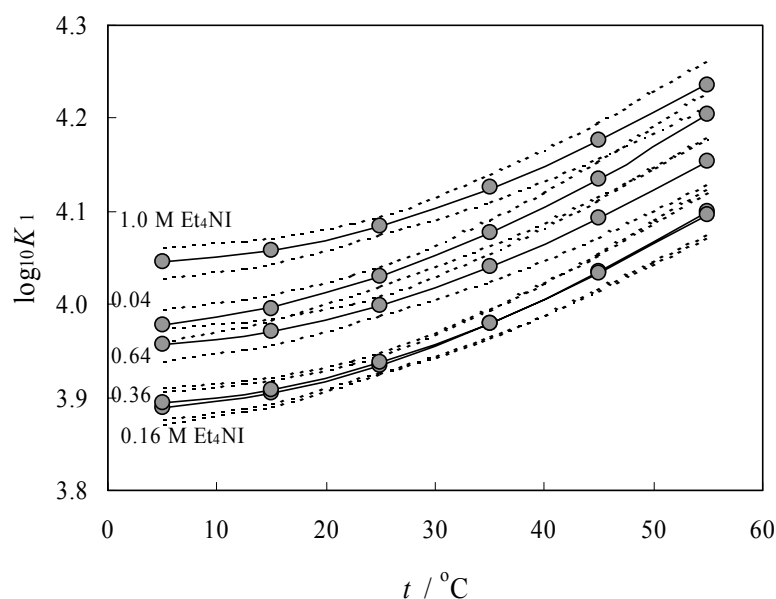
The spectra of the solution of *ca.* 1 mM  $\text{NpO}_2\text{ClO}_4$  and variable concentration of citric acid were measured at the pH 6–7 keeping the ionic strength constant ( $[\text{NaClO}_4] \cong 2 \text{ M}$ ). Since  $[\text{cit}^{3-}]$  predominates at this pH, the protonation constants used ( $\log_{10} K_1 + \log_{10} K_2 = 9.34$ ) does not affect the result. The experiments and data analysis were done carefully and the reported values of  $\log_{10} \beta_{1(\text{cit})} = (2.49 \pm 0.02)$ ,  $\varepsilon_{\text{M}} = 398 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  at 980.4 nm with FWHM = 7.1 nm and  $\varepsilon_{\text{ML}} = 205 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$  at 985.5 nm with FWHM = 7.5 nm seem to be reliable. Considering the systematic errors which might be derived from the mass balance relationships, this review accepts this value with assigning a little larger uncertainty of  $\pm 0.05$  for  $I = 2.21 \text{ m NaClO}_4$ .

#### [\[90ROB/STE\]](#)

Protonation constants of oxalate and citrate (and 19 other carboxylic acids) were obtained by potentiometric measurements in tetraethylammonium iodide ( $\text{Et}_4\text{NI}$ ) in the ranges  $5 \leq t \leq 55^\circ\text{C}$  and  $0.04 \leq I \leq 1 \text{ M}$ . The solutions were titrated with standard KOH in the case of oxalate, which adds some uncertainty to the results obtained in such a changing ionic medium. Hence, the uncertainties of the constants obtained were increased to  $\pm 0.05 \log_{10}$ -units.

In order to estimate the temperature variation of  $\log_{10} K_1$ , values reported in [\[90ROB/STE\]](#) have been corrected to the molal scale using the parameters of Table V-1 in Chapter V. These molal  $\log_{10} K_1$  values have been fitted in this review to a temperature function assuming  $\Delta_{\text{r}} C_{p,\text{m}} = \text{const}$ . According to the rules of error propagation discussed in Section VI.3.4, assuming an uncertainty of  $\pm 0.02$  in the  $\log_{10} K_1$  values, determined over the temperature range 5 to  $55^\circ\text{C}$ , the overall uncertainty in  $\Delta_{\text{r}} H_{\text{m}}$  was estimated to be  $\pm 0.7 \text{ kJ} \cdot \text{mol}^{-1}$ . Consequently, the overall uncertainty of  $\Delta_{\text{r}} C_{p,\text{m}}$  was estimated to be  $\pm 14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . The results are included in Table VI-7 and shown in Figure A-29.

Figure A-29: First protonation constant for oxalate determined by [90ROB/STE] in Et<sub>4</sub>Ni medium, corrected to the molal scale in this review, and the constant  $\Delta_r C_{p,m}$  model with the parameters determined in this review.



#### [90ROS/REI]

The continuous horizontal low-voltage electromigration measurement of  $\gamma$ -emitting radionuclide in homogeneous aqueous electrolyte solutions free of any supporting chromatographic materials was carried out to study the complex formation of carrier-free <sup>241</sup>Am(III). Stoichiometric stability constants for oxalate ligand were obtained to be  $\log_{10} K_1 = (5.01 \pm 0.13)$ ,  $(5.11 \pm 0.13)$  and  $(5.38 \pm 0.18)$ , as well as  $\log_{10} K_2 = (3.15 \pm 0.15)$ ,  $(3.19 \pm 0.14)$  and  $(3.58 \pm 0.26)$  at  $I = 0.10$ ,  $0.05$  and  $0.01$  M Na(H)ClO<sub>4</sub> at 298.1 K and pH  $(5.5 \pm 0.5)$ , respectively. The protonation constants of  $\log_{10} K_{(H)} = 3.82$  and  $1.26$  were used. Since oxalate is completely dissociated at this pH, the errors in the measurement of pH (conversion to  $-\log_{10} [H^+]$ ) and in the values of  $\log_{10} K_{(H)}$  would not affect the estimated  $[ox^{2-}]$ . In the electromigration experiment, the potential given to the solution may slightly affect the homogeneous constancy of the media. Moreover, the change in the composition of the ionic media would affect the migration mobility of each species. Unfortunately, Figure 1 of the paper, which was intended to give the experimental results on the overall mobility of Am(III) as a function of  $\log_{10} [ox^{2-}]$ , was replaced mistakenly by the results of sulphate complexation (Figure 3 of the paper). If the results of oxalate complexation are similar to that of sulphate, five parameters (three

mobilities for  $\text{Am}^{3+}$ ,  $\text{Am}(\text{ox})^+$  and  $\text{Am}(\text{ox})_2^-$  and two stability constants) must be obtained from the rather smoothly changing plots of overall mobility versus  $\log_{10}[\text{ox}^{2-}]$ . Because of the impossibility of verifying the experimental results and the suspected large uncertainty in the values and in the constancy of the mobility of the species, the results of this paper are not considered in this review.

#### [91BAP]

This paper reports binary and ternary complexes of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  with edta and citric acid. However, the experimental information comprises only two lines of text in this paper. There is no indication on the composition of the used reagents, on checking their purities, on the compositions of the used solutions, or on the ionic strengths reached in the experiments. For citric acid protonation constants at 25, 35 and 45°C are given without any comparison with the rather large number of protonation constants reported in the literature. Values of  $\log_{10} K$  are reported for  $[\text{Ni}(\text{B})]^{2+}$ ,  $[\text{Ni}(\text{B})_2]^{2+}$ ,  $[\text{Ni}(\text{B})_3]^{2+}$  and  $[\text{Ni}(\text{A})(\text{B})]^{2+}$ , where A represents edta and B corresponds to citric acid. The chemical equilibria are not defined by [91BAP], especially the meaning of  $\log_{10} K$  for the ternary complex is not clear. The author erroneously seems to assume that edta and citric acid are complexed by Ni in their fully protonated form. In view of all these shortcomings the values reported by [91BAP] are considered as totally unreliable and are discarded by this review.

#### [91BEI/GRA]

Titration calorimetry has been employed by [91BEI/GRA] to investigate the aqueous solution chemistry of the Th(IV) - oxalate system. Enthalpies of formation of  $\text{H}_2\text{ox}$  and  $\text{Hox}^-$  were determined by introducing the  $\text{Na}_2\text{ox}$  titrant into a solution of pH = 1.4,  $I = 1.0 \text{ M HClO}_4$  to measure enthalpy,  $\Delta_r H_m(\text{A.100})$  and  $\Delta_r H_m(\text{A.101})$  at 25°C for the reactions:



The results are reported as  $\Delta_r H_m(\text{A.100}) = +(4.68 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r H_m(\text{A.101}) = -(13 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$ . The authors state that “errors in the enthalpy measurements are  $1\sigma$  standard deviations and represent only uncertainties in the calorimeter measurements of temperature. Since errors in the input parameters required for the speciation calculations have not been included, the uncertainties in enthalpy values should be considered but minimum errors associated with these experiments.” Starting the titration experiments at pH 1.4 in pure  $\text{HClO}_4$  means that oxalic acid is already dissociated to a large extent. In addition, adding  $\text{Na}_2\text{ox}$  as titrant rapidly increases the pH while changing the medium from  $\text{HClO}_4$  to  $\text{NaClO}_4$ . The second protonation step of oxalate is probably a very minor effect in the experiments of [91BEI/GRA] and thus, the value derived for the second protonation enthalpy is a mere error absorber in the data fitting routine than a

thermodynamic quantity. Hence, the  $\Delta_r H_m$  (A.101) value reported by [91BEI/GRA] is not credited in this review. Considering other reliable calorimetric measurements discussed in this review, and the ambiguity due fitting an additional error absorber ( $\Delta_r H_m$  (A.101)) to the experimental data, an uncertainty of  $\Delta_r H_m$  (A.100) =  $(4.7 \pm 0.8)$  kJ·mol<sup>-1</sup> seems appropriate.

#### [91BOU/PHI]

Processing of bauxites (Al ores) containing organic matter by the so-called “Bayer process” generates soluble organic sodium salts of various molecular weights. These organics accumulate in Bayer liquors and degrade to low molecular weight products, the ultimate species being sodium oxalate and carbonate. This paper presents a solubility model of sodium oxalate under Bayer decomposition conditions, based on physical chemistry considerations of complexes formed in solution.

In order to determine the sodium oxalate solubility product, 100 cm<sup>3</sup> of pure oxalic acid solution (1 M) were added to 100 cm<sup>3</sup> of pure NaOH solution at different concentrations (2 – 10 M) at 25, 40 and 60°C. The experimental data (some of them are shown in Fig.1 of the paper) were fitted to a speciation model in such a way that the “ion–pair constant of the sodium oxalate complex was adjusted in the calculation to give the theoretical slope (2 sodium for 1 oxalate) of oxalate activity as a function of sodium activity”. The model comprises the sodium complexes Na(ox)<sup>-</sup>, NaOH(aq), NaCl(aq), NaSO<sub>4</sub><sup>-</sup> and NaCO<sub>3</sub><sup>-</sup>. For the calculation of activity coefficients the authors used the Davies equation and state: “It is a simple expression of the extended Debye–Hückel formula that will be employed beyond its usual limits recommended by the author. However, unpublished work has shown that when a complete set of chemical equations is used, good results are obtained in liquors with high ionic strength”.

This argument is not accepted by this review and the results of the fitting procedure,  $K(25^\circ\text{C}) = 12.5$ ,  $K(40^\circ\text{C}) = 2.75$  and  $K(60^\circ\text{C}) = 0.5$  for  $\text{Na}^+ + \text{ox}^{2-} \rightleftharpoons \text{Na}(\text{ox})^-$ , and  $\log_{10}K(40^\circ\text{C}) = -2.21$ ,  $\log_{10}K(60^\circ\text{C}) = -1.24$  for the reaction  $\text{Na}_2\text{ox}(\text{s}) \rightleftharpoons 2\text{Na}^+ + \text{ox}^{2-}$  are rejected. No attempt was made in this review to develop a thermodynamic model for the highly soluble salt Na<sub>2</sub>ox(s) using SIT at high concentrations up to 10 M NaOH, which may even exceed the range of validity of SIT.

#### [91KET/PAL]

In this careful study the first and second molal dissociation constants of oxalic acid were measured potentiometrically in a concentration cell fitted with hydrogen electrodes. Measurements were made at temperatures ranging from 5°C to 175°C at ionic strengths ranging from 0.1 mol·kg<sup>-1</sup> to 5.0 mol·kg<sup>-1</sup> NaCl. The dissociation constants were obtained from measured emf data by an iterative fitting process: The precise evaluation of the first dissociation constant at a certain temperature and ionic strength involves, among other parameters, the oxalate speciation and thus, the knowledge of the second dissociation constant, and vice versa. The iterative fitting process relied heavily

on previously published data in order to extrapolate the molal dissociation constants to infinite dilution. These data included conductance measurements at 25°C [41DAR], glass electrode measurements [69KUR/FAR], potentiometric data obtained using electrochemical cells without liquid junctions [39PAR/GIB], [61MCA/NAN] and titration calorimetry measurements [96CHO/CHE]. The experimental emf data reported in this study have been later refitted together with new measurements by the same authors [98KET/WES] and other previously published data. For a detailed discussion see [98KET/WES].

#### [91LOO/KOP]

The authors used the cation-exchange method at 20°C to study the complex formation between copper(II), nickel(II) and uranium(VI) with oxalate and with degradation products of bitumen. For Ni(II)-oxalate the study was performed with  $[\text{Ni(II)}]_{\text{TOT}} = 10^{-6} \text{ M}$ ,  $[\text{ox}]_{\text{TOT}} \leq 0.18 \text{ mM}$ ,  $\text{pH} = 5$ , and in an ionic medium consisting of 0.1 M  $\text{NaClO}_4$  and 0.01 M Na-acetate, used to buffer the pH. The value  $\log_{10} K_1^\circ = (4.27 \pm 0.05)$  was reported. This constant included a small correction (0.03  $\log_{10}$ -units) for the complex formation between  $\text{Ni}^{2+}$  and the acetate ions in the background electrolyte. This equilibrium constant is included in the review procedure with an uncertainty increased to  $\pm 0.1 \log_{10}$ -units.

The authors also determined the stability constant of  $\text{UO}_2\text{ox(aq)}$  for comparison. The value of  $\log_{10} \beta_1$  was determined to be  $(6.10 \pm 0.11)$  at  $I = 0.11 \text{ M}$  (0.10 M  $\text{NaClO}_4$  + 0.01 M Na-acetate) and  $\text{pH} = 5$ . Since the stability constant was obtained at a single pH (5) and the calculation appears to be based on the assumption that oxalate was completely deprotonated at this pH, the uncertainty provided in the paper might be too optimistic. In addition, the medium is a mixed electrolyte system (10% Na-acetate), though the complexation of U(VI) by acetate was properly taken into consideration. The value from this study is accepted with increased uncertainty ( $\pm 0.20$ ) by this review. Since the ionic strength is low, the correction from molarity to molality is negligible.

#### [91POC]

This paper is a continuation of the Pu(III) edta studies of Poczynajło. In the first paper [89POC] potentiometric titrations were reported, now [91POC] extraction equilibria in a two-phase system (with 2-thenoylfluoroacetone in the organic phase) are presented. The constant composition of the initial aqueous solutions was  $4.2 \cdot 10^{-5} \text{ M}$  Pu(III),  $1.0 \cdot 10^{-2} \text{ M}$   $\text{NH}_3\text{OHCl}$  (to maintain Pu in the reduced +3 state) and 0.1 M KCl. The variable parameters were pH and total edta concentration.

The entire information about pH measurements reads as follows: “The pH value of separated aqueous phases were determined on a digital pH meter with combined glass-calomel electrode”. No information is given by Poczynajło about the pH scale and the calibration of the pH meter. The origin of the edta protonation constants



used in this study is not clear. Some data fitting exercises seem to have been carried out, but they are not described in the paper, only the remark “the calculated pK values for  $I = 0.1$  are shown in Table 4” can be found in [91POC].

At 25°C seven distribution ratios have been measured, five at constant total edta concentration of  $5 \cdot 10^{-4}$  M and “pH” 2.00, 2.04, 4.75, 4.93 and 5.03, and two at “pH” 5.06 and  $1 \cdot 10^{-3}$  M edta and “pH” 5.24 and  $1.75 \cdot 10^{-3}$  M edta. From these 7 data points the author derives three stability constants,  $K_{ML} = 3.29 \cdot 10^{16}$ ,  $K_{MHL} = 1.20 \cdot 10^9$  and  $K_{MH_2L} = 1.82 \cdot 10^5$ . The author reports: “Confidence intervals of the above stability constants are rather wide. Due to difficulties in their accurate determination, they are not given here”. Considering that the measurements actually comprise only 4 different conditions concerning pH and edta concentration, and 3 constants have been derived there from, it is not astonishing that the confidence intervals of these constants are “rather wide”. The obtained results are not put in perspective with other studies of the Pu(III) edta system. In fact, not a single paper on this topic is cited by Poczynajło.

In view of all these shortcomings, the results reported in this paper are considered as unreliable and thus rejected by this review.

#### [91SIN/YEB]

In this study  $2.4 \cdot 10^{-3}$  calcium chloride solutions were titrated with  $\text{Na}_3\text{cit}$  at 18 – 45 °C,  $I = 0.0198 - 0.170$  M NaCl and pH higher than 8. Free concentrations of  $\text{Ca}^{2+}$  were determined with a calcium ion-selective electrode. Conditional stability constants  $\beta_1$  (without consideration of  $\text{Na}(\text{cit})^{2-}$  formation, denoted by  $K'$  in the paper) were calculated from the total and free concentrations of  $\text{Ca}^{2+}$  by assuming:

$$K' = \frac{[\text{Ca}(\text{cit})^-]}{[\text{Ca}^{2+}][\text{cit}^{3-}]} = \frac{(C_{\text{Ca}} - [\text{Ca}^{2+}])}{[\text{Ca}^{2+}](C_{\text{L}} - [\text{Ca}^{2+}])}.$$

Then the values were corrected for the formation of  $\text{Na}(\text{cit})^{2-}$  by using  $K = 8.5$  for  $\text{Na}^+ + \text{cit}^{3-} \rightleftharpoons \text{Na}(\text{cit})^{2-}$  at all temperatures. Moreover, solubilities of  $\text{Ca}(\text{ox}) \cdot \text{H}_2\text{O}$  in the presence of  $(0.25 - 5) \times 10^{-3}$  M  $\text{Na}_3\text{cit}$  were measured at 37°C,  $I = 0.15$  M NaCl. In this case, the obtained apparent stability constant was corrected also for the formation of  $\text{Na}(\text{ox})^-$  and  $\text{Ca}(\text{ox})(\text{aq})$  by using their respective stability constants of 13.2 and 2746. Using the Davies equation for the estimation of the activity coefficients of mono-, di- and trivalent ions, Singh *et al.* obtained the values of  $\log_{10} \beta_1 = 4.83 - 4.85$  for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$  at 18 – 45°C and then  $\Delta_r G_m^\circ$ ,  $\Delta_r H_m^\circ$ ,  $\Delta_r S_m^\circ$  and  $\Delta_r C_{p,m}^\circ$ . However, in typical results of a potentiometric titration shown in Table 1 of [91SIN/YEB], estimated values of  $[\text{Na}(\text{cit})^{2-}]$  and  $[\text{cit}^{3-}]$  (denoted by  $f''(\text{Cit}^{3-})$  in the paper) are inconsistent with the value of 8.5 for  $\text{Na}(\text{cit})^{2-}$  and  $[\text{Na}^+] \approx 0.15$  M. This review considers that only the conditional stability constants reported are meaningful. In this review, the interaction of  $\text{Na}^+$  with  $\text{cit}^{3-}$  is treated as the SIT interaction with concentration-dependent  $\varepsilon$  ( $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$ ). Thus, this review accepts the conditional stability constants obtained from titration experiments. Among the values of  $\log_{10} \beta_1 = 3.27$

(18°C,  $I = 0.154$ ), 3.26 (25°C,  $I = 0.154$ ), 3.27 (37°C,  $I = 0.154$ ), 3.25 (45°C,  $I = 0.154$ ), and 3.23 (37°C,  $I = 0.0198$ ), 3.27 (37°C,  $I = 0.056$ ), 3.69 (37°C,  $I = 0.15$ ), 4.08 (37°C,  $I = 0.17$ ), the values at  $I = 0.0198$  and 0.056 are not accepted by this review since the contributions of  $\text{Ca}^{2+}$  and  $\text{cit}^{3-}$  to the ionic strengths are too large. The temperature dependence of  $\log_{10} \beta_1$  is smaller than the experimental error. Thus we will take  $\log_{10} \beta_1 = (3.25 \pm 0.10)$  at  $I = 0.15 - 0.17$  M NaCl and at 18 – 45°C. From the relation,  $|\Delta \log_{10} K / \Delta T| < 0.1 / (45 - 18)$ , we will also take  $\Delta_r H_m^\circ = (0 \pm 6) \text{ kJ} \cdot \text{mol}^{-1}$ .

### [\[92GLA/HUL\]](#)

The authors applied a coulometric technique to determine protonation constants of several ligands, including  $\text{edta}^{4-}$  and citrate. Complex formation constants with  $\text{Ca}^{2+}$  and  $\text{Cd}^{2+}$  were also determined. The proposed method can be used with success when the metal ions are reduced at the working electrode. The validity of the procedure was checked by studying well-known systems.

The reported value of  $\log_{10} K_1(\text{edta})$  for the first protonation of  $\text{edta}^{4-}$ , equal to 10.15 at 0.1 M  $\text{NaClO}_4$  and 25°C, is  $> 0.6$   $\log_{10}$ -units larger than any other literature value under similar conditions. No apparent reason for this discrepancy can be found in the publication. Curiously, the reported value is close to the value expected in 0.1 M  $\text{KNO}_3$  (10.17, see Table VIII-8-b) and hence, 0.8  $\log_{10}$ -units larger than the value expected in 0.1 M  $\text{NaClO}_4$  (9.38, see Table VIII-8-b). This outlier value has not been included in the selection procedure for  $\log_{10} K_1^\circ$  of  $\text{edta}^{4-}$ .

The stability constant for  $\text{Ca}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ca}(\text{edta})^{2-}$  is reported as  $\log_{10} \beta_1(\text{edta}) = 10.75$ . This value is in good agreement with results obtained in 0.1 M  $\text{KNO}_3$  (10.73 [\[75AND/POD\]](#), 10.78 [\[73HAN/RUZ\]](#)). However, a 0.7  $\log_{10}$ -units smaller value is expected in 0.1 M  $\text{NaClO}_4$  due to the difference in the stability of  $\text{Kedta}^{3-}$  and  $\text{Na}(\text{edta})^{3-}$  complexes. This discrepancy probably is a direct consequence of applying the erroneous value of  $\log_{10} K_1(\text{edta})$  for deriving  $\log_{10} \beta_1(\text{edta})$  from experimental data. Unfortunately, this hypothesis cannot be checked due to the lack of experimental raw data in [\[92GLA/HUL\]](#) and hence,  $\log_{10} \beta_1(\text{edta})$  had to be discarded in this review.

The stability constant for  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$  is reported as  $\log_{10} \beta_1(\text{cit}) = 3.5$ . The citrate experiments and subsequent data evaluation seem to be carried out properly and the protonation constant reported in this study,  $\log_{10} K_{1(\text{H})} = 5.70$ , is in good agreement with other literature values under similar conditions. Both values,  $\log_{10} K_{1(\text{H})}$  and  $\log_{10} \beta_1(\text{cit})$ , have been accepted in this review with uncertainties of  $\pm 0.1$  and  $\pm 0.2$   $\log_{10}$ -units, respectively.

[\[92NGU/BEG\]](#)

The frequencies of the stretching vibration of O=U=O were studied in solutions of various ligands at different concentrations and pH by Raman spectroscopy. The results suggest that complex formation with the ligands leads to the weakening of the uranium axial oxygen bonds in the order:  $\text{OH}^- > \text{CO}_3^{2-} > \text{ox}^{2-} > \text{F}^- > \text{SO}_4^{2-}$ ,  $\text{CH}_3\text{COO}^- > \text{Cl}^- > \text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{HSO}_4^-$ . Linear correlations between the shift in the Raman frequency and the average ligand number were found for each ligand. The stability constants of the U(VI) complexes were also found to be proportional to the shift in the Raman frequency.

[\[92ROB/STE\]](#)

Protonation constants of oxalate for the reactions:



were obtained by potentiometric measurements in NaCl, KCl and tetraethylammonium iodide ( $\text{Et}_4\text{NI}$ ) in the ranges  $10 \leq t \leq 45^\circ\text{C}$ . The solutions were titrated with standard NaOH, KOH and  $\text{Me}_4\text{NOH}$ , respectively.

In order to estimate the temperature variation of  $\log_{10}K_1(\text{A.102})$ , values reported in [\[92ROB/STE\]](#) as “apparent” quantities, *i.e.*, without considering Na or K oxalate complexes, have been fitted in this review to a temperature function assuming  $\Delta_r C_{p,m}(\text{A.102}) = \text{constant}$ . According to the rules of error propagation discussed in Section VI.3.4, assuming an uncertainty of  $\pm 0.02$  in the  $\log_{10}K_1(\text{A.102})$  values, determined over the temperature range 10 to  $45^\circ\text{C}$ , the minimum uncertainty in  $\Delta_r H_m(\text{A.102})$  was estimated to be  $\pm 0.9 \text{ kJ}\cdot\text{mol}^{-1}$ . Consequently, the minimum uncertainty of  $\Delta_r C_{p,m}(\text{A.102})$  was estimated to be  $\pm 27 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The results are included in Table VI-7 and shown in Figure A-30, Figure A-31 and Figure A-32.

Values reported in [\[92ROB/STE\]](#) for the second protonation constant of oxalate,  $\log_{10}K_2(\text{A.103})$  in all cases exhibit some increase with increasing temperature. However, the total temperature variation of  $\log_{10}K_2(\text{A.103})$  is of the same magnitude as the uncertainty of the individual measurements, which was estimated by [\[92ROB/STE\]](#) to be  $\pm 0.1 \log_{10}$ -units. The uncertainty of  $\Delta_r H_m(\text{A.103})$  and  $\Delta_r C_{p,m}(\text{A.103})$  values derived from these  $\log_{10}K_2(\text{A.103})$  data is larger than the actual  $\Delta_r H_m(\text{A.103})$  and  $\Delta_r C_{p,m}(\text{A.103})$  values and hence, no conclusions can be drawn from such data.

Figure A-30: First protonation constant for oxalate determined by [92ROB/STE] in NaCl medium and the constant  $\Delta_r C_{p,m}$  (A.102) model with the parameters determined in this review.

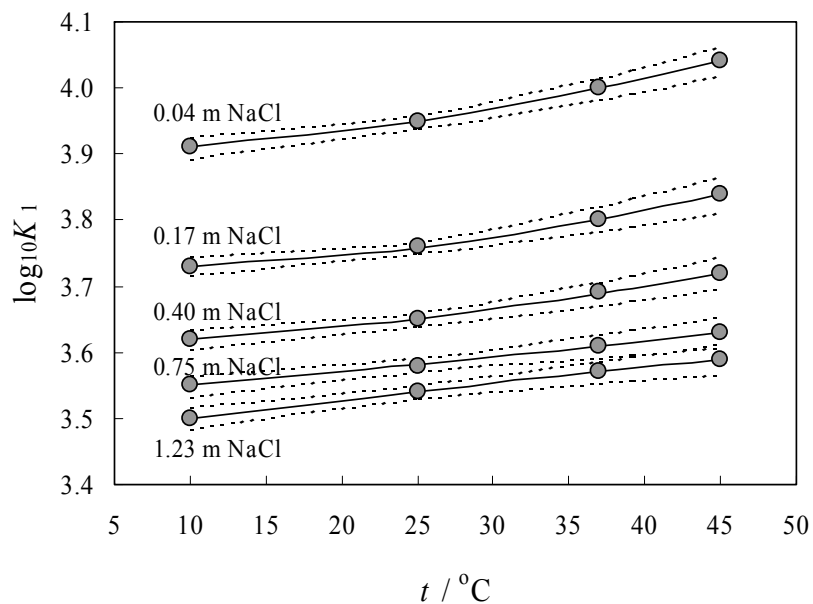


Figure A-31: First protonation constant for oxalate determined by [92ROB/STE] in KCl medium and the constant  $\Delta_r C_{p,m}$  (A.102) model with the parameters determined in this review.

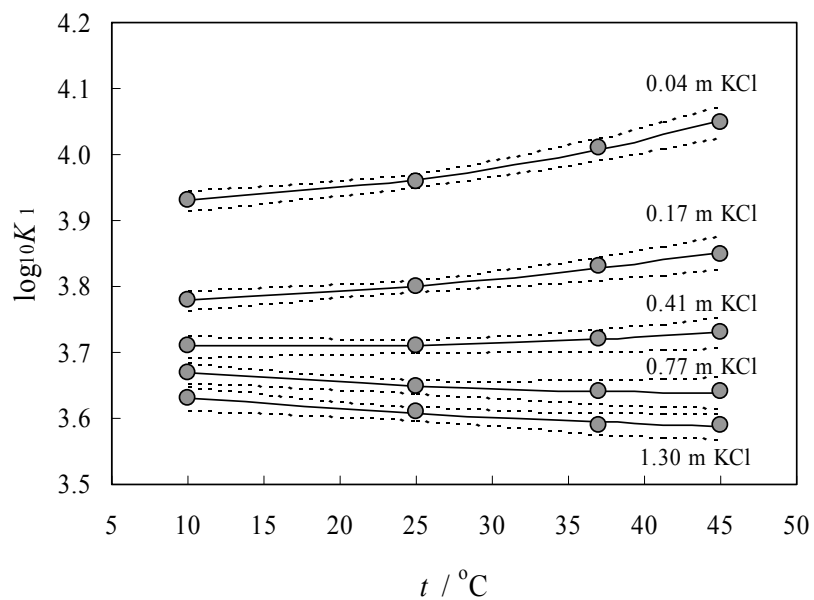
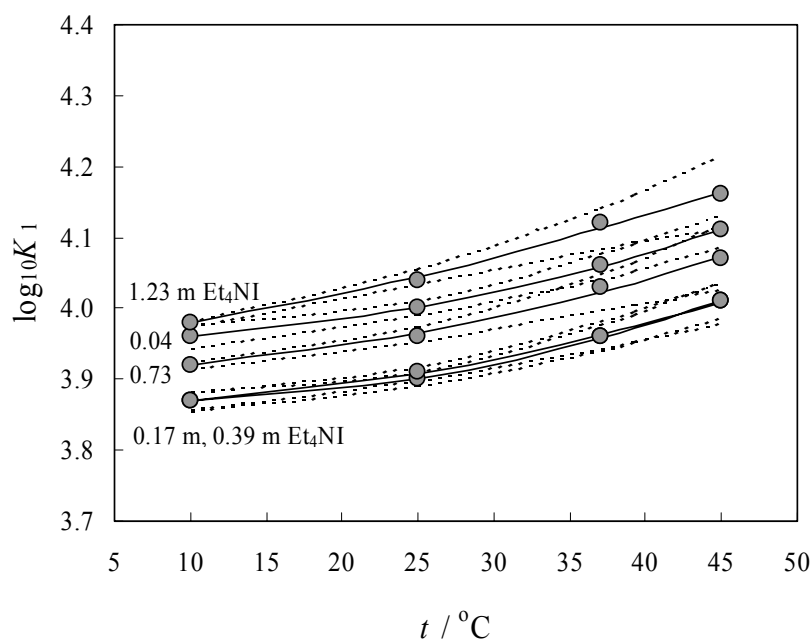


Figure A-32: First protonation constant for oxalate determined by [92ROB/STE] in Et<sub>4</sub>NI medium and the constant  $\Delta_f C_{p,m}$  (A.102) model with the parameters determined in this review.



#### [92THA/KUM]

The standard enthalpy of formation of UO<sub>2</sub>(ox)·3H<sub>2</sub>O(cr) was reported to be  $-2688 \text{ kJ}\cdot\text{mol}^{-1}$ , obtained from the heat of combustion determined by bomb calorimetry. No uncertainty was assigned in the paper. Thus, the data were reanalysed by this review to assign the uncertainty. The calculation was based on the equation:

$$\Delta_f H_m^\circ (\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}, \text{cr}) = \frac{1}{3} \Delta_f H_m^\circ (\text{U}_3\text{O}_8, \text{cr}) + 2 \Delta_f H_m^\circ (\text{CO}_2, \text{g}) + 3 \Delta_f H_m^\circ (\text{H}_2\text{O}, \text{l}) - \Delta_{\text{comb}} H_m$$

where the combustion heat  $\Delta_{\text{comb}} H_m = -(148 \pm 4) \text{ kJ}\cdot\text{mol}^{-1}$ . Using the following values of standard enthalpy of formation from [2003GUI/FAN],  $(1/3) \Delta_f H_m^\circ (\text{U}_3\text{O}_8, \text{cr}) = \Delta_f H_m^\circ (\text{UO}_{2.6667}, \text{cr}) = -(1191.6 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_f H_m^\circ (\text{CO}_2, \text{g}) = -(393.51 \pm 0.13) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_f H_m^\circ (\text{H}_2\text{O}, \text{l}) = -(285.83 \pm 0.04) \text{ kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_f H_m^\circ (\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$  is calculated to be  $-(2688.1 \pm 4.1) \text{ kJ}\cdot\text{mol}^{-1}$  from this study.

A value of  $\Delta_f H_m^\circ (\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$  was determined to be  $-(2715.3 \pm 2.4) \text{ kJ}\cdot\text{mol}^{-1}$  by a different method [77OHA]. Based on the two values, the  $\Delta_f H_m^\circ (\text{UO}_2\text{ox}\cdot 3\text{H}_2\text{O}, \text{cr}, 298.15 \text{ K})$  is selected to be  $-(2701.7 \pm 17.7) \text{ kJ}\cdot\text{mol}^{-1}$  by this review.

[\[92TOC/INO\]](#)

This paper describes the study of neptunyl(V) complexation with 20 different aliphatic and aromatic carboxylic acids.  $^{239}\text{Np}$  in trace concentration was extracted at  $(25 \pm 1)^\circ\text{C}$  synergically using thenoyltrifluoroacetone (TTA) and 1,10-phenanthroline in isoamyl-alcohol. The background electrolyte was 1.0 M  $\text{NaClO}_4$ . The pH was adjusted to 5.6 and 7.4 by the addition of two buffers (morpholinoethanesulphonic acid, MES, and tris(hydroxymethyl)aminomethane, THAM). The authors verified that these buffers had no effect on the results. For oxalate the ligand concentration was varied between 0.002 to 20 mM. Corrections were applied for the complex formation between  $\text{NpO}_2^+$  and TTA in the aqueous phase, although this correction was less than 0.01  $\log_{10}$ -units in the equilibrium constants for complex formation with the carboxylic acids studied. No details are given on the pH measurements (*e.g.*, the calibration of electrodes). The protonation constants for oxalate used in calculating the free ligand concentration were 3.55 and 1.04, which agree within the uncertainties with the values selected by this review.

The influence of the extraction procedure, forward or backward, was also evidenced from plots of distribution ratios in absence of carboxylic ligands and from calculated complex formation constants, *cf.* Table A-13. The difference between the values obtained by forward and backward extraction was explained by the presence of small amounts of unextractable neptunium species in the aqueous phase, which might have been introduced during the preparation of  $^{239}\text{Np}$  from  $^{243}\text{Am}$ , or as a result of unfavourable reactions, such as sorption of minute amounts of foreign colloidal particles, hydrolysis and redox reactions. This is also indicated by the higher uncertainties found for the stability constants obtained from forward solvent extraction data.

Table A-13: Stability constants for the Np(V)-oxalate system in 1.0 M  $\text{NaClO}_4$  at  $25^\circ\text{C}$

[\[92TOC/INO\]](#).

Extraction method	pH = $(5.7 \pm 0.2)$	pH = $(7.4 \pm 0.2)$
forward	$\log_{10} \beta_1 = (3.62 \pm 0.05)$	$\log_{10} \beta_1 = (3.46 \pm 0.05)$
backward	$\log_{10} \beta_1 = (3.73 \pm 0.02)$	$\log_{10} \beta_1 = (3.70 \pm 0.01)$
forward	$\log_{10} \beta_2 = (6.04 \pm 0.04)$	$\log_{10} \beta_2 = (5.74 \pm 0.05)$
backward	$\log_{10} \beta_2 = (6.16 \pm 0.02)$	$\log_{10} \beta_2 = (6.14 \pm 0.01)$

As a consequence the authors studied the complex formation between Np(V) and carboxylic acids by the backward extraction method. The values obtained from backward extraction for oxalate were:

$$\log_{10} \beta_1 = (3.71 \pm 0.02) \quad \log_{10} \beta_2 = (6.15 \pm 0.02).$$

These values are included in the review process with the uncertainty increased

to  $\pm 0.1 \log_{10}$ -units to include the possibility of other systematic errors that might have been overlooked by the authors. In addition the authors also determined the stability constants in 0.1 M NaClO<sub>4</sub> in order to check the contribution of the ionic medium to the solvent extraction process:

$$\log_{10} \beta_1 = (3.71 \pm 0.05) \quad \log_{10} \beta_2 = (5.84 \pm 0.01).$$

Because of difficulties with keeping the ionic strength constant during the measurements, this review increases their uncertainty to  $\pm 0.2 \log_{10}$ -units.

### [\[92TOC/INO3\]](#)

This is a conference contribution reporting some of the data also published in [\[92TOC/INO\]](#) and also some additional distribution coefficients in figures. Methylisobutyl ketone, MIBK, was tested as an organic phase solvent in addition to isoamylalcohol, but at high ligand concentrations MIBK gave unexpectedly high distribution ratios and this solvent was therefore disused. The results obtained using isoamylalcohol are discussed in this Appendix under the [\[92TOC/INO\]](#) entry.

### [\[92TRI/TRI\]](#)

The complex formation between oxalate or nitrilotriacetate (nta) and Cu<sup>2+</sup>, Ni<sup>2+</sup>, and Co<sup>2+</sup> was studied at 30°C by electrophoresis. Mixed complexes with oxalate and nta were also studied. This study is similar to [\[76YAD/GHO\]](#): the authors used solutions that initially had 0.005 M H<sub>2</sub>ox and 0.1 M HClO<sub>4</sub> and the pH was varied between 1 and 5 by the addition of aqueous NaOH. This suggests that the ionic strength and total oxalate concentration were perhaps not kept constant. No information about the pH calibration and about the pH scale is given. In the oxalate systems the authors assumed the formation of two complexes from two plateaus of the mobility curve *versus* pH. For the Ni(II)-oxalate system two equilibrium constants are reported,  $\log_{10} K_1 = 2.3$  and  $\log_{10} K_2 = 2.2$ . The first constant corresponds to the formation of the bioxalate complex, Ni(Hox)<sup>+</sup>. There is however a contradiction in [\[92TRI/TRI\]](#) about the composition of the second complex. In the text it is stated that  $K_2$  corresponds to the “normal” oxalate complex, while in their Table 1, the values given are listed for “ $K_1^{M_{MHL}}$ ” and “ $K_2^{M_{MHL}}$ ”, indicating that  $K_2$  might correspond to the stepwise formation of Ni(Hox)<sub>2</sub>(aq). If  $K_2$  corresponds to the formation of a “normal” oxalate complex, it is not clear if the constant corresponds to the overall equilibrium constant (Ni<sup>2+</sup> + 2 ox<sup>2-</sup>  $\rightleftharpoons$  Ni(ox)<sub>2</sub><sup>2-</sup>), or to the second stepwise constant (Ni(ox)(aq) + ox<sup>2-</sup>  $\rightleftharpoons$  Ni(ox)<sub>2</sub><sup>2-</sup>). The electrophoresis method is of limited accuracy and the experimental conditions were not well defined in this study, and therefore the reported equilibrium constants are not considered in this review.

[\[93APE\]](#)

Solubilities of commercially supplied salts,  $\text{Mg}(\text{ac})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mg}(\text{aspa})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Mg}_3(\text{cit})_2 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ca}_3(\text{cit})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}(\text{lac})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}(\text{cit}) \cdot \text{H}_2\text{O}$  and  $\text{Mg}_3(\text{cit})_2 \cdot 14\text{H}_2\text{O}$ , were measured in water at 283–330 K by using EDTA complexometry. The solubility of  $\text{Mg}_3(\text{cit})_2 \cdot 9\text{H}_2\text{O}$  increased from  $0.0467 \text{ mol} \cdot \text{kg}^{-1}$  at 286.19 K to  $0.0705 \text{ mol} \cdot \text{kg}^{-1}$  at 331.19 K. The solubility of  $\text{Mg}_3(\text{cit})_2 \cdot 14\text{H}_2\text{O}$  increased from  $0.0295 \text{ mol} \cdot \text{kg}^{-1}$  at 286.35 K to  $0.1077 \text{ mol} \cdot \text{kg}^{-1}$  at 326.29 K. On the other hand, the solubility of  $\text{Ca}_3(\text{cit})_2 \cdot 4\text{H}_2\text{O}$  decreased from  $0.0017 \text{ mol} \cdot \text{kg}^{-1}$  at 283.39 K to  $0.0014 \text{ mol} \cdot \text{kg}^{-1}$  at 331.77 K. The enthalpies of solution at 298.15 K were estimated to be  $\Delta_{\text{sol}} H_{\text{m}} (m = 0.0483 \text{ mol} \cdot \text{kg}^{-1}) = 4.0 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{Mg}_3(\text{cit})_2 \cdot 9\text{H}_2\text{O}$ ,  $\Delta_{\text{sol}} H_{\text{m}} (m = 0.0443 \text{ mol} \cdot \text{kg}^{-1}) = 25.1 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{Mg}_3(\text{cit})_2 \cdot 14\text{H}_2\text{O}$  and  $\Delta_{\text{sol}} H_{\text{m}} (m = 0.0018 \text{ mol} \cdot \text{kg}^{-1}) = -6.2 \text{ kJ} \cdot \text{mol}^{-1}$  for  $\text{Ca}_3(\text{cit})_2 \cdot 4\text{H}_2\text{O}$ .

Since the speciation of the dissolved species (free metal ion and  $\text{cit}^{3-}$  or complexed species) was not considered, the final equilibrium species in the chemical reaction to which the estimated  $\Delta_{\text{sol}} H_{\text{m}}$  corresponds is not clear. Thus, this review does not accept the results of this paper.

[\[93AZA/HAS\]](#)

In order to study the formation of mixed complexes of  $\text{Ni}^{2+}$  and adenosine-5'-mono-, -di, or triphosphate and malic, maleic, succinic, tartaric, citric or oxalic acid, the stability constants of the  $\text{Ni}^{2+}$  complexes with citrate have been determined by potentiometric titration of a solution containing  $10^{-3} \text{ M Ni}^{2+}$  and  $10^{-3} \text{ M citric acid}$  at  $0.1 \text{ M KNO}_3$  and  $(25.0 \pm 0.1)^\circ\text{C}$ . The single species  $\text{Ni}(\text{cit})^-$  was assumed to be formed and the constant for  $\text{Ni}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})^-$  was obtained to be  $\log_{10} \beta_1 = (4.536 \pm 0.04)$ . Although the standard deviation given to the value is small, the assumption of nonexistence of  $\text{Ni}(\text{Hcit})(\text{aq})$  and  $\text{Ni}(\text{H}_2\text{cit})^+$  in the course of titration is considered to give a considerable error. Thus, this review does not accept this value.

For  $\text{Ni}(\text{II})$ -oxalate the value of  $\log_{10} K_1 = (4.432 \pm 0.030)$  was reported, which is included in this review with an increased uncertainty of  $\pm 0.10$ .

[\[93GLA/MAJ\]](#)

The coulometric method was applied in this study based on alkalimetric titration of solutions containing  $0.05 \text{ mM}$  oxalic acid or citric acid alone, and in the presence of a 10-fold concentration of calcium or magnesium chloride at ionic strength  $0.15 \text{ M NaCl}$  and  $25$  and  $37^\circ\text{C}$ . The experiments were carried out properly and the protonation constants at  $I = 0.15 \text{ M NaCl}$  obtained in this study,  $\log_{10} K_1 = 3.76$  ( $25^\circ\text{C}$ ) and  $3.95$  ( $37^\circ\text{C}$ ) for oxalate, and  $\log_{10} K_n = 5.71, 4.38, 2.92$  ( $25^\circ\text{C}$ ) and  $5.75, 4.42, 2.98$  ( $37^\circ\text{C}$ ) for citrate, are in good agreement with those evaluated in this review.

The equilibrium constants for  $\text{Me} + \text{L} \rightleftharpoons \text{MeL}$  ( $\text{Me} = \text{Mg}^{2+}, \text{Ca}^{2+}$ ;  $\text{L} = \text{ox}^{2-}, \text{cit}^{3-}$ ) reported by [\[93GLA/MAJ\]](#) are  $\log_{10} \beta_1 = 2.18$  ( $25^\circ\text{C}$ ) and  $2.39$  ( $37^\circ\text{C}$ ) for



Mg(ox)(aq), 1.46 (25°C) and 1.47 (37°C) for Ca(ox)(aq), 3.27 (25°C) and 3.24 (37°C) for Mg(cit)<sup>-</sup>, 3.17 (25°C) and 3.28 (37°C) for Ca(cit)<sup>-</sup>. No uncertainty analysis of these values is provided by [93GLA/MAJ]. In the case of Ca and Mg citrate complexes the reported values are compatible with results reported from similar studies and this review accepts these values with an uncertainty of  $\pm 0.2$ .

However, the Ca and Mg oxalate formation constants reported in this study are puzzling. The Ca oxalate constants are one order of magnitude lower than the values reported in [82DAN/MAR] (e.g.,  $\log_{10} \beta_1 = 2.46$  at 37°C and 0.10 M) and also lower than values reported for 25°C and 0.5 M [76MCD/KEL] and 1 M [67HAS/MAK]. Likewise, but less drastic differences are found comparing the Mg oxalate values with results given in [57SCH/AND], [60RAA], [82DAN/MAR] and [2001CHO/BON]. In the case of Ca perhaps the solubility of Ca(ox)·H<sub>2</sub>O was exceeded under some experimental conditions, but as no experimental data are provided in [93GLA/MAJ], neither in a table nor in a figure, there is no way to check or to re-evaluate the results. The largely discrepant Ca and Mg oxalate formation constants are not credited in this review.

#### [93JAN]

The study reports stability constants for a group of divalent metals (Zn<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>2+</sup> and Pb<sup>2+</sup>) with some organic ligands (oxalate, tartrate, citrate, malonate and pyridine-2,6-dicarboxylate). Ion chromatography was used in these experiments at (22  $\pm$  1)°C. The pH was kept equal to 6 for oxalate and to 5.5 for citrate. The author claims that the ionic strength was “almost” constant ( $\approx 0.1$  M NaClO<sub>4</sub>). The concentrations of the metal ions are given to be 0.01 to 0.1 mM, but the concentrations of the ligands are not reported. However, in their figure illustrating the tartrate system, the concentration of ligand is seen to reach values as high as 0.04 M. This resulted in large variations of the ionic strength, and because of this the data reported in [93JAN] is not considered in this review.

#### [94ERT/MOH]

The authors report potentiometric determinations of the first and second protonation of oxalate at 25°C in NaClO<sub>4</sub> media. The concentration of the background electrolyte ranges from 3 M up to 9 M. The reported protonation constants are discrepant with results originating from the same laboratory [96CHO/CHE]. Although [94ERT/MOH] is cited in the introduction of [96CHO/CHE], the latter authors did not consider the results of [94ERT/MOH], neither in their Table 1 comparing their new experimental results with literature data, nor in their discussion of the results. The following table shows a comparison of [94ERT/MOH] with the data determined by [96CHO/CHE]:

Table A-14: Protonation constants obtained by [94ERT/MOH] and [96CHO/CHE]

Medium	<i>I</i> (molar)	$\text{ox}^{2-} + \text{H}^+ \rightleftharpoons \text{Hox}^-$		$\text{Hox}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{ox}(\text{aq})$	
		$\log_{10}K_1$	$\log_{10}K_1$	$\log_{10}K_2$	$\log_{10}K_2$
		[94ERT/MOH]	[96CHO/CHE]	[94ERT/MOH]	[96CHO/CHE]
NaClO <sub>4</sub>	3	(3.85 ± 0.1)	(3.84 ± 0.01)	(2.0 ± 0.3)	(1.49 ± 0.02)
	5	(4.47 ± 0.01)	(4.23 ± 0.01)	(2.19 ± 0.04)	(1.42 ± 0.04)
	7	(4.91 ± 0.01)	(4.71 ± 0.01)	(2.61 ± 0.04)	(1.75 ± 0.01)
	9	(5.20 ± 0.01)	(5.11 ± 0.04)	(2.26 ± 0.08)	(2.13 ± 0.04)

Although there is no apparent reason for this inconsistency, the data from [94ERT/MOH] are clearly discrepant, especially the  $\log_{10}K_2$  values, and they were not considered in this review.

The formation constants of U(VI) and Th(IV) oxalate complexes were determined by solvent extraction at 25°C, at  $I = 3, 5, 7$  and 9 M (NaClO<sub>4</sub>) for U(VI) and  $I = 1, 3, 5, 7$  and 9 M (NaClO<sub>4</sub>) for Th(IV). U-233 and Th-230 tracers were used. No raw data on the U(VI) experiments were presented in the paper. The concentration of oxalate used in the U(VI) experiments is unknown, but it appears that the concentration of oxalate used in the Th(V) experiments ranges from 0 to  $1 \times 10^{-5}$  M. By conducting the experiments at different  $pC_H$  (1.6 – 3.5), the stability constants for four U(VI) oxalate complexes,  $\beta_{101}$ ,  $\beta_{111}$ ,  $\beta_{102}$  and  $\beta_{122}$ , at different ionic strengths were calculated. The SIT method was used to obtain the constants at  $I = 0$ . The authors found it necessary to add a term of  $\Delta\delta I^2$  in order to fit the data for  $I > 3$  M.

Only the formation constants of U(VI) oxalate at  $I = 3$  M are accepted by this review, since the other ionic strengths ( $\geq 5$  M, or 6.58 m) exceeds the applicable range of the SIT method. Besides, the formation of protonated U(VI) oxalate complexes in the  $pC_H$  region from 1.6 to 3.5 is questionable. The raw data at different  $pC_H$  (Table 4 of the paper) are scattered and insufficient to allow reliable determination of the constants for such complexes, if they formed at  $pC_H = 1.6 - 3.5$ . In fact, an earlier study [83CHO/BOK] of solvent extraction indicates that no protonated U(VI) oxalate complexes formed in 1 – 4 M HNO<sub>3</sub>. Therefore, the data from this work are re-evaluated by this review, using a model excluding protonated complexes. The new values are  $\log_{10} \beta_{101} = (6.13 \pm 0.22)$  and  $\log_{10} \beta_{102} = (11.08 \pm 0.18)$  at  $I = 3$  M. These were then converted from molarity to molality unit by the method in Chapter II and accepted for SIT analysis in conjunction with other accepted values at different ionic strengths (Table VI–39).

#### [94KUM/CHA]

The authors determined the protonation constants of  $\text{edta}^{4-}$  using three different background electrolytes: NaCl, KCl, and tetramethylammonium chloride (Me<sub>4</sub>NCl), at a concentration of 0.1 M. The titrant is however reported to be tetramethylammonium

hydroxide in all cases. The glass electrode was first calibrated using standard buffers. Subsequently, a correction factor was used to convert pH values to  $[H^+]$  values. This factor was obtained from a strong acid-base titration at  $[Me_4NCl] = 0.1$  M, but was apparently used in all titrations, independently of the nature of the background electrolyte. It is quite probable, however, that the value for this correction factor changes with the ionic media, as it includes a junction potential that should depend on the nature of the electrolyte. Because of the uncertainties in the nature of the background electrolyte, and in the calibration of the glass electrode, the data obtained in  $Na^+$  and  $K^+$  media in [\[94KUM/CHA\]](#) are not considered in this review.

#### [\[94RED/SHI\]](#)

The authors report a potentiometric study on the ternary complex formation between 3-methyl-1,2-cyclopentanedione and several ligands, including oxalate. The metals studied were Cu(II), Ni(II), Co(II) and Zn(II). Protonation constants were determined in 0.1 M  $KNO_3$  at 30°C. In addition to the equilibrium constants for ternary metal ion complexes, the stability constants of the binary complexes, including  $Ni(ox)(aq)$ , were also determined. No details are given in this paper on the calibration procedure of the glass electrode. Although the authors refer to a previous paper for experimental details, [\[91RED/DEV\]](#), no information on the measuring equipment is given there either. The results of this study are not credited in this review.

#### [\[94TOC/SIR\]](#)

The stability constants of Np(V) complexes with several nitrogen-containing carboxylates (including edta) have been obtained in 1 M  $NaClO_4$  at 25°C by a solvent extraction method using TTA (thenoyl trifluoroacetone) and 1,10-phenantroline in isoamyl alcohol. Ligand protonation constants have been taken from [\[82MAR/SMI\]](#). In the case of edta these are 8.78, 6.23, 2.38 and 2.00, as reported in Table 1 of [\[94TOC/SIR\]](#). Unfortunately, no details are reported about the pH measurements, *i.e.*, the pH scale used or the calibration of the pH meter. For this reason, the reported Np(V) edta stability constant is not further considered in this review.

#### [\[95LIS/CHO\]](#)

See the comments under [\[96BOR/LIS\]](#).

#### [\[95MIR/SAD\]](#)

The authors report a potentiometric study of the first protonation of oxalate at 25°C in NaCl and  $NaClO_4$  media. The concentration of the background electrolyte ranges from 0.01 M up to 4.0 M. The authors do not give any estimates of the uncertainties of the reported constants. This review assigns uncertainties of  $\pm 0.06 \log_{10}$ -units to the values of [\[95MIR/SAD\]](#) in the multi-dimensional regression analysis of protonation constants. Data measured in electrolyte concentrations of  $I < 0.1$  M have not been included in the

regression analyses.

#### [95PII/LAJ]

Potentiometric titrations of citric acid (0.003 – 0.008 M) in the absence and presence of Mg(II) or Ca(II) ions (0.002 – 0.004 M) were conducted at  $I = 0.5$  M NaClO<sub>4</sub> and 25°C. The experiments covered the pH range  $3.5 < -\log_{10} [H^+] < 6.5$  and ligand to metal ratios 1 – 4. Experiments and data treatment were done properly. Using the protonation constants obtained in this study (  $\log_{10} K_{(H)} = (5.317 \pm 0.007), (4.147 \pm 0.010), (2.832 \pm 0.011)$  ), the constants for  $M^{2+} + H_r \text{cit}^{r-3} \rightleftharpoons M(H_r \text{cit})^{r-1}$  were calculated to be  $\log_{10} \beta_1 = (2.71 \pm 0.01)$  for Mg(cit)<sup>−</sup>,  $(1.23 \pm 0.12)$  for Mg(Hcit)(aq),  $(2.71 \pm 0.01)$  for Ca(cit)<sup>−</sup> and  $(1.38 \pm 0.09)$  for Ca(Hcit)(aq) where the errors were 3σ estimated from the deviations of the potentiometric data. Considering the errors in the potentiometry, purities of the reagents *etc.*, this review accepts these values but with assigning larger uncertainties as,  $\log_{10} \beta_1 = (2.71 \pm 0.1)$  for Mg(cit)<sup>−</sup>,  $(1.23 \pm 0.2)$  for Mg(Hcit)(aq),  $(2.71 \pm 0.1)$  for Ca(cit)<sup>−</sup> and  $(1.38 \pm 0.2)$  for Ca(Hcit)(aq).

#### [95ROB/GIA2]

Known amounts of Ca<sub>3</sub>cit<sub>2</sub> and NaOH or HCl were mixed at 25°C. In some cases, NaCl or (CH<sub>3</sub>)<sub>4</sub>NCl was also added to adjust ionic strength. The total concentrations of Ca<sup>2+</sup> and H<sup>+</sup> in the solution after separating the precipitation were determined by titration with EDTA and NaOH, respectively. By assuming that the decrease in H<sup>+</sup> in the solution is due to the precipitation of Ca(Hcit)(s), and that the decrease in Ca<sup>2+</sup> in the solution is due to the precipitation of Ca<sub>3</sub>(cit)<sub>2</sub>(s) and Ca(Hcit)(s), the total concentration of citrate in the solution was calculated. Then, from these values of the total concentrations of Ca<sup>2+</sup>, H<sup>+</sup> and citrate in the solution, free concentrations of Ca<sup>2+</sup>, H<sup>+</sup> and cit<sup>3−</sup> were calculated with considering the protonation of cit<sup>3−</sup>, complex formation of Na<sup>+</sup> and Ca<sup>2+</sup> with cit<sup>3−</sup>, and the formation of NaCl(aq) and CaCl<sup>+</sup>. From these values, the values of  $\log_{10} K_{s,0}$  were calculated for the reactions  $\text{Ca(Hcit)(s)} \rightleftharpoons \text{Ca}^{2+} + \text{H}^+ + \text{cit}^{3-}$  and  $\text{Ca}_3(\text{cit})_2(\text{s}) \rightleftharpoons 3 \text{Ca}^{2+} + 2 \text{cit}^{3-}$  at  $I = 0.01 - 0.54$  M (NaCl) or ((CH<sub>3</sub>)<sub>4</sub>NCl). These data were treated as a function of the ionic strength and the solubility products were reported to be  $\log_{10} K_{s,0} = -11.35 + 14g(I) - 5.95I$  for  $\text{Ca(Hcit)(s)} \rightleftharpoons \text{Ca}^{2+} + \text{H}^+ + \text{cit}^{3-}$  and  $\log_{10} K_{s,0} = -16.95 + 30g(I) - 8.52I$  for  $\text{Ca}_3(\text{cit})_2(\text{s}) \rightleftharpoons 3 \text{Ca}^{2+} + 2 \text{cit}^{3-}$ , where  $g(I) = \sqrt{I} / (2 + 3\sqrt{I}) + 0.1I^{3/2}$ . As given by the above results in their functional form,  $\log_{10} K_{s,0}$  reported are strongly dependent on the ionic strength. The data of  $\log_{10} K_{s,0}$  given in Table A9 in the paper indicate that both  $\log_{10} K_{s,0}$  begin to deviate significantly (more than 0.5) from  $\log_{10} K_{s,0}^o + \Delta z^2 D$  at such a low ionic strength as  $I = 0.1$  M. Although this is explained by the term  $(0.1\Delta z^2 I^{3/2} - CI)$  in the paper, it is unlikely for the ionic interaction term to have such a large contribution. According to the specific interaction theory expressed by:

$$\log_{10} K_{s,0} = \log_{10} K_{s,0}^o + \Delta z^2 D - \Delta \epsilon I_m$$

$$\Delta \epsilon = 3\epsilon(\text{Ca}^{2+}, \text{X}^-) + 2\epsilon(\text{cit}^{3-}, \text{Na}^+),$$

it is expected that  $\Delta\epsilon$  does not exceed 2. Since the constants used for the protonation of  $\text{cit}^{3-}$ , complex formation of  $\text{Na}^+$  and  $\text{Ca}^{2+}$  with  $\text{cit}^{3-}$ , the formation of  $\text{NaCl}(\text{aq})$  and  $\text{CaCl}^+$ , and their dependences on ionic strength are not given, this review cannot estimate the uncertainties derived from such treatment and from the dependences of the constants on the ionic strength. Although the reviewer cannot assign the origin of this anomalous ionic strength dependence to be experimental or to the treatment of the data, this review does not accept the values reported in this paper.

#### [\[96ARA/ARC\]](#)

The ionisation constants of a series organic acids, including oxalic acid, were determined by potentiometric and spectrophotometric methods in 0.1 M KCl at 25°C. For oxalic acid  $\log_{10}K_1 = 3.38$ ,  $\log_{10}K_2 = 1.00$  are given in Table 2 of [\[96ARA/ARC\]](#) without further details how they were obtained. Some unknown errors in the measurements or in the data treatment are suspected by this review, as the reported  $\log_{10}K_1 = 3.38$  is clearly discrepant by more than 0.4  $\log_{10}$ -units with all other data reported for the same conditions, e.g., [\[92ROB/STE\]](#), [\[95LU/MOT\]](#). It is tempting to assume a typo error, i.e.,  $\log_{10}K_1 = 3.83$ , but this review prefers to reject the suspicious data.

#### [\[96BOR/LIS\]](#)

The authors determined the acid dissociation constants and complex formation constants with U(VI) and Np(V) for a series of organic ligands, including oxalic and citric acids, and edta at  $I = 5$  m NaCl and 25°C.

Simultaneously, Choppin *et al.* [\[96CHO/ERT\]](#) published in the same volume of the journal another study on the complex formation between citrate and thorium(IV) where Choppin *et al.* also determined the acid dissociation constants for citric acid at several ionic strengths in sodium chloride and perchlorate media at 25°C. The values reported in [\[96CHO/ERT\]](#) were also reported later in a SANDIA report [\[2001CHO/BON\]](#).

Large discrepancies are found for the protonation constants of citrate between the two publications at  $I = 5$  m NaCl and 25°C (see Table A-15). There is no apparent reason for these discrepancies. However, in [\[96CHO/ERT\]](#) the description of the experimental procedures is more detailed and shows that greater care was taken to obtain accurate data than in [\[96BOR/LIS\]](#). For example, in [\[96CHO/ERT\]](#) it is described that nitrogen gas was used to avoid contamination with atmospheric  $\text{CO}_2(\text{g})$ , while such precaution is not mentioned in [\[96BOR/LIS\]](#). Because of this, and because the data of Borkowski *et al.* is in disagreement with all other data available in NaCl media, the protonation constants of citrate reported in [\[96BOR/LIS\]](#) are not included in the evaluation procedure of this review.

Table A-15: Literature data for the protonation of citrate in 5 m NaCl.

	<a href="#">[96BOR/LIS]</a>	<a href="#">[96CHO/ERT]</a> <a href="#">[2001CHO/BON]</a>
$\log_{10} K_1$	$(8.20 \pm 0.16)$	$(5.35 \pm 0.01)$
$\log_{10} K_2$	$(5.88 \pm 0.03)$	$(4.49 \pm 0.01)$
$\log_{10} K_3$	$(3.36 \pm 0.02)$	$(3.13 \pm 0.02)$

Similarly to the problems encountered with the protonation constants of citrate, the data by Borkowski, Lis and Choppin for  $\text{ox}^{2-}$  and  $\text{edta}^{4-}$  [\[95LIS/CHO\]](#), [\[96BOR/LIS\]](#) show discrepancies when compared with other publications from the same group, cf. Table A-16 and the discussion in this Appendix of [\[2001CHO/BON\]](#). Although there is no apparent reason for this inconsistency, the data from [\[95LIS/CHO\]](#), [\[96BOR/LIS\]](#) are clearly discrepant, and they were not considered in this review.

Table A-16: Literature data for the protonation of  $\text{ox}^{2-}$  and  $\text{edta}^{4-}$ .

	<a href="#">[95LIS/CHO]</a> , <a href="#">[96BOR/LIS]</a>	<a href="#">[99MIZ/BON]</a>	<a href="#">[2001CHO/BON]</a>
	$I = 5 \text{ m NaCl}$	$I = 5 \text{ m NaCl}$	$I = 5 \text{ m NaCl}$
$\text{ox}^{2-}$			
$\log_{10} K_1$	$(4.68 \pm 0.02)$	$(3.86 \pm 0.02)$	$(3.95 \pm 0.02)$
$\log_{10} K_2$	$(2.08 \pm 0.01)$	$(1.2 \pm 0.02)$	
$\text{edta}^{4-}$			
$\log_{10} K_1$	$(9.11 \pm 0.14)$	$(8.96 \pm 0.02)$	$(9.01 \pm 0.03)$
$\log_{10} K_2$	$(6.82 \pm 0.03)$	$(7.01 \pm 0.02)$	$(6.95 \pm 0.01)$
$\log_{10} K_3$	$(3.21 \pm 0.03)$	$(2.625 \pm 0.009)$	$(2.46 \pm 0.01)$
$\log_{10} K_4$	$(1.85 \pm 0.02)$	$(2.26 \pm 0.06)$	$(1.97 \pm 0.01)$

Distribution ratios of *ca.*  $1 \times 10^{-6} \text{ M } ^{237}\text{Np(V)}$  and  $1 \times 10^{-7} \text{ M } ^{233}\text{U(VI)}$  between  $2 \times 10^{-2} \text{ M}$  HDEHP in heptane and citric acid in 5.0 m NaCl were obtained at  $\text{pH} = (5.8 \pm 0.1)$  and the constant of  $\log_{10} \beta_1(\text{cit}) = (2.40 \pm 0.06)$  for  $\text{NpO}_2^+ + \text{cit}^{3-} \rightleftharpoons \text{NpO}_2(\text{cit})^{2-}$ ,  $\log_{10} \beta_1(\text{cit}) = (6.04 \pm 0.01)$  and  $\log_{10} \beta_2(\text{cit}) = (10.98 \pm 0.03)$  for  $\text{UO}_2^{2+} + 2\text{cit}^{3-} \rightleftharpoons \text{UO}_2(\text{cit})_2^{4-}$  were estimated from the plots of  $(D_0 / D - 1)$  against  $[\text{cit}^{3-}]$ , where  $D_0$  and  $D$  are the distribution ratio of Np(V) or U(VI) in the absence and presence of citrate, respectively. The protonation constants of citric acid in 5.0 m NaCl were obtained by potentiometry (Table A-15), they seem too high as compared with generally accepted values. A first protonation constant  $\log_{10} K_1 = 8.20$  would give lower concentrations of  $\text{cit}^{3-}$  at pH 5.8, which in turn would give larger  $\log_{10} \beta_1(\text{cit})$ . But  $\log_{10} \beta_1(\text{cit}) = 2.40$  seems smaller as compared with those in other reports. So there is no obvious reason for the inconsistent complex formation constant.

The same experimental technique and conditions were used for other  $^{237}\text{Np(V)}$

and  $^{233}\text{U(VI)}$  systems of interest for this review and again the data are found to be discrepant for all these systems. For example when looking at the values of  $\log_{10} \beta_1$  (all at 5 molal NaCl and 25°C):

- $\text{Np(V)}\text{-ox}^{2-}$  ( $3.04 \pm 0.08$ ) [96BOR/LIS] and ( $4.63 \pm 0.05$ ) [2001BOR/MOO]
- $\text{U(VI)}\text{-cit}^{3-}$  ( $6.04 \pm 0.01$ ) [96BOR/LIS] and ( $7.03 \pm 0.02$ ) [99BRO/POK]
- $\text{Np(V)}\text{-edta}^{4-}$  ( $3.56 \pm 0.04$ ) [96BOR/LIS] and ( $5.45 \pm 0.1$ ) [98POK/BRO]
- $\text{U(VI)}\text{-edta}^{4-}$  ( $3.68 \pm 0.03$ ) [96BOR/LIS] and ( $10.48 \pm 0.15$ ) [98POK/BRO].

Because of these discrepancies the above mentioned data reported in [96BOR/LIS] are not considered in this review.

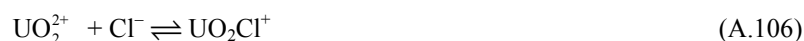
The formation constants of U(VI) oxalate complexes were determined by solvent extraction at 25°C, at  $I = 5$  m (NaCl). U-233 tracers were used. Neither the experimental details including the concentration range of oxalate nor the data on the solvent extraction of U(VI) oxalate systems are provided. It appears, from Table 2 of the paper, that the extraction experiments were conducted at a single pH ( $5.8 \pm 0.1$ ). The stability constants of  $\text{UO}_2\text{ox(aq)}$  and  $\text{UO}_2(\text{ox})_2^{2-}$ ,  $\log_{10} \beta_1$  and  $\log_{10} \beta_2$ , were calculated to be ( $5.50 \pm 0.02$ ) and ( $10.60 \pm 0.02$ ). The dissociation constants of oxalic acid at  $I = 5$  m (NaCl) were measured by potentiometry:  $\text{p}K_{a1} = (2.08 \pm 0.01)$  and  $\text{p}K_{a2} = (4.68 \pm 0.02)$ .

The data from this study (and from [2001BOR/MOO]) are corrected for the complexation of U(IV) by chloride and accepted by this review (Table VI-39). Details of the correction are described as follows.

$$\log_{10} \beta_{\text{corr.}} = \log_{10} \beta_{\text{exp.}} + \log_{10} C \quad (\text{A.104})$$

$$C = 1 + K_{1,\text{Cl}} [\text{Cl}^-] + K_{2,\text{Cl}} [\text{Cl}^-]^2 \quad (\text{A.105})$$

where  $C$  is the correction factor,  $K_{1,\text{Cl}}$  and  $K_{2,\text{Cl}}$  are the formation constants of  $\text{UO}_2\text{Cl}^+$  and  $\text{UO}_2\text{Cl}_2(\text{aq})$  at specific ionic strengths, and can be calculated from the thermodynamic parameters for the complexation:



$\log_{10} K_{1,\text{Cl}}^\circ = (0.17 \pm 0.02)$ ,  $\Delta\varepsilon(\text{A.106}) = -(0.16 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\log_{10} K_{2,\text{Cl}}^\circ = -(1.1 \pm 0.4)$  and  $\Delta\varepsilon(\text{A.107}) = -(0.52 \pm 0.17) \text{ kg}\cdot\text{mol}^{-1}$  [2003GUI/FAN]. The corrections are shown in Table A-17.

Table A-17: Corrections of  $\log_{10} \beta_{\text{exp.}}$  from [96BOR/LIS] and [2001BOR/MOO] for the complexation of U(VI) with chloride.

$I_m$	$\log_{10} K_{1,\text{Cl}}$	$\log_{10} K_{2,\text{Cl}}$	$\log_{10} C$	$\log_{10} \beta_1$		$\log_{10} \beta_2$	
				Exp.	Corr.	Exp.	Corr.
0.0 <sup>a</sup>	(0.17 ± 0.02)	– (1.1 ± 0.4)	0				
5.0 <sup>b</sup>	– (0.08 ± 0.11)	– (0.07 ± 0.94)	(1.42 ± 0.76)	(5.50 ± 0.04)	(6.92 ± 0.76)	(10.60 ± 0.04)	(12.02 ± 0.76)
0.3 <sup>c</sup>	– (0.39 ± 0.02)	– (1.86 ± 0.40)	(0.05 ± 0.01)	(5.94 ± 0.02)	(5.99 ± 0.02)	(10.10 ± 0.12)	(10.15 ± 0.12)
1.0 <sup>c</sup>	– (0.48 ± 0.03)	– (1.80 ± 0.43)	(0.13 ± 0.01)	(5.92 ± 0.02)	(6.05 ± 0.02)		
2.0 <sup>c</sup>	– (0.43 ± 0.05)	– (1.44 ± 0.52)	(0.27 ± 0.04)	(5.89 ± 0.02)	(6.16 ± 0.05)	(10.20 ± 0.16)	(10.47 ± 0.17)
3.0 <sup>c</sup>	– (0.33 ± 0.07)	– (1.01 ± 0.65)	(0.52 ± 0.18)	(6.61 ± 0.04)	(7.13 ± 0.18)	(11.00 ± 0.14)	(11.52 ± 0.22)
4.0 <sup>c</sup>	– (0.21 ± 0.09)	– (0.55 ± 0.79)	(0.90 ± 0.45)	(6.70 ± 0.02)	(7.60 ± 0.45)		
5.0 <sup>c</sup>	– (0.08 ± 0.11)	– (0.07 ± 0.94)	(1.42 ± 0.76)	(5.82 ± 0.04)	(7.24 ± 0.76)		

a: [2003GUI/FAN]

b: [96BOR/LIS]

c: [2001BOR/MOO].

The corrected values are accepted by this review, and included in the SIT analysis in conjunction with other values in Table VI-39.

#### [96CHO/CHE]

The authors report a potentiometric study of the first and second protonation of oxalate at 25°C in NaClO<sub>4</sub> media. The concentration of the background electrolyte ranges from 0.1 M up to 9 M. The SIT formalism is not suitable to describe media effects in very concentrated solutions. Hence, data measured in NaClO<sub>4</sub> at  $I > 5$  M are not included in the multi-dimensional regression analyses of protonation constants.

The complex formation of Am(III) by oxalate has been investigated by solvent extraction with dibenzoylmethane and TBP in toluene at 25°C at  $I = 1.0, 3.0$  and  $5.0$  M NaClO<sub>4</sub>. The considerations on the hydrolysis of Am(III), adsorption of Am(III) on the glass wall, conversion of pH to pcH ( $-\log_{10}[\text{H}^+]$ ) were conducted in a proper way. The stability constants of  $\text{Am}(\text{ox})^+$  and  $\text{Am}(\text{ox})_2^-$  obtained at pcH from 6.3 to 8.3 are reported in Table 3 of the paper and those at pcH below 7.0 were confirmed not to depend on pcH. From the values obtained at pcH below 7.0 listed in Table 3 of the paper, mean values are estimated in this review and the uncertainties are increased considering the possible systematic errors introduced in each series of solvent extraction experiments. The values selected are:

$$\begin{aligned} \log_{10} \beta_1 = & (4.66 \pm 0.10) \text{ at } I = 1.0 \text{ M NaClO}_4, \\ & (4.64 \pm 0.10) \text{ at } I = 3.0 \text{ M NaClO}_4 \\ & (4.83 \pm 0.20) \text{ at } I = 5.0 \text{ M NaClO}_4 \end{aligned} \quad \text{for } \text{Am}^{3+} + \text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})^+$$



$$\begin{aligned} \log_{10} \beta_2 = & (8.35 \pm 0.20) \text{ at } I = 1.0 \text{ M NaClO}_4, \\ & (8.64 \pm 0.10) \text{ at } I = 3.0 \text{ M NaClO}_4 \\ & (9.24 \pm 0.30) \text{ at } I = 5.0 \text{ M NaClO}_4 \end{aligned} \quad \text{for } \text{Am}^{3+} + 2\text{ox}^{2-} \rightleftharpoons \text{Am}(\text{ox})_2^-.$$

### [96CHO/ERT]

As no reliable experimental data exists for  $\text{Pu}^{4+}$  citrate complexes, this paper on thorium citrate complexes is considered as a chemical analogy. Since  $\text{Pu}^{4+}$  and  $\text{Th}^{4+}$  are considered to be similar in complex formation and  $\text{Th}^{4+}$  is known not to hydrolyse up to pH around 4, the stability constants of  $\text{Th}^{4+}$  citrates may be used as alternative for  $\text{Pu}^{4+}$  citrates. In this paper, distribution ratios of  $^{230}\text{Th}$  between TTA or DBM in toluene and the aqueous phase containing  $3.2 \times 10^{-7} \sim 1.9 \times 10^{-6}$  M citric acid were measured at pH 1.8 ~ 4.0, 25°C. The ionic strengths were varied up to 5 m (NaCl) and 14 m ( $\text{NaClO}_4$ ), and the data in the  $\text{NaClO}_4$  system were used to obtain thermodynamic stability constants using SIT. The experiments and calculations were carefully done and considered to be reliable. The values are reported in the following table.

Table A-18: Citrate equilibrium constants and SIT interaction parameters as reported in [96CHO/ERT].

Reaction	$\log_{10} \beta^o$	$\Delta\epsilon$
$\text{Th}^{4+} + \text{cit}^{3-} \rightleftharpoons \text{Th}(\text{cit})^+$	$(13.7 \pm 0.1)$	$(0.21 \pm 0.01)$
$\text{Th}^{4+} + \text{H}^+ + \text{cit}^{3-} \rightleftharpoons \text{Th}(\text{Hcit})^{2+}$	$(16.6 \pm 0.1)$	$(0.30 \pm 0.01)$
$\text{Th}^{4+} + 2\text{H}^+ + 2\text{cit}^{3-} \rightleftharpoons \text{Th}(\text{Hcit})_2(\text{aq})$	$(31.9 \pm 0.1)$	$(0.46 \pm 0.01)$

### [96MIR/PAS]

The enthalpies  $\Delta_r H_m$  of the reaction  $\text{Ca}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ca}(\text{cit})^-$  were measured in  $I = 0.10, 0.20, 0.30, 0.40$  and  $0.50$  M NaCl at pH 12 and 25°C using an isothermal calorimeter. To the solutions containing  $0$  to  $2 \times 10^{-3}$  M  $\text{CaCl}_2$  in  $I$  M NaCl, solutions containing  $I/12$  M  $\text{Na}_3\text{cit}$  and  $I/2$  M NaCl were added until the ratio of the total concentrations of citrate and  $\text{Ca}(\text{II})$  ions reached  $0.8 - 1.0$ . The pH of the solutions was maintained at 12 with sodium hydroxide. The changes in enthalpy ( $\Delta \bar{H}_m$ ) were corrected for the change in enthalpy by mixing similar solutions in the absence of calcium chloride ( $\Delta_{\text{sol}} \bar{H}_m$ ). By fitting the values of  $\Delta \bar{H}_m - \Delta_{\text{sol}} \bar{H}_m$  at various  $[\text{cit}^{3-}]$  to the equation,

$$\Delta \bar{H}_m - \Delta_{\text{sol}} \bar{H}_m = \frac{\Delta_r H_m \times \beta_1 [\text{cit}^{3-}]}{1 + \beta_1 [\text{cit}^{3-}]}$$

the stability constant of  $\text{Ca}(\text{cit})^-$ ,  $\beta_1$ , and  $\Delta_r H_m$  were obtained. Also, from these values,  $\Delta_r G_m$  and  $\Delta_r S_m$  for the reaction were calculated and listed. Using the values of  $\beta_1$ ,  $\Delta_r H_m$ ,  $\Delta_r G_m$  and  $\Delta_r S_m$  at various ionic strengths, the authors estimated the values at zero ionic strength as  $\log_{10} \beta_1^o = (4.80 \pm 0.03)$ ,  $\Delta_r G_m^o = -(27.4 \pm 0.2) \text{ kJ} \cdot \text{mol}^{-1}$ ,

$\Delta_r H_m^\circ = -(0.6 \pm 0.2) \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_r S_m^\circ = (90 \pm 1) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  by using the Vasil'ev extrapolation equation. Although the values of  $\log_{10} \beta_1$  are in fair agreement with the values selected as reliable in this review, there is some doubt about the effect of the formation of hydroxide complexes of  $\text{Ca}^{2+}$  at the pH of 12 adopted in this work and of the formation of chloride complexes at higher ionic strength. Since the detailed experimental data are not given in the paper and we cannot judge the reliability of the reported  $\Delta_r H_m^\circ$  values, and hence, this review does not credit the values reported in this paper.

#### [\[96XUE/TRA\]](#)

The authors reported the protonation constants for oxalate, citrate and ethylenediamine-tetraacetate in 0.1 M  $\text{Me}_4\text{NCl}$  (tetramethylammonium chloride) at 25°C. The titrant was however KOH. Because of complex formation between  $\text{edta}^{4-}$  and  $\text{K}^+$ , a systematic error was introduced. As no details are given on the ligand and titrant concentrations, the magnitude of this error can not be estimated, and therefore the protonation constants for  $\text{edta}^{4-}$  are not included in the review procedure. For oxalate and citrate, the reported data in 0.1 M  $\text{Me}_4\text{NCl}$  media are included in this review with an assigned uncertainty of  $\pm 0.1 \log_{10}$ -units.

#### [\[97BAG/GAR\]](#)

The new polymer  $[\text{K}_2\{\text{Zr}(\text{ox})_3\}\text{H}_2\text{ox}\cdot\text{H}_2\text{O}]_n$  was isolated from an aqueous mixture of  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$  and  $\text{H}_2\text{ox}$  adjusted to pH  $\sim 2$  by addition of KOH. X-ray crystallographic data indicated the simultaneous presence of two different coordination modes of the oxalate ligands to zirconium metal center; *i.e.* bidentate and bridging bisbidentate.

#### [\[97BAG/GAR2\]](#)

The crystal structure of  $\text{K}_6[\{\text{Zr}(\text{ox})_3\}_2(\mu\text{-ox})]\cdot 4\text{H}_2\text{O}$  prepared by the reaction of  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$ , oxalic acid, and potassium oxalate at pH  $\sim 1.5$  was investigated by X-ray crystallography. The result indicated that oxalate strongly complexes Zr(IV) and displaces the  $\mu$ -hydroxyl groups in the tetranuclear species  $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]^{8+}$  present in the Zr(IV) acidic aqueous solution, likely producing a large number of species.

#### [\[97BEN/PAL\]](#)

In this study the authors investigated the acid dissociation constants of citric acid in NaCl solutions at ionic strengths  $0.1 \text{ molal} < I_m < 1 \text{ molal}$  and at temperatures of  $5^\circ\text{C} < t < 150^\circ\text{C}$ . The experimental technique consisted in measuring the emf of a concentration cell with two  $\text{H}_2$ -electrodes in compartments separated by a porous Teflon liquid junction.

For each temperature and ionic strength only a few measurements were performed ( $\approx 5$  determinations of  $[\text{H}^+]$ ). Checks performed in this review showed that there was a good agreement between the  $\log_{10} K_n$  that can be calculated from the reported

experimental data ( $\log_{10} [\text{H}^+]$ ,  $[\text{H}^+]_{\text{TOT}}$  and  $[\text{cit}^{3-}]_{\text{TOT}}$ ) and the corresponding equilibrium constants listed in Tables IV to VI in [97BEN/PAL].

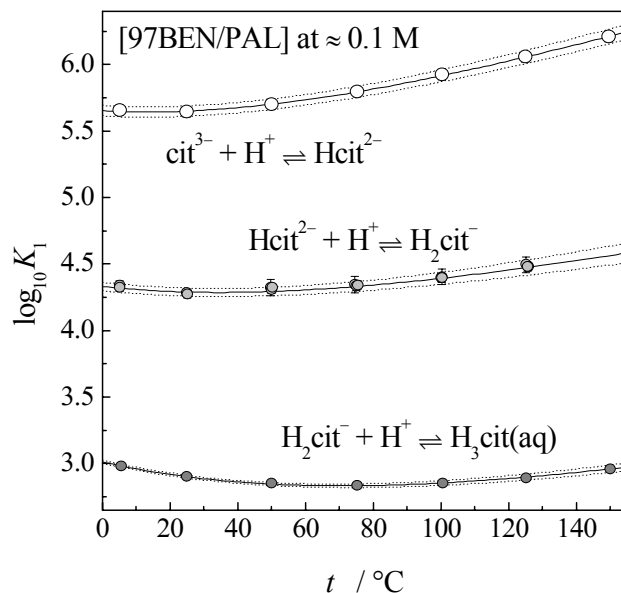
The authors fitted the reported equilibrium constants to functions of  $I_m$  and  $T$ . Numerical differentiation of these functions with respect to temperature, produced values for the corresponding enthalpy and heat capacity changes. These functions produced however slight deviations between the original data and the smoothed values. Values of  $\Delta_r H_m$  and  $\Delta_r C_{p,m}$  were instead obtained in this review by fitting the original equilibrium constants at various temperatures assuming that  $\Delta_r C_{p,m}$  was constant. The results are given in the Table A-19.

Table A-19: Values of  $\Delta_r H_m$  and  $\Delta_r C_{p,m}$  obtained in this review by fitting the original equilibrium constants of [97BEN/PAL] at various temperatures assuming that  $\Delta_r C_{p,m}$  was constant.

$I_m$ (molal)	$\Delta_r H_m$ (kJ·mol <sup>-1</sup> )	$\Delta_r C_{p,m}$ (J·K <sup>-1</sup> ·mol <sup>-1</sup> )
$\text{cit}^{3-} + \text{H}^+ \rightleftharpoons \text{Hcit}^{2-}$		
0.095	(1.84 ± 0.49)	(164 ± 11)
0.299	(1.28 ± 0.45)	(142 ± 12)
0.597	− (0.64 ± 0.34)	(141 ± 9)
0.994	− (1.07 ± 0.25)	(123 ± 5)
$\text{Hcit}^{2-} + \text{H}^+ \rightleftharpoons \text{H}_2\text{cit}^-$		
0.099	− (1.10 ± 0.70)	(116 ± 19)
0.298	− (3.32 ± 0.50)	(113 ± 14)
0.598	− (4.03 ± 0.32)	(113 ± 8)
0.995	− (4.90 ± 0.54)	(100 ± 15)
$\text{H}_2\text{cit}^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{cit}(\text{aq})$		
0.096	− (5.53 ± 0.33)	(121 ± 7)
0.301	− (5.24 ± 0.85)	(94 ± 17)
0.601	− (3.87 ± 0.80)	(63 ± 17)
1.001	− (4.93 ± 0.62)	(77 ± 12)

Figure A-33 shows a comparison between the protonation constants determined by [97BEN/PAL] and the fit using the constant  $\Delta_r C_{p,m}$  model. The values of  $\Delta_r H_m$  were used in Section VII.3.7. Because of the relatively small number of experimental measurements, the uncertainties in  $\Delta_r H_m$  were increased to ± 1 kJ·mol<sup>-1</sup>.

Figure A-33: Protonation constants for citrate in  $\approx 0.1$  molal NaCl determined by [97BEN/PAL] and the constant  $\Delta_r C_{p,m}$  model with the parameters determined in this review.



#### [97POK/CHO]

Distribution ratios of *ca.*  $1 \times 10^{-6}$  M  $^{237}\text{Np(V)}$  between  $2 \times 10^{-4}$  M HDEHP in heptane and the aqueous phase containing an inorganic ligand (acetate, oxalate or citrate) and 0.1 – 9.0 molal  $\text{NaClO}_4$  were obtained and the plots of  $D_0/D-1$  against the free ligand concentration were used to obtain the stability constants, where  $D_0$  and  $D$  are the distribution ratio of  $\text{Np(V)}$  in the absence and presence of organic ligand. The buffer 4-morpholineethanesulfonic acid was used to keep constant pH values. The authors converted the pH meter readings to the pcH values at each ionic strength and they also corrected the measured distribution ratios to that at the averaged pcH. The protonation constants of oxalate and citrate, used to calculate the free ligand concentrations, were those reported in [96CHO/CHE] and [96CHO/ERT].

For citrate, the values of  $\log_{10} \beta_1(\text{cit})$  obtained for  $\text{NpO}_2^+ + \text{cit}^{3-} \rightleftharpoons \text{NpO}_2\text{cit}^{2-}$  ranged from  $(3.03 \pm 0.17)$  to  $(3.11 \pm 0.02)$  as  $I_m$  increased from 0.10 to 9.00 molal  $\text{NaClO}_4$  at  $25^\circ\text{C}$ . No dependence of the stability constant on pcH in the pcH range 5 to 6.5 was observed in accordance with the result by [85SEV] that at  $\text{pH} > 5$   $\text{NpO}_2\text{cit}^{2-}$  is the predominant complex species of neptunium citrate. Since systematic errors might have been introduced from the solvent extraction procedure, this review takes the results of this paper with uncertainties of  $\pm 0.10$  for  $\log_{10} \beta_1(\text{cit})$  at  $I_m = 0.30$  – 9.0 and  $\pm 0.20$  for  $\log_{10} \beta_1(\text{cit})$  at  $I_m = 0.10$ .

The Np(V)-oxalate system was investigated in the oxalate concentration range 0.1 - 10 mM and in a pH range 4 to 6.5. The authors interpreted their data assuming the formation of  $\text{NpO}_2\text{ox}^-$ . No stability constants were reported for the complex  $\text{NpO}_2(\text{ox})_2^{3-}$ , although it might be expected to be formed under these conditions. The data at each pH was analysed separately, and the constants averaged. At 3 molal  $\text{NaClO}_4$ , the values of  $\log_{10} \beta_1$  had a slight dependency with pH. This was interpreted by the authors as an indication of the formation of  $\text{NpO}_2\text{Hox}(\text{aq})$ , with an upper limit for its stability constant of  $\log_{10} \beta_{1,1,1} < 7.3$ . However, the scatter in the  $\log_{10} \beta_1$  values,  $\pm 0.2$ , was of similar magnitude as the alleged change in  $\log_{10} \beta_1$ . The slight tendency of increased  $\log_{10} \beta_1$  values with increased acidities might instead reflect an unknown systematic error.

Because the authors did not include  $\text{NpO}_2(\text{ox})_2^{3-}$  in the interpretation of the experimental data, although this complex should be expected in the range of oxalate concentrations studied and because of possible problems with the solvent extraction technique (possible traces of impurities coming from radionuclide  $^{237}\text{Np}$  preparation, leading to systematic errors as discussed in [92TOC/INO]) this review accepts the stability constants for oxalate reported in [97POK/CHO] with an increased uncertainty of  $\pm 0.2 \log_{10}$ -units.

#### [98ALD/BIA]

This paper reports thermodynamic data for the coordination chemistry of beryllium with dicarboxylic acids. The protonation constants of oxalate have been taken from the literature and thus, are not considered in this review. The enthalpy changes associated with oxalate protonation have been determined by a micro-calorimeter in 0.5 M  $\text{NaClO}_4$  at 25°C. Note that the headings of Table 2 in [98ALD/BIA] are misleading:  $-\Delta_r G_m^\circ$ ,  $-\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$  do not refer to infinite dilution (zero ionic strength) but are valid for 0.5 M  $\text{NaClO}_4$  as a recalculation of  $-\Delta_r G_m^\circ$  from  $\log_{10} K$  in the same table proved. The values reported for the following reactions:



are  $\Delta_r H_m^\circ (\text{A.108}) = (4.7 \pm 0.1)$  and  $\Delta_r H_m^\circ (\text{A.109}) = (4.6 \pm 0.1)$  where the uncertainties are given as one standard deviation. The pH range for the calorimetric measurements leading to these numbers is not reported in [98ALD/BIA]. Hence, some doubts are in place whether the value  $\Delta_r H_m^\circ (\text{A.109})$  derived for the second protonation enthalpy is a reliable thermodynamic quantity or should be regarded as a mere error absorber in the data fitting routine. Hence, the  $\Delta_r H_m^\circ (\text{A.109})$  value reported by [91BEI/GRA] is not credited in this review. Considering other reliable calorimetric measurements discussed in this review, an uncertainty of  $\Delta_r H_m^\circ (\text{A.108}) = (4.7 \pm 0.8) \text{ kJ}\cdot\text{mol}^{-1}$  seems appropriate.

[\[98KET/WES\]](#)

In this careful study the first and second molal dissociation constants of oxalic acid, for the reactions:



were measured potentiometrically in a concentration cell fitted with hydrogen electrodes. Measurements were made at six temperatures ranging from 5°C to 125°C at four ionic strengths ranging from 0.1 mol·kg<sup>-1</sup> to 1.0 mol·kg<sup>-1</sup> (NaCl and NaCF<sub>3</sub>SO<sub>3</sub>). The second molal dissociation constant was measured in NaCF<sub>3</sub>SO<sub>3</sub> media only. The dissociation constants were obtained from measured emf data by an iterative fitting process: The precise evaluation of the first dissociation constant at a certain temperature and ionic strength involves, among other parameters, the oxalate speciation and thus, the knowledge of the second dissociation constant, and vice versa. This iterative fitting process comprised not only data measured in the present study [\[98KET/WES\]](#) but also emf data from [\[91KET/PAL\]](#), [\[48PIN/BAT\]](#) and [\[39HAR/FAL\]](#). Hence, for the sake of internal consistency, we have the choice of either accept the procedure used by [\[98KET/WES\]](#) and considering all the refitted data sets of these studies as a single consistent data set, or to repeat the fitting procedure from scratch. All data for the first acid dissociation constant obtained by the iterative fitting process for individual temperature and ionic strength were subsequently fitted simultaneously yielding a five-parameter function of temperature and ionic strength. A similar overall fit was applied to all data for the second acid dissociation constant yielding a nine-parameter function of temperature and ionic strength. Values of  $\Delta_r H_m$ ,  $\Delta_r S_m$  and  $\Delta_r C_{p,m}$  were obtained by differentiation of these five-parameter and nine-parameter functions. A detailed re-examination of these overall fitting results in terms of the SIT formalism seemed to be necessary for the present review.

In order to estimate the temperature variation of  $\log_{10} K$ , values reported in [\[98KET/WES\]](#) have been fitted in this review to a temperature function assuming  $\Delta_r C_{p,m} = \text{constant}$ . The results are given in Table A-20 and are shown in Figure A-34, Figure A-35 and Figure A-36. According to the rules of error propagation discussed in Section VI.3, assuming an uncertainty of  $\pm 0.02$  in the  $\log_{10} K(\text{A.110})$  values, and  $\pm 0.1$  in the  $\log_{10} K(\text{A.111})$  values, determined over the temperature range 0 to 175°C ( $\log_{10} K(\text{A.110})$  in NaCl) or to 125°C (all other data), the minimum uncertainty in  $\Delta_r H_m$  (A.110) was estimated to be  $\pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$  (NaCl) and  $\pm 0.4 \text{ kJ}\cdot\text{mol}^{-1}$  (NaCF<sub>3</sub>SO<sub>3</sub>), whereas the minimum uncertainty in  $\Delta_r H_m$  (A.111) was estimated to be  $\pm 1.9 \text{ kJ}\cdot\text{mol}^{-1}$ .

Table A-20: Thermodynamic quantities for the first and second protonation reaction of oxalic acid

Medium	$\text{ox}^{2-} + \text{H}^+ \rightleftharpoons \text{Hox}^-$			$\text{Hox}^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{ox}(\text{aq})$		
	$I_m$ (molal)	$\Delta_r H_m$ (A.110) $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_r C_{p,m}$ (A.110) $\text{J}\cdot\text{K}\cdot\text{mol}^{-1}$	$I_m$ (molal)	$\Delta_r H_m$ (A.111) $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_r C_{p,m}$ (A.111) $\text{J}\cdot\text{K}\cdot\text{mol}^{-1}$
NaCl	0.10	$(5.1 \pm 0.8)$	$(190 \pm 12)$	0.10	$(0.0 \pm 2.6)$	$(122 \pm 68)$
	0.19	$(4.9 \pm 0.7)$	$(195 \pm 13)$			
	0.33	$(4.8 \pm 0.3)$	$(159 \pm 5)$	0.32	$(0.3 \pm 2.0)$	$(128 \pm 52)$
				0.60	$(2.3 \pm 1.9)$	$(95 \pm 31)$
	1.00	$(1.3 \pm 1.0)$	$(161 \pm 12)$	1.00	$(1.4 \pm 1.9)$	$(98 \pm 30)$
	2.00	$(0.8 \pm 0.8)$	$(122 \pm 14)$	2.0	$-(2.5 \pm 2.1)$	$(148 \pm 35)$
	3.15	$-(0.6 \pm 0.3)$	$(95 \pm 5)$	3.1	$(0.4 \pm 2.9)$	$(68 \pm 70)$
				4.0	$-(2.2 \pm 1.9)$	$(122 \pm 32)$
NaCF <sub>3</sub> SO <sub>3</sub>	5.00	$-(4.8 \pm 0.4)$	$(78 \pm 6)$	5.0	$-(7.0 \pm 1.9)$	$(152 \pm 18)$
	0.10	$(6.1 \pm 0.4)$	$(177 \pm 7)$	0.10	$-(2.2 \pm 1.9)$	$(187 \pm 25)$
	0.27	$(5.1 \pm 0.4)$	$(168 \pm 3)$			
	0.32	$(5.1 \pm 0.4)$	$(167 \pm 3)$	0.32	$-(0.3 \pm 1.9)$	$(170 \pm 14)$
	0.60	$(4.3 \pm 0.4)$	$(158 \pm 3)$	0.60	$-(0.3 \pm 1.9)$	$(144 \pm 53)$
	1.00	$(3.5 \pm 0.4)$	$(149 \pm 5)$	1.00	$(1.0 \pm 1.9)$	$(120 \pm 27)$

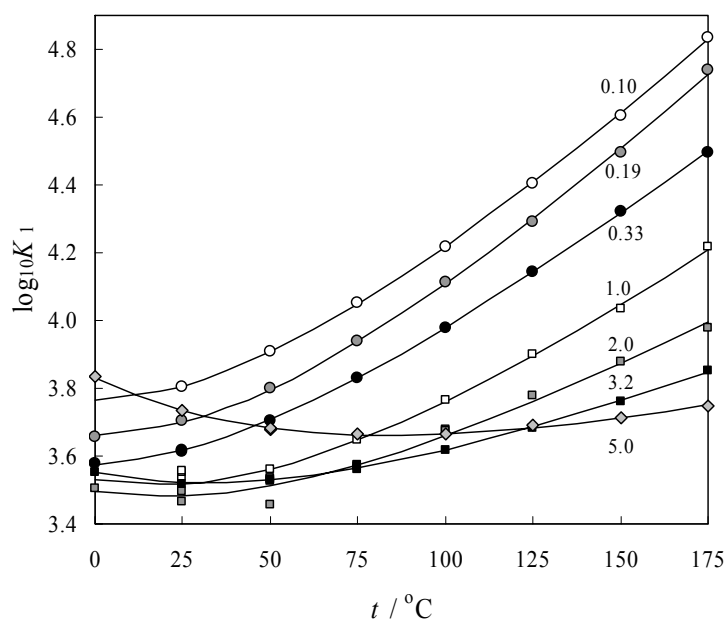
Figure A-34: First protonation constant for oxalate determined by [98KET/WES] in NaCF<sub>3</sub>SO<sub>3</sub> medium and the constant  $\Delta_r C_{p,m}$  model with the parameters determined in this review.

Figure A-35: First protonation constant for oxalate determined by [98KET/WES] in NaCl medium and the constant  $\Delta_r C_{p,m}$  model with the parameters determined in this review.

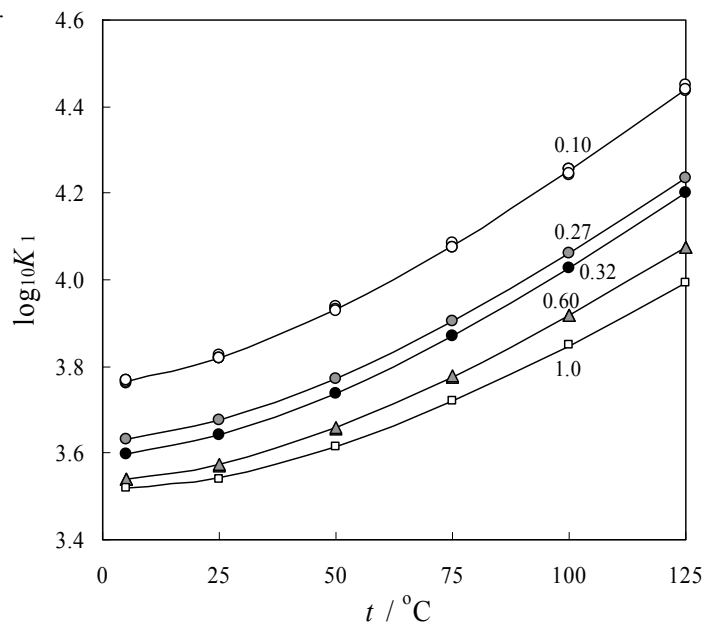
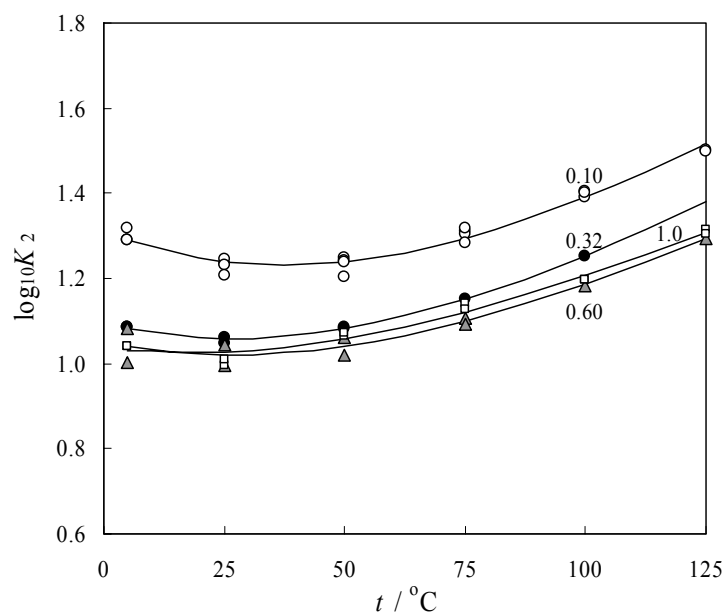


Figure A-36: Second protonation constant for oxalate determined by [98KET/WES] in NaCl medium and the constant  $\Delta_r C_{p,m}$  model with the parameters determined in this review.





[\[98KHA/RAD\]](#)

The authors report a potentiometric study at 25°C on the ternary complex formation between inosine and several ligands, including oxalate. The metals studied were Cu(II) and Ni(II). Protonation constants were determined in 0.1 M NaNO<sub>3</sub>. The first protonation constant for oxalate was determined,  $\log_{10} K_1 = (4.25 \pm 0.08)$ . Some experimental or computational errors seem to have affected the results, as the expected protonation constant should instead be  $\log_{10} K_1 = (3.81 \pm 0.01)$ . Based on this protonation constant and a literature value for the second protonation constant, the complexes formed in the binary and ternary systems were studied. Equilibrium constants for Ni(ox)(aq) and Ni(ox)<sub>2</sub><sup>2-</sup> were reported. The results of this study are not credited in this review.

[\[98KOC/VAS\]](#)

The authors report calorimetric data for the dissociation of H<sub>3</sub>edta<sup>-</sup> at 15 and 35°C in LiNO<sub>3</sub>, KNO<sub>3</sub> and NaClO<sub>4</sub> and at  $I = 0.2, 0.5$  and  $0.75$ . However, the paper contains almost no details on how the calorimetric measurements were performed. The enthalpy changes were calculated using protonation constants obtained in potentiometric titrations at 25°C. No details are presented about the potentiometric titrations, and the values of the protonation constants are not given. The enthalpy of dissociation of H<sub>3</sub>edta<sup>-</sup> is only reported in a graph. The data were however in part corrected for ionic strength effects with a function  $\psi(I)$  that is unknown to this review. Therefore the results reported in the graph can not be taken into consideration.

[\[98MOR/ALM\]](#)

This is an X-ray crystallographic study on guanidinium zirconium carbonate [(C(NH<sub>2</sub>)<sub>3</sub>)<sub>3</sub>ZrOH(CO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O]<sub>2</sub> and sodium zirconium oxalate Na<sub>6</sub>[ZrOH(ox)<sub>3</sub>]<sub>2</sub>·7H<sub>2</sub>O. In the latter dimer, two zirconium atoms are  $\mu$ -bridged by two hydroxyl groups and each zirconium is coordinated by three oxalates.

[\[98OBR/MIT\]](#)

Conductivity and pH measurements in the system H<sub>2</sub>ox – Na<sub>2</sub>SeO<sub>3</sub> are reported in this conference contribution. The measurements were done in three series of solutions: (a)  $x$  cm<sup>3</sup> H<sub>2</sub>ox and  $(10 - x)$  cm<sup>3</sup> Na<sub>2</sub>SeO<sub>3</sub> solutions, (b)  $x$  cm<sup>3</sup> H<sub>2</sub>ox and  $(10 - x)$  cm<sup>3</sup> water and (c)  $(10 - x)$  cm<sup>3</sup> Na<sub>2</sub>SeO<sub>3</sub> and  $x$  cm<sup>3</sup> water. In all series  $x$  was varied from 1 to 9 and the concentration of the initial solutions was 0.02 M. The authors state that the observed decrease in  $[H^+]$  for solutions of the series (a) can be ascribed to an oxalate – selenite complex formation. The authors report in a figure the quantity  $\Delta[H^+] = [H^+]_a - ([H^+]_b + [H^+]_c)$  where  $[H^+]_a$ ,  $[H^+]_b$  and  $[H^+]_c$  are the H<sup>+</sup> ion concentrations in solutions corresponding to the same  $x$  in series (a), (b) and (c), respectively. An analogous difference quantity is reported for conductivity measurements. There are no indications that ionic strength effects were considered by the authors, and because the glass electrode was calibrated using pH-buffers, it may be inferred that the plotted quantity “ $\Delta[H^+]$ ” in fact

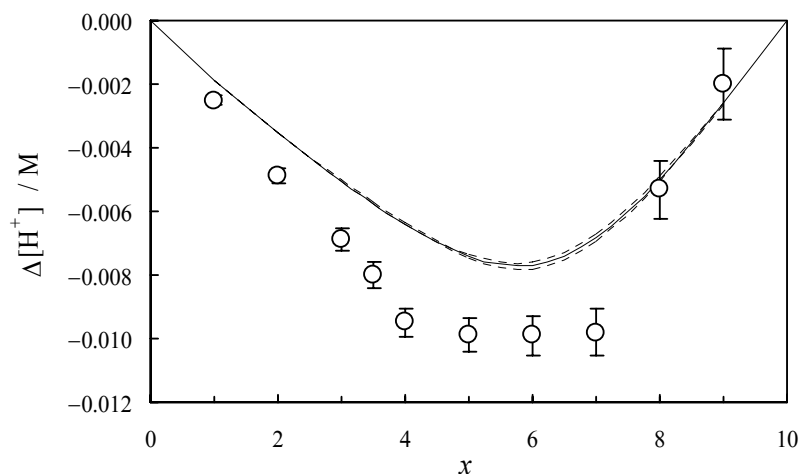
corresponds to  $(a_{\text{H}^+})_{\text{a}} - [(a_{\text{H}^+})_{\text{b}} + (a_{\text{H}^+})_{\text{c}}]$  where  $a_{\text{H}^+}$  indicates the activity of hydrogen ions. The authors state that the curve in their  $\Delta[\text{H}^+]$  versus  $x$  plot indicates the formation of complexes in which the oxalate:selenite ratio is 2:1. The measured pH values are not reported.

The results of simple speciation calculations using the oxalate and selenite protonation constants listed in the tables of recommended values in this review, and ignoring any complex formation, are listed in Table A-21 together with  $\Delta[\text{H}^+]$  values obtained from Fig. 1 in [98OBR/MIT]. As can be seen in Figure A-37, the  $\Delta[\text{H}^+]$  values reported by [98OBR/MIT] are mostly due to the pH difference of solutions (a) and (b) caused by acid-base reactions rather than complex formation. Some effect may nevertheless be seen in Figure A-37 at  $x = 3$  to 7: the experimental values of  $\Delta[\text{H}^+]$  are about  $-2$  mM lower than the calculated ones. However, as the original concentrations and measurements are not reported in this short paper it is not possible to judge the accuracy of the calculated acid-base curve and the possibility of systematic errors cannot be investigated. Therefore, the reported complex formation is not admitted by this review.

Table A-21: Calculated hydrogen ion activities in the system  $\text{H}_2\text{ox} - \text{Na}_2\text{SeO}_3$  and experimental  $\Delta[\text{H}^+]$  values from [98OBR/MIT].

$x$	Series a				Series b		Series c		$\Delta[\text{H}^+] =$	
	$[\text{H}_2\text{ox}]$	$[\text{Na}_2\text{SeO}_3]$	$\text{H}_2\text{ox} + \text{Na}_2\text{SeO}_3$		$\text{H}_2\text{ox}$		$\text{Na}_2\text{SeO}_3$		$[\text{H}^+]_{\text{a}} - ([\text{H}^+]_{\text{b}} + [\text{H}^+]_{\text{c}})$	
	M	M	$\text{pH}_{\text{calc}}$	$I$	$\text{pH}_{\text{calc}}$	$I$	$\text{pH}_{\text{calc}}$	$I$	Calculated	[98OBR/MIT]
1	0.002	0.018	8.64	0.060	2.72	0.002	10.12	0.054	$-0.0019$	$-0.0025$
2	0.004	0.016	8.12	0.052	2.45	0.004	10.11	0.048	$-0.0035$	$-0.0049$
3	0.006	0.014	7.36	0.044	2.29	0.006	10.09	0.042	$-0.0051$	$-0.0069$
3.5	0.007	0.013	4.86	0.036	2.24	0.006	10.07	0.039	$-0.0058$	$-0.0080$
4	0.008	0.012	4.13	0.032	2.19	0.007	10.06	0.036	$-0.0064$	$-0.0095$
5	0.010	0.010	3.41	0.029	2.10	0.009	10.03	0.030	$-0.0075$	$-0.0099$
6	0.012	0.008	2.86	0.022	2.04	0.010	10.00	0.024	$-0.0078$	$-0.0099$
7	0.014	0.006	2.46	0.018	1.98	0.012	9.95	0.018	$-0.0069$	$-0.0098$
8	0.016	0.004	2.18	0.016	1.93	0.013	9.88	0.012	$-0.0050$	$-0.0053$
9	0.018	0.002	1.99	0.016	1.89	0.014	9.75	0.006	$-0.0026$	$-0.0020$

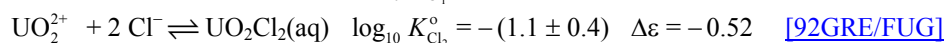
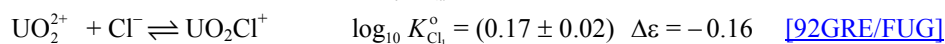
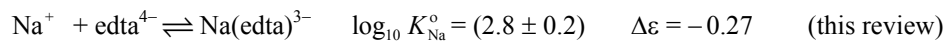
Figure A-37: Plot of  $\Delta[\text{H}^+]$  versus  $x$  in the system  $\text{H}_2\text{Ox} - \text{Na}_2\text{SeO}_3$ : calculated values by this review ignoring complex formation between oxalate and selenite compared with experimental data from [98OBR/MIT]. The uncertainties on the experimental values have been assigned assuming an accuracy of  $\pm 0.03$  pH units.



#### [98POK/BRO]

The complexation of  $\text{UO}_2^{2+}$  ( $10^{-7}$  M) and  $\text{NpO}_2^+$  ( $10^{-6}$  M) with edta ( $0 - 2.5 \cdot 10^{-4}$  M) has been investigated in solutions of 0.3 – 5 m NaCl at 25°C in the pH range 2 – 4.5 (uranium) and 5 – 9 (neptunium). A solvent extraction method with di(2-ethylhexyl)-phosphoric acid (HDEHP) in heptane was used to measure the stability constants of the above cations with  $\text{H}_2\text{edta}^{2-}$ ,  $\text{Hedta}^{3-}$  and  $\text{edta}^{4-}$ . The data are modelled by the authors using the ion-interaction model of Pitzer.

This solvent extraction study is considered as reliable by this review and the stability constants have been included in the final data evaluation. The data measured in 0.3 – 5 m NaCl have been corrected for complexation effects of  $\text{Na}(\text{edta})^{3-}$ ,  $\text{UO}_2\text{Cl}^+$  and  $\text{UO}_2\text{Cl}_2(\text{aq})$ . The following equilibria have been considered:



$$\log_{10} K_{\text{corr}} = \log_{10} K + \log_{10} (1 + K_{\text{Na}} [\text{Na}^+]) + \log_{10} (1 + K_{\text{Cl}_1} [\text{Cl}^-] + K_{\text{Cl}_2} [\text{Cl}^-]^2).$$

Table A-22: Equilibrium constants and correction factors for  $\text{Na}(\text{edta})^{3-}$ ,  $\text{UO}_2\text{Cl}^+$  and  $\text{UO}_2\text{Cl}_2(\text{aq})$  complexation as evaluated in this review.

$I_m$	$\log_{10} K_{\text{Na}}$	$K_{\text{Na}^+}[\text{Na}^+]$	$\log_{10} K_{\text{Cl}_1}$	$K_{\text{Cl}_1} \cdot [\text{Cl}^-]$	$\log_{10} K_{\text{Cl}_2}$	$K_{\text{Cl}_2} \cdot [\text{Cl}^-]^2$
0.0	2.80	0.0	0.17	0.00	-1.10	0.00
0.3	1.66	13.6	-0.39	0.12	-1.86	0.00
1.0	1.44	27.6	-0.48	0.33	-1.80	0.02
2.0	1.49	62.5	-0.43	0.74	-1.44	0.14
3.0	1.65	133.8	-0.33	1.40	-1.01	0.88
4.0	1.84	279.0	-0.21	2.48	-0.55	4.54
5.0	2.06	572.0	-0.08	4.20	-0.07	21.34

For the equilibrium  $\text{UO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons \text{UO}_2\text{edta}^{2-}$  the correction of the original data of [98POK/BRO] is presented below. Note that “ $\pm$  (95%) corr” represents the uncertainty coming from  $K_{\text{Na}}$ ,  $K_{\text{Cl}_1}$  and  $K_{\text{Cl}_2}$ , whereas “ $\pm$  (95%) total” is the total uncertainty of  $\log_{10} K_{\text{corr}}$ .

Table A-23: Correction of the original data of [98POK/BRO] for the equilibrium  $\text{UO}_2^{2+} + \text{edta}^{4-} \rightleftharpoons \text{UO}_2\text{edta}^{2-}$

$I_m$	$\log_{10} K$	$\pm 1\sigma$	$\pm$ (95%)	$\log_{10} K_{\text{corr}}$	$\pm$ (95%) corr	$\pm$ (95%) total	$\log_{10} K_{\text{corr}} + 16D$
0.3	10.72	0.25	0.49	11.93	0.19	0.53	14.38
1.0	9.82	0.04	0.08	11.40	0.21	0.22	14.66
2.0	10.08	0.20	0.39	12.16	0.25	0.47	15.85
3.0	10.20	0.06	0.12	12.85	0.35	0.37	16.77
4.0	10.27	0.15	0.29	13.62	0.47	0.56	17.69
5.0	10.48	0.15	0.29	14.66	0.55	0.62	18.85

For the equilibrium  $\text{UO}_2^{2+} + \text{Hedta}^{3-} \rightleftharpoons \text{UO}_2(\text{Hedta})^-$  only the correction of the original data of [98POK/BRO] for complexation effects of  $\text{UO}_2\text{Cl}^+$  and  $\text{UO}_2\text{Cl}_2(\text{aq})$  are necessary, *i.e.*,  $\log_{10} K_{\text{corr}} = \log_{10} K + \log_{10}(1 + K_{\text{Cl}_1}[\text{Cl}^-] + K_{\text{Cl}_2}[\text{Cl}^-]^2)$ . An overall uncertainty of  $\pm 0.20$  has been assigned to the uncorrected data of [98POK/BRO] in this review.

Table A-24: Correction of the original data of [98POK/BRO] for the equilibrium  $\text{UO}_2^{2+} + \text{Hedta}^{3-} \rightleftharpoons \text{UO}_2(\text{Hedta})^-$ .

$I_m$	$\log_{10} K$	$\pm 1\sigma$	$\pm (95\%)$	$\log_{10} K_{\text{corr}}$	$\pm (95\%) \text{ corr}$	$\pm (95\%) \text{ total}$	$\log_{10} K_{\text{corr}} + 12D$
0.3	6.63	0.03	0.20	6.68	0.00	0.20	8.52
1.0	6.34	0.04	0.20	6.47	0.01	0.20	8.91
2.0	6.50	0.02	0.20	6.77	0.05	0.21	9.54
3.0	6.63	0.02	0.20	7.15	0.15	0.25	10.09
4.0	6.51	0.07	0.20	7.41	0.27	0.34	10.47
5.0	6.43	0.02	0.20	7.85	0.35	0.40	10.99

For the equilibrium  $\text{NpO}_2^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2\text{edta}^{3-}$  the correction of the original data of [98POK/BRO] is presented below. The value for  $I = 0.1$  in the last line is taken from [70EBE/WED]. Note that “ $\pm (95\%) \text{ corr}$ ” represents the uncertainty coming from  $K_{\text{Na}}$ , whereas “ $\pm (95\%) \text{ total}$ ” is the total uncertainty of  $\log_{10} K_{\text{corr}}$ . In the case of  $\text{NpO}_2^+$  no chloride complexes have been selected, see [2001LEM/FUG], and the effect of chloride is entirely attributed to the SIT interaction coefficients. An uncertainty of  $\pm 0.5$  has been assigned to the value reported for the lowest ionic strength of  $I = 0.3$  (first line), in analogy to the uncertainty reported by [98POK/BRO] for the U(VI) edta complexation constant at the lowest ionic strength (see above).

Table A-25: Correction of the original data of [98POK/BRO] for the equilibrium  $\text{NpO}_2^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2\text{edta}^{3-}$ .

$I_m$	$\log_{10} K$	$\pm 1\sigma$	$\pm (95\%)$	$\log_{10} K_{\text{corr}}$	$\pm (95\%) \text{ corr}$	$\pm (95\%) \text{ total}$	$\log_{10} K_{\text{corr}} + 8D$
0.3	7.10	0.10	0.50	8.26	0.19	0.53	9.49
1	6.30	0.10	0.20	7.76	0.19	0.28	9.39
2	6.00	0.10	0.20	7.80	0.20	0.28	9.65
3	5.80	0.10	0.20	7.93	0.20	0.28	9.89
4	5.60	0.10	0.20	8.05	0.20	0.28	10.08
5	5.45	0.10	0.20	8.21	0.20	0.28	10.30
0.1	7.33	0.06	0.12	8.33	0.18	0.22	9.20

For the equilibrium data  $\text{NpO}_2^+ + \text{H}^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2(\text{Hedta})^{2-}$  reported by [98POK/BRO] (below) the same corrections have been applied as for the  $\text{NpO}_2\text{edta}^{3-}$  data. Also the same uncertainty of  $\pm 0.5$  has been assigned to the value reported for the lowest ionic strength of  $I = 0.3$  (first line).

Table A-26: Correction of the original data of [98POK/BRO] for the equilibrium  $\text{NpO}_2^+ + \text{H}^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2(\text{Hedta})^{2-}$ .

$I_m$	$\log_{10} K$	$\pm 1\sigma$	$\pm (95\%)$	$\log_{10} K_{\text{corr}}$	$\pm (95\%) \text{ corr}$	$\pm (95\%) \text{ total}$	$\log_{10} K_{\text{corr}} + 14D$
0.3	13.48	0.06	0.50	14.64	0.19	0.53	16.79
1	13.21	0.03	0.06	14.67	0.19	0.20	17.52
2	13.10	0.05	0.10	14.90	0.20	0.22	18.13
3	12.90	0.05	0.10	15.03	0.20	0.22	18.46
4	12.86	0.06	0.12	15.31	0.20	0.23	18.87
5	12.95	0.05	0.10	15.71	0.20	0.22	19.37

For the equilibrium data  $\text{NpO}_2^+ + 2\text{H}^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2(\text{H}_2\text{edta})^-$  reported by [98POK/BRO] (below) the same corrections have been applied as for the  $\text{NpO}_2\text{edta}^{3-}$  data. An uncertainty of  $\pm 1.0$  has been assigned to the value reported for the lowest ionic strength of  $I = 0.3$  (first line).

Concerning the values reported in [96BOR/LIS] the authors of this paper state that “in the previous measurements in our laboratory [96BOR/LIS] the stability constants measured for  $\text{NpO}_2^+$  and  $\text{UO}_2^{2+}$  complexation with edta correspond to the deprotonated complexes  $\text{NpO}_2(\text{H}_2\text{edta})^-$  and  $\text{UO}_2(\text{H}_2\text{edta})(\text{aq})$ ”, and not  $\text{NpO}_2\text{edta}^{3-}$  and  $\text{UO}_2\text{edta}^{2-}$ , as postulated by [96BOR/LIS]. However, this new interpretation is doubtful. The species  $\text{UO}_2(\text{H}_2\text{edta})(\text{aq})$  prevails at  $\text{pH} < 2.5$  [69STE/MAK2] and the species  $\text{NpO}_2(\text{H}_2\text{edta})^-$  is found at  $\text{pH} < 4$  [98POK/BRO], but the solvent extraction measurements of [96BOR/LIS] have been carried out at higher pH values. In addition, the stability constants listed in Table 1 of [98POK/BRO], taken from other sources [64BHA/KRI], [68SIL/SIM], [84BRI/LAG] in support of their hypothesis, do not refer to the species  $\text{UO}_2(\text{H}_2\text{edta})(\text{aq})$ , as erroneously assumed by [98POK/BRO], but to the species  $(\text{UO}_2)_2\text{edta}(\text{aq})$ .

Table A-27: Correction of the original data of [98POK/BRO] for the equilibrium  $\text{NpO}_2^+ + 2\text{H}^+ + \text{edta}^{4-} \rightleftharpoons \text{NpO}_2(\text{H}_2\text{edta})^-$ .

$I_m$	$\log_{10} K$	$\pm 1\sigma$	$\pm (95\%)$	$\log_{10} K_{\text{corr}}$	$\pm (95\%) \text{ corr}$	$\pm (95\%) \text{ total}$	$\log_{10} K_{\text{corr}} + 18D$
0.3	18.03	0.05	1.00	19.19	0.19	1.02	21.95
1	18.10	0.05	0.10	19.56	0.19	0.22	23.22
2	18.40	0.05	0.10	20.20	0.20	0.22	24.35
3	18.55	0.07	0.14	20.68	0.20	0.24	25.09
4	18.75	0.08	0.16	21.20	0.20	0.25	25.78
5	19.10	0.10	0.20	21.86	0.20	0.28	26.56

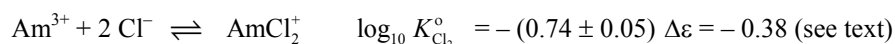
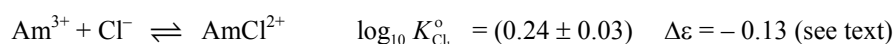
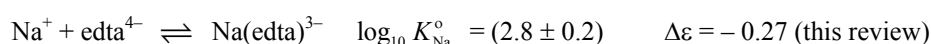
[\[99BRO/POK\]](#)

Distribution ratios of  $10^{-6}$  M  $^{237}\text{NpO}_2^+$  and  $10^{-7}$  M  $^{233}\text{UO}_2^{2+}$  between  $2 \times 10^{-4}$  M HDEHP in heptane and the aqueous phase containing citric acid and 0.1 – 5.0 m NaCl were obtained at pH = 5.0 for Np(V) (pcH changed with ionic strength from 5.0 to 6.8) or pH = 3.0 for U(VI) (pcH 3.0 – 4.5). The plots of  $D_0 / D - 1$  against  $[\text{cit}^{3-}]$  were used to obtain the stability constant, where  $D_0$  and  $D$  are the distribution ratios of Np(V) or U(VI) in the absence and presence of citrate, respectively. The values of  $\log_{10} \beta_1(\text{cit})$  obtained for  $\text{MO}_2^{2+} + \text{cit}^{3-} \rightleftharpoons \text{MO}_2(\text{cit})^{2-3}$  ranged from  $(2.62 \pm 0.05)$  to  $(2.56 \pm 0.03)$  for neptunyl and from  $(7.30 \pm 0.04)$  to  $(7.03 \pm 0.08)$  for uranyl as  $I_m$  increased from 0.3 to 5.0 m NaCl. The conversion of the pH meter readings to the pcH values at each ionic strength and the correction of the measured distribution ratios to that at the averaged pcH were well done. No dependence of the stability constant on pcH in the pcH range studied was observed indicating that  $\text{NpO}_2(\text{cit})^{2-}$  and  $\text{UO}_2(\text{cit})^-$  are the predominant complex species of Np(V) and U(VI) citrate at the pH examined. Since systematic errors might be introduced from the solvent extraction procedure, this review accepts these values with assigning uncertainties of  $\pm 0.10$  for  $\log_{10} \beta_1$  of  $\text{NpO}_2^+ + \text{cit}^{3-} \rightleftharpoons \text{NpO}_2(\text{cit})^{2-}$  and  $\pm 0.30$  for  $\log_{10} \beta_1$  of  $\text{UO}_2^{2+} + \text{cit}^{3-} \rightleftharpoons \text{UO}_2(\text{cit})^-$ .

[\[99CHE/CHO\]](#)

The complexation of  $\text{Am}^{3+}$  with edta (0 – 0.01 M) has been investigated in solutions of 0.3 – 5 m NaCl at 25°C and  $-\log_{10}[\text{H}^+] = 2.4$ . A solvent extraction method with di(2-ethylhexyl)-phosphoric acid (HDEHP) in heptane was used. The authors modelled their data using the ion-interaction model of Pitzer.

This solvent extraction study is considered as reliable by this review and the stability constants have been included in the final data evaluation. The data measured in 0.3 – 5 m NaCl have been corrected for complexation effects of  $\text{Na}(\text{edta})^{3-}$ ,  $\text{AmCl}^{2+}$  and  $\text{AmCl}_2^+$ . The following equilibria have been considered:



$$\log_{10} K_{\text{corr}} = \log_{10} K + \log_{10} (1 + K_{\text{Na}}[\text{Na}^+]) + \log_{10} (1 + K_{\text{Cl}_1}[\text{Cl}^-] + K_{\text{Cl}_2}[\text{Cl}^-]^2)$$

The stability constants  $\log_{10} K_{\text{Cl}_1}^{\circ}$  and  $\log_{10} K_{\text{Cl}_2}^{\circ}$  for the Am chloride complexes have been taken from [\[2003GUI/FAN\]](#). The  $\Delta\varepsilon$  values were calculated from  $\varepsilon(\text{Am}^{3+}, \text{Cl}^-) \approx \varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{AmCl}^{2+}, \text{Cl}^-) \approx \varepsilon(\text{AmCl}^{2+}, \text{ClO}_4^-) = (0.39 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\varepsilon(\text{AmCl}_2^+, \text{Cl}^-) \approx \varepsilon(\text{AmF}_2^+, \text{ClO}_4^-) = (0.17 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$ , and  $\varepsilon(\text{Na}^+, \text{Cl}^-) = (0.03 \pm 0.01) \text{ kg}\cdot\text{mol}^{-1}$ , all values taken from [\[95SIL/BID\]](#).

Note that [\[2003GUI/FAN\]](#) report a value  $\varepsilon(\text{Am}^{3+}, \text{Cl}^-) = (0.23 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  with the remark (footnote G on page 729) that this value “is assumed to be equal to

$\varepsilon(\text{Nd}^{3+}, \text{Cl}^-)$  which is calculated from trace activity coefficients of  $\text{Nd}^{3+}$  ion in 0 – 4 m NaCl. These trace activity coefficients are based on the ion interaction Pitzer parameters evaluated in [97KON/FAN] from osmotic coefficients in aqueous  $\text{NdCl}_3 - \text{NaCl}$  and  $\text{NdCl}_3 - \text{CaCl}_2$ .” Alternatively, inspection by this review of the osmotic coefficients for  $\text{NdCl}_3$  solutions given by [59ROB/STO] also result in  $\varepsilon(\text{Nd}^{3+}, \text{Cl}^-) = (0.23 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$ . This value is derived ignoring Nd – chloride complexation ! Very similar values  $\varepsilon(\text{UO}_2^{2+}, \text{Cl}^-) = (0.21 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  and  $\varepsilon(\text{UO}_2^{2+}, \text{NO}_3^-) = (0.24 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  were obtained from osmotic coefficients reported by [59ROB/STO] for  $\text{UO}_2\text{Cl}_2$  and  $\text{UO}_2(\text{NO}_3)_2$  solutions, respectively. For the latter case [92GRE/FUG] remark (footnote (i) on page 695) “it is recalled that these coefficients are not used in the present review because they were calculated by Ciavatta [80CIA] without taking chloride and nitrate complexation into account”. Instead,  $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  should be used in chloride solutions together with the equilibrium constants for  $\text{UO}_2\text{Cl}^+$  and  $\text{UO}_2\text{Cl}_2(\text{aq})$  as evaluated in [92GRE/FUG]. Hence, in analogy to the U(VI) chloride system, this review used  $\varepsilon(\text{Am}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  together with the equilibrium constants for  $\text{AmCl}^{2+}$  and  $\text{AmCl}_2^+$  given in [2003GUI/FAN].

As can be seen in the Table below, the effect of Am chloride complexation is small (less than 0.5  $\log_{10}$ -units even in 5 m NaCl) compared with the effect of  $\text{Na}(\text{edta})^{3-}$  complexation causing corrections of 1.2 to 2.8  $\log_{10}$ -units in the range  $0.3 < I_m < 5 \text{ m}$ .

For the equilibrium  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$  the correction of the original data of [99CHE/CHO] is presented below. Note that “ $\pm$  (95%) corr” represents the uncertainty coming from  $K_{\text{Na}^+}$ ,  $K_{\text{Cl}^-}$  and  $K_{\text{Cl}_2}$ , whereas “ $\pm$  (95%) total” is the total uncertainty of  $\log_{10}K_{\text{corr}}$ .

The influence of the complex  $\text{Am}(\text{Hedta})(\text{aq})$  on the speciation of the Am edta system at  $-\log_{10}[\text{H}^+] = 2.4$  can be neglected according to the equilibrium constant selected in this review (see Section VIII.13.2.1).

Table A-28: Equilibrium constants and correction factors for  $\text{Na}(\text{edta})^{3-}$ ,  $\text{AmCl}^{2+}$  and  $\text{AmCl}_2^+$  complexation as evaluated in this review.

$I_m$	$\log_{10}K_{\text{Na}}$	$K_{\text{Na}^+} \cdot [\text{Na}^+]$	$\log_{10}K_{\text{Cl}}$	$K_{\text{Cl}^-} \cdot [\text{Cl}^-]$	$\log_{10}K_{\text{Cl}_2}$	$K_{\text{Cl}_2} \cdot [\text{Cl}^-]^2$
0.0	2.80	0.0	0.24	0.00	-0.74	0.00
0.3	1.66	13.6	-0.64	0.07	-2.16	0.00
1.0	1.44	27.6	-0.85	0.14	-2.40	0.00
2.0	1.49	62.5	-0.88	0.26	-2.29	0.02
3.0	1.65	133.8	-0.84	0.43	-2.05	0.08
4.0	1.84	279.0	-0.77	0.68	-1.77	0.27
5.0	2.06	572.0	-0.68	1.05	-1.45	0.88



Table A-29: Correction of the original data of [99CHE/CHO] for the equilibrium  $\text{Am}^{3+} + \text{edta}^{4-} \rightleftharpoons \text{Am}(\text{edta})^-$ .

$I_m$	$\log_{10} K$	$\pm 1\sigma$	$\pm (95\%)$	$\log_{10} K_{\text{corr}}$	$\pm (95\%) \text{ corr}$	$\pm (95\%) \text{ total}$	$\log_{10} K_{\text{corr}} + 24D$
0.3	15.10	0.11	0.22	16.29	0.19	0.29	19.97
1.0	13.96	0.07	0.14	15.48	0.20	0.24	20.36
2.0	14.04	0.09	0.18	15.95	0.21	0.28	21.49
3.0	13.76	0.02	0.10	16.07	0.24	0.26	21.95
4.0	13.89	0.03	0.10	16.63	0.29	0.31	22.74
5.0	14.38	0.05	0.10	17.60	0.37	0.38	23.88

### [99GRI]

Isothermal titration calorimetry is used for the determination of the stability constant of  $\text{Ca}(\text{edta})^{2-}$  and of the involved enthalpy. Buffered edta solutions (0.5 mM, pH mainly 7.5) have been titrated by forty sequential additions of 5 mL volumes of 5 mM  $\text{CaCl}_2$  solution. The ionic strengths of the investigated solutions have not been determined, or at least, they are not mentioned in the paper. Nevertheless, auxiliary constants were taken from the literature for  $I = 0.1$  M without any further discussion. The value obtained for the enthalpy of Ca-edta complex formation for measurements at pH = 7.5 is  $-5.4 \text{ kcal}\cdot\text{mol}^{-1}$  ( $-22.9 \text{ kJ}\cdot\text{mol}^{-1}$ ). From the same measurements the stability constant for  $\text{Ca}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Ca}(\text{edta})^{2-}$  has been derived as  $\log_{10} \beta_1 = 10.7$  but no remarks can be found about the ionic strength and the actually used edta protonation constants. The use of literature values for the protonation constants of the base used in the buffer solutions and of the involved enthalpies further diminishes the reliability of the obtained results. In analysing their results the authors prefer the outdated concept of an octahedral coordination of Ca-edta complexes. The actual coordination of calcium has been found to be 8 due to the coordination of two  $\text{H}_2\text{O}$  molecules forming a  $[\text{Ca}(\text{H}_2\text{O})_2\text{edta}]^{2-}$  complex [79BAR/UCH]. Finally, in contrast to the statement in [99GRI] that “at pH 7.5 only a small proportion of the total edta will be present as  $\text{Hedta}^{3-}$ ”, more than 95% is present as  $\text{Hedta}^{3-}$ , 4.4% as  $\text{H}_2\text{edta}^{2-}$  and 0.016% as  $\text{edta}^{4-}$ . Because of all these deficiencies the values reported in [99GRI] are rejected in this review.

### [99MIZ/BON]

Protonation constants of acetate, oxalate, citrate and edta have been determined potentiometrically using a glass electrode at  $25^\circ\text{C}$  in 0.3 to 5.0 m NaCl. The experimental data have later been published in a SANDIA report [2001CHO/BON] as part of the quality assurance procedure in connection with studies on actinide chemistry in support of the Waste Isolation Pilot Plant (WIPP). Because of the disagreements between these data and those published in [2001CHO/BON] and uncertainties discussed in this appendix under [2001CHO/BON] the error estimates for all data from this report are increased to  $\pm 0.1$ , unless the reported uncertainty is larger.

[\[99ROB/STE\]](#)

The authors determined the protonation constants of several carboxylate ligands at different ionic strengths (0.1 to 5 molal), ionic media (NaCl, KCl and Me<sub>4</sub>NCl) and temperatures (5 to 45°C).

The protonation of citrate was studied in NaCl (0.1 to 5 molal) and KCl (0.1 to 4.5 molal) and at 25°C only. The total citrate concentration was 5 to 10 mM, affecting the ionic media for experiments at  $I = 0.1$  M. Therefore, the protonation constants reported at  $I = 0.1$  M are not considered in this review.

[\[2000BOR/CHO\]](#)

The complexation of Co(II) and Ni(II) by citrate in 0.3 – 5 *m* NaCl solutions has been investigated at  $(20 \pm 1)^\circ\text{C}$  and pH 6.0 by solvent extraction method with HDEHP in toluene. The data were modelled using the Pitzer ion-interaction formalism. The dimensionless standard chemical potential ( $\mu^\circ/RT$ ) for  $\text{Ni}(\text{cit})^-$  was calculated to be  $-0.697$ . With the ( $\mu^\circ/RT$ ) values for  $\text{cit}^{3-}$  (33.4059) and  $\text{Ni}^{2+}$  ( $-18.4$ ) cited in the paper, this corresponds to  $\log_{10} \beta_{1,0,1}^\circ = 6.82$  for the reaction  $\text{Ni}^{2+} + \text{cit}^{3-} \rightleftharpoons \text{Ni}(\text{cit})^-$ . Binary interaction parameters calculated were  $\beta^{(0)} = -0.2249$  and  $C^{\text{p}} = 0.0539$  for  $\text{Ni}(\text{cit})^-$  and  $\text{Na}^+$  interactions. Because of the limited data, the  $\beta^{(1)}$  value for  $\text{Ni}(\text{cit})^-$  with  $\text{Na}^+$  was fixed at 0.29. The experiment and the analysis were well done. Since the formation of  $\text{NiCl}^+$  cannot be neglected, an analysis has been conducted to extrapolate the apparent formation constants  $^{\text{app}}\beta = \beta_{1,0,1}^{\text{cit}}/(1 + \beta_{1,0,1}^{\text{Cl}})$  obtained at  $I = 0.30, 1.00, 2.00, 3.00, 4.00$  and  $5.00$  *m* NaCl to  $I = 0$ , where  $\beta_{1(\text{cit})} = [\text{Ni}(\text{cit})^-]/[\text{Ni}^{2+}][\text{cit}^{3-}]$  and  $\beta_{1(\text{Cl})} = [\text{NiCl}^+]/[\text{Ni}^{2+}][\text{Cl}^-]$ . Thus, this review takes only the value of  $\log_{10} \beta_{1(\text{cit})}^\circ = 6.82$ . Considering the reported standard deviations for  $\log_{10} ^{\text{app}}\beta$  ( $\pm 0.02$  to  $\pm 0.06$ ), this review assigns the uncertainty of  $\pm 0.10$  to  $\log_{10} \beta_{1(\text{cit})}^\circ = 6.82$ .

[\[2000FER/IUL\]](#)

The authors used potentiometry with both a glass electrode and a mercury electrode, based on the Hg/Hg<sub>2</sub>Ox(s) couple, to determine the protonation constants of oxalic acid and the stability constants of U(VI) oxalate complexes in 2 and 3 M NaClO<sub>4</sub> at 25°C. The performance of the mercury electrode was tested in [\[2000VAS/CAR\]](#). The protonation constants of oxalic acid were determined to be:  $\log_{10} K_1 = (3.57 \pm 0.02)$  ( $I = 2$  M) and  $(1.14 \pm 0.03)$  ( $I = 3$  M),  $\log_{10} K_2 = (3.81 \pm 0.02)$  ( $I = 2$  M) and  $(1.14 \pm 0.02)$  ( $I = 3$  M). The stability constants of the 1:1, 1:2 and 1:3 U(VI) oxalate complexes are listed in Table VI-38. It appears to be a carefully conducted study with sufficient experimental details provided. The complex formation function (the average number of ligands on U(VI)) was sufficiently high (0 – 2.4) to allow accurate determination of the three constants. In conjunction with the data at  $I = 1.0$  NaClO<sub>4</sub>, the authors used the SIT approach to obtain the protonation constants of oxalate and the stability constants of U(VI) oxalate complexes at  $I = 0$  M. The following ion interaction parameters were developed:

$$\varepsilon(\text{Na}^+, \text{ox}^{2-}) = 0.05 \text{ kg}\cdot\text{mol}^{-1} \quad \varepsilon(\text{H}^+, \text{ox}^{2-}) = 0.15 \text{ kg}\cdot\text{mol}^{-1}$$

$$\begin{aligned}\varepsilon(\text{Na}^+, \text{Hox}^-) &= 0.12 \text{ kg}\cdot\text{mol}^{-1} & \varepsilon(\text{Na}^+, \text{UO}_2\text{ox}(\text{aq})) &= 0.23 \text{ kg}\cdot\text{mol}^{-1} \\ \varepsilon(\text{Na}^+, \text{UO}_2(\text{ox})_2^{2-}) &= 0.56 \text{ kg}\cdot\text{mol}^{-1} & \varepsilon(\text{Na}^+, \text{UO}_2(\text{ox})_3^{4-}) &= 0.17 \text{ kg}\cdot\text{mol}^{-1}\end{aligned}$$

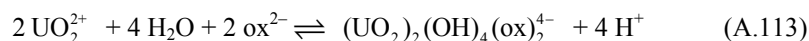
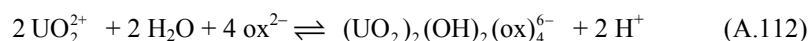
The stability constants at  $I = 1, 2$  and  $3 \text{ M NaClO}_4$  from this study are converted to the constants on the molality scale based on the method described in Chapter II, and accepted by this review with the uncertainties increased to  $\pm 0.10, 0.20$  and  $0.30$  for  $\log_{10} \beta_1$ ,  $\log_{10} \beta_2$  and  $\log_{10} \beta_3$ , respectively.

#### [\[2000LEN/CAB\]](#)

The complexation of U(VI) by citric acid was studied by ion exchange method to check the validity of the method for the study of the interaction of U(VI) with humic and fulvic acids. In the presence of  $0.60$  to  $0.002 \text{ mM}$  citric acid,  $1.0 \text{ }\mu\text{M}$  total U(VI) was distributed between the aqueous solution and Dowex  $50\text{W}\times 8$  at  $(21 \pm 2)^\circ\text{C}$ . The ionic strength of  $0.10 \text{ M}$  was maintained using  $\text{NaClO}_4$  and pH was adjusted to pH  $4.0$  and  $5.0$  with sodium acetate/acetic acid buffer of  $0.006 \text{ M}$  and  $0.0033 \text{ M}$ , respectively. The analysis was conducted by Schubert's method using reported values of protonation constants of citrate [\[74FIE/MCC\]](#) and acetate [\[65RAJ/MAR\]](#), the formation constants of uranyl acetate [\[65RAJ/MAR\]](#), hydroxide [\[95GRE/PUI\]](#), [\[92SIL\]](#) and carbonate [\[95GRE/PUI\]](#). The analysis indicated the formation of only a  $1:1$  uranyl citrate complex and the formation constant was determined to be  $\log_{10} \beta_1 = (6.69 \pm 0.03)$ . Although the experiments and analyses were conducted carefully, there is no description about the calibration of the pH electrode. The measured value of pH should be transformed into  $\log_{10} [\text{H}^+]$  and the use of  $\text{NaClO}_4$  with the usual reference electrode (filled with KCl) might have caused the precipitation of  $\text{KClO}_4$  at the junction of the electrode and given some error in the measured pH. Since this is considered to give serious errors at pH  $4.0$  and  $5.0$ , this review does not accept the reported value.

#### [\[2000PAL\]](#)

The hydrolysis of U(VI) in the absence and presence of oxalate was studied at  $25^\circ\text{C}$  by potentiometry. In the presence of oxalate, the hydrolysis of U(VI) was found to be shifted to a higher pH region, which was interpreted by the author as the result of the formation of two hydroxo-oxalato dinuclear U(VI) complexes represented by the following reactions:



The equilibrium constants for the reactions (A.112) and (A.113) in  $1 \text{ M NaClO}_4$  were determined to be  $(12.48 \pm 0.05)$  and  $-(7.15 \pm 0.08)$ . This is a carefully conducted study and the constants of the hydroxo-oxalato dinuclear U(VI) complexes appear to be reasonable. Also, the hydroxo-oxalato U(VI) complexes are identical to those observed by Curini *et al.* [\[2002CUR/TEN\]](#), though no stability constants were given in

[2002CUR/TEN]. However, it is difficult to reliably identify these ternary polynuclear species and determine their constants without ambiguity. Different models with various combinations of the species should be tested with the data and the goodness of the fits compared. Such information is missing in the paper. Evidently, more experiments with varying concentrations of all the components need to be performed and various models with different combinations of species need to be tested. Therefore, the data on the hydroxo-oxalato dinuclear U(VI) complexes are not accepted by this review.

#### [2000VAS/CAR]

The authors used a mercury electrode, based on the  $\text{Hg}|\text{Hg}_2\text{Ox(s)}$  couple, to determine the protonation constants of oxalic acid and the stability constants of U(VI) oxalate complexes in 1 M  $\text{NaClO}_4$  and at 25°C. The electrode reaction  $(\text{Hg}_2\text{Ox(s)} + 2\text{e}^- \rightleftharpoons 2\text{Hg(l)} + \text{ox}^{2-})$  was found to be fast and reversible. Its Nernstian behaviour was confirmed. The protonation constants of oxalate were determined to be:  $\log_{10} \beta_1 = (3.57 \pm 0.02)$  and  $\log_{10} \beta_2 = (4.57 \pm 0.02)$ . The stability constants of the 1:1, 1:2 and 1:3 U(VI) oxalate complexes are listed in Table VI-38. This appears to be a very carefully conducted study with sufficient experimental details provided. One shortcoming is that the complex formation function (the average number of ligands on U(VI)) was low ( $< 1$ ), which resulted in a high uncertainty in the stability constant of the  $\text{UO}_2(\text{ox})_3^{4-}$  complex. The constants from this study are converted to those in molality according to the method in Chapter II, and accepted by this review, with increased uncertainties.

#### [2001BOR/MOO]

The authors give in this paper values for the equilibrium constants for the formation of oxalate complexes of  $^{230}\text{Th(IV)}$ ,  $^{233}\text{U(VI)}$ ,  $^{237}\text{Np(V)}$  and  $^{241}\text{Am(III)}$ . Except for what appears to be a few typographical errors, the equilibrium constants published here are numerically equal to those published in the technical report [2001CHO/BON] (*cf.* comments for that publication in this Appendix).

Solvent extraction data were obtained using di(2-ethylhexyl)-phosphoric acid (HDEHP) in heptane at 25°C. The aqueous phase contained 0.3 – 5 molal NaCl as background electrolyte. The ionic media in [2001BOR/MOO] was erroneously changed by the printers from molal to molar units (M. Borkowski, personal communication). The measured pH was converted by the authors to  $-\log_{10}[\text{H}^+]$  using a linear function of [NaCl]. The pH and ligand concentration ranges are tabulated in the report [2001CHO/BON]:

- for  $\text{Th}^{4+}$ : pH = 1.8 – 3.0,  $[\text{ox}^{2-}]_{\text{TOT}} = 0 - 0.02$  mM;
- for  $\text{UO}_2^{2+}$ : pH = 3.0 – 3.4,  $[\text{ox}^{2-}]_{\text{TOT}} = 0 - 0.1$  mM;
- for  $\text{NpO}_2^+$ : pH = 4.4 – 5.6,  $[\text{ox}^{2-}]_{\text{TOT}} = 0 - 1$  mM;
- for  $\text{Am}^{3+}$ : pH = 3.7 – 4.9,  $[\text{ox}^{2-}]_{\text{TOT}} = 0 - 0.5$  mM.

The free oxalate concentration was calculated using the protonation constants of [99MIZ/BON], although they differ considerably with those listed in [2001CHO/BON], see also the comments for the latter report in this Appendix. The stability constants of oxalate complexes determined at  $I = 0.3, 1.0, 2.0, 3.0, 4.0$  and  $5.0$  m (NaCl) were used to derive the constants at  $I = 0$  with the Pitzer formalism. Data from this paper and a few earlier publications [94ERT/MOH], [96BOR/LIS], [96CHO/CHE], [96CHO/ERT] and [99MIZ/BON], are also included in [2001CHO/BON]. There are discrepancies between the data from this work and those published earlier. For example, the constant for  $\text{UO}_2\text{ox(aq)}$  at  $5.0$  m NaCl ( $5.82 \pm 0.02$ ) in [2001BOR/MOO] disagrees with that in [96BOR/LIS] ( $5.50 \pm 0.02$ ), but no explanations were given.

The reported constants for the formation of oxalate complexes with  $\text{NpO}_2^+$  are included in the corresponding sections of this review with an uncertainty of  $\pm 0.15$   $\log_{10}$ -units.

The reported constants for the formation of oxalate complexes with U(VI),  $\text{UO}_2\text{ox(aq)}$  and  $\text{UO}_2(\text{ox})_2^{2-}$ , are corrected for the complexation of U(VI) with chloride, according to the method described in Section V.4. The corrections are shown in Table A-17 (in this Appendix). The corrected values are accepted by this review and used in the SIT analysis in conjunction with other accepted data at different ionic strengths (Table VI-39).

The complex formation of Am(III) by oxalate has also been investigated by solvent extraction with HDEHP in heptane at  $25^\circ\text{C}$  at  $I = 0.3, 1, 2, 3, 4$ , and  $5$  m NaCl. Experiments were carried out carefully and the conversion of pH to pCH ( $-\log_{10}[\text{H}^+]$ ) was conducted in a proper way. The values of  $\log_{10} \beta_1$  and  $\log_{10} \beta_2$  were obtained to be:

$$\begin{aligned} \log_{10} \beta_1 &= (4.53 \pm 0.01) \text{ and } \log_{10} \beta_2 = (8.22 \pm 0.02) \text{ at } I = 0.3 \text{ m NaCl,} \\ \log_{10} \beta_1 &= (4.17 \pm 0.05) \text{ and } \log_{10} \beta_2 = (7.77 \pm 0.08) \text{ at } I = 1.0 \text{ m NaCl,} \\ \log_{10} \beta_1 &= (4.40 \pm 0.04) \text{ and } \log_{10} \beta_2 = (8.22 \pm 0.03) \text{ at } I = 2.0 \text{ m NaCl,} \\ \log_{10} \beta_1 &= (4.56 \pm 0.04) \text{ and } \log_{10} \beta_2 = (8.42 \pm 0.07) \text{ at } I = 3.0 \text{ m NaCl,} \\ \log_{10} \beta_1 &= (4.63 \pm 0.04) \text{ and } \log_{10} \beta_2 = (8.46 \pm 0.02) \text{ at } I = 4.0 \text{ m NaCl,} \\ \log_{10} \beta_1 &= (4.57 \pm 0.06) \text{ and } \log_{10} \beta_2 = (8.6 \pm 0.1) \text{ at } I = 5.0 \text{ m NaCl.} \end{aligned}$$

The effects of the complex formation of Am(III) with chloride are not considered. The correction for this complexation is discussed in Section V.4 for Am(III)-edta. According to this discussion, the corrections were estimated to be from  $0.02$  at  $I_m = 0.3$  m to  $0.09$  at  $I_m = 5.0$  m. By giving the correction and considering the systematic errors introduced in each series of experiment, this review takes the following values for  $\log_{10} \beta_1$  and  $\log_{10} \beta_2$ :

$\log_{10} \beta_1 = (4.55 \pm 0.10)$  and  $\log_{10} \beta_2 = (8.24 \pm 0.20)$  at  $I_m = 0.3\text{ m}$ ,  
 $\log_{10} \beta_1 = (4.21 \pm 0.10)$  and  $\log_{10} \beta_2 = (7.81 \pm 0.20)$  at  $I_m = 1.0\text{ m}$ ,  
 $\log_{10} \beta_1 = (4.44 \pm 0.15)$  and  $\log_{10} \beta_2 = (8.26 \pm 0.30)$  at  $I_m = 2.0\text{ m}$ ,  
 $\log_{10} \beta_1 = (4.61 \pm 0.20)$  and  $\log_{10} \beta_2 = (8.47 \pm 0.30)$  at  $I_m = 3.0\text{ m}$ ,  
 $\log_{10} \beta_1 = (4.70 \pm 0.20)$  and  $\log_{10} \beta_2 = (8.53 \pm 0.40)$  at  $I_m = 4.0\text{ m}$ ,  
 $\log_{10} \beta_1 = (4.66 \pm 0.30)$  and  $\log_{10} \beta_2 = (8.70 \pm 0.50)$  at  $I_m = 5.0\text{ m NaCl}$ .

### [\[2001CHO/BON\]](#)

This SANDIA report (SAND99-0943) presents raw experimental data provided by Florida State University on thermodynamic parameters required as part of the Waste Isolation Pilot Plant (WIPP). The authors state that “this document has been assembled and organised to comply with the quality assurance and traceability criteria established for data used in performance assessment calculations for WIPP”.

The report contains tables with protonation constants for several ligands including oxalate, citrate and edta, as well as lists of complex formation constants between the ligands and  $\text{Mg}^{2+}$ ,  $\text{Th}^{4+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{NpO}_2^+$  and  $\text{Am}^{3+}$ . The experimental data are provided: results from potentiometric titrations and solvent extraction data. However, not a single experimental detail is given. Most results based on these experimental data have already been published [\[94ERT/MOH\]](#), [\[96BOR/LIS\]](#), [\[96CHO/CHE\]](#), [\[96CHO/ERT\]](#), [\[99MIZ/BON\]](#), [\[2001BOR/MOO\]](#). These publications give the necessary experimental details, and they are discussed in this review.

The protonation constants reported in the Tables in the introduction of [\[2001CHO/BON\]](#) are not always identical to those published elsewhere by the same authors, for example in [\[99MIZ/BON\]](#). There is no explanation given for this in this last report of the series. It is not clear in these publications whether the equilibrium constants refer to Molar or molal concentration units, although the texts and Table captions report ligand and titrant concentrations in molar units. Because of these disagreements and uncertainties the error estimates for all data from this report are increased to  $\pm 0.1$ , unless the reported uncertainty is larger or the individual discussions of the original publications in this Appendix indicate a larger assigned uncertainty.

Several of the values on the protonation of  $\text{edta}^{4-}$  reported in Table 2 of [\[2001CHO/BON\]](#) appear to be misprints. An inspection of Tables AD79 and AD80 in the original report indicates that the values in Table 2, page 85 of [\[2001CHO/BON\]](#), should instead be:  $\text{p}K_{a1} = 2.00$ ;  $\text{p}K_{a2} = 2.44$ ;  $\text{p}K_{a3} = 6.08$ ; and  $\text{p}K_{a4} = 9.21$  (using the nomenclature in the original report). The corrected values have been listed in Table VIII-2.

A series of potentiometric measurements of Mg complexation with oxalate, citrate and edta is not yet published elsewhere. These data have been scrutinised in this

review. In the case of Mg edta data all attempts failed to re-evaluate the reported results from the tables of experimental data. Correspondence with the authors of the report revealed that the table headers of the Mg-edta data in SAND99-0943 contain several mistakes. A correct list of experimental parameters were obtained from Marian Borkowski (personal communication), see Table A-30.

Tests using this new list of parameters showed that the reported Mg-edta stability constants are essentially correct with respect to the reported titration data.

A later attempt failed to obtain a correct list of experimental parameters for Mg oxalate, where the corresponding table headers also contain several mistakes. However, extrapolating from the experience with the edta data in this review it has been assumed that the stability constants reported for Mg oxalate have been derived from the correct data sets.

For the reaction  $\text{Mg}^{2+} + \text{edta}^{4-} \rightleftharpoons \text{Mg}(\text{edta})^{2-}$  the uncertainties associated with the reported constants have been estimated to  $\pm 0.1 \log_{10}$ -units. These constants were corrected in this review for  $\text{Na}(\text{edta})^{3-}$  complexation using values evaluated in this review (see Table VIII-8-a). At 25°C the correction range is  $1.1 < \Delta \log_{10} K_1 < 2.8$  depending on  $I$ . The estimated uncertainty of the resulting constants have been doubled in order to account for the uncertainty of the  $\text{Na}(\text{edta})^{3-}$  complexation constant.

The reaction  $\text{Mg}(\text{edta})^{2-} + \text{H}^+ \rightleftharpoons \text{Mg}(\text{Hedta})^-$  is always a very minor effect in the titration experiments of [2001CHO/BON]. Hence, the uncertainties associated with the reported constants have been estimated to  $\pm 0.5 \log_{10}$ -units.

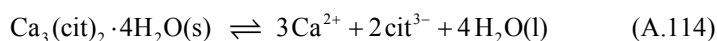
The reliability of the studies on  $\text{UO}_2^{2+}$ -citrate and  $\text{NpO}_2^{2+}$ -citrate systems has been discussed in [99BRO/POK]. For the  $\text{Am}^{3+}$ -citrate system, the values will be taken with corrections for the formation of  $\text{AmCl}^{2+}$ , where the apparent formation constants are  $^{\text{app}}\beta = \beta_{\text{cit}} / (1 + \beta_{\text{Cl}})$ . This discussion is given in the main text. For the  $\text{Mg}^{2+}$ -citrate system, the reported values for the formation of  $\text{Mg}(\text{cit})^-$  and  $\text{Mg}(\text{Hcit})(\text{aq})$  will be taken without considering the complex formation of  $\text{Mg}^{2+}$  with chloride, since the degree of complex formation is expected to be smaller or similar as compared with the complex formation of  $\text{UO}_2^{2+}$  with chloride (see discussion for  $\text{UO}_2^{2+}$ -citrate system in the main text). Considering the reported standard deviations for  $\log_{10} ^{\text{app}}\beta$  ( $\pm 0.02$  to  $\pm 0.06$ ), this review assigns the uncertainty of  $\pm 0.2$  to the reported values of  $\log_{10} \beta$  for  $\text{Mg}(\text{cit})^-$  and  $\pm 0.3$  to the reported values of  $\log_{10} \beta$  for  $\text{Mg}(\text{Hcit})(\text{aq})$ .

Table A-30: Correct list of experimental parameters for the Mg edta data in [\[2001CHO/BON\]](#). These values are to replace those appearing in the table captions of the original report.

pcH = slope · pHr + intercept				
Table #	m NaCl	slope	intercept	Acid (HCl) mmols
Mg68	0.3	0.98678	0.16348	0.152
Mg69	0.3	0.98573	0.17111	0.152
Mg70	1	0.98323	0.32485	0.1365
Mg71	1	0.98063	0.34588	− 0.0025
Mg72	1	0.97694	0.38295	0
Mg73	1	0.97950	0.38157	0
Mg74	2	0.97597	0.59497	0.00518
Mg75	2	0.98025	0.57497	0.0055
Mg76	2	0.97482	0.59471	0.005
Mg77	2	0.97568	0.59212	0.0049
Mg78	3	0.97954	0.77533	0.0594
Mg79	3	0.96919	0.84836	0.059
Mg80	4	0.98293	0.97450	0.0103
Mg81	4	0.97776	1.00582	0.0103
Mg82	4	0.97774	1.00179	0.0106
Mg83	4	0.97732	1.00272	0.0108
Mg84	5	0.98105	1.16008	0.0032
Mg85	5	0.97900	1.17022	0.0055

### [\[2001CIA/TOM\]](#)

The solubility of  $\text{Ca}_3(\text{cit})_2 \cdot 4\text{H}_2\text{O}$  in  $\text{NaClO}_4$  solutions at 0, 0.10, 0.25, 0.51, 1.05, 2.20 and 3.50 m  $\text{NaClO}_4$  has been determined at 25°C by potentiometric titration with EDTA. Since pH of these solutions should be high enough, the reactions,



have been taken into consideration, and the solubility,  $s$ , is related with the concentrations of the species,

$$3s = [\text{Ca}^{2+}] + [\text{Ca}(\text{cit})^-]$$

$$2s = [\text{cit}^{3-}] + [\text{Ca}(\text{cit})^-]$$

where the concentrations are in molality units. The values of  $\log_{10} K_{s,0}^\circ = -(17.81 \pm 0.03)$  for (A.114), and  $\varepsilon(\text{cit}^{3-}, \text{Na}^+) = -(0.08 \pm 0.03) - (0.06 \pm 0.01)m_{\text{Na}}$  have been obtained to explain the change of solubility with  $I_m$ , using the specific ion interaction theory, values of  $\log_{10} \beta^\circ$  (A.115) = 4.85,  $\varepsilon(\text{Ca}^{2+}, \text{ClO}_4^-) = 0.27 \text{ kg} \cdot \text{mol}^{-1}$  and the assumption,  $\varepsilon(\text{Ca}(\text{cit})^-, \text{Na}^+) = \frac{1}{2} \{ \varepsilon(\text{Ca}^{2+}, \text{ClO}_4^-) + \varepsilon(\text{cit}^{3-}, \text{Na}^+) \}$ . The



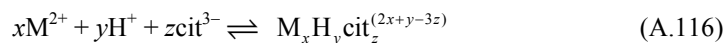
experiment and analysis of the data seem to have been done carefully. However, as compared with  $\varepsilon(\text{cit}^{3-}, \text{Na}^+) = -(0.16 \pm 0.03) + (0.11 \pm 0.03) \log_{10} I_m$  selected in the present review, the values of  $\varepsilon(\text{cit}^{3-}, \text{Na}^+) I_m$  are significantly different (more than 0.1) at  $I_m \geq 2.2$  m. Since  $[\text{Ca}(\text{cit})^-]$  in the above reaction is calculated using  $\log_{10} \beta^\circ$  and  $\Delta\varepsilon = \varepsilon(\text{Ca}(\text{cit})^-, \text{Na}^+) - \varepsilon(\text{Ca}^{2+}, \text{ClO}_4^-) - \varepsilon(\text{cit}^{3-}, \text{Na}^+)$  for the reaction (A.115), the estimated values for  $\log_{10} K_{s,0}^\circ$  and  $\varepsilon(\text{cit}^{3-}, \text{Na}^+)$  are strongly dependent on the values of  $\log_{10} \beta^\circ$  and  $\varepsilon$  used in the data analysis. In this paper,  $\varepsilon(\text{cit}^{3-}, \text{Na}^+)$  is assumed to be dependent on  $I_m$  and  $\varepsilon(\text{Ca}(\text{cit})^-, \text{Na}^+)$  is assumed to be equal to  $\frac{1}{2} \{ \varepsilon(\text{Ca}^{2+}, \text{ClO}_4^-) + \varepsilon(\text{cit}^{3-}, \text{Na}^+) \}$ . This means that  $\varepsilon(\text{Ca}(\text{cit})^-, \text{Na}^+)$  is also dependent on  $I_m$  and would compensate the contribution of  $\varepsilon(\text{cit}^{3-}, \text{Na}^+)$  in  $\Delta\varepsilon = \varepsilon(\text{Ca}(\text{cit})^-, \text{Na}^+) - \varepsilon(\text{Ca}^{2+}, \text{ClO}_4^-) - \varepsilon(\text{cit}^{3-}, \text{Na}^+)$  for the reaction (A.115) at high  $I_m$ . The  $\varepsilon$  values proposed in this paper are not in agreement with the copious experimental data on the ionic strength dependence of the first protonation constant of citrate. Since the only point of discrepancy between this NEA-TDB review and the experimental data in this paper is the solubility determined in 3 M  $\text{NaClO}_4$ , and there is a slight possibility that the experimental determination in 3 M  $\text{NaClO}_4$  is incorrect due to some unknown error such as the change in the nature of the solid phase, this review does not accept the value for  $\varepsilon(\text{cit}^{3-}, \text{Na}^+)$  proposed in this paper but accept the reported values of  $\log_{10} K_{s,0}$  at  $I_m \leq 0.5$  m where the contribution of  $\Delta\varepsilon$  for the reactions (A.114) and (A.115) are negligible, namely,  $\log_{10} K_{s,0} = -(17.8 \pm 0.2)$ ,  $-(14.5 \pm 0.2)$ ,  $-(13.6 \pm 0.2)$  and  $-(12.8 \pm 0.2)$  at  $I_m = 0, 0.10, 0.25$  and  $0.51$  m ( $\text{NaClO}_4$ ), respectively (the values were retrieved from Fig. 2 in the paper). Larger uncertainties of  $\pm 0.2$  are assigned by this review since  $\log_{10} \beta^\circ$  (A.115) = 4.85 is different from  $(4.75 \pm 0.03)$  selected in this review.

#### [\[2001GUO/LIA\]](#)

The authors determined the precipitation kinetics and solubility of Pu(IV) oxalate at  $(25 \pm 0.2)^\circ\text{C}$  in solutions containing both  $\text{HNO}_3$  and oxalic acid. Extraction with TTA showed that Pu(IV) was  $\geq 99.5\%$  of total plutonium. Solid Pu(IV) oxalate was prepared by mixing a Pu(IV) solution in 4 M  $\text{HNO}_3$  with a 1 M solution of  $\text{H}_2\text{ox}$ . The solid phase was not characterised. In the solubility measurements solid Pu(IV) oxalate was washed three times with the solution to be equilibrated with, and then equilibrated with the nitric-oxalic solution for 40 hours. The solution was then separated by centrifugation and the Pu was analysed radiometrically. The authors do not specify if anoxic conditions were used during the experiments.

#### [\[2001SAR\]](#)

Stability constants for magnesium, calcium, copper, nickel and zinc citrate complexes have been determined by potentiometric titration at  $(25.0 \pm 0.5)^\circ\text{C}$  and  $I = 0.1$  M NaCl. Protonation constants of citrate were obtained to be  $\log_{10} K_{(\text{H})} = (5.666 \pm 0.02)$ ,  $(4.303 \pm 0.01)$  and  $(2.853 \pm 0.02)$  in 0.1 M NaCl. By analysing the data with SUPERQUAD, the constants  $\log_{10} \beta_{\text{xyz}}$  for the reaction:



were obtained and reported in Table A-31.

Table A-31: Stability constants for the Reaction (A.116) with M = Mg, Ca and Ni.

$\log_{10} \beta_{xyz}$	$Mg_xH_yCit_z^{(2x+y-3z)}$	$Ca_xH_yCit_z^{(2x+y-3z)}$	$Ni_xH_yCit_z^{(2x+y-3z)}$
$\log_{10} \beta_{1,0,1}$	$(3.313 \pm 0.015)$	$(3.383 \pm 0.010)$	
$\log_{10} \beta_{1,0,2}$	$(5.166 \pm 0.023)$	$(5.444 \pm 0.024)$	$(7.747 \pm 0.015)$
$\log_{10} \beta_{1,1,1}$	$(7.843 \pm 0.020)$	$(7.736 \pm 0.014)$	
$\log_{10} \beta_{1,2,1}$	$(11.629 \pm 0.036)$	$(11.146 \pm 0.036)$	
$\log_{10} \beta_{1,2,2}$			$(18.053 \pm 0.041)$
$\log_{10} \beta_{1,3,2}$			$(21.550 \pm 0.055)$
$\log_{10} \beta_{1,4,2}$			$(24.927 \pm 0.105)$
$\log_{10} \beta_{1,1,2}$	$(10.999 \pm 0.020)$	$(10.601 \pm 0.035)$	$(13.549 \pm 0.028)$
$\log_{10} \beta_{1,-1,1}$	$-(8.505 \pm 0.027)$	$-(9.060 \pm 0.008)$	
$\log_{10} \beta_{1,-1,2}$			$-(2.340 \pm 0.014),$
$\log_{10} \beta_{1,-2,1}$	$-(21.130 \pm 0.072)$		
$\log_{10} \beta_{1,-2,2}$			$-(13.554 \pm 0.021).$

The pH calibration was done only by using standard buffer solution(s) and the conversion of pH to  $-\log_{10} [H^+]$  was not done. Therefore mixed activity-concentration constants were obtained. No details are given on the concentrations used for the ligand, metal or titrant. Furthermore, no details are given on the fitting procedure followed to obtain the equilibrium constants.

Because of all these shortcomings the values reported in [2001SAR] are not credited in this review.

#### [2002HAV/SOT]

The protonation of oxalate and the complexation of U(VI) with oxalate in aqueous solutions of 3.0 M NaClO<sub>4</sub> at  $(25.0 \pm 0.2)^\circ\text{C}$  were studied by UV-Vis spectrophotometry in this work. The overall protonation constants of oxalate were determined to be:  $\log_{10} K_1 = (3.83 \pm 0.01)$  and  $\log_{10} \beta_2 = (4.92 \pm 0.01)$ . The stability constants for the  $(\text{UO}_2)_p(\text{ox})_q^{2(p-q)}$  species were determined to be:  $\log_{10} \beta_{11} = (6.31 \pm 0.02)$ ,  $\log_{10} \beta_{12} = (11.21 \pm 0.07)$ ,  $\log_{10} \beta_{13} = (13.8 \pm 0.04)$ ,  $\log_{10} \beta_{23} = (18.5 \pm 0.2)$ , and  $\log_{10} \beta_{25} = (28.5 \pm 0.1)$ . Negligible difference in  $\log_{10} \beta_{11}$  at different acidities ( $-\log_{10}[H^+] = 0.5, 1.0$  and  $1.5$ ) suggested no formation of protonated U(VI) oxalate complexes. Thus, the protonated U(VI) oxalate species were not included in the calculation. The authors used the data at  $I = 3.0$  M NaClO<sub>4</sub> from this work and other data from the literature ( $I = 0.1 - 9.0$  M), to obtain the stability constants at  $I = 0$  mol·kg<sup>-1</sup> by the SIT approach. In the calculation with SIT, two new interaction parameters were developed:  $\varepsilon(\text{UO}_2\text{ox}(\text{aq}), \text{Na}^+ + \text{ClO}_4^-) = -(0.151 \pm 0.033)$  kg·mol<sup>-1</sup> and  $\varepsilon(\text{UO}_2(\text{ox})_2^{2-}, \text{Na}^+) = -(0.072 \pm 0.061)$  kg·mol<sup>-1</sup>. In addition, the interaction parameter  $\varepsilon(\text{UO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+)$  was used as the

analog for  $\varepsilon(\text{UO}_2(\text{ox})_3^{4-}, \text{Na}^+)$ .

The inclusion of the dimeric species,  $(\text{UO}_2)_2(\text{ox})_3^{2-}$  and  $(\text{UO}_2)_2(\text{ox})_5^{6-}$ , slightly improved the overall fitting. Besides, the results from vapour pressure osmometry and conductivity experiments seem to support the presence of polynuclear species when the concentration of U(VI) is at or above 0.06 M, where the vapour pressure and electric conductance of a solution of  $(2 \text{UO}_2(\text{NO}_3)_2 + 3 \text{K}_2\text{ox})$  start to deviate from a linear correlation between the vapour pressure or conductance and the concentration of the solutes. It is noted that the vapour pressure and electric conductance experiments were performed without background electrolyte ( $\text{NaClO}_4$ ).

The spectrophotometric experiments appear to be well conducted and the data analysis is reasonable. The stability constants of the mononuclear species,  $\text{UO}_2(\text{ox})_q^{2-q}$  where ( $q = 1, 2$  and  $3$ ), at  $I = 3.0 \text{ M NaClO}_4$  and  $(25.0 \pm 0.2)^\circ\text{C}$  from this work are accepted by this review and included in the SIT analysis, in conjunction with other selected data at different ionic strengths from the literature.

Despite that the vapour pressure and conductance experiments seem to support the presence of polynuclear species, the stability constants for the dimeric U(VI) oxalate species from this work are not accepted by this review based on the following considerations: 1) inclusion of the dimeric species only slightly improves the overall fit; 2) the concentration of U(VI) in the spectrophotometric experiments was much lower than 0.06 M where the vapour pressure or conductance started to deviate from the linear dependence on the solute concentration. As shown in the paper, the concentration of U(VI) in the spectrophotometric experiments was 8.3 mM (Figure 2), 0 – 16.6 mM (Figure 3) and 1.7 mM (Figure 4). At such concentrations, the  $(\text{UO}_2)_2(\text{ox})_3^{2-}$  species is minor and the  $(\text{UO}_2)_2(\text{ox})_5^{6-}$  species does not become significant until the concentration of oxalate becomes high, thus raising doubts on the reliability of the stability constants for these species. In fact, the authors pointed out in the paper that these values should be regarded only as upper limits of the real values. Similar dinuclear U(VI) oxalate complexes were reported in the earlier literature [56GRI/PTI], [59TEK/VIN2]. Evidently, more studies are needed to confirm the presence of such complexes and obtain reliable stability constants.

#### [\[2002MAK/MER\]](#)

Electrochemical reduction of U(VI) in the presence of  $\text{Na}_3\text{cit}$ ,  $\text{Na}_2\text{ox}$  and  $\text{Na}_4\text{P}_2\text{O}_7$  were studied by polarography, cyclic voltammetry and constant potential coulometry in 0.5 M  $\text{HClO}_4$ . It was observed that the disproportionation of U(V) was facilitated in the presence of the ligands, oxalate and pyrophosphate in particular. In the presence of oxalate, the disproportionation of U(V) was complete, resulting in the reduction of U(VI) to U(IV). Mechanisms involving the formation of oxalate complexes with U(VI) and U(IV) were proposed, but no stability constants were provided.

[\[2002SOT\]](#)

The author studied the uranium(VI)-oxalate system by absorption spectrophotometry ( $I = 3 \text{ M NaClO}_4$ ) and capillary electrophoresis ( $I \approx 0.02 \text{ M}$ ) and at  $25^\circ\text{C}$ . Stability constants of three mononuclear and two dinuclear U(VI) oxalate complexes were determined by spectrophotometry. For the  $(\text{UO}_2)_p(\text{ox})_q^{2(p-q)}$  species,  $\log_{10} \beta_{11} = (6.31 \pm 0.02)$ ,  $\log_{10} \beta_{12} = (11.21 \pm 0.07)$ ,  $\log_{10} \beta_{13} = (13.8 \pm 0.04)$ ,  $\log_{10} \beta_{23} = (18.5 \pm 0.2)$ , and  $\log_{10} \beta_{25} = (28.5 \pm 0.1)$ . These results have been published in [\[2002HAV/SOT\]](#), see discussion in this Appendix.

In the capillary electrophoresis (CE) study, dilute solutions ( $C_U = 0.2 \text{ mM}$ ,  $C_{\text{ox}} = 0.25 - 5 \text{ mM}$ ) were used and the pH was adjusted to be 3.2 with  $20 \text{ mM}$  acetate. The formation of  $\text{UO}_2(\text{ox})(\text{aq})$  and  $\text{UO}_2(\text{ox})_2^{2-}$  was proved by the CE experiments.  $\log_{10} \beta_2 (\text{UO}_2(\text{ox})_2^{2-})$  was estimated to be  $(11.89 \pm 0.04)$  from the respective mobility  $(2 \pm 4) \text{ m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ . Since the ionic strength in the CE experiments was not maintained constant and the formation of ternary U(VI)-acetato-oxalate complexes was not taken into consideration, the results from the CE experiments are not accepted by this review.

[\[2004SCH/MAU\]](#)

The activity of water,  $a_{\text{H}_2\text{O}}$ , has been measured by the authors at  $25^\circ\text{C}$  in solutions of  $\text{NaCl}$ ,  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$  containing also a variable amount of  $\text{H}_3\text{cit}$ . The concentration range (molal units) was  $\approx 0.2$  to  $\approx 3$  for the electrolytes and  $\approx 0.1$  to  $\approx 5.7$  for citric acid. Mixtures containing both an excess of electrolyte and an excess of  $\text{H}_3\text{cit}$  were investigated. Furthermore activities of water were also reported for  $\text{Na}_3\text{cit}$  solutions and for mixtures of sodium citrate and citric acid. The data for mixtures of  $\text{H}_3\text{cit}$  and  $\text{NaCl}$ , and for  $\text{Na}_3\text{cit}$  solutions will be analysed here to support or discard the selections made in this review for specific ion interaction coefficients, *i.e.*, to check the assumption that  $\varepsilon(\text{H}_3\text{cit}(\text{aq}), \text{NaCl}) \approx 0$ .

In order to interpret the activities of water in solutions containing citric acid and sodium chloride, the dissociation of the acid must be taken into account. Preliminary calculations indicate that it is enough to consider the first dissociation step:  $\text{H}_3\text{cit}(\text{aq}) \rightleftharpoons \text{H}^+ + \text{H}_2\text{cit}^-$ ,  $\log_{10} K^\circ = -\log_{10} K_3^\circ = -(3.13 \pm 0.01)$ , *cf.* Table VII-3. The medium effects on this equilibrium constant are obtained by means of the SIT model described in Appendix B. Given the large excess of citric acid over the electrolyte in many of the mixtures (up to  $4.5 \text{ M}$ ), the effects of  $\text{H}_3\text{cit}(\text{aq})$  on the activity coefficients should be taken into account:

$$\log_{10} \gamma_{\text{H}^+} = -D + \varepsilon(\text{H}^+, \text{Cl}^-) m_{\text{Cl}^-}$$

$$\log_{10} \gamma_{\text{H}_2\text{cit}^-} = -D + \varepsilon(\text{Na}^+, \text{H}_2\text{cit}^-) m_{\text{Na}^+}$$

$$\log_{10} \gamma_{\text{H}_3\text{cit}} = \varepsilon(\text{H}_3\text{cit}, \text{NaCl}) m_{\text{NaCl}} + \varepsilon(\text{H}_3\text{cit}) m_{\text{H}_3\text{cit}}$$

$D$  is a function of the ionic strength defined in Eq. (B.2). The coefficients  $\varepsilon(\text{H}^+, \text{Cl}^-)$  and  $\varepsilon(\text{Na}^+, \text{H}_2\text{cit}^-)$  are listed in Tables B-4 and B-5, respectively. The coefficient describing

the interaction between citric acid molecules is denoted here by  $\varepsilon(\text{H}_3\text{cit})$ . This coefficient may be obtained from the activity coefficients of aqueous solutions of citric acid reported in [95APE/DOV2],  $\varepsilon(\text{H}_3\text{cit}) = (0.057 \pm 0.005) \text{ kg} \cdot \text{mol}^{-1}$ . In the expressions for  $\gamma_{\text{H}^+}$  and  $\gamma_{\text{H}_3\text{cit}^-}$  the interactions with  $\text{H}_3\text{cit}(\text{aq})$  are unknown and have been neglected here, although exploratory calculations show that if included, these terms have almost no impact on the calculated dissociation of citric acid. Using these approximations, a couple of interactions are sufficient to evaluate the ionic strength, the acid dissociation constant and the degree of dissociation for each of the  $\text{H}_3\text{cit}$ -NaCl mixtures studied in [2004SCH/MAU]. The degree of dissociation of  $\text{H}_3\text{cit}$  is found to be at maximum 12% in the most diluted solutions ( $\approx 0.1 \text{ M}$  in  $\text{H}_3\text{cit}$ ) and  $< 3\%$  for solutions with  $[\text{H}_3\text{cit}] > 1 \text{ M}$ . Once the equilibrium composition of the  $\text{H}_3\text{cit}$ -NaCl mixtures is established their osmotic coefficients may be calculated by:

$$\phi = 1 - \frac{1}{\sum m_i} \sum_j m_j \left[ \frac{A_\gamma \ln(10) z_j^2}{I_m (1.5)^3} \sigma(I_m) - \frac{\ln(10)}{2} \sum_k \varepsilon(j, k) m_k \right]$$

where

$$\sigma(I_m) = \left(1 + 1.5\sqrt{I_m}\right) - \frac{1}{\left(1 + 1.5\sqrt{I_m}\right)} - 2 \ln\left(1 + 1.5\sqrt{I_m}\right)$$

and “ $i$ ”, “ $j$ ” and “ $k$ ” in the summations are made for all species in the solution, including neutral species. For solutions of a single electrolyte these expressions are equivalent to Eq. (B.11). For mixtures of NaCl and  $\text{H}_3\text{cit}$ , the expression for the osmotic coefficient is therefore:

$$\begin{aligned} \phi = 1 - & \frac{m_{\text{Na}^+}}{\sum_i m_i} \left[ \frac{A_\gamma \ln(10)}{I_m (1.5)^3} \sigma(I_m) - \frac{\ln(10)}{2} \left( \varepsilon(\text{Na}^+, \text{Cl}^-) m_{\text{Cl}^-} + \varepsilon(\text{H}_3\text{cit}, \text{NaCl}) m_{\text{H}_3\text{cit}} \right) \right] \\ & - \frac{m_{\text{Cl}^-}}{\sum_i m_i} \left[ \frac{A_\gamma \ln(10)}{I_m (1.5)^3} \sigma(I_m) - \frac{\ln(10)}{2} \left( \varepsilon(\text{Na}^+, \text{Cl}^-) m_{\text{Na}^+} + \varepsilon(\text{H}_3\text{cit}, \text{NaCl}) m_{\text{H}_3\text{cit}} \right) \right] \\ & + \frac{m_{\text{H}_3\text{cit}}}{\sum_i m_i} \frac{\ln(10)}{2} \left( \varepsilon(\text{H}_3\text{cit}, \text{NaCl}) m_{\text{NaCl}} + \varepsilon(\text{H}_3\text{cit}) m_{\text{H}_3\text{cit}} \right) \\ & - \frac{m_{\text{H}_2\text{cit}^-}}{\sum_i m_i} \left[ \frac{A_\gamma \ln(10)}{I_m (1.5)^3} \sigma(I_m) - \frac{\ln(10)}{2} \varepsilon(\text{Na}^+, \text{H}_2\text{cit}^-) m_{\text{Na}^+} \right] \\ & - \frac{m_{\text{H}^+}}{\sum_i m_i} \left[ \frac{A_\gamma \ln(10)}{I_m (1.5)^3} \sigma(I_m) + \frac{\ln(10)}{2} \varepsilon(\text{H}^+, \text{Cl}^-) m_{\text{Cl}^-} \right] \end{aligned}$$

with  $\sum_i m_i = (m_{\text{Na}^+} + m_{\text{Cl}^-} + m_{\text{H}_3\text{cit}} + m_{\text{H}_2\text{cit}^-} + m_{\text{H}^+})$ . In the equation given above several

$\epsilon$ -terms have been excluded: those multiplied by either  $m_{\text{H}^+}$  or  $m_{\text{H}_2\text{cit}^-}$  since these concentrations are negligible compared to those of  $\text{Na}^+$ ,  $\text{Cl}^-$  or  $\text{H}_3\text{cit}(\text{aq})$ ; the interactions between  $\text{H}_3\text{cit}(\text{aq})$  and  $\text{H}^+$  or  $\text{H}_2\text{cit}^-$  are also neglected but test calculations indicate that these terms have no appreciable impact on the calculated value of  $\phi$ . From the calculated values of the osmotic coefficient the corresponding activities of water are evaluated using Eq. (B.9). Only one parameter,  $\epsilon(\text{H}_3\text{cit}, \text{NaCl})$ , needs to be adjusted to fit the experimental data with the expression for  $\phi$  given above, because the value of  $\epsilon(\text{Na}^+, \text{H}_2\text{cit}^-)$  may be obtained from  $\Delta\epsilon_3^*(\text{VII.5}) = \epsilon(\text{H}_3\text{cit}, \text{NaCl}) - \epsilon(\text{Na}^+, \text{H}_2\text{cit}^-) = (0.05 \pm 0.01)$  listed in Table VII-3,  $\epsilon(\text{H}^+, \text{Cl}^-)$  and  $\epsilon(\text{Na}^+, \text{Cl}^-)$  are listed in Tables B-4 and B-5, respectively, and  $\epsilon(\text{H}_3\text{cit})$  has been defined above. It is found that the experimental data for the  $\text{H}_3\text{cit}$ - $\text{NaCl}$  mixtures reported in [2004SCH/MAU] are well described with  $\epsilon(\text{H}_3\text{cit}, \text{NaCl}) = (0.03 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ , *cf.* Figure A-38. It may be therefore concluded that the assumption  $\epsilon(\text{H}_3\text{cit}(\text{aq}), \text{NaCl}) \approx 0$  made in this review is corroborated by these experimental data on water activities.

Activities of water are also reported in [2004SCH/MAU] for sodium citrate solutions at 25°C in the concentration range 0.5 to 1.7 molal. These data may be used to confirm the selected value of  $\epsilon(\text{Na}^+, \text{cit}^{3-}) = -(0.15 \pm 0.03) + (0.13 \pm 0.03) \log_{10} I_m$  reported in Table VII-9. Preliminary calculations show that the protonation of citrate may be neglected, *i.e.*, citrate is a weak base. Under such conditions  $\text{Na}_3\text{cit}$  may be considered to be a strong electrolyte and its osmotic coefficient and water activities are then given by Eqs. (B.9) and (B.11). Figure A-39 shows a comparison with the experimental data and the curves calculated using  $\epsilon(\text{Na}^+, \text{cit}^{3-}) = -(0.12 \pm 0.01) + (0.145 \pm 0.020) \log_{10} m_{\text{Na}^+}$ . This value agrees with that selected by this review within the uncertainties.

It should be noted however that the expression given in Table VII-9, where the ionic strength substitutes  $m_{\text{Na}^+}$ , results in a much worse fit of the experimental data. For 1:1 electrolytes the expression  $\epsilon = \epsilon_1 + \epsilon_2 \log_{10} I_m$  is appropriate, but for the unsymmetrical electrolyte studied here the correct expression appears to be  $\epsilon = \epsilon_1 + \epsilon_2 \log_{10} [M^+]$ .

Figure A-38: Experimental activities of water for mixtures of  $\text{H}_3\text{cit}$  and  $\text{NaCl}$  at  $25^\circ\text{C}$  [2004SCH/MAU] compared with values calculated using  $\varepsilon(\text{H}_3\text{cit}, \text{NaCl}) = (0.03 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ .

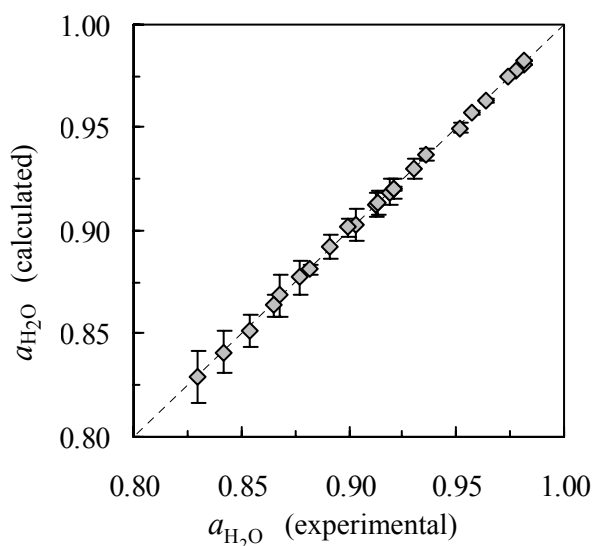
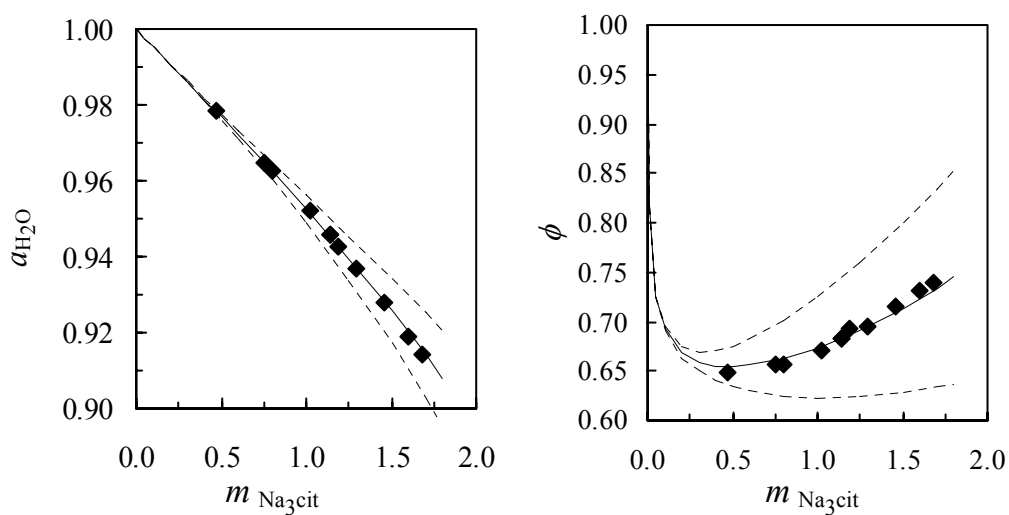


Figure A-39: Experimental activities of water and corresponding osmotic coefficients for  $\text{Na}_3\text{cit}$  solutions at  $25^\circ\text{C}$  [2004SCH/MAU] compared with values calculated using  $\varepsilon(\text{Na}^+, \text{cit}^{3-}) = -(0.12 \pm 0.01) + (0.145 \pm 0.020) \log_{10} m_{\text{Na}^+}$ .







# Appendix B

## Ionic strength corrections<sup>1</sup>

Thermodynamic data always refer to a selected standard state. The definition given by IUPAC [82LAF] is adopted in this review as outlined in Section II.3.1. According to this definition, the standard state for a solute B in a solution is a hypothetical solution, at the standard state pressure, in which  $m_B = m^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$ , and in which the activity coefficient  $\gamma_B$  is unity. However, for many reactions, measurements cannot be made accurately (or at all) in dilute solutions from which the necessary extrapolation to the standard state would be simple. This is invariably the case for reactions involving ions of high charge. Precise thermodynamic information for these systems can only be obtained in the presence of an inert electrolyte of sufficiently high concentration that ensures activity factors are reasonably constant throughout the measurements. This appendix describes and illustrates the method used in this review for the extrapolation of experimental equilibrium data to zero ionic strength.

The activity factors of all the species participating in reactions in high ionic strength media must be estimated in order to reduce the thermodynamic data obtained from the experiment to the state  $I = 0$ . Two alternative methods can be used to describe the ionic medium dependence of equilibrium constants:

- One method takes into account the individual characteristics of the ionic media by using a medium dependent expression for the activity coefficients of the species involved in the equilibrium reactions. The medium dependence is described by virial or ion interaction coefficients as used in the Pitzer equations [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

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<sup>1</sup> This Appendix essentially contains the text of the TDB-2 Guideline written by Grenthe and Wanner [2000GRE/WAN], earlier versions of which have been printed in the previous NEA TDB reviews. The equations presented here are an essential part of the review procedure and are required to use the selected thermodynamic values. The contents of Tables B-4, B-5, B-6 and B-7 have been revised.

and the ionic strength, but it accounts for the medium specific properties by introducing ion pairing between the medium ions and the species involved in the equilibrium reactions. Earlier, this approach has been used extensively in 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 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 [2000GRE/WAN].

The specific ion interaction methods are reliable for intercomparison of experimental data in a given concentration range. In many cases this includes data at rather low ionic strengths,  $I = 0.01$  to  $0.1 \text{ M}$ , *cf.* Figure B-1, while in other cases, notably for cations of high charge ( $\geq +4$  and  $\leq -4$ ), the lowest available ionic strength is often  $0.2 \text{ M}$  or higher, see for example Figures V.12 and V.13 in [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, and the other due to model errors. The model errors seem to be rather small for many systems, less than  $0.1$  units in  $\log_{10} K^\circ$ . For reactions involving ions of high charge, which may be extensively hydrolysed, one cannot perform experiments at low ionic strengths. Hence, it is impossible to estimate the extrapolation error. This is true for all methods used to estimate activity corrections. Systematic model errors of this type are not included in the uncertainties assigned to the selected data in this review.

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 [22BRO], [22BRO2] and elaborated by Scatchard [36SCA] and Guggenheim [66GUG]. Biedermann [75BIE] highlighted its practical value, especially for the estimation of ionic medium effects on equilibrium constants. The two basic assumptions in the specific ion interaction theory are described below.

• **Assumption 1:** The activity coefficient  $\gamma_j$  of an ion  $j$  of charge  $z_j$  in the solution of ionic strength  $I_m$  may be described by Eq. (B.1):

$$\log_{10} \gamma_j = -z_j^2 D + \sum_k \varepsilon(j, k, I_m) m_k \quad (\text{B.1})$$

$D$  is the Debye-Hückel term:

$$D = \frac{A \sqrt{I_m}}{1 + B a_j \sqrt{I_m}} \quad (\text{B.2})$$

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 is correlated to the value of  $\varepsilon(j, k, I_m)$ . Hence, this variety of values for  $Ba_j$  does not represent an uncertainty range, but rather indicates that several different sets of  $Ba_j$  and  $\varepsilon(j, k, I_m)$  may describe equally well the experimental mean activity coefficients of a given electrolyte. The ion interaction coefficients at 25°C listed in Table B-4, Table B-5, Table B-6 and Table B-7 have thus to be used with  $Ba_j = 1.5 \text{ kg}^{1/2} \cdot \text{mol}^{-1/2}$ .

The summation in Eq. (B.1) extends over all ions  $k$  present in solution. Their molality is denoted by  $m_k$ , and the specific ion interaction parameters,  $\varepsilon(j, k, I_m)$ , in

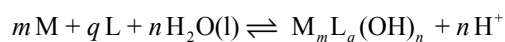
general depend only slightly on the ionic strength. The concentrations of the ions of the ionic medium are often very much larger than those of the reacting species. Hence, the ionic medium ions will make the main contribution to the value of  $\log_{10}\gamma_j$  for the reacting ions. This fact often makes it possible to simplify the summation  $\sum \epsilon(j, k, I_m) m_k$ , 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,  $\epsilon(j, k, I_m)$  are zero for ions of the same charge sign and for uncharged species. The rationale behind this is that  $\epsilon$ , 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 reproduce accurately their activity coefficient data, concentration dependent ion interaction coefficients have to be used, *cf.* Lewis *et al.* [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 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  $M_m L_q (OH)_n$ ,  $^* \beta_{q,n,m}$ , 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,  $M_m L_q (OH)_n$ . If the concentrations of N and X are much greater than the concentrations of M, L,  $M_m L_q (OH)_n$  and  $H^+$ , only the molalities  $m_N$  and  $m_X$  have to be taken into account for the calculation of the term,  $\sum \varepsilon(j,k,I_m) m_k$  in Eq. (B.1). For example, for the activity coefficient of the metal cation M,  $\gamma_M$ , Eq. (B.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:

$$\log_{10} ^* \beta_{q,n,m} - \Delta z^2 D - n \log_{10} a_{H_2O} = \log_{10} ^* \beta_{q,n,m}^\circ - \Delta \varepsilon I_m \quad (B.5)$$

where, at 25°C and 1 bar:

$$\Delta z^2 = (m z_M - q z_L - n)^2 + n - m z_M^2 - q z_L^2 \quad (B.6)$$

$$D = \frac{0.509 \sqrt{I_m}}{1 + 1.5 \sqrt{I_m}} \quad (B.7)$$

$$\Delta \varepsilon = \varepsilon(q, n, m, N \text{ or } X) + n \varepsilon(H, X) - q \varepsilon(N, L) - m \varepsilon(M, X) \quad (B.8)$$

Here  $(m z_M - q z_L - n)$ ,  $z_M$  and  $z_L$  are the charges of the complex,  $M_m L_q (OH)_n$ , 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:

$$\log_{10} a_{H_2O} = \frac{-\phi \sum_k m_k}{\ln(10) \cdot 55.51} \quad (B.9)$$

where  $\phi$  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 as the dominant species, 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:

$$\log_{10} a_{H_2O} = \frac{-2 m_{NX} \phi}{\ln(10) \times 55.51} \quad (B.10)$$

Alternatively, water activities can be taken from Table B-1. These have been calculated for the most common ionic media at various concentrations applying Pitzer's ion interaction model and the interaction parameters given in [91PIT]. Data in *italics* have been calculated for concentrations beyond the validity of the parameter set applied. These data are therefore extrapolations and should be used with care.

Table B-1: Water activities  $a_{\text{H}_2\text{O}}$  for the most common ionic media at various concentrations applying Pitzer's ion interaction approach and the interaction parameters given in [91PIT]. Data in *italics* have been calculated for concentrations beyond the validity of the parameter set applied. These data are therefore extrapolations and should be used with care.

Water activities $a_{\text{H}_2\text{O}}$								
c (M)	HClO <sub>4</sub>	NaClO <sub>4</sub>	LiClO <sub>4</sub>	NH <sub>4</sub> ClO <sub>4</sub>	Ba(ClO <sub>4</sub> ) <sub>2</sub>	HCl	NaCl	LiCl
0.10	0.9966	0.9966	0.9966	0.9967	0.9953	0.9966	0.9966	0.9966
0.25	0.9914	0.9917	0.9912	0.9920	0.9879	0.9914	0.9917	0.9915
0.50	0.9821	0.9833	0.9817	0.9844	0.9740	0.9823	0.9833	0.9826
0.75	0.9720	0.9747	0.9713	0.9769	0.9576	0.9726	0.9748	0.9731
1.00	0.9609	0.9660	0.9602	0.9694	0.9387	0.9620	0.9661	0.9631
1.50	0.9357	0.9476	0.9341	0.9542	0.8929	0.9386	0.9479	0.9412
2.00	0.9056	0.9279	0.9037		<i>0.8383</i>	0.9115	0.9284	0.9167
3.00	0.8285	0.8840	0.8280		<i>0.7226</i>	0.8459	0.8850	0.8589
4.00	0.7260	0.8331	<i>0.7309</i>			0.7643	0.8352	0.7991
5.00	<i>0.5982</i>	<i>0.7744</i>				0.6677	0.7782	0.7079
6.00	<i>0.4513</i>	<i>0.7075</i>				<i>0.5592</i>		<i>0.6169</i>

(Continued on next page)

Table B-1: (continued)

c (M)	KCl	NH <sub>4</sub> Cl	MgCl <sub>2</sub>	CaCl <sub>2</sub>	NaBr	HNO <sub>3</sub>	NaNO <sub>3</sub>	LiNO <sub>3</sub>
0.10	0.9966	0.9966	0.9953	0.9954	0.9966	0.9966	0.9967	0.9966
0.25	0.9918	0.9918	0.9880	0.9882	0.9916	0.9915	0.9919	0.9915
0.50	0.9836	0.9836	0.9744	0.9753	0.9830	0.9827	0.9841	0.9827
0.75	0.9754	0.9753	0.9585	0.9605	0.9742	0.9736	0.9764	0.9733
1.00	0.9671	0.9669	0.9399	0.9436	0.9650	0.9641	0.9688	0.9635
1.50	0.9500	0.9494	0.8939	0.9024	0.9455	0.9439	0.9536	0.9422
2.00	0.9320	0.9311	0.8358	0.8507	0.9241	0.9221	0.9385	0.9188
3.00	0.8933	0.8918	0.6866	0.7168	0.8753	0.8737	0.9079	0.8657
4.00	0.8503	0.8491	0.5083	0.5511	0.8174	0.8196	0.8766	0.8052
5.00		0.8037		0.3738	0.7499	0.7612	0.8446	0.7390
6.00					0.6728	0.7006	0.8120	0.6696
c (M)	NH <sub>4</sub> NO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Na <sub>2</sub> CO <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	NaSCN		
0.10	0.9967	0.9957	0.9958	0.9956	0.9955	0.9966		
0.25	0.9920	0.9900	0.9902	0.9896	0.9892	0.9915		
0.50	0.9843	0.9813	0.9814	0.9805	0.9789	0.9828		
0.75	0.9768	0.9732	0.9728	0.9720	0.9683	0.9736		
1.00	0.9694	0.9653	0.9640	0.9637	0.9570	0.9641		
1.50	0.9548	0.9491	0.9455	0.9467	0.9316	0.9438		
2.00	0.9403		0.9247	0.9283	0.9014	0.9215		
3.00	0.9115		0.8735		0.8235	0.8708		
4.00	0.8829		0.8050		0.7195	0.8115		
5.00	0.8545				0.5887	0.7436		
6.00	0.8266					0.6685		

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,  $N_{v+} X_{v-}$ , 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]).

$$1 - \phi = \frac{A \ln(10) |z_+ z_-|}{I_m (B a_j)^3} \left[ 1 + B a_j \sqrt{I_m} - 2 \ln(1 + B a_j \sqrt{I_m}) - \frac{1}{1 + B a_j \sqrt{I_m}} \right] - \ln(10) \varepsilon(N, X) m_{NX} \left( \frac{\nu_+ \nu_-}{\nu_+ + \nu_-} \right) \quad (\text{B.11})$$

where  $\nu_+$  and  $\nu_-$  are the number of cations and anions in the salt formula ( $\nu_+ z_+ = \nu_- z_-$ ) and in this case:

$$I_m = \frac{1}{2} |z_+ z_-| m_{NX} (\nu_+ + \nu_-)$$

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 might be necessary to use Pitzer's equation to calculate the activity of water. On the other hand,  $a_{\text{H}_2\text{O}}$  is nearly constant in most experimental studies of equilibria in dilute aqueous solutions, where an ionic medium is used in large excess with respect to the reactants. The medium electrolyte thus determines the osmotic coefficient of the solvent.

In natural waters the situation is similar; the ionic strength of most surface waters is so low that the activity of  $\text{H}_2\text{O}(\text{l})$  can be set equal to unity. A correction may be necessary in the case of seawater, where a sufficiently good approximation for the osmotic coefficient may be obtained by considering NaCl as the dominant electrolyte.

In more complex solutions of high ionic strengths with more than one electrolyte at significant concentrations, *e.g.*, ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ), Pitzer's equation (*cf.* [\[2000GRE/WAN\]](#)) may be used to estimate the osmotic coefficient; the necessary interaction coefficients are known for most systems of geochemical interest.

Note that in all ion interaction approaches, the equation for the mean activity coefficients can be split up to give equations for conventional single ion activity coefficients in mixtures, *e.g.*, Eq. (B.1). The latter are strictly valid only when used in combinations which yield electroneutrality. Thus, while estimating medium effects on standard potentials, a combination of redox equilibria with,  $\text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2} \text{H}_2(\text{g})$ , is necessary (*cf.* Example B.3).

### B.1.2 Ionic strength corrections at temperatures other than 298.15 K

Values of the Debye-Hückel parameters  $A$  and  $B$  in Eqs. (B.2) and (B.11) are listed in Table B-2 for a few temperatures at a pressure of 1 bar below 100°C and at the steam saturated pressure for  $t \geq 100^\circ\text{C}$ . The values in Table B-2 may be calculated from the static dielectric constant and the density of water as a function of temperature and pres-



sure, 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-2.
- The value  $Ba_j$  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-2, this implies a temperature dependence for ion size parameters. Assuming for the ion size is in reality constant, then it is seen that this simplification introduces an error in  $D$ , which increases with temperature and ionic strength (this error is less than  $\pm 0.01$  at  $t \leq 100^\circ\text{C}$  and  $I < 6 \text{ m}$ , and less than  $\pm 0.006$  at  $t \leq 50^\circ\text{C}$  and  $I \leq 4 \text{ m}$ ).
- The value of  $Ba_j$  is calculated at each temperature assuming a given temperature variation for  $a_j$  and using the values of  $B$  listed in Table B-2. For example, in the aqueous ionic model of Helgeson and co-workers ([\[88TAN/HEL\]](#), [\[88SHO/HEL\]](#), [\[89SHO/HEL\]](#), [\[89SHO/HEL2\]](#)) 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 *et al.* [\[61LEW/RAN\]](#), 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  $\leq 0.13$ . It is clear that in order to reduce the uncertainties in solubility calculations at  $t \neq 25^\circ\text{C}$ , studies on the variation of  $\varepsilon(j, k, I_m)$  values with temperature should be undertaken.

Table B-2: Debye-Hückel constants as a function of temperature at a pressure of 1 bar below 100°C and at the steam saturated pressure for  $t \geq 100^\circ\text{C}$ . The uncertainty in the  $A$  parameter is estimated by this review to be  $\pm 0.001$  at 25°C, and  $\pm 0.006$  at 300°C, while for the  $B$  parameter the estimated uncertainty ranges from  $\pm 0.0003$  at 25°C to  $\pm 0.001$  at 300°C.

$t(^{\circ}\text{C})$	$p(\text{bar})$	$A \text{ ( kg}^{\frac{1}{2}} \cdot \text{mol}^{-\frac{1}{2}} \text{ )}$	$B \times 10^{-10} \text{ ( kg}^{\frac{1}{2}} \cdot \text{mol}^{-\frac{1}{2}} \cdot \text{mol}^{-1} \text{ )}$
0	1.00	0.491	0.3246
5	1.00	0.494	0.3254
10	1.00	0.498	0.3261
15	1.00	0.501	0.3268
20	1.00	0.505	0.3277
25	1.00	0.509	0.3284
30	1.00	0.513	0.3292
35	1.00	0.518	0.3300
40	1.00	0.525	0.3312
50	1.00	0.534	0.3326
75	1.00	0.564	0.3371
100	1.013	0.600	0.3422
125	2.32	0.642	0.3476
150	4.76	0.690	0.3533
175	8.92	0.746	0.3593
200	15.5	0.810	0.365
250	29.7	0.980	0.379
300	85.8	1.252	0.396

### B.1.3 Estimation of ion interaction coefficients

#### B.1.3.1 Estimation from mean activity coefficient data

##### Example B.1:

The ion interaction coefficient  $\varepsilon(\text{H}^+, \text{Cl}^-)$  can be obtained from published values of  $\gamma_{\pm, \text{HCl}}$  versus  $m_{\text{HCl}}$ :

$$\begin{aligned}
 2 \log_{10} \gamma_{\pm, \text{HCl}} &= \log_{10} \gamma_{\text{H}^+} + \log_{10} \gamma_{\text{Cl}^-} \\
 &= -D + \varepsilon(\text{H}^+, \text{Cl}^-) m_{\text{Cl}^-} - D + \varepsilon(\text{Cl}^-, \text{H}^+) m_{\text{H}^+} \\
 \log_{10} \gamma_{\pm, \text{HCl}} &= -D + \varepsilon(\text{H}^+, \text{Cl}^-) m_{\text{HCl}}
 \end{aligned}$$

By plotting  $(\log_{10} \gamma_{\pm, \text{HCl}} + D)$  versus  $m_{\text{HCl}}$  a straight line with the slope  $\varepsilon(\text{H}^+, \text{Cl}^-)$  is obtained. The degree of linearity should in itself indicate the range of validity of the specific ion interaction approach. Osmotic coefficient data can be treated in an analogous way.

### B.1.3.2 Estimations based on experimental values of equilibrium constants at different ionic strengths

#### Example B.2:

Equilibrium constants are given in Table B-3 for the reaction:



The following formula is deduced from Eq. (B.5) for the extrapolation to  $I = 0$ :

$$\log_{10} \beta_1 + 4D = \log_{10} \beta_1^\circ - \Delta\epsilon I_m \quad (\text{B.13})$$

The linear regression is done as described in Appendix C. The following results are obtained:

$$\log_{10} \beta_1^\circ = (0.170 \pm 0.021)$$

$$\Delta\epsilon(\text{B.12}) = -(0.248 \pm 0.022) \text{ kg}\cdot\text{mol}^{-1}.$$

The experimental data are depicted in Figure B-1, where the area enclosed by the dotted lines represents the uncertainty range that is obtained by using the results in  $\log_{10} \beta_1^\circ$  and  $\Delta\epsilon$  and correcting back to  $I \neq 0$ .

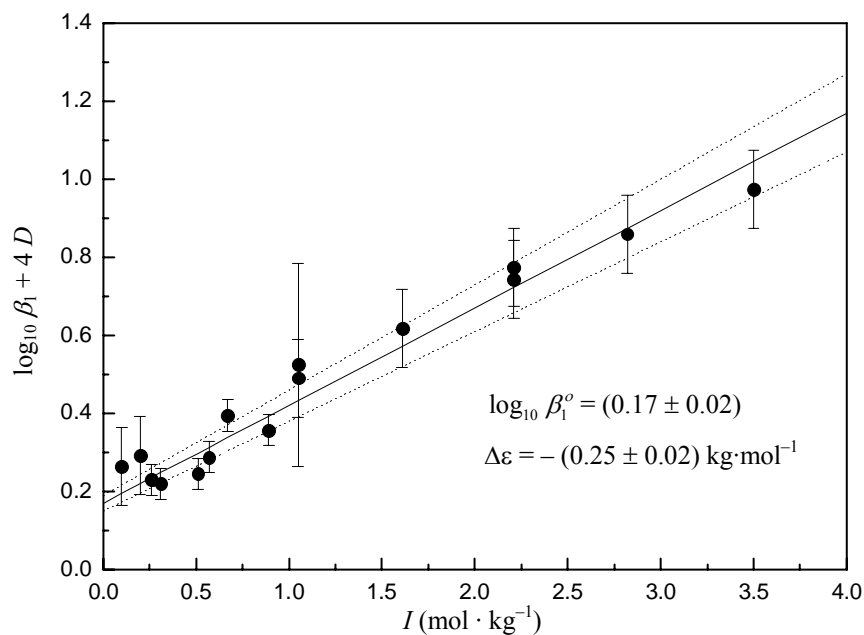
Table B-3: The preparation of the experimental equilibrium constants for the extrapolation to  $I = 0$  with the specific ion interaction method at 25°C and 1 bar, according to Reaction (B.12). The linear regression of this set of data is shown in Figure B-1.

$I_m$	$\log_{10} \beta_1 \text{ (exp)}^{(a)}$	$\log_{10} \beta_{1,m}^{(b)}$	$\log_{10} \beta_{1,m} + 4D$
0.1	$-(0.17 \pm 0.10)$	-0.174	$(0.264 \pm 0.100)$
0.2	$-(0.25 \pm 0.10)$	-0.254	$(0.292 \pm 0.100)$
0.26	$-(0.35 \pm 0.04)$	-0.357	$(0.230 \pm 0.040)$
0.31	$-(0.39 \pm 0.04)$	-0.397	$(0.220 \pm 0.040)$
0.41	$-(0.41 \pm 0.04)$	-0.420	$(0.246 \pm 0.040)$
0.51	$-(0.32 \pm 0.10)$	-0.331	$(0.371 \pm 0.100)$
0.57	$-(0.42 \pm 0.04)$	-0.432	$(0.288 \pm 0.040)$
0.67	$-(0.34 \pm 0.04)$	-0.354	$(0.395 \pm 0.040)$
0.89	$-(0.42 \pm 0.04)$	-0.438	$(0.357 \pm 0.040)$
1.05	$-(0.31 \pm 0.10)$	-0.331	$(0.491 \pm 0.100)$
1.05	$-(0.277 \pm 0.260)$	-0.298	$(0.525 \pm 0.260)$
1.61	$-(0.24 \pm 0.10)$	-0.272	$(0.618 \pm 0.100)$
2.21	$-(0.15 \pm 0.10)$	-0.193	$(0.744 \pm 0.100)$
2.21	$-(0.12 \pm 0.10)$	-0.163	$(0.774 \pm 0.100)$
2.82	$-(0.06 \pm 0.10)$	-0.021	$(0.860 \pm 0.100)$
3.5	$(0.04 \pm 0.10)$	-0.021	$(0.974 \pm 0.100)$

(a) Equilibrium constants for Reaction (B.12) with assigned uncertainties, corrected to 25°C where necessary.

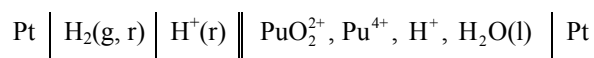
(b) Equilibrium constants corrected from molarity to molality units, as described in Section II.2

Figure B-1: Plot of  $\log_{10} \beta_1 + 4D$  versus  $I_m$  for Reaction (B.12), 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.

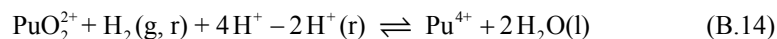


### Example B.3:

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 "r" is used to indicate that  $\text{H}_2(\text{g})$  and  $\text{H}^+$  are at the chemical conditions in the reference electrode compartment, *i.e.*, standard conditions when the reference electrode is the SHE. However, activities of  $\text{H}^+$ ,  $\text{H}_2\text{O}(\text{l})$  and the ratio of activity of  $\text{PuO}_2^{2+}$  to  $\text{Pu}^{4+}$  depend on the conditions of the experimental measurements (*i.e.*, non-standard conditions, usually high ionic strength to improve the accuracy of the measurement).

For Reaction (B.14):

$$\log_{10} K^{\circ} = \log_{10} \left( \frac{a_{\text{Pu}^{4+}} \cdot a_{\text{H}_2\text{O}}^2 \cdot a_{\text{H}^+(\text{r})}}{a_{\text{PuO}_2^{2+}} \cdot a_{\text{H}^+}^4 \cdot f_{\text{H}_2(\text{r})}} \right).$$

Since by definition of the SHE,  $f_{\text{H}_2(\text{r})} = 1$  and  $\gamma_{\text{H}^+(\text{r})} = 1$ ,

$$\log_{10} K^{\circ} = \log_{10} K + \log_{10} \gamma_{\text{Pu}^{4+}} - \log_{10} \gamma_{\text{PuO}_2^{2+}} - 4 \log_{10} \gamma_{\text{H}^+} + 2 \log_{10} a_{\text{H}_2\text{O}},$$

and

$$\log_{10} \gamma_{\text{Pu}^{4+}} = -16D + \varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-) m_{\text{ClO}_4^-}$$

$$\log_{10} \gamma_{\text{PuO}_2^{2+}} = -4D + \varepsilon(\text{PuO}_2^{2+}, \text{ClO}_4^-) m_{\text{ClO}_4^-}$$

$$\log_{10} \gamma_{\text{H}^+} = -D + \varepsilon(\text{H}^+, \text{ClO}_4^-) m_{\text{ClO}_4^-}$$

Hence,

$$\begin{aligned} \log_{10} K^{\circ} = \log_{10} K - 8D + (\varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-) - \varepsilon(\text{PuO}_2^{2+}, \text{ClO}_4^-) \\ - 4\varepsilon(\text{H}^+, \text{ClO}_4^-)) m_{\text{ClO}_4^-} + 2 \log_{10} a_{\text{H}_2\text{O}} \end{aligned} \quad (\text{B.15})$$

The relationship between the equilibrium constant and the redox potential is:

$$\ln K = \frac{nF}{RT} E^{\circ'} \quad (\text{B.16})$$

$$\ln K^{\circ} = \frac{nF}{RT} E^{\circ}. \quad (\text{B.17})$$

$E^{\circ'}$  is the redox potential in a medium of ionic strength  $I$ ,  $E^{\circ}$  is the corresponding standard potential at  $I = 0$ , and  $n$  is the number of transferred electrons in the reaction considered. Combining Eqs. (B.15), (B.16) and (B.17) and rearranging them leads to Eq.(B.18):

$$E^{\circ'} - (8D - 2 \log_{10} a_{\text{H}_2\text{O}}) \left( \frac{RT \ln(10)}{nF} \right) = E^{\circ} - \Delta\varepsilon m_{\text{ClO}_4^-} \left( \frac{RT \ln(10)}{nF} \right) \quad (\text{B.18})$$

For  $n = 2$  in the present example and  $T = 298.15$  K, Eq.(B.18) becomes:

$$E^{\circ'} [\text{mV}] - 236.6 D + 59.16 \log_{10} a_{\text{H}_2\text{O}} = E^{\circ} [\text{mV}] - 29.58 \Delta\varepsilon m_{\text{ClO}_4^-}$$

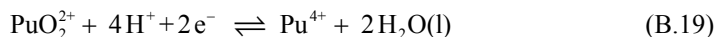
where

$$\Delta\varepsilon = \varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-) - \varepsilon(\text{PuO}_2^{2+}, \text{ClO}_4^-) - 4\varepsilon(\text{H}^+, \text{ClO}_4^-).$$

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 II.1.6.5, as exemplified in Tables V.2 and V.3 of the uranium NEA review [\[92GRE/FUG\]](#). In that case, the  $\text{H}^+$  appearing in the reduction reaction is

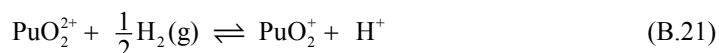
already at standard conditions. For example, experimental data are available on the formal potentials for reactions:



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  $\text{H}^+$  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)  $\text{H}^+$  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). Reactions (B.20) and (B.21) are equivalent, as are Reactions (B.14) and (B.19), as can be seen if any of these equations are combined with Reaction (II.27). Hence Eq. (B.18) can be obtained more simply by using Eq. (II.34) 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 *et al.* [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 determining the magnitude of the ion interaction coefficient. Ions of the same charge type have similar ion interaction coefficients with a given counter-ion. Based on the tabulated data, Grenthe *et al.* [92GRE/FUG] proposed that it is possible to estimate, with an error of at most  $\pm 0.1 \text{ kg} \cdot \text{mol}^{-1}$  in  $\epsilon$ , 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  $\pm 0.1 \text{ kg} \cdot \text{mol}^{-1}$  in  $\Delta\epsilon$  in most cases, based on comparison with  $\Delta\epsilon$  values of various reactions of the same charge type.

Ciavatta [90CIA] has proposed an alternative method to estimate values of  $\epsilon$  for a first or second complex, ML or  $\text{ML}_2$ , in an ionic media NX, according to the following relationships:

$$\epsilon(\text{ML}, \text{N or X}) \approx (\epsilon(\text{M}, \text{X}) + \epsilon(\text{L}, \text{N}))/2 \quad (\text{B.22})$$

$$\epsilon(\text{ML}_2, \text{N or X}) \approx (\epsilon(\text{M}, \text{X}) + 2\epsilon(\text{L}, \text{N}))/3 \quad (\text{B.23})$$

Ciavatta obtained [90CIA] an average deviation of  $\pm 0.05 \text{ kg} \cdot \text{mol}^{-1}$  between  $\varepsilon$  estimates according to Eqs. (B.22) and (B.23), and the  $\varepsilon$  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-4. This review takes chloride and nitrate complex formation into account when these ions are part of the ionic medium and uses the value of the ion interaction coefficient,  $\varepsilon(\text{M}^{n+}, \text{ClO}_4^-)$ , as a substitute for  $\varepsilon(\text{M}^{n+}, \text{Cl}^-)$  and  $\varepsilon(\text{M}^{n+}, \text{NO}_3^-)$ . In this way, the medium dependence of the activity coefficients is described with a combination of a specific ion interaction model and an ion pairing model. It is evident that the use of NEA recommended data with ionic strength correction models that differ from those used in the evaluation procedure can lead to inconsistencies in the results of the speciation calculations.

It should be mentioned that complex formation may also occur between negatively charged complexes and the cation of the ionic medium. An example is the stabilisation of the complex ion,  $\text{UO}_2(\text{CO}_3)_3^{5-}$ , at high ionic strength, see for example Section V.7.1.2.1.d (p. 322) in the uranium review [92GRE/FUG].

## B.3 Tables of ion interaction coefficients

Table B-4, Table B-5, Table B-6 and Table B-7 contain the selected specific ion interaction coefficients used in this review, according to the specific ion interaction theory described. Table B-4 contains cation interaction coefficients with  $\text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ , Table B-5 anion interaction coefficients with  $\text{Li}^+$ ,  $\text{Na}^+$  (or  $\text{NH}_4^+$ ) and  $\text{K}^+$ , and Table B-7 neutral species – electroneutral combination of ions. The coefficients have the units of  $\text{kg} \cdot \text{mol}^{-1}$  and are valid for 298.15 K and 1 bar. The species are ordered by charge and appear, within each charge class, in standard order of arrangement, *cf.* Section II.1.8.

In some cases, the ionic interaction can be better described by assuming ion interaction coefficients as functions of the ionic strength rather than as constants. Ciavatta [80CIA] proposed the use of Eq. (B.24) for cases where the uncertainties in Table B-4 and Table B-5 are  $\pm 0.03 \text{ kg} \cdot \text{mol}^{-1}$  or greater.

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m \quad (\text{B.24})$$

For these cases, and when the uncertainty can be improved with respect to the use of a constant value of  $\varepsilon$ , the values  $\varepsilon_1$  and  $\varepsilon_2$  given in Table B-6 should be used.

It should be noted that ion interaction coefficients tabulated in Table B-4, Table B-5 and Table B-6 may also involve ion pairing effects, as described in Section B.3. In direct comparisons of ion interaction coefficients, or when estimates are made by analogy, this aspect must be taken into account.



Table B-4: Ion interaction coefficients  $\varepsilon(j,k)$  ( $\text{kg}\cdot\text{mol}^{-1}$ ) for cations  $j$  with  $k = \text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ , taken from Ciavatta [80CIA], [88CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with  $\dagger$  can be described more accurately with an ionic strength dependent function, listed in Table B-6. The coefficients  $\varepsilon(\text{M}^{n+}, \text{Cl}^-)$  and  $\varepsilon(\text{M}^{n+}, \text{NO}_3^-)$  reported by Ciavatta [80CIA] were evaluated without taking chloride and nitrate complexation into account, as discussed in Section B.2.

$j \quad k \rightarrow$ $\downarrow$	$\text{Cl}^-$	$\text{ClO}_4^-$	$\text{NO}_3^-$
$\text{H}^+$	$(0.12 \pm 0.01)$	$(0.14 \pm 0.02)$	$(0.07 \pm 0.01)$
$\text{NH}_4^+$	$-(0.01 \pm 0.01)$	$-(0.08 \pm 0.04)^\dagger$	$-(0.06 \pm 0.03)^\dagger$
$\text{H}_2\text{gly}^+$	$-(0.06 \pm 0.02)$		
$\text{H}_5\text{edta}^+$	$-(0.23 \pm 0.15)$	$-(0.23 \pm 0.15)$	$-(0.23 \pm 0.15)$
$\text{Ti}^+$		$-(0.21 \pm 0.06)^\dagger$	
$\text{ZnHCO}_3^+$	$0.2^{(a)}$		
$\text{CdCl}^+$		$(0.25 \pm 0.02)$	
$\text{CdI}^+$		$(0.27 \pm 0.02)$	
$\text{CdSCN}^+$		$(0.31 \pm 0.02)$	
$\text{HgCl}^+$		$(0.19 \pm 0.02)$	
$\text{Cu}^+$		$(0.11 \pm 0.01)$	
$\text{Ag}^+$		$(0.00 \pm 0.01)$	$-(0.12 \pm 0.05)^\dagger$
$\text{NiOH}^+$	$-(0.01 \pm 0.07)^{(K)}$	$(0.14 \pm 0.07)^{(L)}$	
$\text{NiF}^+$		$(0.34 \pm 0.08)^{(M)}$	
$\text{NiCl}^+$		$(0.47 \pm 0.06)^{(N)}$	
$\text{NiNO}_3^+$		$(0.44 \pm 0.14)^{(O)}$	
$\text{Ni}(\text{H}_2\text{cit})^+$		$(0.12 \pm 0.5)$	
$\text{NiBr}^+$		$(0.59 \pm 0.10)^{(P)}$	
$\text{NiHS}^+$		$-(0.85 \pm 0.39)^{(Q)}$	
$\text{NiSCN}^+$		$(0.31 \pm 0.04)^{(R)}$	
$\text{YCO}_3^+$		$(0.17 \pm 0.04)^{(b)}$	
$\text{Am}(\text{OH})_2^+$	$-(0.27 \pm 0.20)^{(q)}$	$(0.17 \pm 0.04)^{(c)}$	
$\text{AmF}_2^+$		$(0.17 \pm 0.04)^{(c)}$	
$\text{AmSO}_4^+$		$(0.22 \pm 0.08)^{(d)}$	
$\text{AmCO}_3^+$	$(0.01 \pm 0.05)^{(r)}$	$(0.17 \pm 0.04)^{(c)}$	
$\text{Am}(\text{ox})^+$		$(0.08 \pm 0.10)$	
$\text{PuO}_2^+$		$(0.24 \pm 0.05)^{(e)}$	
$\text{PuO}_2\text{F}^+$		$(0.29 \pm 0.11)^{(f)}$	
$\text{PuO}_2\text{Cl}^+$		$(0.50 \pm 0.09)^{(g)}$	

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Table B-4 (continued)

$j \downarrow k \rightarrow$	$\text{Cl}^-$	$\text{ClO}_4^-$	$\text{NO}_3^-$
$\text{NpO}_2^+$	$(0.09 \pm 0.05)$	$(0.25 \pm 0.05)^{(h)}$	
$\text{NpO}_2\text{OH}^+$		$-(0.06 \pm 0.40)^{(i)}$	
$(\text{NpO}_2)_3(\text{OH})_5^+$		$(0.45 \pm 0.20)$	
$\text{NpO}_2\text{F}^+$		$(0.29 \pm 0.12)^{(j)}$	
$\text{NpO}_2\text{Cl}^+$		$(0.50 \pm 0.14)^{(k)}$	
$\text{NpO}_2\text{IO}_3^+$		$(0.33 \pm 0.04)^{(l)}$	
$\text{Np}(\text{SCN})_3^+$		$(0.17 \pm 0.04)^{(m)}$	
$\text{UO}_2^+$		$(0.26 \pm 0.03)^{(n)}$	
$\text{UO}_2\text{OH}^+$		$-(0.06 \pm 0.40)^{(n)}$	$(0.51 \pm 1.4)^{(n)}$
$(\text{UO}_2)_3(\text{OH})_5^+$	$(0.81 \pm 0.17)^{(n)}$	$(0.45 \pm 0.15)^{(n)}$	$(0.41 \pm 0.22)^{(n)}$
$\text{UF}_3^+$	$(0.1 \pm 0.1)^{(o)}$	$(0.1 \pm 0.1)^{(o)}$	
$\text{UO}_2\text{F}^+$	$(0.04 \pm 0.07)^{(p)}$	$(0.28 \pm 0.04)$	
$\text{UO}_2\text{Cl}^+$		$(0.33 \pm 0.04)^{(n)}$	
$\text{UO}_2\text{ClO}_3^+$		$(0.33 \pm 0.04)^{(o)}$	
$\text{UO}_2\text{Br}^+$		$(0.24 \pm 0.04)^{(o)}$	
$\text{UO}_2\text{BrO}_3^+$		$(0.33 \pm 0.04)^{(o)}$	
$\text{UO}_2\text{IO}_3^+$		$(0.33 \pm 0.04)^{(o)}$	
$\text{UO}_2\text{N}_3^+$		$(0.3 \pm 0.1)^{(o)}$	
$\text{UO}_2\text{NO}_3^+$		$(0.33 \pm 0.04)^{(o)}$	
$\text{UO}_2\text{SCN}^+$		$(0.22 \pm 0.04)^{(o)}$	
$\text{H}_6\text{edta}^{2+}$	$-(0.20 \pm 0.16)$	$-(0.20 \pm 0.16)$	$-(0.20 \pm 0.16)$
$\text{Pb}^{2+}$		$(0.15 \pm 0.02)$	$-(0.20 \pm 0.12)^\dagger$
$\text{AlOH}^{2+}$	$0.09^{(s)}$	$0.31^{(s)}$	
$\text{Al}_2\text{CO}_3(\text{OH})_2^{2+}$	$0.26^{(s)}$		
$\text{Zn}^{2+}$		$(0.33 \pm 0.03)$	$(0.16 \pm 0.02)$
$\text{ZnCO}_3^{2+}$	$(0.35 \pm 0.05)^{(a)}$		
$\text{Cd}^{2+}$			$(0.09 \pm 0.02)$
$\text{Hg}^{2+}$		$(0.34 \pm 0.03)$	$-(0.1 \pm 0.1)^\dagger$
$\text{Hg}_2^{2+}$		$(0.09 \pm 0.02)$	$-(0.2 \pm 0.1)^\dagger$
$\text{Cu}^{2+}$	$(0.08 \pm 0.01)$	$(0.32 \pm 0.02)$	$(0.11 \pm 0.01)$
$\text{Ni}^{2+}$	$(0.17 \pm 0.02)$	$(0.370 \pm 0.032)^{(s)}$	$(0.182 \pm 0.010)^{(t)}$
$\text{Co}^{2+}$	$(0.16 \pm 0.02)$	$(0.34 \pm 0.03)$	$(0.14 \pm 0.01)$

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Table B-4 (continued)

$j \downarrow k \rightarrow$	$\text{Cl}^-$	$\text{ClO}_4^-$	$\text{NO}_3^-$
$\text{FeOH}^{2+}$		0.38 <sup>(b)</sup>	
$\text{FeSCN}^{2+}$		0.45 <sup>(b)</sup>	
$\text{Mn}^{2+}$	(0.13 ± 0.01)		
$\text{YHCO}_3^{2+}$		(0.39 ± 0.04) <sup>(b)</sup>	
$\text{AmOH}^{2+}$	− (0.04 ± 0.07) <sup>(q)</sup>	(0.39 ± 0.04) <sup>(c)</sup>	
$\text{AmF}^{2+}$		(0.39 ± 0.04) <sup>(c)</sup>	
$\text{AmCl}^{2+}$		(0.39 ± 0.04) <sup>(c)</sup>	
$\text{AmN}_3^{2+}$		(0.39 ± 0.04) <sup>(c)</sup>	
$\text{AmNO}_2^{2+}$		(0.39 ± 0.04) <sup>(c)</sup>	
$\text{AmNO}_3^{2+}$		(0.39 ± 0.04) <sup>(c)</sup>	
$\text{AmH}_2\text{PO}_4^{2+}$		(0.39 ± 0.04) <sup>(c)</sup>	
$\text{AmSCN}^{2+}$		(0.39 ± 0.04) <sup>(c)</sup>	
$\text{PuO}_2^{2+}$		(0.46 ± 0.05) <sup>(t)</sup>	
$\text{PuF}_2^{2+}$		(0.36 ± 0.17) <sup>(j)</sup>	
$\text{PuCl}^{2+}$		(0.39 ± 0.16) <sup>(u)</sup>	
$\text{PuI}^{2+}$		(0.39 ± 0.04) <sup>(v)</sup>	
$\text{PuSCN}^{2+}$		(0.39 ± 0.04) <sup>(B)</sup>	
$\text{NpO}_2^{2+}$		(0.46 ± 0.05) <sup>(w)</sup>	
$(\text{NpO}_2)_2(\text{OH})_2^{2+}$		(0.57 ± 0.10)	
$\text{NpF}_2^{2+}$		(0.38 ± 0.17) <sup>(j)</sup>	
$\text{NpSO}_4^{2+}$		(0.48 ± 0.11)	
$\text{Np}(\text{SCN})_2^{2+}$		(0.38 ± 0.20) <sup>(j)</sup>	
$\text{UO}_2^{2+}$	(0.21 ± 0.02) <sup>(x)</sup>	(0.46 ± 0.03)	(0.24 ± 0.03) <sup>(v)</sup>
$(\text{UO}_2)_2(\text{OH})_2^{2+}$	(0.69 ± 0.07) <sup>(n)</sup>	(0.57 ± 0.07) <sup>(n)</sup>	(0.49 ± 0.09) <sup>(n)</sup>
$(\text{UO}_2)_3(\text{OH})_4^{2+}$	(0.50 ± 0.18) <sup>(n)</sup>	(0.89 ± 0.23) <sup>(n)</sup>	(0.72 ± 1.0) <sup>(n)</sup>
$\text{UF}_2^{2+}$		(0.3 ± 0.1) <sup>(o)</sup>	
$\text{USO}_4^{2+}$		(0.3 ± 0.1) <sup>(o)</sup>	
$\text{U}(\text{NO}_3)_2^{2+}$		(0.49 ± 0.14) <sup>(y)</sup>	
$\text{Mg}^{2+}$	(0.19 ± 0.02)	(0.33 ± 0.03)	(0.17 ± 0.01)
$\text{Ca}^{2+}$	(0.14 ± 0.01)	(0.27 ± 0.03)	(0.02 ± 0.01)
$\text{Ba}^{2+}$	(0.07 ± 0.01)	(0.15 ± 0.02)	− (0.28 ± 0.03)

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Table B-4 (continued)

$j \downarrow k \rightarrow$	$\text{Cl}^-$	$\text{ClO}_4^-$	$\text{NO}_3^-$
$\text{Al}^{3+}$	$(0.33 \pm 0.02)$		
$\text{Ni}_2\text{OH}^{3+}$		$(0.59 \pm 0.15)^{(U)}$	
$\text{Fe}^{3+}$		$(0.56 \pm 0.03)$	$(0.42 \pm 0.08)$
$\text{Cr}^{3+}$	$(0.30 \pm 0.03)$		$(0.27 \pm 0.02)$
$\text{La}^{3+}$	$(0.22 \pm 0.02)$	$(0.47 \pm 0.03)$	
$\text{La}^{3+} \rightarrow \text{Lu}^{3+}$		$0.47 \rightarrow 0.52^{(b)}$	
$\text{Am}^{3+}$	$(0.23 \pm 0.02)^{(G)}$	$(0.49 \pm 0.03)^{(c)}$	
$\text{Pu}^{3+}$		$(0.49 \pm 0.05)^{(z)}$	
$\text{PuOH}^{3+}$		$(0.50 \pm 0.05)^{(i)}$	
$\text{PuF}^{3+}$		$(0.56 \pm 0.11)^{(i)}$	
$\text{PuCl}^{3+}$		$(0.85 \pm 0.09)^{(\#)}$	
$\text{PuBr}^{3+}$		$(0.58 \pm 0.16)^{(A)}$	
$\text{Np}^{3+}$		$(0.49 \pm 0.05)^{(z)}$	
$\text{NpOH}^{3+}$		$(0.50 \pm 0.05)^{(i)}$	
$\text{NpF}^{3+}$		$(0.58 \pm 0.07)^{(C)}$	
$\text{NpCl}^{3+}$		$(0.81 \pm 0.09)^{(D)}$	
$\text{NpI}^{3+}$		$(0.77 \pm 0.26)^{(E)}$	
$\text{NpSCN}^{3+}$		$(0.76 \pm 0.12)^{(j)}$	
$\text{U}^{3+}$		$(0.49 \pm 0.05)^{(y)}$	
$\text{UOH}^{3+}$		$(0.48 \pm 0.08)^{(y)}$	
$\text{UF}^{3+}$		$(0.48 \pm 0.08)^{(o)}$	
$\text{UCl}^{3+}$		$(0.50 \pm 0.10)^{(k)}$	
$\text{UBr}^{3+}$		$(0.52 \pm 0.10)^{(o)}$	
$\text{UI}^{3+}$		$(0.55 \pm 0.10)^{(o)}$	
$\text{UNO}_3^{3+}$		$(0.62 \pm 0.08)^{(y)}$	
$\text{Be}_2\text{OH}^{3+}$		$(0.50 \pm 0.05)^{(F)}$	
$\text{Be}_3(\text{OH})_3^{3+}$	$(0.30 \pm 0.05)^{(F)}$	$(0.51 \pm 0.05)^{(y)}$	$(0.29 \pm 0.05)^{(F)}$
$\text{Al}_3\text{CO}_3(\text{OH})_4^{4+}$	$0.41^{(8)}$		
$\text{Ni}_4(\text{OH})_4^{4+}$		$(1.08 \pm 0.08)^{(V)}$	
$\text{Fe}_2(\text{OH})_2^{4+}$		$0.82^{(b)}$	

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Table B-4: (continued)

$j \quad k \rightarrow$ $\downarrow$	$\text{Cl}^-$	$\text{ClO}_4^-$	$\text{NO}_3^-$
$\text{Y}_2\text{CO}_3^{4+}$		$(0.80 \pm 0.04)^{(b)}$	
$\text{Pu}^{4+}$		$(0.82 \pm 0.07)^{(H)}$	
$\text{Np}^{4+}$		$(0.84 \pm 0.06)^{(I)}$	
$\text{U}^{4+}$		$(0.76 \pm 0.06)^{(J)(o)}$	
$\text{Th}^{4+}$	$(0.25 \pm 0.03)$		$(0.11 \pm 0.02)$
$\text{Al}_3(\text{OH})_4^{5+}$	$0.66^{(s)}$	$1.30^{(s)}$	

- (a) Taken from Ferri *et al.* [85FER/GRE].
- (b) Taken from Spahiu [83SPA].
- (c) Estimated in [95SIL/BID].
- (d) Evaluated in [95SIL/BID].
- (e) Derived from  $\Delta\epsilon = \epsilon(\text{PuO}_2^{2+}, \text{ClO}_4^-) - \epsilon(\text{PuO}_2^+, \text{ClO}_4^-) = (0.22 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  [95CAP/VIT]. In [92GRE/FUG],  $\epsilon(\text{PuO}_2^+, \text{ClO}_4^-) = (0.17 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  was tabulated based on [89ROB], [89RIG/ROB] and [90RIG]. Capdevila and Vitorge's data [92CAP], [94CAP/VIT] and [95CAP/VIT] were unavailable at that time.
- (f) Estimated in [2001LEM/FUG] by analogy with  $\Delta\epsilon$  of the corresponding Np(IV) reaction.
- (g) From  $\Delta\epsilon$  evaluated by Giffaut [94GIF].
- (h) As in [92GRE/FUG], derived from  $\Delta\epsilon = \epsilon(\text{NpO}_2^{2+}, \text{ClO}_4^-) - \epsilon(\text{NpO}_2^+, \text{ClO}_4^-) = (0.21 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$  [87RIG/VIT], [89RIG/ROB] and [90RIG].
- (i) Estimated in [2001LEM/FUG].
- (j) Estimated in [2001LEM/FUG] by analogy with  $\Delta\epsilon$  of the corresponding U(IV) reaction.
- (k) Estimated in [2001LEM/FUG] by analogy with  $\Delta\epsilon$  of the corresponding P(VI) reaction.
- (l) Estimated in [2001LEM/FUG] by assuming  $\epsilon(\text{NpO}_2\text{IO}_3^+, \text{ClO}_4^-) \approx \epsilon(\text{UO}_2\text{IO}_3^+, \text{ClO}_4^-)$ .
- (m) Estimated in [2001LEM/FUG] by assuming  $\epsilon(\text{Np}(\text{SCN})_3^+, \text{ClO}_4^-) \approx \epsilon(\text{AmF}_2^+, \text{ClO}_4^-)$ .
- (n) Evaluated in the uranium review [92GRE/FUG], using  $\epsilon(\text{UO}_2^{2+}, \text{X}) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ , where  $\text{X} = \text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ .
- (o) Estimated in the uranium review [92GRE/FUG].
- (p) Taken from Riglet *et al.* [89RIG/ROB], where the following assumptions were made:  $\epsilon(\text{Np}^{3+}, \text{ClO}_4^-) \approx \epsilon(\text{Pu}^{3+}, \text{ClO}_4^-) = 0.49 \text{ kg}\cdot\text{mol}^{-1}$  as for other  $(\text{M}^{3+}, \text{ClO}_4^-)$  interactions, and  $\epsilon(\text{NpO}_2^{2+}, \text{ClO}_4^-) \approx \epsilon(\text{PuO}_2^{2+}, \text{ClO}_4^-) \approx \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = 0.46 \text{ kg}\cdot\text{mol}^{-1}$ .
- (q) Evaluated in [2003GUI/FAN] (*cf.* Section 12.3.1.1) from  $\Delta\epsilon$  (in NaCl solution) for the reactions  $\text{An}^{3+} + n\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{An}(\text{OH})_n^{(3-n)} + n\text{H}^+$ .
- (r) Evaluated in [2003GUI/FAN] (*cf.* Section 12.6.1.1.1) from  $\Delta\epsilon$  (in NaCl solution) for the reactions  $\text{An}^{3+} + n\text{CO}_3^{2-} \rightleftharpoons \text{An}(\text{CO}_3)_n^{(3-n)}$  (based on  $\epsilon(\text{Am}^{3+}, \text{Cl}^-) = (0.23 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  and  $\epsilon(\text{Na}^+, \text{CO}_3^{2-}) = -(0.08 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ ).
- (s) Taken from Hedlund [88HED].

- (t) 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.
- (u) Estimated in [2001LEM/FUG] by analogy with  $\Delta\varepsilon$  of the corresponding Am(III) reaction.
- (v) Estimated in [2001LEM/FUG] by assuming  $\varepsilon(\text{Pu}^{2+}, \text{ClO}_4^-) \approx \varepsilon(\text{AmSCN}^{2+}, \text{ClO}_4^-)$  and  $\varepsilon(\text{I}^-, \text{NH}_4^+) \approx \varepsilon(\text{SCN}^-, \text{Na}^+)$ .
- (w) By analogy with  $\varepsilon(\text{UO}_2^{2+}, \text{ClO}_4^-)$  as derived from isopiestic measurements noted in [92GRE/FUG]. The uncertainty is increased because the value is estimated by analogy.
- (x) 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  $\varepsilon(\text{UO}_2^{2+}, \text{X}) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ , for  $\text{X} = \text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$ .
- (y) Evaluated in the uranium review [92GRE/FUG] using  $\varepsilon(\text{U}^{4+}, \text{X}) = (0.76 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ .
- (z) 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.
- (#) Derived from the  $\Delta\varepsilon$  evaluated in [2001LEM/FUG].
- (A) Estimated in [2001LEM/FUG] 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 [2001LEM/FUG] by assuming  $\varepsilon(\text{PuSCN}^{2+}, \text{ClO}_4^-) \approx \varepsilon(\text{AmSCN}^{2+}, \text{ClO}_4^-)$ .
- (C) Evaluated in [2001LEM/FUG].
- (D) Derived from the  $\Delta\varepsilon$  selected in [2001LEM/FUG].
- (E) Estimated in [2001LEM/FUG] 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  $\varepsilon(\text{M}^{2+}, \text{NO}_3^-)$ .
- (G) The ion interaction coefficient  $\varepsilon(\text{An}^{3+}, \text{Cl}^-)$  for  $\text{An} = \text{Am}$  and  $\text{Cm}$  is assumed to equal to  $\varepsilon(\text{Nd}^{3+}, \text{Cl}^-)$  which is calculated from trace activity coefficients of  $\text{Nd}^{3+}$  ion in 0–4 m NaCl. These trace activity coefficients are based on the ion interaction Pitzer parameters evaluated in [97KON/FAN] from osmotic coefficients in aqueous  $\text{NdCl}_3 - \text{NaCl}$  and  $\text{NdCl}_3 - \text{CaCl}_2$ .
- (H) 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 [2001LEM/FUG] (see Appendix A). In the first book of this series [92GRE/FUG],  $\varepsilon(\text{Pu}^{3+}, \text{ClO}_4^-) \approx (1.03 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  was tabulated based on references [89ROB], [89RIG/ROB], [90RIG]. Capdevila and Vitorge's data [92CAP], [94CAP/VIT] and [95CAP/VIT] were unavailable at that time.
- (I) 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].
- (J) Using the measured value of  $\Delta\varepsilon = \varepsilon(\text{U}^{4+}, \text{ClO}_4^-) - \varepsilon(\text{U}^{3+}, \text{ClO}_4^-) = (0.35 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$  p.89 [90RIG], where the uncertainty is recalculated in [2001LEM/FUG] from the data given in this thesis, and  $\varepsilon(\text{U}^{3+}, \text{ClO}_4^-) = (0.49 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  (see footnote (y)), a value for  $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-)$  can be calculated in the same way as is done for  $\varepsilon(\text{Np}^{4+}, \text{ClO}_4^-)$  and  $\varepsilon(\text{Pu}^{4+}, \text{ClO}_4^-)$ . This value,  $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.84 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$  is consistent with that tabulated  $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-) = (0.76 \pm 0.06) \text{ kg}\cdot\text{mol}^{-1}$ , since the uncertainties overlap. The authors of [2001LEM/FUG] do not believe that a change in the previously selected value for  $\varepsilon(\text{U}^{4+}, \text{ClO}_4^-)$  is justified at present.
- (K) Evaluated in Section V.3.1.1 of [2005GAM/BUG] from  $\Delta\varepsilon$  in chloride media for the reaction  $\text{Ni}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NiOH}^+ + \text{H}^+$ .

- (L) Evaluated in Section V.3.1.1 of [2005GAM/BUG] from  $\Delta\epsilon$  in perchlorate media for the reaction  $\text{Ni}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NiOH}^+ + \text{H}^+$ .
- (M) Derived from  $\Delta\epsilon = \epsilon(\text{NiF}^+, \text{ClO}_4^-) - \epsilon(\text{Ni}^{2+}, \text{ClO}_4^-) - \epsilon(\text{Na}^+, \text{F}^-) = -(0.049 \pm 0.060) \text{ kg}\cdot\text{mol}^{-1}$  (see Section V.4.2.3 of [2005GAM/BUG]).
- (N) See details in Section V.4.2.4 of [2005GAM/BUG].
- (O) See details in Section V.6.1.2 of [2005GAM/BUG], specially sub-section V.6.1.2.1 for an alternative treatment of this system.
- (P) See details in Section V.4.2.5 of [2005GAM/BUG], specially sub-section V.4.2.5.1 for an alternative treatment of this system.
- (Q) See details in Section V.5.1.1.2 of [2005GAM/BUG].
- (R) Derived from  $\Delta\epsilon = \epsilon(\text{NiSCN}^-, \text{Na}^+) - \epsilon(\text{SCN}^-, \text{Na}^+) - \epsilon(\text{Ni}^{2+}, \text{ClO}_4^-) = -(0.109 \pm 0.025) \text{ kg}\cdot\text{mol}^{-1}$  (see [2005GAM/BUG], Section V.7.1.3.1).
- (S) Derived from the ionic strength dependence of the osmotic and mean activity coefficient of  $\text{Ni}(\text{ClO}_4)_2$  solution (see [2005GAM/BUG], Section V.4.3).
- (T) Derived from the ionic strength dependence of the osmotic and mean activity coefficient of  $\text{Ni}(\text{NO}_3)_2$  solution (see [2005GAM/BUG], Section V.6.1.2.1).
- (U) By assuming  $\epsilon(\text{Ni}_2\text{OH}^{3+}, \text{ClO}_4^-) \approx \epsilon(\text{Be}_2\text{OH}^{3+}, \text{ClO}_4^-)$ , see Section V.3.1.1 ([2005GAM/BUG]).
- (V) Derived from  $\Delta\epsilon = 4 \cdot \epsilon(\text{H}^+, \text{ClO}_4^-) - \epsilon(\text{Ni}_4\text{OH}_4^{4+}, \text{ClO}_4^-) - 4 \cdot \epsilon(\text{Ni}^{2+}, \text{ClO}_4^-) = (0.16 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$  (see [2005GAM/BUG], Section V.3.1.1.1).

Table B-5: Ion interaction coefficients,  $\epsilon(j,k)$   $\text{kg} \cdot \text{mol}^{-1}$ , for anions  $j$  with  $k = \text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ , 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-6.

$j \downarrow k \rightarrow$	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$
$\text{OH}^-$	$-(0.02 \pm 0.03)^\dagger$	$(0.04 \pm 0.01)$	$(0.09 \pm 0.01)$
$\text{F}^-$		$(0.02 \pm 0.02)^{(a)}$	$(0.03 \pm 0.02)$
$\text{HF}_2^-$		$-(0.11 \pm 0.06)^{(a)}$	
$\text{Cl}^-$	$(0.10 \pm 0.01)$	$(0.03 \pm 0.01)$	$(0.00 \pm 0.01)$
$\text{ClO}_3^-$		$-(0.01 \pm 0.02)$	
$\text{ClO}_4^-$	$(0.15 \pm 0.01)$	$(0.01 \pm 0.01)$	
$\text{Br}^-$	$(0.13 \pm 0.02)$	$(0.05 \pm 0.01)$	$(0.01 \pm 0.02)$
$\text{BrO}_3^-$		$-(0.06 \pm 0.02)$	
$\text{I}^- \text{ (p)}$	$(0.16 \pm 0.01)$	$(0.08 \pm 0.02)$	$(0.02 \pm 0.01)$
$\text{IO}_3^-$		$-(0.06 \pm 0.02)^{(b)}$	
$\text{HSO}_4^-$		$-(0.01 \pm 0.02)$	
$\text{N}_3^-$		$(0.0 \pm 0.1)^{(b)}$	
$\text{NO}_2^-$	$(0.06 \pm 0.04)^\dagger$	$(0.00 \pm 0.02)$	$-(0.04 \pm 0.02)$
$\text{NO}_3^-$	$(0.08 \pm 0.01)$	$-(0.04 \pm 0.03)^\dagger$	$-(0.11 \pm 0.04)^\dagger$
$\text{H}_2\text{PO}_4^-$		$-(0.08 \pm 0.04)^\dagger$	$-(0.14 \pm 0.04)^\dagger$
$\text{HCO}_3^-$		$(0.00 \pm 0.02)^{(d)}$	$-(0.06 \pm 0.05)^{(i)}$
$\text{Hox}^-$	$-(0.28 \pm 0.09)$	$-(0.07 \pm 0.01)$	$-(0.01 \pm 0.08)$
$\text{H}_2\text{cit}^-$	$-(0.11 \pm 0.03)$	$-(0.05 \pm 0.01)$	$-(0.04 \pm 0.01)$
$\text{CN}^-$		$(0.07 \pm 0.03)^{(x)}$	
$\text{SCN}^-$		$(0.05 \pm 0.01)$	$-(0.01 \pm 0.01)$
$\text{HCOO}^-$		$(0.03 \pm 0.01)$	
$\text{CH}_3\text{COO}^-$	$(0.05 \pm 0.01)$	$(0.08 \pm 0.01)$	$(0.09 \pm 0.01)$
$\text{H}_3\text{edta}^-$		$-(0.33 \pm 0.14)$	$-(0.14 \pm 0.17)$
$\text{SiO(OH)}_3^-$		$-(0.08 \pm 0.03)^{(a)}$	
$\text{Si}_2\text{O}_2(\text{OH})_5^-$		$-(0.08 \pm 0.04)^{(b)}$	
$\text{B(OH)}_4^-$		$-(0.07 \pm 0.05)^\dagger$	
$\text{Ni(SCN)}_3^-$		$(0.66 \pm 0.13)^{(t)}$	
$\text{Ni(cit)}^-$		$(0.22 \pm 0.5)$	
$\text{Am(SO}_4)_2^-$		$-(0.05 \pm 0.05)^{(c)}$	
$\text{Am(CO}_3)_2^-$		$-(0.14 \pm 0.06)^{(r)}$	
$\text{Am(ox)}_2^-$		$-(0.21 \pm 0.08)$	
$\text{Am(edta)}^-$		$(0.01 \pm 0.16)$	$(0.01 \pm 0.16)^{(E)}$
$\text{PuO}_2\text{CO}_3^-$		$-(0.18 \pm 0.18)^{(o)}$	
$\text{Pu(edta)}^-$			$(0.01 \pm 0.16)^{(D)}$
$\text{NpO}_2(\text{OH})_2^-$		$-(0.01 \pm 0.07)^{(q)}$	

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Table B-5 (continued)

$j \quad k \rightarrow$ $\downarrow$	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$
$\text{NpO}_2\text{CO}_3^-$		$-(0.18 \pm 0.15)^{(f)}$	
$\text{NpO}_2(\text{ox})^-$		$-(0.4 \pm 0.1)$	
$\text{NpO}_2(\text{H}_2\text{edta})^-$		$-(0.18 \pm 0.16)$	
$(\text{NpO}_2)_2\text{CO}_3(\text{OH})_3^-$		$(0.00 \pm 0.05)^{(k)}$	
$\text{UO}_2(\text{OH})_3^-$		$-(0.09 \pm 0.05)^{(b)}$	
$\text{UO}_2\text{F}_3^-$		$-(0.14 \pm 0.05)^{(w)}$	
$\text{UO}_2(\text{N}_3)_3^-$		$(0.0 \pm 0.1)^{(b)}$	
$(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$		$(0.00 \pm 0.05)^{(b)}$	
$\text{UO}_2\text{cit}^-$		$-(0.11 \pm 0.09)$	
$\text{Mg}(\text{cit})^-$		$(0.03 \pm 0.03)$	
$\text{UO}_2(\text{Hedta})^-$		$-(0.18 \pm 0.16)$	
$\text{Mg}(\text{Hedta})^-$		$(0.11 \pm 0.20)$	
$\text{SO}_3^{2-}$		$-(0.08 \pm 0.05)^\dagger$	
$\text{SO}_4^{2-}$	$-(0.03 \pm 0.04)^\dagger$	$-(0.12 \pm 0.06)^\dagger$	$-(0.06 \pm 0.02)$
$\text{S}_2\text{O}_3^{2-}$		$-(0.08 \pm 0.05)^\dagger$	
$\text{HPO}_4^{2-}$		$-(0.15 \pm 0.06)^\dagger$	$-(0.10 \pm 0.06)^\dagger$
$\text{CO}_3^{2-}$		$-(0.08 \pm 0.03)^{(d)}$	$(0.02 \pm 0.01)$
$\text{ox}^{2-}$	$-(0.51 \pm 0.09)$	$-(0.08 \pm 0.01)$	$(0.07 \pm 0.08)$
$\text{Hcit}^{2-}$	$-(0.17 \pm 0.04)$	$-(0.04 \pm 0.02)$	$-(0.01 \pm 0.02)$
$\text{H}_2\text{edta}^{2-}$		$-(0.37 \pm 0.14)$	$-(0.17 \pm 0.18)$
$\text{SiO}_2(\text{OH})_2^{2-}$		$-(0.10 \pm 0.07)^{(a)}$	
$\text{Si}_2\text{O}_3(\text{OH})_4^{2-}$		$-(0.15 \pm 0.06)^{(b)}$	
$\text{Ni}(\text{ox})_2^{2-}$		$-(0.26 \pm 0.03)$	
$\text{Ni}(\text{CN})_4^{2-}$		$(0.185 \pm 0.081)^{(u)}$	
$\text{CrO}_4^{2-}$		$-(0.06 \pm 0.04)^\dagger$	$-(0.08 \pm 0.04)^\dagger$
$\text{NpO}_2(\text{HPO}_4)_2^{2-}$		$-(0.1 \pm 0.1)$	
$\text{NpO}_2(\text{CO}_3)_2^{2-}$		$-(0.02 \pm 0.14)^{(k)}$	
$\text{NpO}_2\text{cit}^{2-}$		$-(0.06 \pm 0.03)$	
$\text{NpO}_2(\text{Hedta})^{2-}$		$(0.07 \pm 0.16)$	
$\text{UO}_2\text{F}_4^{2-}$		$-(0.30 \pm 0.06)^{(w)}$	
$\text{UO}_2(\text{SO}_4)_2^{2-}$		$-(0.12 \pm 0.06)^{(b)}$	
$\text{UO}_2(\text{N}_3)_4^{2-}$		$-(0.1 \pm 0.1)^{(b)}$	
$\text{UO}_2(\text{ox})_2^{2-}$		$-(0.18 \pm 0.07)$	
$\text{UO}_2\text{edta}^{2-}$		$-(0.22 \pm 0.18)$	
$\text{UO}_2(\text{CO}_3)_2^{2-}$		$-(0.02 \pm 0.09)^{(d)}$	
$(\text{UO}_2)_2(\text{OH})_2(\text{SO}_4)_2^{2-}$		$-(0.14 \pm 0.22)$	
$\text{Mg}(\text{ox})_2^{2-}$		$-(0.15 \pm 0.03)$	$-(0.15 \pm 0.10)^{(y)}$
$\text{Mg}(\text{edta})^{2-}$		$-(0.01 \pm 0.15)$	

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Table B-5 (continued)

$j \quad k \rightarrow$ $\downarrow$	$\text{Li}^+$	$\text{Na}^+$	$\text{K}^+$
$\text{Ca(ox)}_2^{2-}$		$-(0.15 \pm 0.10)^{(z)}$	$-(0.15 \pm 0.10)^{(A)}$
$\text{cit}^{3-}$	$-(0.44 \pm 0.15)^\dagger$	$-(0.076 \pm 0.030)^\dagger$	$(0.02 \pm 0.02)$
$\text{Hedta}^{3-}$		$-(0.10 \pm 0.14)$	$(0.31 \pm 0.18)$
$\text{PO}_4^{3-}$		$-(0.25 \pm 0.03)^\dagger$	$-(0.09 \pm 0.02)$
$\text{Si}_3\text{O}_6(\text{OH})_3^{3-}$		$-(0.25 \pm 0.03)^{(b)}$	
$\text{Si}_3\text{O}_5(\text{OH})_5^{3-}$		$-(0.25 \pm 0.03)^{(b)}$	
$\text{Si}_4\text{O}_7(\text{OH})_5^{3-}$		$-(0.25 \pm 0.03)^{(b)}$	
$\text{Ni(CN)}_5^{3-}$		$(0.25 \pm 0.14)^{(v)}$	
$\text{Am(CO}_3)_3^{3-}$		$-(0.23 \pm 0.07)^{(r)}$	
$\text{Am(ox)}_3^{3-}$		$-(0.23 \pm 0.10)^{(C)}$	
$\text{Np(CO}_3)_3^{3-}$			$-(0.15 \pm 0.07)^{(n)}$
$\text{NpO}_2(\text{CO}_3)_2^{3-}$		$-(0.33 \pm 0.17)^{(f)}$	
$\text{NpO}_2(\text{ox})_2^{3-}$		$-(0.3 \pm 0.2)$	
$\text{NpO}_2\text{edta}^{3-}$		$(0.20 \pm 0.16)$	
$\text{edta}^{4-}$		$(0.32 \pm 0.14)$	$(1.07 \pm 0.19)$
$\text{P}_2\text{O}_7^{4-}$		$-(0.26 \pm 0.05)$	$-(0.15 \pm 0.05)$
$\text{Fe(CN)}_6^{4-}$			$-(0.17 \pm 0.03)$
$\text{NpO}_2(\text{CO}_3)_3^{4-}$		$-(0.40 \pm 0.19)^{(e)}$	$-(0.62 \pm 0.42)^{(g)(h)}$
$\text{NpO}_2(\text{CO}_3)_2\text{OH}^{4-}$		$-(0.40 \pm 0.19)^{(m)}$	
$\text{U(CO}_3)_4^{4-}$		$-(0.09 \pm 0.10)^{(b)(d)}$	
$\text{UO}_2(\text{CO}_3)_3^{4-}$		$-(0.01 \pm 0.11)^{(d)}$	
$\text{UO}_2(\text{ox})_3^{4-}$		$-(0.01 \pm 0.11)^{(B)}$	
$(\text{UO}_2)_3(\text{OH})_4(\text{SO}_4)_3^{4-}$		$(0.6 \pm 0.6)$	
$\text{NpO}_2(\text{CO}_3)_3^{5-}$		$-(0.53 \pm 0.19)^{(f)}$	$-(0.22 \pm 0.03)^{(s)}$
$\text{UO}_2(\text{CO}_3)_3^{5-}$		$-(0.62 \pm 0.15)^{(d)}$	
$\text{Np(CO}_3)_5^{6-}$			$-(0.73 \pm 0.68)^{(j)}$
$(\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$		$-(0.46 \pm 0.73)^{(e)}$	
$\text{U(CO}_3)_5^{6-}$		$-(0.30 \pm 0.15)^{(d)}$	$-(0.70 \pm 0.31)^{(i)}$
$(\text{UO}_2)_3(\text{CO}_3)_6^{6-}$		$(0.37 \pm 0.11)^{(d)}$	
$(\text{UO}_2)_2\text{NpO}_2(\text{CO}_3)_6^{6-}$		$(0.09 \pm 0.71)^{(l)}$	
$(\text{UO}_2)_5(\text{OH})_8(\text{SO}_4)_4^{6-}$		$(1.10 \pm 0.5)$	
$(\text{UO}_2)_4(\text{OH})_7(\text{SO}_4)_4^{7-}$		$(2.80 \pm 0.7)$	

(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  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  are based on [80CIA].
- (e) Calculated in [2001LEM/FUG] (Section 12.1.2.1.2).
- (f) Calculated in [2001LEM/FUG] (Section 12.1.2.1.3).
- (g) Calculated in [2001LEM/FUG] (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 [2001LEM/FUG] (Section 12.1.2.2.1).
- (i) Calculated in [2001LEM/FUG] from Pitzer coefficients [98RAI/FEL].
- (j) Calculated in [2001LEM/FUG] (Section 12.1.2.1.4).
- (k) Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.2).
- (l) Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.2.1).
- (m) Estimated in [2001LEM/FUG] by analogy with  $\text{NpO}_2(\text{CO}_3)_3^{4-}$ .
- (n) Estimated by analogy in [2001LEM/FUG] (Section 12.1.2.1.5).
- (o) Estimated in [2001LEM/FUG] by analogy with  $\varepsilon(\text{NpO}_2\text{CO}_3^-, \text{Na}^+)$ .
- (p)  $\varepsilon(\text{I}^-, \text{NH}_4^+) \approx \varepsilon(\text{SCN}^-, \text{Na}^+) = (0.05 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}$ .
- (q) Estimated in [2001LEM/FUG] (Section 8.1.3).
- (r) Evaluated in [2003GUI/FAN], Section 12.6.1.1.1 from  $\Delta\epsilon_n$  (in NaCl solution) for the reactions  $\text{An}^{3+} + n\text{CO}_3^{2-} \rightleftharpoons \text{An}(\text{CO}_3)_n^{(3-n)-}$  (based on  $\varepsilon(\text{Am}^{3+}, \text{Cl}^-) = (0.23 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$  and  $\varepsilon(\text{Na}^+, \text{CO}_3^{2-}) = - (0.08 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1}$ ).
- (s) Evaluated in [2003GUI/FAN] in Appendix A, discussion of [98ALM/NOV] from  $\Delta\epsilon$  for the reactions  $\text{KNpO}_2\text{CO}_3(\text{s}) + 2\text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{2-} + \text{K}^+$  (in  $\text{K}_2\text{CO}_3$ –KCl solution) and  $\text{K}_3\text{NpO}_2(\text{CO}_3)_2(\text{s}) + \text{CO}_3^{2-} \rightleftharpoons \text{NpO}_2(\text{CO}_3)_3^{5-} + 3\text{K}^+$  (in  $\text{K}_2\text{CO}_3$  solution) (based on  $\varepsilon(\text{K}^+, \text{CO}_3^{2-}) = (0.02 \pm 0.01) \text{ kg} \cdot \text{mol}^{-1}$ ).
- (t) Evaluated in the NEA-TDB nickel review [2005GAM/BUG] (see Section V.7.1.3.1).
- (u) Evaluated in the NEA-TDB nickel review [2005GAM/BUG] (see Section V.7.1.2.1.1).
- (v) Evaluated in the NEA-TDB nickel review [2005GAM/BUG] (see Section V.7.1.2.1.1).
- (w) Evaluated in [2003GUI/FAN], Section 9.4.2.2.1.1.
- (x) As reported in [92BAN/BLI].
- (y) Estimated in Section VI.5.1 by assuming  $\varepsilon(\text{Mg}(\text{ox})_2^{2-}, \text{K}^+) \approx \varepsilon(\text{Mg}(\text{ox})_2^{2-}, \text{Na}^+)$ .
- (z) Estimated in Section VI.5.2 by assuming  $\varepsilon(\text{Ca}(\text{ox})_2^{2-}, \text{Na}^+) \approx \varepsilon(\text{Mg}(\text{ox})_2^{2-}, \text{Na}^+)$ .
- (A) Estimated in Section VI.5.2 by assuming  $\varepsilon(\text{Ca}(\text{ox})_2^{2-}, \text{K}^+) \approx \varepsilon(\text{Mg}(\text{ox})_2^{2-}, \text{Na}^+)$ .
- (B) Estimated in Section VI.10.2.4.1 by assuming  $\varepsilon(\text{UO}_2(\text{ox})_3^{4-}, \text{Na}^+) \approx \varepsilon(\text{UO}_2(\text{CO}_3)_3^{4-}, \text{Na}^+)$ .
- (C) Estimated in Section VI.13.2.1 by assuming  $\varepsilon(\text{Am}(\text{ox})_3^{3-}, \text{Na}^+) \approx \varepsilon(\text{Am}(\text{CO}_3)_3^{3-}, \text{Na}^+)$ .
- (D) Estimated in Section VIII.12.2.1 by assuming  $\varepsilon(\text{Pu}(\text{edta})^-, \text{K}^+) \approx \varepsilon(\text{Am}(\text{edta})^-, \text{Na}^+)$ .
- (E) Estimated in Section VIII.13.2.1 by assuming  $\varepsilon(\text{Am}(\text{edta})^-, \text{K}^+) \approx \varepsilon(\text{Am}(\text{edta})^-, \text{Na}^+)$ .

Table B-6: Ion interaction coefficients,  $\varepsilon(1,j,k)$  and  $\varepsilon(2,j,k)$   $\text{kg} \cdot \text{mol}^{-1}$ , for cations  $j$  with  $k = \text{Cl}^-$ ,  $\text{ClO}_4^-$  and  $\text{NO}_3^-$  (first part), and for anions  $j$  with  $k = \text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  (second part), according to the relationship  $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$ . The data are taken from Ciavatta [80CIA], [88CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level.

$j \ k \rightarrow$ $\downarrow$	$\text{Cl}^-$		$\text{ClO}_4^-$		$\text{NO}_3^-$	
	$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_1$	$\varepsilon_2$
$\text{NH}_4^+$			$-(0.088 \pm 0.002)$	$(0.095 \pm 0.012)$	$-(0.075 \pm 0.001)$	$(0.057 \pm 0.004)$
$\text{Ti}^+$			$-(0.18 \pm 0.02)$	$(0.09 \pm 0.02)$		
$\text{Ag}^+$					$-(0.1432 \pm 0.0002)$	$(0.0971 \pm 0.0009)$
$\text{Pb}^{2+}$					$-(0.329 \pm 0.007)$	$(0.288 \pm 0.018)$
$\text{Hg}^{2+}$					$-(0.145 \pm 0.001)$	$(0.194 \pm 0.002)$
$\text{Hg}_2^{2+}$					$-(0.2300 \pm 0.0004)$	$(0.194 \pm 0.002)$
$j \ k \rightarrow$ $\downarrow$	$\text{Li}^+$		$\text{Na}^+$		$\text{K}^+$	
	$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_1$	$\varepsilon_2$	$\varepsilon_1$	$\varepsilon_2$
$\text{OH}^-$	$-(0.039 \pm 0.002)$	$(0.072 \pm 0.006)$				
$\text{NO}_2^-$	$(0.02 \pm 0.01)$	$(0.11 \pm 0.01)$				
$\text{NO}_3^-$			$-(0.049 \pm 0.001)$	$(0.044 \pm 0.002)$	$-(0.131 \pm 0.002)$	$(0.082 \pm 0.006)$
$\text{H}_2\text{PO}_4^-$			$-(0.109 \pm 0.001)$	$(0.095 \pm 0.003)$	$-(0.1473 \pm 0.0008)$	$(0.121 \pm 0.004)$
$\text{B}(\text{OH})_4^-$			$-(0.092 \pm 0.002)$	$(0.103 \pm 0.005)$		
$\text{SO}_3^{2-}$			$-(0.125 \pm 0.008)$	$(0.106 \pm 0.009)$		
$\text{SO}_4^{2-}$	$-(0.068 \pm 0.003)$	$(0.093 \pm 0.007)$	$-(0.184 \pm 0.002)$	$(0.139 \pm 0.006)$		
$\text{S}_2\text{O}_3^{2-}$			$-(0.125 \pm 0.008)$	$(0.106 \pm 0.009)$		
$\text{HPO}_4^{2-}$			$-(0.19 \pm 0.01)$	$(0.11 \pm 0.03)$	$-(0.152 \pm 0.007)$	$(0.123 \pm 0.016)$
$\text{CrO}_4^{2-}$			$-(0.090 \pm 0.005)$	$(0.07 \pm 0.01)$	$-(0.123 \pm 0.003)$	$(0.106 \pm 0.007)$
$\text{cit}^{3-}$	$-(0.55 \pm 0.11)^{(a)}$	$(0.3 \pm 0.2)^{(a)}$	$-(0.15 \pm 0.03)^{(a)}$	$(0.13 \pm 0.03)^{(a)}$		
$\text{PO}_4^{3-}$			$-(0.29 \pm 0.02)$	$(0.10 \pm 0.01)$		

(a): See Section VII.3.6 of this review.

Table B-7: SIT interaction coefficient  $\varepsilon(j,k)$   $\text{kg} \cdot \text{mol}^{-1}$  for neutral species,  $j$ , with  $k$ , electroneutral combination of ions.

$j \quad k \rightarrow$ $\downarrow$	$\text{Na}^+ + \text{ClO}_4^-$	$\text{Na}^+ + \text{Cl}^-$	$\text{K}^+ + \text{NO}_3^-$
$\text{H}_2\text{ox}(\text{aq})$	$(0.00 \pm 0.01)^{(b)}$	$(0.00 \pm 0.01)^{(b)}$	$(0.00 \pm 0.01)^{(b)}$
$\text{H}_3\text{cit}(\text{aq})$	$(0.00 \pm 0.01)^{(b)}$	$(0.00 \pm 0.01)^{(b)}$	$(0.00 \pm 0.01)^{(b)}$
$\text{H}_4\text{edta}(\text{aq})$	$-(0.29 \pm 0.14)$	$-(0.29 \pm 0.14)$	$-(0.29 \pm 0.14)$
$\text{Ni}(\text{ox})(\text{aq})$	$-(0.07 \pm 0.03)$	$-(0.07 \pm 0.03)$	
$\text{Ni}(\text{Hcit})(\text{aq})$	$-(0.07 \pm 0.05)$		
$\text{Ni}(\text{SCN})_2(\text{aq})$	$(0.38 \pm 0.06)^{(a)}$		
$\text{Am}(\text{cit})(\text{aq})$		$(0.00 \pm 0.05)$	
$\text{Np}(\text{edta})(\text{aq})$	$-(0.19 \pm 0.19)^{(g)}$		
$\text{UO}_2\text{ox}(\text{aq})$	$-(0.05 \pm 0.06)$	$-(0.05 \pm 0.06)$	
$\text{Uedta}(\text{aq})$	$-(0.19 \pm 0.19)$		
$\text{Mg}(\text{ox})(\text{aq})$		$(0.00 \pm 0.03)$	$(0.0 \pm 0.1)^{(c)}$
$\text{Mg}(\text{Hcit})(\text{aq})$	$(0.02 \pm 0.05)$	$(0.02 \pm 0.05)$	
$\text{Ca}(\text{ox})(\text{aq})$	$(0.0 \pm 0.1)^{(d)}$	$(0.0 \pm 0.1)^{(e)}$	$(0.0 \pm 0.1)^{(f)}$

(a): See Section V.7.1.3.1 in [\[2005GAM/BUG\]](#).

(b): Basic assumption of this review, see Sections VI.3.5 and VII.3.6 for discussions.

(c): Estimated in Section VI.5.2 by assuming  $\varepsilon(\text{Mg}(\text{ox})(\text{aq}), \text{KNO}_3) \approx \varepsilon(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl})$ .

(d): Estimated in Section VI.5.2 by assuming  $\varepsilon(\text{Ca}(\text{ox})(\text{aq}), \text{NaClO}_4) \approx \varepsilon(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl})$ .

(e): Estimated in Section VI.5.1 by assuming  $\varepsilon(\text{Ca}(\text{ox})(\text{aq}), \text{NaCl}) \approx \varepsilon(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl})$ .

(f): Estimated in Section VI.5.2 by assuming  $\varepsilon(\text{Ca}(\text{ox})(\text{aq}), \text{KNO}_3) \approx \varepsilon(\text{Mg}(\text{ox})(\text{aq}), \text{NaCl})$ .

(g): Estimated in Section VIII.11.2.2 by assuming  $\varepsilon(\text{Np}(\text{edta})(\text{aq}), \text{NaClO}_4) \approx \varepsilon(\text{Uedta}(\text{aq}), \text{NaClO}_4)$ .



# Appendix C

## Assigned uncertainties<sup>1</sup>

This Appendix describes the origin of the uncertainty estimates that are given in the TDB tables of selected data. The original text in [\[92GRE/FUG\]](#) has been retained in [\[95SIL/BID\]](#), [\[99RAR/RAN\]](#) and [\[2001LEM/FUG\]](#), except for some minor changes. Because of the importance of the uncertainty estimates, the present review offers a more comprehensive description of the procedures used.

### C.1 The general problem

The focus of this section is on the uncertainty estimates of equilibria in solution, where the key problem is analytical, *i.e.*, the determination of the stoichiometric composition and equilibrium constants of complexes that are in rapid equilibrium with one another. We can formulate analyses of the experimental data in the following way: From  $N$  measurements,  $y_i$ , of the variable  $y$  we would like to determine a set of  $n$  equilibrium constants  $k_r$ ,  $r = 1, 2, \dots, n$ , assuming that we know the functional relationship:

$$y = f(k_1, k_2, \dots, k_n; a_1, a_2, \dots) \quad (\text{C.1})$$

where  $a_1, a_2, \dots$  are quantities that can be varied but whose values ( $a_{1i}, a_{2i}, \dots$ ) are assumed to be known accurately in each experiment from the data sets  $(y_i, a_{1i}, a_{2i}, \dots)$ ,  $i = 1, 2, \dots, N$ . The functional relationship (C.1) is obtained from the chemical model proposed and in general several different models have to be tested before the "best" one is selected. Details of the procedures are given in Rossotti and Rossotti [\[61ROS/ROS\]](#).

When selecting the functional relationship (C.1) and determining the set of equilibrium constants that best describes the experiments one often uses a least-squares method. Within this method, the "best" description is the one that will minimise the residual sum of squares,  $U$ :

$$U = \sum_i w_i [y_i - f(k_1 \dots k_n; a_{1i}, a_{2i} \dots)]^2 \quad (\text{C.2})$$

where  $w_i$  is the weight of each experimental measurement  $y_i$ .

---

<sup>1</sup> This Appendix essentially contains the text of the TDB-3 Guideline, [99WAN/OST], earlier versions of which have been printed in the previous NEA TDB reviews [92GRE/FUG], [95SIL/BID], [99RAR/RAN] [2001LEM/FUG] and [2003GUI/FAN]. Because of its importance in the selection of data and to guide the users of the values in Chapters VI, VII, VIII and IV the text is reproduced here with minor revisions.

The minimum of the function (C.2) is obtained by solving a set of normal equations:

$$\frac{\partial U}{\partial k_r} = 0, r = 1, \dots, n \quad (\text{C.3})$$

A "true" minimum is only obtained if:

- the functional relationship (C.1) is correct, *i.e.*, if the chemical model is correct.
- all errors are random errors in the variable  $y$ , in particular there are no systematic errors.
- the random errors in  $y$  follow a Gaussian (normal) distribution.
- the weight  $w_i(y_i, a_{1i}, a_{2i}, \dots)$  of an experimental determination is an exact measure of its inherent accuracy.

To ascertain that the first condition is fulfilled requires chemical insight, such as information of the coordination geometry, relative affinity between metal ions and various donor atoms, *etc.* It is particularly important to test if the chemical equilibrium constants of complexes that occur in small amounts are chemically reasonable. Too many experimentalists seem to look upon the least-squares refinement of experimental data more as an exercise in applied mathematics than as a chemical venture. One of the tasks in the review of the literature is to check this point. An erroneous chemical model is one of the more serious type of systematic error.

The experimentalist usually selects the variable that he/she finds most appropriate to fulfill the second condition. If the estimated errors in  $a_{1i}, a_{2i} \dots$  are smaller than the error in  $y_i$ , the second condition is reasonably well fulfilled. The choice of the error-carrying variable is a matter of choice based on experience, but one must be aware that it has implications, especially in the estimated uncertainty.

The presence of systematic errors is, potentially, the most important source of uncertainty. There is no possibility to handle systematic errors using statistics; statistical methods may indicate their presence, no more. Systematic errors in the chemical model have been mentioned. In addition there may be systematic errors in the methods used. By comparing experimental data obtained with different experimental methods one can obtain an indication of the presence and magnitude of such errors. The systematic errors of this type are accounted for both in the review of the literature and when taking the average of data obtained with different experimental methods. This type of systematic error does not seem to affect the selected data very much, as judged by the usually very good agreement between the equilibrium data obtained using spectroscopic, potentiometric and solubility methods.



The electrode calibration, especially the conversion between measured pH and  $-\log_{10}[\text{H}^+]$  is an important source of systematic error. The reviewers have when possible corrected this error, as seen in many instances in Appendix A.

The assumption of a normal distribution of the random errors is a choice made in the absence of better alternatives.

Finally, a comment on the weights used in least-squares refinements; this is important because it influences the uncertainty estimate of the equilibrium constants. The weights of individual experimental points can be obtained by repeating the experiment several times and then calculating the average and standard deviation of these data. This procedure is rarely used, instead most experimentalists seem to use unit weight when making a least-squares analysis of their data. However, also in this case there is a weighting of the data by the number of experimental determinations in the parameter range where the different complexes are formed. In order to have comparable uncertainty estimates for the different complexes, one should try to have the same number of experimental data points in the concentration ranges where each of these complexes is predominant; a procedure very rarely used.

As indicated above, the assignment of uncertainties to equilibrium constants is not a straightforward procedure and it is complicated further when there is lack of primary experimental data. The uncertainty estimates given for the individual equilibrium constants reported by the authors and for some cases re-estimated by this review are given in the tables of this and previous reviews. The procedure used to obtain these estimates is given in the original publications and in the Appendix A discussions. However, this uncertainty is still a subjective estimate and to a large extent based on "expert judgment".

## C.2 Uncertainty estimates in the selected thermodynamic data.

The uncertainty estimate in the selected thermodynamic data is based on the uncertainty of the individual equilibrium constants or other thermodynamic data, calculated as described in the following sections. A weighted average of the individual  $\log_{10}K$  values is calculated using the estimated uncertainty of the individual experimental values to assign its weight. The uncertainty in this average is then calculated using the formulae given in the following text. This uncertainty depends on the number of experimental data points – for  $N$  data point with the same estimated uncertainty,  $\sigma$ , the uncertainty in the average is  $\sigma/\sqrt{N}$ . The average and the associated uncertainty reported in the tables of selected data are reported with many more digits than justified only in order to allow the users to back-track the calculations. The reported uncertainty is much smaller than the estimated experimental uncertainty and the users of the tables should look at the discussion of the selected constants in order to get a better estimate of the uncertainty in an experimental determination using a specific method.

One of the objectives of the NEA Thermochemical Data Base (TDB) project is to provide an idea of the uncertainties associated with the data selected in this review. As a rule, the uncertainties define the range within which the corresponding data can be reproduced with a probability of 95% at any place and by any appropriate method. In many cases, the statistical treatment is limited or impossible due to the availability of only one or few data points. A particular problem has to be solved when significant discrepancies occur between different source data. This appendix outlines the statistical procedures, which were used for fundamentally different problems, and explains the philosophy used in this review when statistics were inapplicable. These rules are followed consistently throughout the series of reviews within the TDB Project. Four fundamentally different cases are considered:

1. One source datum available
2. Two or more independent source data available
3. Several data available at different ionic strengths
4. Data at non-standard conditions: Procedures for data correction and recalculation.

### C.3 One source datum

The assignment of an uncertainty to a selected value that is based on only one experimental source is a highly subjective procedure. In some cases, the number of data points, on which the selected value is based, allows the use of the “root mean square” [82TAY] deviation of the data points,  $X_i$ , to describe the standard deviation,  $s_X$ , associated with the average,  $\bar{X}$ :

$$s_X = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (X_i - \bar{X})^2} \quad (\text{C.4})$$

The standard deviation,  $s_X$ , is thus calculated from the dispersion of the equally weighted data points,  $X_i$ , around the average  $\bar{X}$ , and the probability is 95% that an  $X_i$  is within  $\bar{X} \pm 1.96 s_X$ , see Taylor [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.4) (but often not multiplied by 1.96), but these do not represent the quality of the reported values in absolute terms. Therefore, it is thus important not to confuse the standard deviation,  $s_X$ , with the uncertainty,  $\sigma$ . The latter reflects the reliability and reproducibility of an experimental value and also includes all kinds of systematic errors,  $s_j$ , that may be involved. The uncertainty,  $\sigma$ , can be calculated with Eq. (C.5), assuming that the systematic errors are independent.

$$\sigma_X = \sqrt{s_X^2 + \sum_j (s_j^2)} \quad (\text{C.5})$$

The estimation of the systematic errors  $s_j$  (which, of course, have to relate to  $\bar{X}$  and be expressed in the same units) can only be made by a person who is familiar with the experimental method. The uncertainty,  $\sigma$ , has to correspond to the 95% confidence level preferred in this review. It should be noted that for all the corrections and recalculations made (*e.g.*, temperature or ionic strength corrections) the rules of the propagation of errors have to be followed, as outlined in Section C.6.2.

More often, the determination of  $s_X$  is impossible because either only one or two data points are available, or the authors did not report the individual values. The uncertainty  $\sigma$  in the resulting value can still be estimated using Eq. (C.5) assuming that  $s_X^2$  is much smaller than  $\sum_j (s_j^2)$ , which is usually the case anyway.

## C.4 Two or more independent source data

Frequently, two or more experimental data sources are available, reporting experimental determinations of the desired thermodynamic data. In general, the quality of these determinations varies widely, and the data have to be weighted accordingly for the calculation of the mean. Instead of assigning weight factors, the individual source data,  $X_i$ , are provided with an uncertainty,  $\sigma_i$ , that also includes all systematic errors and represents the 95% confidence level, as described in Section C.3. The weighted mean  $\bar{X}$  and its uncertainty,  $\sigma_{\bar{X}}$ , are then calculated according to Eqs. (C.6) and (C.7).

$$\bar{X} \equiv \frac{\sum_{i=1}^N \left( \frac{X_i}{\sigma_i^2} \right)}{\sum_{i=1}^N \left( \frac{1}{\sigma_i^2} \right)} \quad (\text{C.6})$$

$$\sigma_{\bar{X}} = \sqrt{\frac{1}{\sum_{i=1}^N \left( \frac{1}{\sigma_i^2} \right)}} \quad (\text{C.7})$$

Eqs. (C.6) and (C.7) may only be used if all the  $X_i$  belong to the same parent distribution. If there are serious discrepancies among the  $X_i$ , one proceeds as described below under Section C.4.1. It can be seen from Eq. (C.7) that  $\sigma_{\bar{X}}$  is directly dependent on the absolute magnitude of the  $\sigma_i$  values, and not on the dispersion of the data points around the mean. This is reasonable because there are no discrepancies among the  $X_i$ , and because the  $\sigma_i$  values already represent the 95% confidence level. The selected uncertainty,  $\sigma_{\bar{X}}$ , will therefore also represent the 95% confidence level.

In cases where all the uncertainties are equal,  $\sigma_i = \sigma$ , Eqs. (C.6) and (C.7) reduce to Eqs. (C.8) and (C.9).

$$\bar{X} = \frac{1}{N} \sum_{i=1}^N X_i \quad (\text{C.8})$$

$$\sigma_{\bar{X}} = \frac{\sigma}{\sqrt{N}} \quad (\text{C.9})$$

**Example C.1:**

Five data sources report values for the thermodynamic quantity,  $X$ . The reviewer has assigned uncertainties that represent the 95% confidence level as described in Section C.3.

$i$	$X_i$	$\sigma_i$
1	25.3	0.5
2	26.1	0.4
3	26.0	0.5
4	24.85	0.25
5	25.0	0.6

According to Eqs.(C.6) and (C.7), the following result is obtained:

$$\bar{X} = (25.3 \pm 0.2).$$

The calculated uncertainty,  $\sigma_{\bar{X}} = 0.2$ , appears relatively small, but is statistically correct, as the values are assumed to follow a Gaussian distribution. As a consequence of Eq. (C.7),  $\sigma_{\bar{X}}$  will always come out smaller than the smallest  $\sigma_i$ . Assuming  $\sigma_4 = 0.10$  instead of 0.25 would yield  $\bar{X} = (25.0 \pm 0.1)$  and  $\sigma_4 = 0.60$  would result in  $\bar{X} = (25.6 \pm 0.2)$ . In fact, the values  $(X_i \pm \sigma_i)$  in this example are at the limit of consistency, *i.e.*, the range  $(X_4 \pm \sigma_4)$  does not overlap with the ranges  $(X_2 \pm \sigma_2)$  and  $(X_3 \pm \sigma_3)$ . There might be a better way to solve this problem. Three possible choices seem more reasonable:

- i. The uncertainties,  $\sigma_i$ , are reassigned because they appear too optimistic after further consideration. Some assessments may have to be reconsidered and the uncertainties reassigned. For example, multiplying all the  $\sigma_i$  by 2 would yield  $\bar{X} = (25.3 \pm 0.3)$ .
- ii. If reconsideration of the previous assessments gives no evidence for reassigning the  $X_i$  and  $\sigma_i$  (95% confidence level) values listed above, the statistical conclusion will be that all the  $X_i$  do not belong to the same parent distribution and cannot therefore be treated in the same group (*cf.* item iii below for a non-statistical explanation). The values for  $i = 1, 4$  and 5 might be considered as belonging to Group A and the values for  $i = 2$  and 3 to Group B. The weighted average of the values in Group A is  $X_A$  ( $i = 1, 4, 5$ ) =  $(24.95 \pm 0.21)$  and of those in Group B,  $X_B$  ( $i = 2, 3$ ) =  $(26.06 \pm 0.31)$ , the second digit after the decimal point being carried over to avoid loss of information. The selected value is now determined as described below under “Discrepancies” (Section C.4.1, Case I).  $X_A$  and  $X_B$  are averaged (straight average, there is no reason for giving  $X_A$  a larger weight than  $X_B$ ), and  $\sigma_{\bar{X}}$  is chosen in such a way that it covers the complete ranges of expectancy of  $X_A$  and  $X_B$ . The selected value is then  $\bar{X} = (25.5 \pm 0.9)$ .

- iii. Another explanation could be that unidentified systematic errors are associated with some values. If this seems likely to be the case, there is no reason for splitting the values up into two groups. The correct way of proceeding would be to calculate the unweighted average of all the five points and assign an uncertainty that covers the whole range of expectancy of the five values. The resulting value is then  $\bar{X} = (25.45 \pm 1.05)$ , which is rounded according to the rules in Section C.6.3 to  $\bar{X} = (25.4 \pm 1.1)$ .

### C.4.1 Discrepancies

Two data are called discrepant if they differ significantly, *i.e.*, their uncertainty ranges do not overlap. In this context, two cases of discrepancies are considered. Case I: Two significantly different source data are available. Case II: Several, mostly consistent source data are available, one of them being significantly different, *i.e.*, an “outlier”.

**Case I. Two discrepant data:** This is a particularly difficult case because the number of data points is obviously insufficient to allow the preference of one of the two values. If there is absolutely no way of discarding one of the two values and selecting the other, the only solution is to average the two source data in order to obtain the selected value, because the underlying reason for the discrepancy must be unrecognised systematic errors. There is no point in calculating a weighted average, even if the two source data have been given different uncertainties, because there is obviously too little information to give even only limited preference to one of the values. The uncertainty,  $\sigma_{\bar{X}}$ , assigned to the selected mean,  $\bar{X}$ , has to cover the range of expectation of both source data,  $X_1, X_2$ , as shown in Eq.(C.10),

$$\sigma_{\bar{X}} = |X_i - \bar{X}| + \sigma_{\max} \quad (\text{C.10})$$

where  $i = 1, 2$ , and  $\sigma_{\max}$  is the larger of the two uncertainties  $\sigma_i$ , see Example C.1.ii and Example C.2.

#### Example C.2:

The following credible source data are given:

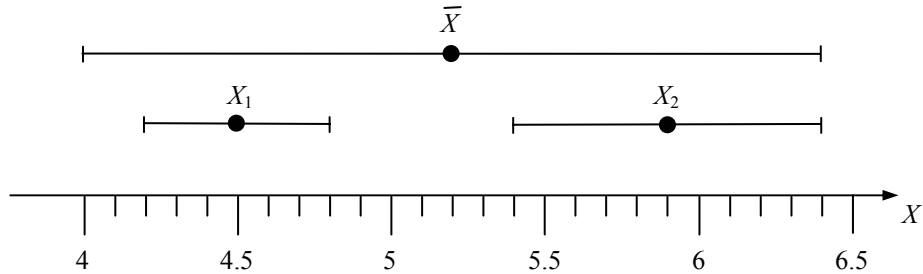
$$X_1 = (4.5 \pm 0.3)$$

$$X_2 = (5.9 \pm 0.5).$$

The uncertainties have been assigned by the reviewer. Both experimental methods are satisfactory and there is no justification to discard one of the data. The selected value is then:

$$\bar{X} = (5.2 \pm 1.2).$$

Figure C-1: Illustration for Example C.2



**Case II. Outliers:** This problem can often be solved by either discarding the outlying data point, or by providing it with a large uncertainty to lower its weight. If, however, the outlying value is considered to be of high quality and there is no reason to discard all the other data, this case is treated in a way similar to Case I. Example C.3 illustrates the procedure.

#### Example C.3:

The following data points are available. The reviewer has assigned the uncertainties and sees no justification for any change.

$i$	$X_i$	$\sigma_i$
1	4.45	0.35
2	5.9	0.5
3	5.7	0.4
4	6.0	0.6
5	5.2	0.4

There are two data sets that, statistically, belong to different parent distributions, A and B. According to Eqs. (C.6) and (C.7), the following average values are found for the two groups:  $X_A(i=1) = (4.45 \pm 0.35)$  and  $X_B(i=2, 3, 4, 5) = (5.62 \pm 0.23)$ . The selected value will be the straight average of  $X_A$  and  $X_B$ , analogous to Example C.1:

$$\bar{X} = (5.0 \pm 0.9).$$

## C.5 Several data at different ionic strengths

The extrapolation procedure for aqueous equilibria used in this review is the specific ion interaction model outlined in Appendix B. The objective of this review is to provide selected data sets at standard conditions, *i.e.*, among others, at infinite dilution for aqueous species. Equilibrium constants determined at different ionic strengths can, according to the specific ion interaction equations, be extrapolated to  $I = 0$  with a linear regression model, yielding as the intercept the desired equilibrium constant at  $I = 0$ , and as the slope the stoichiometric sum of the ion interaction coefficients,  $\Delta\epsilon$ . The ion interaction coefficient of the target species can usually be extracted from  $\Delta\epsilon$  and would be listed in the corresponding table of Appendix B.

The available source data may sometimes be sparse or may not cover a sufficient range of ionic strengths to allow a proper linear regression. In this case, the correction to  $I = 0$  should be carried out according to the procedure described in Section C.6.1.

If sufficient data are available at different ionic strengths and in the same inert salt medium, a weighted linear regression will be the appropriate way to obtain both the constant at  $I = 0$ ,  $\bar{X}^o$ , and  $\Delta\epsilon$ . The first step is the conversion of the ionic strength from the frequently used molar ( $\text{mol}\cdot\text{dm}^{-3}$ , M) to the molal ( $\text{mol}\cdot\text{kg}^{-1}$ ,  $m$ ) scale, as described in Section II.2. The second step is the assignment of an uncertainty,  $\sigma_i$ , to each data point  $X_i$  at the molality,  $m_{k,i}$ , according to the rules described in Section C.3. A large number of commercial and public domain computer programs and routines exist for weighted linear regressions. The subroutine published by Bevington [69BEV] (*pp.* 104 – 105) has been used for the calculations in the examples of this appendix. Eqs. (C.11) through (C.15) present the equations that are used for the calculation of the intercept  $\bar{X}^o$  and the slope  $-\Delta\epsilon$ :

$$\bar{X}^o = \frac{1}{\Delta} \left( \sum_{i=1}^N \frac{m_{k,i}^2}{\sigma_i^2} \sum_{i=1}^N \frac{X_i}{\sigma_i^2} - \sum_{i=1}^N \frac{m_{k,i}}{\sigma_i^2} \sum_{i=1}^N \frac{m_{k,i} X_i}{\sigma_i^2} \right) \quad (\text{C.11})$$

$$-\Delta\epsilon = \frac{1}{\Delta} \left( \sum_{i=1}^N \frac{1}{\sigma_i^2} \sum_{i=1}^N \frac{m_{k,i} X_i}{\sigma_i^2} - \sum_{i=1}^N \frac{m_{k,i}}{\sigma_i^2} \sum_{i=1}^N \frac{X_i}{\sigma_i^2} \right) \quad (\text{C.12})$$

$$\sigma_{\bar{X}^o} = \sqrt{\frac{1}{\Delta} \sum_{i=1}^N \frac{m_{k,i}^2}{\sigma_i^2}} \quad (\text{C.13})$$

$$\sigma_{\Delta\epsilon} = \sqrt{\frac{1}{\Delta} \sum_{i=1}^N \frac{1}{\sigma_i^2}} \quad (\text{C.14})$$

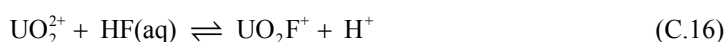
where

$$\Delta = \sum_{i=1}^N \frac{1}{\sigma_i^2} \sum_{i=1}^N \frac{m_{k,i}^2}{\sigma_i^2} - \left( \sum_{i=1}^N \frac{m_{k,i}}{\sigma_i^2} \right)^2. \quad (\text{C.15})$$

In this way, the uncertainties,  $\sigma_i$ , are not only used for the weighting of the data in Eqs. (C.11) and (C.12), but also for the calculation of the uncertainties,  $\sigma_{\bar{X}^o}$  and  $\sigma_{\Delta\epsilon}$ , in Eqs. (C.13) and (C.14). If the  $\sigma_i$  represents the 95% confidence level,  $\sigma_{\bar{X}^o}$  and  $\sigma_{\Delta\epsilon}$  will also do so. In other words, the uncertainties of the intercept and the slope do not depend on the dispersion of the data points around the straight line, but rather directly on their absolute uncertainties,  $\sigma_i$ .

#### Example C.4:

Ten independent determinations of the equilibrium constant,  $\log_{10}^* \beta$ , for the reaction:



are available in  $\text{HClO}_4/\text{NaClO}_4$  media at different ionic strengths. Uncertainties that represent the 95% confidence level have been assigned by the reviewer. A weighted linear regression,  $(\log_{10}^* \beta + 2D)$  vs.  $m_k$ , according to the formula,  $\log_{10}^* \beta$  (C.16) +  $2D = \log_{10}^* \beta^o$  (C.16) -  $\Delta\epsilon m_k$ , will yield the correct values for the intercept,  $\log_{10}^* \beta^o$  (C.16), and the slope,  $\Delta\epsilon$ . In this case,  $m_k$  corresponds to the molality of  $\text{ClO}_4^-$ .  $D$  is the Debye-Hückel term, *cf.* Appendix B.

$i$	$m_{\text{ClO}_4^-,i}$	$\log_{10}^* \beta + 2D$	$\sigma_i$
1	0.05	1.88	0.10
2	0.25	1.86	0.10
3	0.51	1.73	0.10
4	1.05	1.84	0.10
5	2.21	1.88	0.10
6	0.52	1.89	0.11
7	1.09	1.93	0.11
8	2.32	1.78	0.11
9	2.21	2.03	0.10
10	4.95	2.00	0.32

The results of the linear regression are:

$$\text{intercept} = (1.837 \pm 0.054) = \log_{10}^* \beta^o \text{ (C.16)}$$

$$\text{slope} = (0.029 \pm 0.036) = -\Delta\epsilon$$

Calculation of the ion interaction coefficient  $\epsilon(\text{UO}_2\text{F}^+, \text{ClO}_4^-) = \Delta\epsilon + \epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) - \epsilon(\text{H}^+, \text{ClO}_4^-)$ : from  $\epsilon(\text{UO}_2^{2+}, \text{ClO}_4^-) = (0.46 \pm 0.03) \text{ kg}\cdot\text{mol}^{-1}$ ,  $\epsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg}\cdot\text{mol}^{-1}$  (see Appendix B) and the slope of the linear re-



gression,  $\Delta\varepsilon = -(0.03 \pm 0.04) \text{ kg}\cdot\text{mol}^{-1}$ , it follows that  $\varepsilon(\text{UO}_2\text{F}^+, \text{ClO}_4^-) = (0.29 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}$ . Note that the uncertainty ( $\pm 0.05$ )  $\text{kg}\cdot\text{mol}^{-1}$  is obtained based on the rules of error propagation as described in Section C.6.2:

$$\sigma = \sqrt{(0.04)^2 + (0.03)^2 + (0.02)^2}$$

The resulting selected values are thus:

$$\log_{10} {}^*\beta^\circ (\text{C.16}) = (1.84 \pm 0.05)$$

$$\varepsilon(\text{UO}_2\text{F}^+, \text{ClO}_4^-) = (0.29 \pm 0.05) \text{ kg}\cdot\text{mol}^{-1}.$$

### C.5.1 Discrepancies or insufficient number of data points

Discrepancies are principally treated as described in Section C.4. Again, two cases can be defined. Case I: Only two data points are available. Case II: An “outlier” cannot be discarded. If only one data point is available, the procedure for correction to zero ionic strength outlined in Section C.6 should be followed.

**Case I. Too few molalities:** If only two source data are available, there will be no straightforward way to decide whether or not these two data points belong to the same parent distribution unless either the slope of the straight line is known or the two data refer to the same ionic strength. Drawing a straight line right through the two data points is an inappropriate procedure because all the errors associated with the two source data would accumulate and may lead to highly erroneous values of  $\log_{10} K^\circ$  and  $\Delta\varepsilon$ . In this case, an ion interaction coefficient for the key species in the reaction in question may be selected by analogy (charge is the most important parameter), and a straight line with the slope  $\Delta\varepsilon$  as calculated may then be drawn through each data point. If there is no reason to discard one of the two data points based on the quality of the underlying experiment, the selected value will be the unweighted average of the two standard state data point obtained by this procedure, and its uncertainty must cover the entire range of expectancy of the two values, analogous to Case I in Section C.4. It should be mentioned that the ranges of expectancy of the corrected values at  $I = 0$  are given by their uncertainties, which are based on the uncertainties of the source data at  $I \neq 0$  and the uncertainty in the slope of the straight line. The latter uncertainty is not an estimate, but is calculated from the uncertainties in the ion interaction coefficients involved, according to the rules of error propagation outlined in Section C.6.2. The ion interaction coefficients estimated by analogy are listed in the table of selected ion interaction coefficients (Appendix B), but they are flagged as estimates.

**Case II. Outliers and inconsistent data sets:** This case includes situations where it is difficult to decide whether or not a large number of points belong to the same parent distribution. There is no general rule on how to solve this problem, and decisions are left to the judgment of the reviewer. For example, if eight data points follow a straight line reasonably well and two lie way out, it may be justified to discard the “out-

liers”. If, however, the eight points are scattered considerably and two points are just a bit further out, one can probably not consider them as “outliers”. It depends on the particular case and on the judgment of the reviewer whether it is reasonable to increase the uncertainties of the data to reach consistency, or whether the slope,  $\Delta\epsilon$ , 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:

$I_c = 0.1 \text{ M (KNO}_3\text{)}$	$\log_{10} \beta \text{ (C.17)} = (1.19 \pm 0.03)$
$I_c = 0.33 \text{ M (KNO}_3\text{)}$	$\log_{10} \beta \text{ (C.17)} = (0.90 \pm 0.10)$
$I_c = 1.0 \text{ M (NaClO}_4\text{)}$	$\log_{10} \beta \text{ (C.17)} = (0.75 \pm 0.03)$
$I_c = 1.0 \text{ M (NaClO}_4\text{)}$	$\log_{10} \beta \text{ (C.17)} = (0.76 \pm 0.03)$
$I_c = 1.0 \text{ M (NaClO}_4\text{)}$	$\log_{10} \beta \text{ (C.17)} = (0.93 \pm 0.03)$
$I_c = 2.5 \text{ M (NaNO}_3\text{)}$	$\log_{10} \beta \text{ (C.17)} = (0.72 \pm 0.03)$

The uncertainties are assumed to represent the 95% confidence level. From the values at  $I_c = 1 \text{ M}$ , it can be seen that there is a lack of consistency in the data, and that a linear regression similar to that shown in Example C.4 would be inappropriate. Instead, the use of  $\Delta\epsilon$  values from reactions of the same charge type is encouraged. Analogies with  $\Delta\epsilon$  are more reliable than analogies with single  $\epsilon$  values due to canceling effects. For the same reason, the dependency of  $\Delta\epsilon$  on the type of electrolyte is often smaller than for single  $\epsilon$  values.

A reaction of the same charge type as Reaction (C.17), and for which  $\Delta\epsilon$  is well known, is:



The value of  $\Delta\epsilon \text{ (C.18)} = -(0.25 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}$  was obtained from a linear regression using 16 experimental values between  $I_c = 0.1 \text{ M}$  and  $I_c = 3 \text{ M Na(Cl,ClO}_4\text{)}$  [\[92GRE/FUG\]](#). It is thus assumed that:

$$\Delta\epsilon \text{ (C.17)} = \Delta\epsilon \text{ (C.18)} = -(0.25 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}.$$

The correction of  $\log_{10} \beta \text{ (C.17)}$  to  $I_c = 0$  is done using the specific ion interaction equation, *cf.* TDB-2, which uses molal units:

$$\log_{10} \beta + 4D = \log_{10} \beta^\circ - \Delta\epsilon I_m. \quad (\text{C.19})$$

$D$  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 Table II-5. The following list

gives the details of this calculation. The resulting uncertainties in  $\log_{10} \beta$  are obtained based on the rules of error propagation as described in Section C.6.2.

Table C-1: Details of the calculation of equilibrium constant corrected to  $I = 0$ , using (C.19).

$I_m$	electrolyte	$\log_{10} \beta$	$4D$	$\Delta\epsilon I_m$	$\log_{10} \beta^\circ$
0.101	KNO <sub>3</sub>	$(1.19 \pm 0.03)$	0.438	$-0.025$	$(1.68 \pm 0.03)^{(a)}$
0.335	KNO <sub>3</sub>	$(0.90 \pm 0.10)$	0.617	$-0.084$	$(1.65 \pm 0.10)^{(a)}$
1.050	NaClO <sub>4</sub>	$(0.75 \pm 0.03)$	0.822	$-0.263$	$(1.31 \pm 0.04)$
1.050	NaClO <sub>4</sub>	$(0.76 \pm 0.03)$	0.822	$-0.263$	$(1.32 \pm 0.04)$
1.050	NaClO <sub>4</sub>	$(0.93 \pm 0.03)$	0.822	$-0.263$	$(1.49 \pm 0.04)$
2.714	NaNO <sub>3</sub>	$(0.72 \pm 0.03)$	0.968	$-0.679$	$(1.82 \pm 0.13)^{(a)}$

(a) These values were corrected for the formation of the nitrate complex,  $\text{UO}_2\text{NO}_3^+$ , 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.4. That is, the selected value will be the unweighted average of  $\log_{10} \beta^\circ$ , and its uncertainty will cover the entire range of expectancy of the six values. A weighted average would only be justified if the six values of  $\log_{10} \beta^\circ$  were consistent. The result is:

$$\log_{10} \beta^\circ = (1.56 \pm 0.39).$$

## C.6 Procedures for data handling

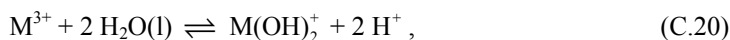
### C.6.1 Correction to zero ionic strength

The correction of experimental data to zero ionic strength is necessary in all cases where a linear regression is impossible or appears inappropriate. The method used throughout the review is the specific ion interaction equations described in detail in Appendix B. Two variables are needed for this correction, and both have to be provided with an uncertainty at the 95% confidence level: the experimental source value,  $\log_{10} K$  or  $\log_{10} \beta$ , and the stoichiometric sum of the ion interaction coefficients,  $\Delta\epsilon$ . The ion interaction coefficients (see Tables B-4, B-5, B-6 and B-7 of Appendix B) required to calculate  $\Delta\epsilon$  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  $\Delta\epsilon$  from known reactions of the same charge type, rather than to estimate single  $\Delta\epsilon$  values. The uncertainty of the corrected value at  $I = 0$  is calculated by taking into account the

propagation of errors, as described below. It should be noted that the ionic strength is frequently given in moles per dm<sup>3</sup> of solution (molar, M) and has to be converted to moles per kg H<sub>2</sub>O (molal, *m*), as the model requires. Conversion factors for the most common inert salts are given in Table II.5.

### Example C.6:

For the equilibrium constant of the reaction:



only one credible determination in 3 M NaClO<sub>4</sub> solution is known to be,  $\log_{10} {}^*\beta$  (C.20) = −6.31, to which an uncertainty of ±0.12 has been assigned. The ion interaction coefficients are as follows:

$$\varepsilon(\text{M}^{3+}, \text{ClO}_4^-) = (0.56 \pm 0.03) \text{ kg} \cdot \text{mol}^{-1},$$

$$\varepsilon(\text{M}(\text{OH})_2^+, \text{ClO}_4^-) = (0.26 \pm 0.11) \text{ kg} \cdot \text{mol}^{-1},$$

$$\varepsilon(\text{H}^+, \text{ClO}_4^-) = (0.14 \pm 0.02) \text{ kg} \cdot \text{mol}^{-1}.$$

The values of  $\Delta\varepsilon$  and  $\sigma_{\Delta\varepsilon}$  can be obtained readily (*cf.* Eq. (C.22)):

$$\Delta\varepsilon = \varepsilon(\text{M}(\text{OH})_2^+, \text{ClO}_4^-) + 2\varepsilon(\text{H}^+, \text{ClO}_4^-) - \varepsilon(\text{M}^{3+}, \text{ClO}_4^-) = -0.22 \text{ kg} \cdot \text{mol}^{-1},$$

$$\sigma_{\Delta\varepsilon} = \sqrt{(0.11)^2 + (2 \times 0.02)^2 + (0.03)^2} = 0.12 \text{ kg} \cdot \text{mol}^{-1}.$$

The two variables are thus:

$$\log_{10} {}^*\beta \text{ (C.20)} = -(6.31 \pm 0.12),$$

$$\Delta\varepsilon = -(0.02 \pm 0.12) \text{ kg} \cdot \text{mol}^{-1}.$$

According to the specific ion interaction model the following equation is used to correct for ionic strength for the reaction considered here:

$$\log_{10} {}^*\beta \text{ (C.20)} + 6D = \log_{10} {}^*\beta^\circ \text{ (C.20)} - \Delta\varepsilon m_{\text{ClO}_4^-}$$

*D* is the Debye-Hückel term:

$$D = \frac{0.509\sqrt{I_m}}{(1 + 1.5\sqrt{I_m})}.$$

The ionic strength,  $I_m$ , and the molality,  $m_{\text{ClO}_4^-}$  ( $I_m \approx m_{\text{ClO}_4^-}$ ), have to be expressed in molal units, 3 M NaClO<sub>4</sub> corresponding to 3.5 *m* NaClO<sub>4</sub> (see Section II.2), giving  $D = 0.25$ . This results in:

$$\log_{10} {}^*\beta^\circ \text{ (C.20)} = -4.88.$$

The uncertainty in  $\log_{10} {}^*\beta^\circ$  is calculated from the uncertainties in  $\log_{10} {}^*\beta$  and  $\Delta\varepsilon$  (*cf.* Eq. (C.22)):

$$\sigma_{\log_{10} \beta^{\circ}} = \sqrt{\sigma_{\log_{10} \beta}^2 + (m_{\text{ClO}_4} \sigma_{\Delta \varepsilon})^2} = \sqrt{(0.12)^2 + (3.5 \times 0.12)^2} = 0.44$$

The selected, rounded value is:

$$\log_{10} \beta^{\circ} (\text{C.20}) = -(4.9 \pm 0.4).$$

## C.6.2 Propagation of errors

Whenever data are converted or recalculated, or other algebraic manipulations are performed that involve uncertainties, the propagation of these uncertainties has to be taken into account in a correct way. A clear outline of the propagation of errors is given by Bevington [69BEV]. A simplified form of the general formula for error propagation is given by Eq.(C.21), supposing that  $X$  is a function of  $Y_1, Y_2, \dots, Y_N$ .

$$\sigma_X^2 = \sum_{i=1}^N \left( \frac{\partial X}{\partial Y_i} \sigma_{Y_i} \right)^2 \quad (\text{C.21})$$

Eq. (C.21) can be used only if the variables,  $Y_1, Y_2, \dots, Y_N$ , are independent or if their uncertainties are small, *i.e.*, the covariances can be disregarded. One of these two assumptions can almost always be made in chemical thermodynamics, and Eq. (C.21) can thus almost universally be used in this review. Eqs. (C.22) through (C.26) present explicit formulas for a number of frequently encountered algebraic expressions, where  $c, c_1, c_2$  are constants.

$$X = c_1 Y_1 \pm c_2 Y_2 : \quad \sigma_X^2 = (c_1 \sigma_{Y_1})^2 + (c_2 \sigma_{Y_2})^2 \quad (\text{C.22})$$

$$X = \pm c Y_1 Y_2 \text{ and } X = \pm \frac{c Y_1}{Y_2} : \quad \left( \frac{\sigma_X}{X} \right)^2 = \left( \frac{\sigma_{Y_1}}{Y_1} \right)^2 + \left( \frac{\sigma_{Y_2}}{Y_2} \right)^2 \quad (\text{C.23})$$

$$X = c_1 Y^{\pm c_2} : \quad \frac{\sigma_X}{X} = c_2 \frac{\sigma_Y}{Y} \quad (\text{C.24})$$

$$X = c_1 e^{\pm c_2 Y} : \quad \frac{\sigma_X}{X} = c_2 \sigma_Y \quad (\text{C.25})$$

$$X = c_1 \ln(\pm c_2 Y) : \quad \sigma_X = c_1 \frac{\sigma_Y}{Y} \quad (\text{C.26})$$

### Example C.7:

A few simple calculations illustrate how these formulas are used. The values have not been rounded.

$$\begin{aligned} \text{Eq. (C.22): } \Delta_r G_m &= 2 \cdot [-(277.4 \pm 4.9)] \text{ kJ} \cdot \text{mol}^{-1} - [-(467.3 \pm 6.2)] \text{ kJ} \cdot \text{mol}^{-1} \\ &= -(87.5 \pm 11.6) \text{ kJ} \cdot \text{mol}^{-1}. \end{aligned}$$

$$\text{Eq. (C.23): } K = \frac{(0.038 \pm 0.002)}{(0.0047 \pm 0.0005)} = (8.09 \pm 0.96)$$

$$\text{Eq. (C.24): } K = 4 \cdot (3.75 \pm 0.12)^3 = (210.9 \pm 20.3)$$

$$\text{Eq. (C.25): } K^\circ = e^{\frac{-\Delta_r G_m^\circ}{RT}}; \quad \Delta_r G_m^\circ = -(2.7 \pm 0.3) \text{ kJ} \cdot \text{mol}^{-1}$$

$$R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T = 298.15 \text{ K}$$

$$K^\circ = (2.97 \pm 0.36).$$

Note that powers of 10 have to be reduced to powers of  $e$ , *i.e.*, the variable has to be multiplied by  $\ln(10)$ , *e.g.*,

$$\log_{10} K = (2.45 \pm 0.10); \quad K = 10^{\log_{10} K} = e^{(\ln(10) \cdot \log_{10} K)} = (282 \pm 65).$$

$$\text{Eq. (C.26): } \Delta_r G_m^\circ = -RT \ln K^\circ; \quad K^\circ = (8.2 \pm 1.2) \times 10^6$$

$$R = 8.3145 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T = 298.15 \text{ K}$$

$$\Delta_r G_m^\circ = -(39.46 \pm 0.36) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln K^\circ = (15.92 \pm 0.15)$$

$$\log_{10} K^\circ = \ln K^\circ / \ln(10) = (6.91 \pm 0.06).$$

Again, it can be seen that the uncertainty in  $\log_{10} K^\circ$  cannot be the same as in  $\ln K^\circ$ . The constant conversion factor of  $\ln(10) = 2.303$  is also to be applied to the uncertainty.

### C.6.3 Rounding

The standard rules to be used for rounding are:

1. When the digit following the last digit to be retained is less than 5, the last digit retained is kept unchanged.
2. When the digit following the last digit to be retained is greater than 5, the last digit retained is increased by 1.
3. When the digit following the last digit to be retained is 5 and
  - a) there are no digits (or only zeroes) beyond the 5, an odd digit in the last place to be retained is increased by 1 while an even digit is kept unchanged.
  - b) other non-zero digits follow, the last digit to be retained is increased by 1, whether odd or even.

This procedure avoids introducing a systematic error from always dropping or not dropping a 5 after the last digit retained.

When adding or subtracting, the result is rounded to the number of decimal places (not significant digits) in the term with the least number of places. In multiplication and division, the results are rounded to the number of significant digits in the term with the least number of significant digits.

In general, all operations are carried out in full, and only the final results are rounded, in order to avoid the loss of information from repeated rounding. For this reason, several additional digits are carried in all calculations until the final selected data set is developed, and only then are data rounded.

#### C.6.4 Significant digits

The uncertainty of a value basically defines the number of significant digits a value should be given.

Example:  $(3.478 \pm 0.008)$

$(3.48 \pm 0.01)$

$(2.8 \pm 0.4)$

$(10 \pm 1)$

$(105 \pm 20)$ .

In the case of auxiliary data or values that are used for later calculations, it is often inconvenient to round to the last significant digit. In the value  $(4.85 \pm 0.26)$ , for example, the “5” is close to being significant and should be carried along a recalculation path in order to avoid loss of information. In particular cases, where the rounding to significant digits could lead to slight internal inconsistencies, digits with no significant meaning in absolute terms are nevertheless retained. The uncertainty of a selected value always contains the same number of digits after the decimal point as the value itself.





# Bibliography

- [1808THO] Thomson, T., On oxalic acid, *Philos. Trans. R. Soc. London*, **98**, (1808), 63-95. Cited on page: 105.
- [1820DUB/SIL] Dubois, F., de Silveira, A. A., Note sur un nouveau procédé pour obtenir la zircone pure, *Ann. Chim. Phys.*, série 2, **14**, (1820), 110-111, in French. Cited on pages: 202, 543.
- [1842EBE] Ebelmen, M., Recherches sur quelques composés de l'urane, *Ann. Chim. Phys.*, série 3, **5**, (1842), 189-223, in French. Cited on pages: 213, 215, 216, 218, 219, 543.
- [1862SEE] Seekamp, W., Ueber die Zersetzung der Oxalsäure durch das Sonnenlicht, *Ann. Chem. (Justus Liebig)*, **122**, (1862), 113-118, in German. Cited on pages: 206, 230.
- [1864ALL] Alluard, De la solubilité des sels, *C. R. Acad. Sci., Chimie*, **59**, (1864), 500-504, in French. Cited on pages: 153, 155, 156.
- [1875BER3] Berthelot, M., Sur la chaleur de combustion des acides formique et oxalique, *Ann. Chim. Phys.*, série 5, **5**, (1875), 289-318, in French. Cited on pages: 107, 109.
- [1880REC] von Rechenberg, C., Ueber die Verbrennungswärme organischer Verbindungen, *J. Prakt. Chem.*, **22**, (1880), 1-45, in German. Cited on pages: 107, 109.
- [1882THO] Thomsen, J., *Thermochemische Untersuchungen*, J. A. Barth, Leipzig, (1882), in German. Cited on pages: 107, 109.
- [1884STO/REC] Stohmann, F., von Rechenberg, C., Wilsing, H., Rodatz, P., Die Wärmewerthe der wichtigsten Nährstoffe und Körperbestandtheile, *Landwirtsch. Jahrb.*, (1884), 549-581, in German. Cited on pages: 107, 109.
- [1885STO] Stohmann, F., Calorimetrische Untersuchungen, *J. Prakt. Chem.*, **31**, (1885), 273-306, in German. Cited on pages: 107, 109.

- [1886LOU] Louguinine, W., Sur la mesure des chaleurs de combustion des éthers de quelques acides organiques comme moyen de déterminer la chaleur de formation de ces acides, *Ann. Chim. Phys.*, série 6, **8**, (1886), 128-144, in French. Cited on pages: 107, 109.
- [1889JAH] Jahn, H., Beiträge zur Electrochemie und Thermochemie einiger organischer Säuren, *Ann. Phys. (Berlin)*, **37**, (1889), 408-443, in German. Cited on pages: 107, 109.
- [1889STO/KLE] Stohmann, F., Kleber, C., Langbein, H., Ueber den Wärmewerth der Säuren der Oxalsäure-Reihe und der Fumar- und Maleinsäure, *J. Prakt. Chem.*, **40**, (1899), 202-229, in German. Cited on pages: 107, 109.
- [1894NAS] Nass, G., Über die quantitative Bestimmung von Mangan, Magnesium, Zink, Kobalt und Nickel mittels der Oxalatmethode nach Prof. A. Classen, *Z. Angew. Chem.*, **7**, (1894), 501-508, in German. Cited on pages: 191, 543, 544.
- [1895JOR/STA] Jorissen, W. J., van de Stadt, E., Ueber die Bindungswärme des Krystallwassers von organischen Verbindungen, *J. Prakt. Chem.*, **51**, (1895), 102-106, in German. Cited on pages: 110, 111.
- [01GER] Gérard, Solubilité de l'oxalate de chaux urinaire dans le chlorure de sodium et dans le phosphate acide de soude, *Ann. Chim. Anal.*, **6**, (1901), 59-60, in French. Cited on pages: 166, 167.
- [01KOH] Kohlschütter, V., Ueber Oxalouranoverbindungen, *Ber. Dtsch. Chem. Ges.*, **34**, (1901), 3619-3635, in German. Cited on page: 207.
- [01KOH/ROS] Kohlschütter, V., Rossi, H., Ueber die Uranooxalsäure, *Ber. Dtsch. Chem. Ges.*, **34**, (1901), 1472-1479, in German. Cited on page: 207.
- [01RIC/MCC] Richards, T. W., McCaffrey, C. F., Bisbee, H., Die Okklusion von Magnesiumoxalat durch Calciumoxalat und die Löslichkeit von Calciumoxalat, *Z. Anorg. Chem.*, **28**, (1901), 71-89, in German. Cited on pages: 161, 166, 167.
- [02ORL] Orlov, N. A., On characterisation of tetravalent uranium compounds, *Zh. Russ. Fiz.-Khim. Obsh.*, **34**, (1902), 375-380, in Russian. Cited on pages: 207, 210, 544.

- [03HER/MUH] Herz, W., Muhs, G., Ueber die Löslichkeit einiger Salze der Erdalkalimetalle mit organischen Säuren in Essigsäure, *Ber. Dtsch. Chem. Ges.*, **36**, (1903), 3715-3718, in German. Cited on pages: 161, 166, 167.
- [03KOH] Kohlrausch, F., Über gesättigte wässrige Lösungen schwerlöslicher Salze. I. Teil: Die elektrischen Leitvermögen, *Z. Phys. Chem.*, **44**, (1903), 197-249, in German. Cited on pages: 159, 160, 161, 162, 166, 167, 555, 556.
- [05FOO/AND] Foote, H. W., Andrew, I. A., The acid oxalates of lithium, sodium, potassium and caesium and their solubility, *Am. Chem. J.*, **34**, (1905), 153-164. Cited on pages: 152, 153, 155.
- [08KOH] Kohlrausch, F., Über gesättigte wässrige Lösungen schwerlöslicher Salze. II. Teil: Die gelösten Mengen mit ihrem Temperaturgang, *Z. Phys. Chem.*, **64**, (1908), 129-169, in German. Cited on pages: 159, 160, 161, 162, 166, 167, 555, 556, 712.
- [08KOP/CAH] Koppel, J., Cahn, M., Gleichgewichte im System:  $K_2O-C_2O_3-H_2O$  (Kaliumoxalat - Oxalsäure - Wasser), *Z. Anorg. Chem.*, **60**, (1908), 53-112, in German. Cited on pages: 153, 154, 155, 156.
- [09DEA/SCO] Deakin, S., Scott, M., Steele, B. D., On the complex oxalates of cobalt and nickel, *Z. Phys. Chem. (Munich)*, **69**, (1909), 123-135. Cited on pages: 190, 562.
- [10JOR] Jorissen, W. P., Etwas über die Hydratationswärme, *Z. Phys. Chem.*, **71**, (1910), 308-324, in German. Cited on pages: 109, 111.
- [11DOD] Dodgson, J. W., The stability of the double oxalates of sodium and nickel, and sodium and cobalt, *Proc. Chem. Soc.*, **27**, (1911), 260-262. Cited on page: 190.
- [12MAS] Masson, J. I. O., The solubility of electrolytes in aqueous solutions. Part II. Solubility of oxalic acid in other acids, *J. Chem. Soc.*, **101**, (1912), 103-108. Cited on page: 112.
- [13HAR/DRU] Hartley, H., Drugman, J., Vlieland, C. A., Bouhdillon, R., The neutral and acid oxalates of potassium, *J. Chem. Soc.*, **103**, (1913), 1747-1751. Cited on pages: 153, 155.

- [16COL] Colani, A., Oxalates d'uranyle et de potassium, *C. R. Hebd. Séances Acad. Sci.*, **163**, (1916), 123-125, in French. Cited on pages: 153, 155, 213, 215, 544, 545, 552.
- [16COL2] Colani, A., Solubilité des oxalates alcalins en présence de quelques sels alcalins, *Bull. Soc. Chim. Fr., Mem.*, (1916), 405-407, in French. Cited on pages: 152, 153, 155.
- [16HEN/TAY] Henderson, W. N., Taylor, H. S., Neutral salt action on acid solubilities, *J. Phys. Chem.*, **20**, (1916), 660-679. Cited on pages: 161, 166, 167.
- [17COL] Colani, A., Etude du système eau, oxalate d'uranyle, oxalate de sodium, *C. R. Hebd. Séances Acad. Sci.*, **165**, (1917), 111-113, in French. Cited on pages: 152, 153, 213, 215, 544.
- [17COL2] Colani, A., Etude du système eau, oxalate d'uranyle, oxalate d'ammonium, *C. R. Hebd. Séances Acad. Sci.*, **165**, (1917), 234-236, in French. Cited on pages: 213, 215, 544, 545.
- [19RIV/OCO] Rivett, A. C. D., O'Connor, E. A., Some ternary systems containing alkali oxalates and water, *J. Chem. Soc.*, **115**, (1919), 1346-1354. Cited on pages: 152, 153, 155.
- [22BRO] Brønsted, J. N., Studies of solubility: IV. The principle of specific interaction of ions, *J. Am. Chem. Soc.*, **44**, (1922), 877-898. Cited on page: 821.
- [22BRO2] Brønsted, J. N., Calculation of the osmotic and activity functions in solutions of uni-univalent salts, *J. Am. Chem. Soc.*, **44**, (1922), 938-948. Cited on page: 821.
- [23HER/NEU] Herz, W., Neukirch, E., Die Beeinflussung der Oxalsäurelöslichkeit durch starke Säuren, *Z. Anorg. Allg. Chem.*, **131**, (1923), 303-309, in German. Cited on page: 112.
- [23LEW/RAN] Lewis, G. N., Randall, M., *Thermodynamics and the free energy of chemical substances*, McGraw-Hill Book Company, Inc., New York, (1923), 653 pp. Cited on page: 579.

- [24CHA/DHA] Chatterjee, K. P., Dhar, N. R., Studies of sparingly soluble salts, readily obtained from hot solutions of reacting substances, *J. Phys. Chem.*, **28**, (1924), 1009-1028. Cited on pages: 159, 160, 162.
- [24HOF/MAR] Hoffmann, H., Mark, H., Das Gitter der Oxalsäure, *Z. Phys. Chem.*, **111**, (1924), 321-356, in German. Cited on pages: 106, 110.
- [24LAR] Larsson, E., Zur elektrolytischen Dissoziation der zweibasischen Säuren. II. Die zweiten Dissoziationskonstanten einiger Säuren, *Z. Anorg. Allg. Chem.*, **140**, (1924), 292-300, in German. Cited on page: 114.
- [25COL] Colani, A., Etude de l'oxalate d'uranyle, *Bull. Soc. Chim. Fr., Mem.*, (1925), 856-861, in French. Cited on pages: 213, 215, 216, 217, 218, 219, 544, 545, 563, 570, 578.
- [25WAL] Walker, O. J., Solubility of bi-bivalent salts in solutions containing a common ion, *J. Chem. Soc.*, **127**, (1925), 61-66. Cited on pages: 159, 160, 162.
- [26VER/HAR] Verkade, P. E., Hartman, H., Coops, J., Calorimetric researches. X. Heats of combustion of successive terms of homologous series: Dicarboxylic acids of the oxalic acid series, *Rec. Trav. Chim.*, **45**, (1926), 373-393. Cited on pages: 107, 109.
- [26WOS] Woskressenskaja, N., Gleichgewicht des Systems "Kaliumoxalat + Wasser", *Z. Anorg. Allg. Chem.*, **155**, (1926), 115-120, in German. Cited on pages: 153, 155.
- [27AUM2] Auméras, M., Contribution à l'étude des équilibres ioniques. Premier mémoire: Etude de l'équilibre oxalate de calcium - acide chlorhydrique étendu, *J. Chim. Phys. Phys.-Chim. Biol.*, **24**, (1927), 24-49, in French. Cited on pages: 161, 166, 167.
- [27BOB/MAL] Bobtelsky, M., Malkowa-Janowski, Über die Löslichkeit von Magnesiumoxalat und ihre Bedeutung für die Calcium-Magnesium-Trennung, *Z. Angew. Chem.*, **40**, (1937), 1343-1436, in German. Cited on pages: 159, 160, 162.
- [27DAV] Davies, C. W., The extent of dissociation of salts in water, *Trans. Faraday Soc.*, **23**, (1927), 351-356. Cited on pages: 178, 181, 547, 549, 556.

- [27SCH2] Scholder, R., Über den teilweisen Ersatz des Oxalsäure-Restes in Oxalato-Anionen zweiwertiger Metalle, *Ber. Dtsch. Chem. Ges.*, **60**, (1927), 1499-1509, in German. Cited on page: 177.
- [27SCH3] Scholder, R., Über Selbstkomplexbildung bei Oxalaten zweiwertiger Metalle, I.: Leitfähigkeits- und Löslichkeits- Bestimmungen, *Ber. Dtsch. Chem. Ges.*, **60**, (1927), 1510-1525, in German. Cited on pages: 160, 161, 162, 166, 191, 547, 549.
- [27SCH/GAD] Scholder, R., Gadenne, E., Niemann, H., Über Oxalato-Verbindungen der Erdalkalien und des Bleis, *Ber. Dtsch. Chem. Ges.*, **60**, (1927), 1489-1499, in German. Cited on pages: 177, 598.
- [28FLO] Flöttmann, F., Über Löslichkeitsgleichgewichte, *Z. Anal. Chem.*, **73**, (1928), 1-39, in German. Cited on pages: 112, 152, 153, 548.
- [28KOL/BOS] Kolthoff, I. M., Bosch, W., The influence of neutral salts on acid-salt equilibria. II. The three dissociation constants of citric acid, *Recl. Trav. Chim. Pays-Bas*, **47**, (1928), 558-575. Cited on pages: 308, 323.
- [28SIM] Simms, H. S., The effect of salts on weak electrolytes. II. Calculation of overlapping constants, *J. Phys. Chem.*, **32**, (1928), 1495-1515. Cited on pages: 114, 308, 323.
- [28SIM2] Simms, H. S., The effect of salts on weak electrolytes. I. Dissociation of weak electrolytes in the presence of salts, *J. Phys. Chem.*, **32**, (1928), 1121-1141. Cited on page: 114.
- [29BJE/UNM] Bjerrum, N., Unmack, A., Elektrometrische Messungen mit Wasserstoffelektroden in Mischungen von Säuren und Basen mit Salzen. Die Dissoziationskonstanten von Wasser, Phosphorsäure, Citronensäure und Glycin, *Math.-Fys. Medd. - Kong. Danske Vidensk. Selsk.*, **9**, (1929), 1-208, in German. Cited on pages: 308, 323, 326, 328.
- [29HAM] Hammarsten, G., On calcium oxalate and its solubility in the presence of inorganic salts with special reference to the occurrence of oxaluria, *Compt. Rend. Travaux Lab. Carlsberg*, **17**, (1929), 1-85. Cited on pages: 166, 167, 169, 170, 555.

- [29RIC/MAI] Richards, T. W., Mair, B. J., A study of the thermochemical behavior of weak electrolytes, *J. Am. Chem. Soc.*, **51**, (1929), 740-748. Cited on page: 326.
- [30RUF] Ruff, O., Fraktionierte Fällung. V. Der Einschluß von Fremdstoffen in Kristallgitter, *Z. Anorg. Allg. Chem.*, **185**, (1930), 387-402, in German. Cited on pages: 167, 169.
- [31BAN/RIG] Banks, W. H., Righellato, E. C., Davies, C. W., The extent of dissociation of salts in water. Part III, *Trans. Faraday Soc.*, **27**, (1931), 621-627. Cited on pages: 157, 548.
- [31CHA/BEL] Chapin, E. M., Bell, J. M., The solubility of oxalic acid in aqueous solutions of hydrochloric acid, *J. Am. Chem. Soc.*, **53**, (1931), 3284-3287. Cited on page: 112.
- [31GAB] Gable, H. S., Zirconium. II. Zirconium oxalate and diphenyldinitrogen zirconium, *J. Am. Chem. Soc.*, **53**, (1931), 1276-1278. Cited on pages: 202, 548.
- [31GAN/ING] Gane, R., Ingold, C. K., Electrometric titration curves of dibasic acids. Part IV. Corrections for interionic effects and for solvent electrostriction. First and second dissociation constants of some n-paraffin  $\alpha\omega$ -dicarboxylic acids, alkyl- and dialkyl-malonic acids, s-di- and -tetra-alkylsuccinic acids,  $\beta$ -alkyl- and  $\beta\beta$ -dialkyl-glutaric acids, and cyclic 1:1-diacetic acids. Remarks on the configurations and molecular dimensions of these acids in dilute aqueous solutions, *J. Chem. Soc.*, (1931), 2153-2169. Cited on pages: 114, 626.
- [32MON/DAV] Money, R. W., Davies, C. W., The extent of dissociation of salts in water. Part IV: Bi-bivalent salts, *Trans. Faraday Soc.*, **28**, (1932), 609-614. Cited on pages: 178, 179, 181, 187, 194, 196, 549, 556.
- [33FOO/VAN] Foote, H. W., Vance, J. E., The system: sodium iodate, sodium oxalate, water, *Am. J. Sci.*, **226**, (1933), 16-18. Cited on pages: 152, 153, 549.
- [33KOL/SAN] Kolthoff, I. M., Sandell, E. B., Exchange adsorption and its influence upon the solubility of precipitates with ionic lattices in electrolyte solutions, *J. Am. Chem. Soc.*, **55**, (1933), 2170-2171. Cited on pages: 161, 166, 167.

- [33LAT/SCH] Latimer, W. M., Schutz, P. W., Hicks Jr, J. F. G., The heat capacity and entropy of calcium oxalate from 19 to 300° absolute. The entropy and free energy of oxalate ion, *J. Am. Chem. Soc.*, **55**, (1933), 971-975. Cited on pages: 164, 549, 550, 551.
- [33MAL/GLU] Maljaroff, K. L., Gluschakoff, A. J., Die Löslichkeit des Calciumoxalats in einigen Salzlösungen, *Z. Anal. Chem.*, **93**, (1933), 265-268, in German. Cited on pages: 166, 167.
- [34BAS] Basset, H., Notes on the system lime - water, and on the determination of calcium, *J. Chem. Soc.*, (1934), 1270-1275. Cited on pages: 161, 166, 167.
- [34BEC/ROT] Becker, G., Roth, W. A., Die Bildungswärme von Ammoniak und Salpetersäure, *Z. Elektrochem.*, **40**, (1934), 836-843, in German. Cited on pages: 107, 109, 110, 111, 112, 113.
- [34COL] Colani, A., Combinaisons de l'oxalate d'uranyle avec les oxalates alcalino-terreux, *C. R. Hebd. Séances Acad. Sci.*, **198**, (1934), 1510-1512, in French. Cited on pages: 213, 215, 551.
- [34FRE] Fredholm, H., Das Verhalten des Magnesiumions zu Ammoniak in wäßriger Lösung. III. Löslichkeitsveränderung einiger Salze in H<sub>3</sub>N-haltiger Lösung., *Z. Anorg. Allg. Chem.*, **218**, (1934), 225-234, in German. Cited on pages: 159, 160, 162.
- [34HAS/MCL] Hastings, A. B., McLean, F. C., Eichelberger, L., Hall, J. L., Da Costa, E., The ionization of calcium, magnesium, and strontium citrates, *J. Biol. Chem.*, **107**, (1934), 351-370. Cited on pages: 335, 337, 340, 342, 552, 600.
- [34SAR] Sartori, G., Applicazione del metodo polarografico allo studio di anioni complessi, *Gazz. Chim. Ital.*, **64**, (1934), 3-16, in Italian. Cited on pages: 195, 196, 552.
- [35GUG] Guggenheim, E. A., The specific thermodynamic properties of aqueous solutions of strong electrolytes, *Philos. Mag.*, **19**, (1935), 588-643. Cited on page: 821.
- [35HEN] Hendricks, S. B., The orientation of the oxalate group in oxalic acid and some of its salts, *Z. Kristallogr.*, **91**, (1935), 48-64. Cited on pages: 106, 153, 154, 155.



- [36BOU] Boulanger, J., Sur les systèmes oxalate de zirconyle, oxalates alcalins et eau, *C. R. Acad. Sci., Chimie*, **202**, (1936), 2156-2159, in French. Cited on pages: 153, 155, 202, 552, 553.
- [36BOU2] Boulanger, J., Suite de l'étude des systèmes oxalate de zirconyle, oxalates alcalins et eau, *C. R. Acad. Sci., Chimie*, **203**, (1936), 87-90, in French. Cited on pages: 152, 153, 202, 552, 553.
- [36BRI/JAR] Britton, H. T. S., Jarrett, M. E. D., Physicochemical studies of complex formation involving weak acids. Part XVI. (a) Isotherms at 18° of the systems: sodium oxalate-copper (or zinc or magnesium) oxalate-water. (b) The solubility of copper, zinc, and magnesium oxalates in solutions of oxalic acid and sulphuric acid. (c) A potentiometric investigation of the complex anion,  $\text{Cu}(\text{C}_2\text{O}_4)_2^{2-}$ , *J. Chem. Soc.*, (1936), 1489-1493. Cited on pages: 114, 152, 153, 159, 160, 162, 167.
- [36MUU/LEB] Muus, J., Lebel, H., On complex calcium citrate, *Math.-Fys. Medd. - Kong. Danske Vidensk. Selsk.*, **13**, (1936), 1-17. Cited on pages: 337, 339, 342, 553.
- [36PIT/GOR] Pitzer, E. C., Gordon, N. E., Wilson, D. A., The reduction of uranyl ion in the uranyl oxalate actinometer, *J. Am. Chem. Soc.*, **58**, (1936), 67-70. Cited on page: 234.
- [36SCA] Scatchard, G., Concentrated solutions of strong electrolytes, *Chem. Rev.*, **19**, (1936), 309-327. Cited on page: 821.
- [36TRA] Trapp, H., Über die Löslichkeit der Oxalsäure und der Oxalate der alkalischen Erden in Mineralsäuren, I, *J. Prakt. Chem.*, **144**, (1936), 193-210, in German. Cited on page: 112.
- [36VOS/ISR] Vosburgh, W. C., Israel, K., Birch, O. G., The system nickel oxalate, potassium oxalate and water at 30°C, *J. Am. Chem. Soc.*, **58**, (1936), 2282-2283. Cited on pages: 155, 190, 562.
- [37CLA/VOS] Clayton, W. J., Vosburgh, W. C., Equilibria in solutions of cadmium and zinc oxalates, *J. Am. Chem. Soc.*, **59**, (1937), 2414-2421. Cited on page: 114.

- [37DAL] Dalman, L. H., The solubility of citric and tartaric acids in water, *J. Am. Chem. Soc.*, **59**, (1937), 2547-2549. Cited on pages: 303, 305.
- [37LED/HAU] Ledrut, J., Hauss, L., Dosage du nickel par permanganatométrie, *Bull. Soc. Chim. Fr.*, série 5, **4**, (1937), 1136-1141, in French. Cited on page: 191.
- [38CAN/KIB] Cannan, R. K., Kibrick, A., Complex formation between carboxylic acids and divalent metal cations, *J. Am. Chem. Soc.*, **60**, (1938), 2314-2320. Cited on pages: 114, 178, 179, 181, 182, 183, 553, 616.
- [39HAR/FAL] Harned, H. S., Fallon, L. D., The second ionization constant of oxalic acid from 0 to 50°C, *J. Am. Chem. Soc.*, **61**, (1939), 3111-3113. Cited on pages: 115, 116, 133, 136, 143, 145, 149, 554, 555, 556, 607, 612, 638, 682, 792.
- [39NOR] Nordbö, R., The concentration of ionized magnesium and calcium in milk, *J. Biol. Chem.*, **128**, (1939), 745-757. Cited on pages: 335, 337, 342, 555, 600.
- [39PAR/GIB] Parton, H. N., Gibbons, R. C., The thermodynamic dissociation constants of oxalic acid, *Trans. Faraday Soc.*, **35**, (1939), 542-545. Cited on pages: 115, 555, 638, 770.
- [39PAR/NIC] Parton, H. N., Nicholson, A. J. C., The thermodynamic dissociation constants of oxalic acid in water and methanol-water mixtures, *Trans. Faraday Soc.*, **35**, (1939), 546-550. Cited on pages: 115, 555, 638, 733.
- [39PED] Pedersen, K. J., Ionic equilibria in aqueous solutions of magnesium oxalate, *Trans. Faraday Soc.*, **35**, (1939), 277-283. Cited on pages: 178, 182, 183, 555.
- [39PED2] Pedersen, K. J., The solubility of calcium oxalate in aqueous solutions of urea, *J. Am. Chem. Soc.*, **61**, (1939), 334-336. Cited on pages: 161, 166, 167.
- [39SAT/SOG] Satoh, S., Sogabe, T., The specific heats of some solid aliphatic acids and their ammonium salts and the atomic heat of nitrogen, *Sci. Pap. Inst. Phys. Chem. Res. (Jpn.)*, **36**, (1939), 97-105. Cited on page: 108.

- [40ADE] Adell, B., Die elektrolytische Dissoziation der Citronensäure in Natriumchloridlösungen, *Z. Phys. Chem. (Leipzig)*, **187A**, (1940), 66-78, in German. Cited on pages: 310, 314, 600.
- [40SHE/PAL] Shehyn, H., Pall, D. B., The solubility of calcium oxalate in various salt solutions, *J. Phys. Chem.*, **44**, (1940), 166-171. Cited on pages: 161, 166.
- [40VOS/BEC] Vosburgh, W. C., Beckman, J. F., The solubility of cadmium and zinc oxalates in salt solutions, *J. Am. Chem. Soc.*, **62**, (1940), 1028-1031. Cited on page: 114.
- [41DAR] Darken, L. S., The ionization constants of oxalic acid at 25°C from conductance measurements, *J. Am. Chem. Soc.*, **63**, (1941), 1007-1011. Cited on pages: 116, 556, 676, 770.
- [41LAR/TOM] Larson W. D., Tomsicek W. J., The activity coefficients of the undissociated part of weak acids. II. Oxalic acid, *J. Am. Chem. Soc.*, **63**, (1941), 3329-3331. Cited on page: 151.
- [42BEN] Benrath A., Über die Löslichkeit von Salzen und Salzgemischen bei Temperaturen oberhalb von 100°. IV, *Z. Anorg. Allg. Chem.*, **249**, (1942), 245-250, in German. Cited on pages: 153, 155, 156.
- [42BRI/HES] Brintzinger, H., Hesse, G., Kupfer-, Nickel- und Uranylverbindungen der Äthylendiamintetraessigsäure, *Z. Anorg. Allg. Chem.*, **249**, (1942), 113-118, in German. Cited on pages: 460, 477.
- [42HEI] Heidt, L. J., The photosensitive complexes in the photolysis of uranyl oxalate and their dissociation constants, *J. Phys. Chem.*, **46**, (1942), 624-630. Cited on pages: 230, 231, 232, 233, 234, 235, 556, 557, 576.
- [42KAR] Karaoglanov, Z., Die Empfindlichkeit chemischer Reaktionen. V. Teil. Empfindlichkeit der Reaktion  $\text{Mg}^{2+} + \text{C}_2\text{O}_4^{2-}$ , *Z. Anal. Chem.*, **124**, (1942), 92-102, in German. Cited on pages: 159, 160, 162.
- [42KLE/RAD] Klemm, W., Raddatz, K.-H., Notiz über das magnetische Verhalten der Nickelkomplexe der Nitrilotriessigsäure und der Äthylendiamintetraessigsäure, *Z. Anorg. Allg. Chem.*, **250**, (1942), 204-206, in German. Cited on page: 460.

- [42MCC/RIE] McComas, Jr., W. H., Rieman III, W., The solubility of calcium oxalate monohydrate in pure water and various neutral salt solutions at 25°, *J. Am. Chem. Soc.*, **64**, (1942), 2946-2947. Cited on pages: 161, 166, 167, 169, 170.
- [42PFE/OFF] Pfeiffer, P., Offermann, W., Calcium- und Kupfer- Komplexsalze von Trilon A und B, *Ber. Dtsch. Chem. Ges. B*, **75**, (1942), 1-12, in German. Cited on page: 443.
- [43BRI/THI] Brintzinger, H., Thiele, H., Müller, U., Komplexverbindungen und Salze der Äthylendiamintetraessigsäure, *Z. Anorg. Allg. Chem.*, **251**, (1943), 285-294, in German. Cited on page: 476.
- [43PFE/SIM] Pfeiffer, P., Simons, H., Innere Komplexsalze der Erdalkalimetalle, *Ber. Dtsch. Chem. Ges. B*, **76**, (1943), 847-855, in German. Cited on page: 443.
- [44OCO2] O'Connor, P., Solubilities of plutonium(III) and (IV) oxalates, in: *Chemical Research - Basic Chemistry of Plutonium. Report CN-1702*, pp.7-10, Chicago University Metallurgical Laboratory, Chicago, Illinois, (1944). Cited on pages: 268, 269, 270.
- [45BOB/JOR] Bobtelsky, M., Jordan, J., The metallic complexes of tartrates and citrates, their structure and behavior in dilute solutions. I. The cupric and nickelous complexes, *J. Am. Chem. Soc.*, **67**, (1945), 1824-1831. Cited on pages: 353, 354, 358, 557, 760.
- [45HOO/WIJ] Hoover, A. A., Wijesinha, G. S., Influence of pH and salts on the solubility of calcium oxalate, *Nature (London)*, **155**, (1945), 638. Cited on pages: 166, 167.
- [46HIL/GOU] Hill, L. M., Goulden, T. P., Hatton, E., Equilibria in ternary systems containing oxalates, *J. Chem. Soc.*, (1946), 78-81. Cited on pages: 152, 153.
- [46JOS] Joseph, N. R., The dissociation constants of organic calcium complexes, *J. Biol. Chem.*, **164**, (1946), 529-541. Cited on pages: 337, 343, 557.

- [46KOL/HAR] Kolthoff, I. M., Harris, W. E., The polarography of uranium. II. Polarography in strongly acid solution, *J. Am. Chem. Soc.*, **68**, (1946), 1175-1179. Cited on page: 228.
- [47DUN/ROB] Dunitz, J. D., Robertson, J. M., The crystal and molecular structure of certain dicarboxylic acids. Part I. Oxalic acid dihydrate, *J. Chem. Soc.*, (1947), 142-149. Cited on page: 110.
- [47PEL/DUV] Peltier, S., Duval, C., Sur la thermogravimétrie des précipités analytiques. II. dosage du calcium, *Anal. Chim. Acta*, **1**, (1947), 345-354. Cited on pages: 164, 165.
- [47SCH/ACK] Schwarzenbach, G., Ackermann, H., Komplexe V. Die Äthylendiamin-tetraessigsäure, *Helv. Chim. Acta*, **30**, (1947), 1798-1804, in German. Cited on pages: 391, 399, 402, 437, 438, 439, 443, 445, 446, 447, 449, 450, 451, 454, 455, 558, 559, 594, 617, 625, 633, 635, 644, 649, 659, 668, 670, 690, 695, 725, 737.
- [47SCH/WIL] Schwarzenbach, G., Willi, A., Bach, R. O., Komplexe IV. Die Acidität und die Erdalkalikomplexe der Anilin-diessigsäure und ihre Substitutionsprodukte, *Helv. Chim. Acta*, **30**, (1947), 1303-1320. Cited on page: 558.
- [48PIN/BAT] Pinching, G. D., Bates, R. G., Second dissociation constant of oxalic acid from 0° to 50°C, and the pH of certain oxalate buffer solutions, *J. Res. Natl. Bur. Stand.*, **40**, (1948), 405-416. Cited on pages: 115, 116, 133, 134, 136, 143, 145, 149, 555, 558, 559, 607, 676, 682, 792.
- [48PYN] Pyne, G. T., Measurement of alkaline earth ion concentrations by Rennet action, *Nature (London)*, **162**, (1948), 925. Cited on pages: 337, 342, 559.
- [48SCH/ACK] Schwarzenbach, G., Ackermann, H., Komplexe XII. Die Homologen der Äthylendiamin-tetraessigsäure und ihre Erdalkalikomplexe, *Helv. Chim. Acta*, **31**, (1948), 1029-1048, in German. Cited on pages: 447, 559.
- [49BAT/PIN] Bates, R. G., Pinching, G. D., Resolution of the dissociation constants of citric acid at 0 to 50°, and determination of certain related thermodynamic functions, *J. Am. Chem. Soc.*, **71**, (1949), 1274-1283. Cited on pages: 308, 323, 326, 328, 331, 565, 729.

- [49CON/MCV] Connick, R. E., McVey, W. H., The aqueous chemistry of zirconium, *J. Am. Chem. Soc.*, **71**, (1949), 3182-3191. Cited on pages: 202, 204, 559, 709.
- [49PAT] Patton, R. L., Note on the preparation of plutonium(III) oxalate, in: *The transuranium elements: Research papers*, Seaborg, G. T., Katz, J. J. and Manning, W. M., Eds., p. 849, McGraw-Hill, New York, USA, (1949). Cited on page: 262.
- [49PAT2] Patton, R. L., Preparation of some organic derivatives of plutonium, in: *The transuranium elements: Research papers*, Seaborg, G. T., Katz, J. J. and Manning, W. M., Eds., pp.851-852, McGraw-Hill, New York, USA, (1949). Cited on page: 262.
- [49PED] Pedersen, K. J., Relations between vapour pressures and solubilities of hydrates, *Acta Chem. Scand.*, **3**, (1949), 65-71. Cited on page: 166.
- [49PFE/SCH] Pfeiffer, P., Schmitz, E., Innerkomplexsalze der Trilon-B-Säure mit 2 zweiwertigen Metallen, *Z. Anorg. Chem.*, **258**, (1949), 247-256, in German. Cited on pages: 443, 460.
- [49REA] Reas, W. H., Identification of plutonium(IV) oxalate complexes in oxalic acid solutions in: *The transuranium elements: Research papers*, Seaborg, G. T. and Katz, J. J. and Manning, W. M., Eds., pp. 423-433, McGraw-Hill, New York, USA, (1949). Cited on pages: 112, 115, 268, 270, 271, 272, 273, 277, 279, 280, 281, 560.
- [50KRA/NEL] Kraus, K. A., Nelson, F., Hydrolytic behavior of metal ions: I. The acid constants of uranium(IV) and plutonium(IV), *J. Am. Chem. Soc.*, **72**, (1950), 3901-3906. Cited on pages: 481, 658.
- [50MEI] Meites, L., Polarographic studies of metal complexes. III. The copper(II) oxalates and carbonates, *J. Am. Chem. Soc.*, **72**, (1950), 184-189. Cited on page: 114.
- [50MEI2] Meites, L., Polarographic studies of metal complexes. II. The copper(II) citrates, *J. Am. Chem. Soc.*, **72**, (1950), 180-183. Cited on page: 114.

- [51BAR/ARG] Barney II, J. E., Argersinger, Jr., W. J., Reynolds, C. A., A study of some complex chlorides and oxalates by solubility measurements, *J. Am. Chem. Soc.*, **73**, (1951), 3785-3788. Cited on pages: 159, 160, 162, 179, 181, 191, 192, 195, 196, 561, 562.
- [51CAB] Cabell, M. J., The complex ions formed by thorium and uranium with complexones, U. K. Atomic Energy Research Establishment, Report AERE C/R 813, (1951). Cited on pages: 398, 572, 573, 581, 582, 583, 662.
- [51CON/REA] Connick, R. E., Reas, W. H., The hydrolysis and polymerization of zirconium in perchloric acid solution, *J. Am. Chem. Soc.*, **73**, (1951), 1171-1176. Cited on pages: 202, 204, 563.
- [51COO/LON] Cook, Jr., C. M., Long, F. A., Determination of dissociation constants of complex ions by a radioactive indicator method, *J. Am. Chem. Soc.*, **73**, (1951), 4119-4121. Cited on pages: 461, 462, 465, 466.
- [51HEI] Heinz, E., Untersuchungen über Komplexverbindungen des Calciums, *Biochem. Z.*, **321**, (1951), 314-342, in German. Cited on pages: 308, 323, 337, 339, 342, 563, 600.
- [51NOR] Norris, W. H. H., The system oxalic acid - sodium hydroxide - water, *J. Chem. Soc.*, (1951), 1708-1715. Cited on pages: 112, 152, 153.
- [51NYD] Nydahl, F., The solubility of calcium oxalate monohydrate in ammonium oxalate solutions at 25°C, *Acta Chem. Scand.*, **5**, (1951), 669-670. Cited on pages: 161, 166, 167, 169.
- [51SCH/FRE] Schwarzenbach, G., Freitag, E., Komplexe XX. Stabilitätskonstanten von Schwermetallkomplexen der Äthylendiamin-tetraessigsäure, *Helv. Chim. Acta*, **34**, (1951), 1503-1508, in German. Cited on pages: 461, 464, 465, 466, 467, 566.
- [52AMP/DAV] Amphlett, C. B., Davidge, O. T., The solubility of uranyl oxalate in nitric acid, *J. Chem. Soc.*, (1952), 2938-2939. Cited on pages: 213, 215, 217, 545, 563, 578.

- [52CAR/MAR] Carini, F. F., Martell, A. E., The effect of potassium chloride on the equilibrium between ethylenediaminetetraacetate and calcium ions, *J. Am. Chem. Soc.*, **74**, (1952), 5745-5748. Cited on pages: 398, 621, 629.
- [52COX/DOU] Cox, E. G., Dougill, M. W., Jeffrey, G. A., The structure of  $\alpha$ -oxalic acid and of the carboxyl group, *J. Chem. Soc.*, (1952), 4854-4864. Cited on page: 106.
- [52ELL2] Ellenbogen, E., Dissociation constants of peptides. I. A survey of the effect of optical configuration, *J. Am. Chem. Soc.*, **74**, (1952), 5198-5201. Cited on page: 308.
- [52GIB/GRU] Gibson, G., Gruen, D. M., Katz, J. J., Some observations on Neptunium(V) compounds, *J. Am. Chem. Soc.*, **74**, (1952), 2103-2104. Cited on page: 248.
- [52LAT] Latimer, W. M., *The oxidation states of the elements and their potentials in aqueous solutions*, 2nd. Edition, Prentice-Hall Inc., Englewood Cliffs, N. J., (1952), 392 pp.. Cited on page: 602.
- [52MAR/PLU] Martell, A. E., Plumb, R. C., Complexes of various metals with ethylenediaminetetraacetic acid, *J. Phys. Chem.*, **56**, (1952), 993-996. Cited on page: 461.
- [52SAT/DIA] Sato, T. R., Diamond, H., Norris, W. P., Strain, H. H., Electrochromatographic separations of rare earths, *J. Am. Chem. Soc.*, **74**, (1952), 6154-6155. Cited on page: 577.
- [52SCH/LIN] Schubert, J., Lindenbaum, A., Stability of alkaline earth-organic acid complexes measured by ion exchange, *J. Am. Chem. Soc.*, **74**, (1952), 3529-3532. Cited on pages: 337, 343, 564, 565, 600, 601.
- [52SPE/MIL] Spedding, F. H., Miller, C. F., Thermochemistry of the rare earths: I. Cerium and neodymium, *J. Am. Chem. Soc.*, **74**, (1952), 4195-4198. Cited on pages: 110, 112.
- [53AHM/CRU] Ahmed, F. R., Cruickshank, D. W. J., A refinement of the crystal structure analyses of oxalaic acid dihydrate, *Acta Crystallogr.*, **6**, (1953), 385-392. Cited on page: 110.



- [53ALL/SCA] Allen, J. A., Scaife, D. E., The dissociation pressure of nickel oxalate dihydrate, *J. Phys. Chem.*, **57**, (1953), 863-864. Cited on page: 190.
- [53AST/VER] Astakhov, K. V., Verenikin, V. B., Some inner complex compounds of nickel and cobalt, and their properties, *Sb. Statei Obshch. Khim.*, **2**, (1953), 1149-1157, in Russian. Cited on pages: 459, 460.
- [53BRA/COT] Bradley, R. S., Cotson, S., The vapour pressure and lattice energy of hydrogen-bonded crystals. Part II.  $\alpha$ - and  $\beta$ -anhydrous oxalic acid and tetragonal pentaerythritol, *J. Chem. Soc.*, (1953), 1684-1688. Cited on pages: 106, 108, 110.
- [53CAR/MAR] Carini, F. F., Martell, A. E., Thermodynamics of metal chelate formation. I. The third and fourth dissociation constants of ethylenediaminetetraacetic acid, *J. Am. Chem. Soc.*, **75**, (1953), 4810-4813. Cited on pages: 398, 428, 432, 439.
- [53DAV/HOY] Davies, C. W., Hoyle, B. E., The interaction of calcium ions with some phosphate and citrate buffers, *J. Chem. Soc.*, (1953), 4134-4136. Cited on pages: 339, 342, 565, 567.
- [53GRU/KAT] Gruen, D. M., Katz, J. J., Spectrophotometric study on Np(V) oxalate complexes, *J. Am. Chem. Soc.*, **75**, (1953), 3772-3776. Cited on pages: 254, 255, 256, 257, 565, 566, 649.
- [53HUG/MAR] Hughes, V. L., Martell, A. E., Spectrophotometric determination of the stabilities of ethylenediaminetetraacetate chelates, *J. Phys. Chem. A*, **57**, (1953), 694-699. Cited on pages: 461, 466, 566.
- [53WAR/WEB] Warner, R. C., Weber, I., The cupric and ferric citrate complexes, *J. Am. Chem. Soc.*, **75**, (1953), 5086-5094. Cited on pages: 308, 598, 667.
- [53WAT/AAR] Watters, J. I., Aaron, A., Spectrophotometric investigation of the complexes formed between copper and pyrophosphate ions in aqueous solution, *J. Am. Chem. Soc.*, **75**, (1953), 611-616. Cited on page: 609.

- [54CAR/MAR] Carini, F. F., Martell, A. E., Thermodynamic quantities associated with the interaction between ethylenediaminetetraacetate and alkaline earth ions, *J. Am. Chem. Soc.*, **76**, (1954), 2153-2157. Cited on pages: 445, 446, 449, 455, 456, 457, 566, 695.
- [54CHA2] Charles, R. G., Heats and entropies of reaction of metal ions with ethylenediaminetetraacetate, *J. Am. Chem. Soc.*, **76**, (1954), 5854-5858. Cited on pages: 439, 455, 456, 457, 468, 469, 569, 639.
- [54CON] Connick, R. E., Oxidation states, potentials, equilibria, and oxidation-reduction reactions of plutonium, in: *The actinide elements*, Seaborg, G. T. and Katz, J. J., Eds., pp.221-300, McGraw-Hill, New York, (1954). Cited on page: 277.
- [54CUN] Cunningham, B. B., Preparation and properties of the compounds of plutonium, in: *The actinide elements*, Seaborg, G. T. and Katz, J. J., Eds., pp.371-434, McGraw-Hill, New York, (1954). Cited on pages: 261, 264, 265.
- [54GRU/HUT] Gruen, D. M., Hutchison, Jr., C. A., Magnetic susceptibilities of  $\text{Np}^{+6}$ ,  $\text{Np}^{+5}$ , and  $\text{Np}^{+4}$ , *J. Chem. Phys.*, **22**, (1954), 386-393. Cited on page: 248.
- [54HEI/BOB] Heitner, C., Bobtelsky, M., Complexes de l'uranium avec le citrate, leurs composition et stabilité, *Bull. Soc. Chim. Fr.*, **21**, (1954), 356-359, in French. Cited on pages: 364, 368, 567.
- [54HIN] Hindman, J. C., Ionic and molecular species of plutonium in solution, in: *The actinide elements*, Seaborg, G. T. and Katz, J. J., Eds., pp. 301-370, McGraw-Hill, New York, USA, (1954). Cited on pages: 264, 265.
- [54JEF/PAR] Jeffrey, G. A., Parry, G. S., The crystal structure of sodium oxalate, *J. Am. Chem. Soc.*, **76**, (1954), 5283-5286. Cited on pages: 152, 153.
- [54SCH/GUT] Schwarzenbach, G., Gut, R., Anderegg, G., Komplexe XXV. Die polarographische Untersuchung von Austauschgleichgewichten. Neue Daten der Bildungskonstanten von Metallkomplexen der Äthylendiamin-tetraessigsäure und der 1,2-Diaminocyclohexan-tetraessigsäure, *Helv. Chim. Acta*, **37**, (1954), 937-957, in German. Cited on pages: 446, 449, 450, 451, 461, 462, 465, 466, 467, 490, 566, 597, 635, 658, 659.

- [54SCH/LAI] Schaap, W. B., Laitinen, H. A., Bailar, Jr., J. C., Polarography of iron oxalates, malonates and succinates, *J. Am. Chem. Soc.*, **76**, (1954), 5868-5872. Cited on page: 114.
- [54YAT/ZOL] Yatsimirskii, K. B., Zolotarev, E. K., On thermodynamics of oxalate complexes, *Zh. Fiz. Khim.*, **28**, (1954), 1292-1298, in Russian. Cited on pages: 195, 196, 199, 567.
- [55DAV/HOY] Davies, C. W., Hoyle, B. E., The interaction of calcium ions with some citrate buffers: A correction, *J. Chem. Soc.*, (1955), 1038. Cited on pages: 339, 567, 600.
- [55LEV] Levien, B. J., A physicochemical study of aqueous citric acid solutions, *J. Phys. Chem.*, **59**, (1955), 640-644. Cited on pages: 305, 306.
- [55MAC/KRI] MacNevin, W. M., Kriege, O. H., Reactions of divalent palladium with ethylenediaminetetraacetic acid, *J. Am. Chem. Soc.*, **77**, (1955), 6149-6151. Cited on page: 737.
- [55MOH/SIN] Mohanty, S. R., Singh, D., Murty, J. G. K., Estimation and complexes of zirconium with oxalates, *Curr. Sci.*, **24**, (1955), 229. Cited on pages: 202, 567.
- [56CAR/STA] Care, R. A., Staveley, L. A. K., The thermodynamics of the formation of complex ions of ethylenediaminetetra-acetic acid and bivalent cations, *J. Chem. Soc.*, (1956), 4571-4579. Cited on pages: 398, 455, 456, 457, 458, 459, 463, 466, 468, 469, 568, 639, 695.
- [56DUT/RAY] Dutta, R. L., Ray, P., A study on the metal complexes of ethylenediamine tetra-acetic acid, *J. Indian Chem. Soc.*, **33**, (1956), 727-731. Cited on page: 460.
- [56FOM/KAR] Fomin, V. V., Kartushova, R. E., Rudenko, T. I., Decomposition of plutonium oxalates by intrinsic alpha radiation, *Sov. At. Energy*, **3**, (1956), 409-413. Cited on page: 262.
- [56GRA/GRA] Grabowski, Z. R., Grabowska, A., Katalizowana redukcja polarograficzna kwasu szczawiowego w obecności soli uranylu, *Rocz. Chem.*, **30**, (1956), 1245-1256, in Polish. Cited on page: 228.

- [56GRI/PET2] Grinberg, A. A., Petrzhak, G. I., Physico-chemical properties of oxalates of quadrivalent uranium, *Trudy Radievogo Inst. im. V. G. Khlopina, Khim. i. Geokhim*, **7**, (1956), 50-73, in Russian. Cited on pages: 207, 208, 209, 210, 218, 568, 579.
- [56GRI/PTI] Grinberg, A. A., Ptitsyn, B. V., Tekster, E. N., Physico-chemical properties of aqueous solutions of complex uranium oxalates, *Trudy Radievogo Inst. im. V. G. Khlopina, Khim. i. Geokhim*, **7**, (1956), 74-86. Cited on pages: 233, 234, 241, 242, 243, 568, 598, 813.
- [56KOR/PET] Kornienko, I. V. P., Petrenko, V. V., Thermal decomposition of nickel oxalate, *Uch. Zap. Khar'kov. Gos. Univ. Tr. Khim. Fak. i Nauchn.-Iss.*, **71**, (1956), 77-87. Cited on page: 192.
- [56MAR] Martell, A. E., Thermodynamic changes associated with the formation of aminopolycarboxylate chelates, *Recl. Trav. Chim.*, **75**, (1956), 781-786. Cited on pages: 466, 569.
- [56MOR/JUS] Morgan, L. O., Justus, N. L., Complex compounds of zirconium(IV) and hafnium(IV) with ethylenediaminetetraacetic acid, *J. Am. Chem. Soc.*, **78**, (1956), 38-41. Cited on pages: 472, 473, 569.
- [56SCH/REI] Schmid, R. W., Reilley, C. N., A rapid electrochemical method for the determination of metal chelate stability constants, *J. Am. Chem. Soc.*, **78**, (1956), 5513-5518. Cited on pages: 445, 446, 449, 450, 451, 452, 633, 635.
- [56STA/CRO3] Staritzky, E., Cromer, D. T., Uranyl oxalate trihydrate,  $\text{UO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ , *Anal. Chem.*, **28**, (1956), 1353-1354. Cited on page: 213.
- [56ZIE/CON] Zielen, A. J., Connick, R. E., The hydrolytic polymerization of zirconium in perchloric acid solutions, *J. Am. Chem. Soc.*, **78**, (1956), 5785-5792. Cited on pages: 202, 204, 569.
- [57BAB/DUB] Babko, A. K., Dubovenko, L. I., Study of cerium oxalate, *Russ. J. Inorg. Chem.*, **2**, (1957), 149-161. Cited on page: 114.
- [57BER/MUL] Bersin, T., Müller, A., Schwarz, H., Zur pharmakologischen Wirkung einiger anorganischer Komplexverbindungen, *Arch. Biochem. Biophys.*, **69**, (1957), 507-513, in German. Cited on page: 443.

- [57BJE/SCH] Bjerrum, J., Schwarzenbach, G., Sillén, L. G., *Stability Constants*, I, Chemical Society, London, (1957). Cited on page: 449.
- [57BOB/RAF] Bobtelsky, M., Rafailoff, R., The zirconium compounds of ethylenediaminetetraacetate. A heterometric study, *Anal. Chim. Acta*, **17**, (1957), 308-313. Cited on page: 472.
- [57BOL/KOR3] Bol'shakov, K. A., Korovin, S. S., Plyushchev, V. E., Ermakova, T. A., Study of solubility in the system  $\text{UO}_2\text{C}_2\text{O}_4\text{-H}_2\text{C}_2\text{O}_4\text{-H}_2\text{O}$ , *Russ. J. Inorg. Chem.*, **2**, (1957), 339-347. Cited on pages: 213, 215, 216, 218, 219, 220, 544, 545, 546, 570.
- [57BOL/KOR4] Bol'shakov, K. A., Korovin, S. S., Solubility in the quaternary reciprocal system  $\text{UO}_2(\text{NO}_3)_2 + \text{H}_2\text{C}_2\text{O}_4 \rightleftharpoons \text{UO}_2\text{C}_2\text{O}_4 + \text{H}_2(\text{NO}_3)_2$  at  $25^\circ\text{C}$ , *Russ. J. Inorg. Chem.*, **2**, (1957), 365-380. Cited on pages: 213, 215, 571.
- [57BRI/PAR] Bricker, C. E., Parker, G. H., Precipitation of magnesium with (ethylenedinitrilo)tetraacetic acid, *Anal. Chem.*, **29**, (1957), 1470-1474. Cited on page: 443.
- [57DUT/SUR] Dutt, N. K., Sur, B., Oxalato- and malonato-complexes of trivalent metals. II. Stabilities of tris-oxalato complexes of iron, chromium, aluminium, and gallium, *Z. Anorg. Allg. Chem.*, **293**, (1957), 195-203. Cited on page: 114.
- [57FOR/SMI] Foreman, J. K., Smith, T. D., The nature and stability of the complex ions formed by ter-, quadri-, and sexa-valent plutonium ions with ethylenediaminetetraacetic acid. Part I. pH titrations and ion-exchange studies, *J. Chem. Soc.*, (1957), 1752-1758. Cited on pages: 498, 499, 501, 502, 571, 572, 573.
- [57FOR/SMI2] Foreman, J. K., Smith, T. D., The nature and stability of the complex ions formed by ter-, quadri-, and sexa-valent plutonium ions with ethylenediaminetetraacetic acid. Part II. spectrophotometric studies, *J. Chem. Soc.*, (1957), 1758-1762. Cited on pages: 498, 499, 501, 502, 572, 573, 593.

- [57GEL/MAT2] Gel'man, A. D., Matorina, N. N., Moskvina, A. I., Determination of the composition and instability constants of complex  $\text{Pu}^{+3}$  oxalate ions, *Sov. At. Energy*, **3**, (1957), 1115-1120. Cited on pages: 115, 262, 264, 265, 266, 276, 277, 574.
- [57GEL/MAT3] Gel'man, A. D., Matorina, N. N., Moskvina, A. I., The formation and stability conditions of the  $\text{Pu(III)}$  oxalate complexes in water solutions, *Dokl. Akad. Nauk SSSR*, **117**, (1957), 88-91, in Russian. Cited on pages: 262, 264, 265, 276, 277, 574.
- [57GEL/MOS] Gel'man, A. D., Moskvina, A. I., Investigation of the formation conditions and stability of complex  $\text{Pu}^{3+}$  compounds by a spectrophotometric method, *Sov. At. Energy*, **3**, (1957), 1121-1123. Cited on pages: 262, 263, 276.
- [57JOR/ALL] Jordan, J., Alleman, T. G., Thermochemical titrations. Enthalpy titrations, *Anal. Chem.*, **29**, (1957), 9-13. Cited on pages: 455, 456, 457, 468, 469, 575.
- [57LEF] Lefebvre, J., Méthode de la surface potentiométrique. II. Application à l'étude de systèmes à deux composants : Borates, Vanadates, Oxalate de magnésium, *J. Chim. Phys. Phys.-Chim. Biol.*, **54**, (1957), 567-580, in French. Cited on pages: 178, 182, 183, 337, 575.
- [57LEF4] Lefebvre, J., Méthode de la surface potentiométrique. III. Application à l'étude des composés maliques et citriques du cuivre, *J. Chim. Phys. Phys.-Chim. Biol.*, **54**, (1957), 581-600, in French. Cited on page: 308.
- [57LI/WES] Li, N. C., Westfall, W. M., Lindenbaum, A., White, J. M., Schubert, J., Manganese-54, Uranium-233 and Cobalt-60 complexes of some organic acids, *J. Am. Chem. Soc.*, **79**, (1957), 5864-5870. Cited on pages: 233, 235, 575.
- [57PAT/PAN2] Patnaik, R. K., Pani, S., Citrate complex of nickel, *J. Indian Chem. Soc.*, **34**, (1957), 619-628. Cited on pages: 322, 353, 354, 355, 358, 576, 760.
- [57RIN/SII] Ringbom, A., Siitonen, S., Skrifvars, B., The ethylenediaminetetraacetate complexes of vanadium(V), *Acta Chem. Scand.*, **11**, (1957), 551-554. Cited on page: 398.

- [57SCH/AND] Schwarzenbach, G., Anderegg, G., Die Verwendung der Quecksilberelektrode zur Bestimmung der Stabilitätskonstanten von Metallkomplexen, *Helv. Chim. Acta*, **40**, (1957), 1773-1792, in German. Cited on pages: 178, 179, 182, 183, 399, 446, 449, 450, 451, 576, 779.
- [57ZAI/SHU2] Zaitsev, L. M., Shubochkin, L. K., Bochkarev, G. S., Zirconyl oxalic acid and its production, *Russ. J. Inorg. Chem.*, **2**, (1957), 423-426. Cited on pages: 202, 577.
- [58BLU] Blumenthal, W. B., *The chemical behavior of zirconium*, Van Nostrand Company, Princeton, New Jersey, (1958). Cited on pages: 202, 577.
- [58BOB/BEN] Bobtelsky, M., Ben-Bassat, A. H. I., Les oxalates de zirconium : composition, structure et propriétés. Etude hétérométrique, *Bull. Soc. Chim. Fr.*, **25**, (1958), 180-184, in French. Cited on pages: 202, 577.
- [58BOL/KOR] Bolshakov, K. A., Korovin, S. S., *Tr. Inst.-Mosk. Inst. Tonkoi Khim.-Tekhnol. im. M. V. Lomonosova*, **7**, (1958), 165-170 (from the citation in [2001HAL/NAV]). Cited on pages: 213, 215, 217, 577, 578.
- [58CHA/HOA] Chappel, F. P., Hoare, F. E., The heat of combustion of citric acid monohydrate, *Trans. Faraday Soc.*, **54**, (1958), 367-371. Cited on page: 303.
- [58COO/FOR] Cook, G. P., Foreman, J. K., Kemp, E. F., Some experiments on the polarography of plutonium(VI) in complexing media, *Anal. Chim. Acta*, **19**, (1958), 174-179. Cited on page: 282.
- [58COO/LON] Cook, Jr., C. M., Long, F. A., Kinetics of the exchange of nickel ethylenediaminetetraacetate ion with nickelous ion, *J. Am. Chem. Soc.*, **80**, (1958), 33-37. Cited on page: 462.
- [58DOR] Dorrough, G. D., The solubility of uranium(IV) oxalate, *Chemistry of uranium. Collected papers*, vol. 2, pp. 535-542, U.S. Atomic Energy Commission, Oak Ridge, Tennessee, (1958). Cited on pages: 207, 208, 210, 579, 610.

- [58DRA/MOS2] Drabkina, L. E., Moskvina, A. I., Gel'man, A. D., Determination of the solubility product of plutonyl oxalate, *Russ. J. Inorg. Chem.*, **3**, (1958), 290-294. Cited on pages: 274, 275, 276, 284, 610.
- [58ERM/BEL] Ermakov, A. N., Belyaeva, V. K., Marov, I. N., Anion exchange study of complex formation of Zr and Hf with oxalate ion, *Tr. Inst.-Mosk. Khim.-Tekhnol. Inst. im. D. I. Mendeleeva*, **9**, (1958), 170-178, in Russian. Cited on pages: 205, 206, 580.
- [58FOM/VOR] Fomin, V. V., Vorob'ev, S. P., Andreeva, M. A., Polarographic investigation of complex plutonium oxalates, *Sov. At. Energy*, **4**, (1958), 63-70. Cited on pages: 262, 264, 277, 278, 279, 580.
- [58FUG] Fuger, J., Ion exchange behaviour and dissociation constants of americium, curium, and californium complexes with ethylenediaminetetra-acetic acid, *J. Inorg. Nucl. Chem.*, **5**, (1958), 332-338. Cited on pages: 504, 505, 581, 582, 583.
- [58GEL/DRA2] Gel'man, A. D., Drabkina, L. E., Moskvina, A. I., Determination of the composition and instability constant of the oxalate complex ions of plutonium(VI), *Russ. J. Inorg. Chem.*, **3**, (1958), 96-101. Cited on pages: 274, 275, 276, 283, 284.
- [58GEL/DRA3] Gel'man, A. D., Drabkina, L. E., Formation and study of the properties of certain oxalate compounds with hexavalent plutonium, *Russ. J. Inorg. Chem.*, **3**, (1958), 57-62. Cited on pages: 263, 274, 276, 283.
- [58GEL/HAY] Gelles, E., Hay, R. W., The interaction of transition-metal ions with oxaloacetic acid. Part I. The role of chelate compounds in the decarboxylation, *J. Chem. Soc.*, (1958), 3673-3683. Cited on page: 187.
- [58GEL/MAT] Gel'man, A. D., Matorina, N. N., Moskvina, A. I., Determination of the composition and instability constants of some oxalate complexes of  $\text{Pu}^{+3}$  by an ion exchange method, *Sov. At. Energy*, **4**, (1958), 55-61. Cited on pages: 114, 276, 277, 574, 583, 605.



- [58GEL/MOS2] Gel'man, A. D., Moskvina, A. I., Investigation of oxalate and carbonate complexes of plutonium(IV) in aqueous solutions by the solubility method, *Proc. Acad. Sci. USSR Chem. Sect. (Doklady Chemistry)*, **118**, (1958), 61-64. Cited on pages: 268, 269, 270, 271, 272, 273, 278, 280, 281, 283, 584, 585, 586, 588.
- [58GEL/SOK] Gel'man, A. D., Sokhina, L. P., Oxalate complex compounds of plutonium (IV), *Russ. J. Inorg. Chem.*, **3**, (1958), 49-56. Cited on pages: 262, 263.
- [58GEL/ZAI3] Gel'man, A. D., Zaitsev, L. M., III. The mixed oxalate-carbonate compounds of plutonium (IV), *Russ. J. Inorg. Chem.*, **3**, (1958), 107-118. Cited on pages: 263, 272, 280.
- [58GRI/PET2] Grinberg, A. A., Petrzhak, G. I., Evteev, L. I., Investigation on the chemistry of uranium and thorium oxalates, *Russ. J. Inorg. Chem.*, **3**, (1958), 315-326. Cited on pages: 207, 209, 210, 225, 584, 601, 602, 623.
- [58HEI/FRI] Heitner-Wirguin, C., Friedman, D., Goldschmidt, J. M. E., Shamir, J., Contribution à l'étude des complexes des citrates et tartrates: 3. Le complexe du nickel avec le citrate, *Bull. Soc. Chim. Fr.*, (1958), 864-867, in French. Cited on pages: 322, 353, 354, 355, 358, 585.
- [58IRV/SHE] Irving, H., Shelton, R., Evans, R., Steric hindrance in analytical chemistry. Part IV. Some sterically hindered complexones, *J. Chem. Soc.*, (1958), 3540-3549. Cited on pages: 399, 402.
- [58MAR2] Markin, T. L., The thermal decomposition of americium(III) oxalate, *J. Inorg. Nucl. Chem.*, **7**, (1958), 290-291. Cited on pages: 284, 585, 764.
- [58MEC/SCH] Mechelynck, P., Schietecatte, W., Solubilité de l'acide éthylènediaminotétraacétique (Complexon II) en fonction du pH. Titration ampérométrique du complexon, *Anal. Chim. Acta*, **19**, (1958), 577-579, in French. Cited on page: 394.
- [58MIG/SYC] Migal, P. K., Sychev, A. Y., Stability of citric acid complexes of some metals, *Russ. J. Inorg. Chem.*, **3**, (1958), 104-117. Cited on pages: 353, 354, 355, 358, 585.

- [58MOS/GEL] Moskvin, A. I., Gel'man, A. D., Determination of the composition and instability constants of oxalate and carbonate complexes of plutonium(IV), *Russ. J. Inorg. Chem.*, **3**, (1958), 198-216. Cited on pages: 114, 268, 269, 270, 271, 272, 273, 278, 280, 281, 584, 585, 586, 587, 588.
- [58MOS/GEL3] Moskvin, A. I., Gel'man, A. D., Study of the physicochemical properties of aqueous solutions of plutonium(IV) oxalate and determination of its solubility product, *Russ. J. Inorg. Chem.*, **3**, (1958), 188-197. Cited on pages: 268, 269, 270, 272, 273, 280, 281, 584, 585, 586, 588.
- [58SAW/PAU] Sawyer, D. T., Paulsen, P. J., Properties and infrared spectra of ethylenediaminetetraacetic acid complexes. I. Alkaline earth chelates, *J. Am. Chem. Soc.*, **80**, (1958), 1597-1600. Cited on page: 443.
- [58TIL/STA] Tillotson, M. J. L., Staveley, L. A. K., The heats of ionization of ethylenediaminetetra-acetic acid and its dissociation as an ammonium-ion acid, *J. Chem. Soc.*, (1958), 3613-3619. Cited on pages: 402, 428, 432.
- [58YAT/KAR] Yatsimirskii, K. B., Karacheva, G. A., Variation of the entropy in the complex-formation reactions with complexons, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, (1958), 13-21, in Russian. Cited on pages: 431, 437, 456, 457, 588.
- [58YOS/IGU] Yoshino, Y., Iguchi, A., Kojima, M., Mizumachi, K., Solubility of ethylenediaminetetraacetic acid in some aqueous solutions, *Bull. Chem. Soc. Jpn.*, **31**, (1958), 892-893. Cited on pages: 394, 395, 399, 402, 589.
- [59BEC/GOR] Beck, M. T., Görög, S., Water solubility of ethylenediamine- and cyclohexanediamine-tetraacetic acids as a function of acidity, *Chem. Anal. (Warsaw)*, **48**, (1959), 90-91. Cited on pages: 394, 398.
- [59BEC/GOR2] Beck, M. T., Görög, S., Amphoteric properties of ethylenediaminetetraacetic acid and its effect on the stability of its metal complexes, *Magy. Tud. Akad. Kem. Tud. Oszt. Kozl.*, **12**, (1959), 265-277, in Hungarian. Cited on pages: 394, 398.

- [59DRA/GEL] Drabkina, L. E., Gel'man, A. D., Stability of sexivalent plutonium in some aqueous solutions, *Radiokhimiya*, **1**, (1959), 136-140, in Russian. Cited on page: 283.
- [59ERM/BEL2] Ermakov, A. N., Belyaeva, V. K., Marov, I. N., Chmutova, M. K., The use of ion exchange in the study of the composition of complex oxalates of Pu(IV), Zr and Hf, *Russ. J. Inorg. Chem.*, **4**, (1959), 222-224. Cited on pages: 279, 580, 589.
- [59GEL/ART] Gel'man, A. D., Artyukhin, P. I., Moskvina, A. I., A study of complex-formation by pentavalent plutonium in ethylenediaminetetraacetate solutions by means of ion exchange, *Russ. J. Inorg. Chem.*, **4**, (1959), 599-601. Cited on pages: 502, 589.
- [59GEL/MEF] Gel'man, A. D., Mefod'eva, M. P., Complex formation of  $\text{Np}^{4+}$  and  $\text{NpO}_2^+$  with trilon B in aqueous solutions, *Dokl. Phys. Chem.*, **124**, (1959), 69-72. Cited on pages: 491, 492, 493, 589, 590.
- [59GRI/PET] Grinberg, A. A., Petrzhak, G. I., Evteev, L. I., The preparation and properties of uranium-oxalic acid salts with rare earth elements, *Radiokhimiya*, **1**, (1959), 300-308, in Russian. Cited on pages: 207, 210, 590.
- [59IGU/YOS] Iguchi, A., Yoshino, Y., Tsunoda, Y., Solubility of ethylenediamine-tetraacetic acid in some aqueous media, *Sci. Pap. Coll. Gen. Educ. Univ. Tokyo*, **9**, (1959), 23-30. Cited on pages: 394, 395, 399, 402, 589, 591.
- [59KIR/TAN] Kirakosyan, A. K., Tanaev, I. V., Ion exchange in the study of zirconium complexes, *Russ. J. Inorg. Chem.*, **4**, (1959), 387-389. Cited on pages: 205, 591.
- [59KLY/SMI3] Klygin, A. E., Smirnova, I. D., Nikol'skaya, N. A., Solubility in the  $\text{UO}_2(\text{NO}_3)_2$ -ethylenediaminetetraacetic acid - water system, *Russ. J. Inorg. Chem.*, **4**, (1959), 1209-1213. Cited on pages: 398, 476, 477, 484, 486, 592.
- [59KLY/SMI4] Klygin, A. E., Smirnova, I. D., Nikol'skaya, N. A., The solubility of ethylenediaminetetraacetic acid in ammonia and hydrochloric acid and its reaction with uranium(IV) and plutonium(IV), *Russ. J. Inorg. Chem.*, **4**, (1959), 1279-1282. Cited on pages: 394, 399, 478, 481, 573, 592, 617, 666.

- [59LI/LIN] Li, N. C., Lindenbaum, A., White, J. M., Some metal complexes of citric and tricarballic acids, *J. Inorg. Nucl. Chem.*, **12**, (1959), 122-128. Cited on pages: 308, 335, 336, 342, 354, 358, 364, 365, 369, 593, 594, 760.
- [59MOS] Moskvina, A. I., Investigation of the plutonium and americium(III) complex formation in aqueous solutions by the solubility and the ion-exchange methods, *Radiokhimiya*, **1**, (1959), 430-434, in Russian. Cited on page: 274.
- [59MOS/ART] Moskvina, A. I., Artyukhin, P. I., Determination of the composition and instability constants of Pu(III) ethylenediaminetetraacetate complexes by ion-exchange, *Russ. J. Inorg. Chem.*, **4**, (1959), 269-271. Cited on pages: 499, 594, 605.
- [59MOS/ZAK] Moskvina, A. I., Zakharova, F. A., Investigation of the formation of uranyl complexes in oxalate solutions by the solubility method, *Russ. J. Inorg. Chem.*, **4**, (1959), 975-979. Cited on pages: 213, 215, 216, 217, 218, 219, 220, 222, 223, 231, 232, 234, 545, 563, 578, 594, 596.
- [59OKA/KOL] Okáč, A., Kolařík, Z., Potentiometrische Untersuchung der Zitratkomplexe des Zinks, *Collect. Czech. Chem. Commun.*, **24**, (1959), 1-8, in German. Cited on pages: 310, 322, 675.
- [59PET/WIE] Peters, H., Wiedemann, H.-G., Untersuchung des thermischen Zerfalls von Calciumoxalat und Calciumcarbonat auf einer Thermowaage hoher Genauigkeit, *Z. Anorg. Allg. Chem.*, **300**, (1959), 142-151, in German. Cited on pages: 164, 165.
- [59PTI/TEK] Ptitsyn, B. V., Tekster, E. N., Determination of the instability constants of complex uranyl oxalates by the displaced equilibrium method, *Russ. J. Inorg. Chem.*, **4**, (1959), 1024-1027. Cited on pages: 231, 232, 234, 596.
- [59ROB/STO] Robinson, R. A., Stokes, R. H., *Electrolyte solutions*, 2nd. Edition, Butterworths, London, (1959, revised 1970), 571 pp. Cited on pages: 99, 102, 802, 825.

- [59SAW/PAU] Sawyer, D. T., Paulsen, P. J., Properties and infrared spectra of ethylenediaminetetraacetic acid complexes. II. Chelates of divalent ions, *J. Am. Chem. Soc.*, **81**, (1959), 816-820. Cited on page: 460.
- [59SMI] Smith, T. D., The effect of fluoride ion on the co-ordination of uranium(IV) by ethylenediaminetetraacetic acid, *J. Inorg. Nucl. Chem.*, **11**, (1959), 314-319. Cited on pages: 480, 482, 597.
- [59SMI/HOA] Smith, G. S., Hoard, J. L., The structure of dihydrogen ethylenediaminetetraacetatoaquonickel(II), *J. Am. Chem. Soc.*, **81**, (1959), 556-561. Cited on page: 460.
- [59TEK/VIN2] Tekster, E. N., Vinogradova, L. I., Ptitsyn, B. V., Determination of instability constants of magnesium and uranyl complex oxalates using a silver oxalate electrode, *Russ. J. Inorg. Chem.*, **4**, (1959), 347-349. Cited on pages: 179, 181, 241, 242, 569, 597, 813.
- [59VIN/GET] Vinogradova, L. I., Getskina, L. L., Ustinskaya, V. I., The solubility of silver citrate in potassium citrate solutions, *Russ. J. Inorg. Chem.*, **4**, (1959), 1308-1309. Cited on page: 301.
- [59VOR] Voříšek, J., Über die Magnesiumkomplexe der Äthylendiamintetraessigsäure, *Collect. Czech. Chem. Commun.*, **24**, (1959), 3921-3925, in German. Cited on page: 443.
- [59YAT/KAR] Yatsimirskii, K. B., Karacheva, G. A., The influence of ionic strength on the heat of reaction in the formation of the complexes of calcium and nickel, *Russ. J. Inorg. Chem.*, **4**, (1959), 127-130. Cited on pages: 456, 457, 468, 469, 598.
- [60ADA/SMI] Adams, A., Smith, T. D., The formation and photochemical oxidation of uranium(IV) citrate complexes, *J. Chem. Soc.*, (1960), 4846-4850. Cited on pages: 361, 362, 363, 598.
- [60ALE/ZHD] Alekperov, A. I., Zhdanov, S. I., Influence of anions on the reduction of uranyl ions at the dropping mercury electrode, *Russ. J. Inorg. Chem.*, **5**, (1960), 846-848. Cited on pages: 225, 228, 229, 599.
- [60BAB/DUB] Babko, A. K., Dubovenko, L. I., Zirconium oxalate complexes, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **3**, (1960), 226-234, in Russian. Cited on pages: 205, 206, 599.

- [60BEC/GOR] Beck, M. T., Görög, S., Amphoteric properties of ethylenediaminetetraacetic acid and the stability of its metal complexes, *Acta Chim. Acad. Sci. Hung.*, **22**, (1960), 159-171. Cited on pages: 394, 398, 646.
- [60BOH/MAR] Bohigian, Jr., T. A., Martell, A. E., Chelation and olation reactions of aqueous metal ions. Part III. Thermodynamics of metal chelate formation, US Atom. Energ. Comm. Contract, Report AT (30-1)-1823, (1960). Cited on pages: 399, 445, 446, 449, 455, 456, 457, 566, 600.
- [60BOU/MAR] Boulet, M., Marier, J. R., Solubility of tricalcium citrate in solutions of variable ionic strength and in milk ultrafiltrates, *J. Dairy Sci.*, **43**, (1960), 155-164. Cited on pages: 350, 600, 601.
- [60FEL/NOR] Feldman, I., North, C. A., Hunter, H. B., Equilibrium constants for the formation of polynuclear tridentate 1:1 chelates in uranyl-malate, -citrate and -tartrate systems, *J. Phys. Chem.*, **64**, (1960), 1224-1230. Cited on pages: 364, 365, 366, 369, 594, 601, 703.
- [60GRI/PET] Grinberg, A. A., Petrzhak, G. I., Evteev, L. I., Instability constants of the complex oxalates of uranium, *Radiokhimiya*, **2**, (1960), 505-506, in Russian. Cited on pages: 225, 226, 601, 623.
- [60KON/GEL] Kondratova, P. I., Gel'man, A. D., Oxalate compounds of quadrivalent neptunium, *Radiokhimiya*, **2**, (1960), 315-319, in Russian. Cited on pages: 246, 247, 248, 250, 251, 602, 603.
- [60KOZ/KRO] Kozlov, A. G., Krot, N. N., Spectrophotometric study of complex formation between the uranyl ion and ethylenediaminetetraacetic acid, *Russ. J. Inorg. Chem.*, **5**, (1960), 954-957. Cited on pages: 484, 485, 486, 603.
- [60LEB/PIR] Lebedev, I. A., Pirozhkov, S. V., Yakovlev, G. N., Determination of the composition and the instability constants of oxalate, nitrate and sulfate complexes of Am(III) and Cm(III) by the method of ion exchange, *Sov. Radiochem.*, **2**, (1960), 39-47. Cited on pages: 286, 603, 691.

- [60LEB/PIR2] Lebedev, I. A., Pirozhkov, S. V., Razbitnoi, V. M., Yakovlev, G. N., Studies on complex formation between  $\text{Am}^{3+}$  and oxalate ions, *Sov. Radiochem.*, **2**, (1960), 89-94. Cited on pages: 284, 285, 286, 287, 604, 718, 757.
- [60MAT/SAF] Matorina, N. N., Safonova, N. D., An ion-exchange study of ethylenediaminetetraacetate complexes of the alkaline-earth elements, *Russ. J. Inorg. Chem.*, **5**, (1960), 151-155. Cited on pages: 446, 447, 449, 604, 605.
- [60MCA/NAN] McAuley, A., Nancollas, G. H., Complex formation in solutions of copper oxalate, *Trans. Faraday Soc.*, **56**, (1960), 1165-1171. Cited on pages: 116, 129.
- [60MOS/KHA] Moskvina, A. I., Khalturin, G. V., Gel'man, A. D., Investigation of the complexing of trivalent americium in oxalate and ethylenediaminetetraacetate solutions by the ion-exchange method, *Sov. Radiochem.*, **1**, (1960), 69-76. Cited on pages: 286, 287, 504, 505, 605.
- [60OLS/MAR] Olson, D. C., Margerum, D. W., Ionization of ethylenediaminetetraacetic acid and its acid salts, *J. Am. Chem. Soc.*, **82**, (1960), 5602-5605. Cited on page: 402.
- [60PAL/UDA] Palei, P. N., Udaltsova, N. I., Solubility of ethylenediaminetetraacetic acid in water and solutions of hydrochloric acid, and sodium and potassium chlorides, *Russ. J. Inorg. Chem.*, **5**, (1960), 1121-1123. Cited on page: 394.
- [60RAA] Raaflaub, J., Untersuchungen über die Magnesiumkomplexverbindungen von Oxalat und Carbonat, *Helv. Chim. Acta*, **43**, (1960), 629-634, in German. Cited on pages: 178, 182, 183, 606, 779.
- [60RYA/ERM] Ryabchikov, D. I., Ermakov, A. N., Belyaeva, V. K., Marov, I. N., Zirconium and hafnium complexes with some hydroxy acids, *Russ. J. Inorg. Chem.*, **5**, (1960), 505-513. Cited on pages: 362, 606, 632.
- [60SCH/FIS] Schwarzenbach, G., Fischer, A., Die Acidität der Sulfane und die Zusammensetzung wässriger Polysulfidlösungen, *Helv. Chim. Acta*, **43**, (1960), 1365-1391, in German. Cited on page: 115.

- [60SOK/GEL] Sokhina, L. P., Gel'man, A. D., Decomposition of oxalato complexes of plutonium by  $\alpha$ -radiation, *Russ. J. Inorg. Chem.*, **5**, (1960), 487-488. Cited on page: 262.
- [60STA3] Starý, J., Bestimmung der Zusammensetzung und der Stabilitätskonstanten von Metallkomplexen durch Extraktionsmethode, *Collect. Czech. Chem. Commun.*, **25**, (1960), 2630-2640, in German. Cited on pages: 232, 235, 236, 237, 239, 484, 486, 607, 608, 624.
- [60WAT/DEW] Watters, J. I., DeWitt, R., The complexes of nickel(II) ion in aqueous solutions containing oxalate ion and ethylenediamine, *J. Am. Chem. Soc.*, **82**, (1960), 1333-1339. Cited on pages: 194, 195, 196, 199, 609, 765.
- [60YAM/DAV] Yamane, T., Davidson, N., Complexes of mercury(I) with polyphosphate and dicarboxylate anions and mercury(II) pyrophosphate complexes, *J. Am. Chem. Soc.*, **82**, (1960), 2123-2129. Cited on page: 114.
- [60ZAK/MOS] Zakharova, F. A., Moskvina, A. I., The solubility product of uranium(IV) oxalate and the composition and dissociation constants of oxalato-uranium(IV) complexes in aqueous solution, *Russ. J. Inorg. Chem.*, **5**, (1960), 592-595. Cited on pages: 207, 208, 209, 210, 225, 226, 568, 579, 609.
- [61BAB/SHT] Babko, A. K., Shtokalo, M. I., Formation and relative stability of some Zr complexes by the metal-indicator method, *Ukr. Khim. Zh. (Russ. Ed.)*, **27**, (1961), 566-574, in Russian. Cited on pages: 205, 610, 659.
- [61BAR/BEC] Barthel, J., Becker, F., Schmahl, N. G., Untersuchungen über die Grundlagen der thermometrischen Titration, *Z. Phys. Chem. (Munich)*, **29**, (1961), 58-76, in German. Cited on pages: 326, 327, 611.
- [61CHE/GOL] Chernyaev, I. I., Golovnya, V. A., Shchelokov, R. N., Carbonato-oxalatoaquo complexes of uranyl [dioxocarbonato-oxalato-diaquouranates], *Russ. J. Inorg. Chem.*, **6**, (1961), 280-283. Cited on pages: 242, 244, 245, 611.



- [61GRI/AST] Grinberg, A. A., Astapovich, V. I., Complex zirconium oxalates, *Russ. J. Inorg. Chem.*, **6**, (1961), 164-167. Cited on pages: 114, 205, 206, 611.
- [61ISH/YOK] Ishibashi, S., Yokoyama, H., Makioka, K., Nickel citrate complex in aqueous solution, *J. Chem. Soc. Jpn.*, **82**, (1961), 442-447, in Japanese. Cited on pages: 354, 358, 612, 760.
- [61KAB] Kabanova, O. L., Plutonium(V) complexes with ethylenediamine-tetra-acetic acid, *Russ. J. Inorg. Chem.*, **6**, (1961), 401-403. Cited on pages: 502, 612.
- [61LEW/RAN] Lewis, G. N., Randall, M., *Thermodynamics, as revised by Pitzer, K. S. and Brewer, L.*, 2nd. Edition, McGraw-Hill, New York, (1961), 723 pp. Cited on pages: 820, 822, 825, 827.
- [61LI/TAN] Li, N. C., Tang, P., Mathur, R., Deuterium isotope effects on dissociation constants and formation constants, *J. Phys. Chem.*, **65**, (1961), 1074-1076. Cited on page: 308.
- [61MAN/FRA] Mandleberg, C. J., Francis, K. E., Smith, R., The solubility of plutonium trifluoride, plutonium tetrafluoride, and plutonium(IV) oxalate in nitric acid mixtures, *J. Chem. Soc.*, (1961), 2464-2468. Cited on pages: 263, 269, 653.
- [61MCA/NAN] McAuley, A., Nancollas, G. H., Thermodynamics of ion association. Part VII. Some transition-metal oxalates, *J. Chem. Soc.*, (1961), 2215-2221. Cited on pages: 115, 116, 143, 145, 194, 197, 199, 200, 607, 612, 613, 670, 682, 770.
- [61MOS/MAR] Moskvina, A. I., Marov, I. N., Zolotov, Y. A., Neptunium(V) complexes with citric and tartaric acids, *Russ. J. Inorg. Chem.*, **6**, (1961), 926-929. Cited on pages: 374, 375, 614.
- [61PAL/HSU] Palei, P. N., Hsü, L. Y., Complex formation between uranium(IV) and complexone-III, *Russ. J. Inorg. Chem.*, **6**, (1961), 1337-1340. Cited on page: 478.
- [61PAT/PAN] Patnaik, R. K., Pani, S., Studies on the citrate complex of calcium, *J. Indian Chem. Soc.*, **38**, (1961), 229-232. Cited on pages: 337, 342, 614.

- [61ROS/ROS] Rossotti, F. J. C., Rossotti, H., *The determination of stability constants and other equilibrium constants in solution*, McGraw-Hill, New York, (1961). Cited on pages: 24, 849.
- [61SIM] Simpson, R. B., Association constants of methylmercury with sulfhydryl and other bases, *J. Am. Chem. Soc.*, **83**, (1961), 4711-4717. Cited on page: 398.
- [61STA/PRA] Starý, J., Prášilová, J., Extraction and ion exchange investigation of uranium(VI) chelates, *J. Inorg. Nucl. Chem.*, **17**, (1961), 361-365. Cited on pages: 484, 486, 614.
- [61WAL] Walser, M., Ion association. V. Dissociation constants for complexes of citrate with sodium, potassium, calcium, and magnesium ions, *J. Phys. Chem.*, **65**, (1961), 159-161. Cited on pages: 332, 335, 337, 342, 615.
- [61ZOL/MAR2] Zolotov, Y. A., Marov, I. N., Moskvina, A. I., Complexes of pentavalent neptunium in oxalic and ethylenediaminetetra-acetic acid solutions, *Russ. J. Inorg. Chem.*, **6**, (1961), 539-543. Cited on pages: 114, 254, 255, 256, 492, 493, 615, 626.
- [62ASA/MOR] Asai, H., Morales, M., Application of interferometry to myosin ATPase and ion binding, *Arch. Biochem. Biophys.*, **99**, (1962), 383-389. Cited on pages: 178, 181, 616.
- [62AXT/HAN] Axt, H., Hansen, H.-J., Sansoni, B., Darstellung von Komplexsalzen durch doppelte Umsetzung mit Kationenaustauschern, *Angew. Chem.*, **74**, (1962), 466-467, in German. Cited on page: 460.
- [62BAE/BEN] Baetslé, L., Bengsch, E., Ion-exchange characteristics of the radium-ethylenediaminetetraacetate complex, *J. Chromatogr., A*, **8**, (1962), 265-273. Cited on page: 398.
- [62BRU/KAI] De Bruin, H. J., Kairaitis, D., Temple, R. B., The extraction of anionic beryllium complexes by tri-iso-octylamine, *Aust. J. Chem.*, **15**, (1962), 457-466. Cited on page: 114.
- [62DAV] Davies, C. W., *Ion association*, Butterworths, London, (1962), 190 pp. Cited on page: 820.

- [62EVA/HOA] Evans, D. M., Hoare, F. E., Melia, T. P., Heat capacity, enthalpy and entropy of citric acid monohydrate, *Trans. Faraday Soc.*, **58**, (1962), 1511-1514. Cited on page: 303.
- [62FUR/CER] Furlani, C., Cervone, E., Constanti di stabilità dei complessi zinco-citrato, zinco-tartrato, cadmio citrato e cadmio tartrato, *Ann. Chim. (Rome)*, **52**, (1962), 564-572, in Italian. Cited on page: 310.
- [62ISH/NAK] Ishimori, T., Nakamura, E., Some complex compounds of neptunium(IV) and related ions, *Radiochim. Acta*, **1**, (1962), 6-11. Cited on pages: 250, 251, 491, 617.
- [62KRO/ERM] Krot, N. N., Ermolaev, N. P., Gel'man, A. D., The behaviour of ethylenediaminetetraacetic acid in acid solutions and its reaction with uranium(IV), *Russ. J. Inorg. Chem.*, **7**, (1962), 1062-1066. Cited on pages: 394, 395, 399, 402, 478, 479, 481, 482, 483, 573, 617, 618, 687.
- [62LEB/PIR2] Lebedev, I. A., Pirozhkov, S. V., Razbitnoi, V. M., Yakovlev, G. N., Investigation of the decomposition of americium oxalate under the action of its own  $\alpha$ -radiation, *Sov. Radiochem.*, **4**, (1962), 276-279. Cited on pages: 284, 619.
- [62MAR/RYA2] Marov, I. N., Ryabchikov, D. I., Complex formation of Zr(IV) and Hf(IV) with chloride, nitrate, and oxalate ions, *Russ. J. Inorg. Chem.*, **7**, (1962), 533-539. Cited on pages: 205, 619, 632.
- [62MCD/LON] McDougall, A. O., Long, F. A., Relative hydrogen bonding of deuterium. II. Acid ionization constants in H<sub>2</sub>O and D<sub>2</sub>O, *J. Phys. Chem.*, **66**, (1962), 429-433. Cited on page: 114.
- [62RYA/MAR] Ryabchikov, D. I., Marov, I. N., Yao, K.-M., Citrato-complexes of indium, *Russ. J. Inorg. Chem.*, **7**, (1962), 1415-1420. Cited on page: 308.
- [62SHV/MAS2] Shvedov, V. P., Maslov, E. I., Determination of the composition and stability constants of complex compounds by electromigration. I. Determination of the composition and stability constants of oxalate complexes of zirconium, *Sov. Radiochem.*, **4**, (1962), 376-381. Cited on pages: 205, 206, 619.

- [62STA/BAL] Starý, J., Balek, V., Untersuchung der Uran(VI)-Komplexe mit  $\alpha$ -Hydroxysäuren durch Extraktionsmethode, *Collect. Czech. Chem. Commun.*, **27**, (1962), 809-815, in German. Cited on pages: 365, 368, 620.
- [62VAS] Vasil'ev, V. P., Influence of ionic strength on the instability constants of complexes, *Russ. J. Inorg. Chem.*, **7**, (1962), 924-927. Cited on page: 821.
- [62ZAI/BOC3] Zaitsev, L. M., Bochkarev, G. S., Peculiarities in the behaviour of zirconyl in solutions, *Russ. J. Inorg. Chem.*, **7**, (1962), 411-414. Cited on pages: 203, 621.
- [63AND] Anderegg, G., Komplexe XXXIII. Reaktionsenthalpie und -entropie bei der Bildung der Metallkomplexe von Äthylendiamin- und Diaminocyclohexan-tetraessigsäure, *Helv. Chim. Acta*, **46**, (1963), 1833-1842, in German. Cited on pages: 428, 432, 455, 456, 458, 459, 468, 469, 621, 635, 639.
- [63BHA/KRI] Bhat, T. R., Krishnamurthy, M., Spectrophotometric studies on protonated, anion and hydroxo complexes of copper(II), nickel(II) and cobalt(II) versenates, *J. Inorg. Nucl. Chem.*, **25**, (1963), 1147-1154. Cited on pages: 462, 463, 466, 621.
- [63BRE/CLA2] Bressat, R., Claudel, B., Trambouze, Y., Etude de la décomposition thermique des oxalates d'uranyle et d'uranium(IV), *Bull. Soc. Chim. Fr.*, (1963), 464-470, in French. Cited on pages: 207, 214.
- [63CHA] Chackraburttty, D. M., X-ray evidence of plutonium(III) oxalate decahydrate, *Acta Crystallogr.*, **16**, (1963), 834. Cited on pages: 262, 263.
- [63ERM/KRO] Ermolaev, N. P., Krot, N. N., Complex formation between uranium(IV) and ethylenediaminetetraacetic acid, *Russ. J. Inorg. Chem.*, **8**, (1963), 1282-1289. Cited on pages: 475, 476, 478, 479, 480, 482, 622.
- [63FRI/VER] Fridman, Y. D., Veresova, R. A., Dolgashova, N. V., Sorochan, R. I., Formation of mixed metal oxalato-complexes in ethylenediamine solution, *Russ. J. Inorg. Chem.*, **8**, (1963), 344-348. Cited on pages: 195, 196, 622.

- [63FUR/GIU] Furlani Donda, A., Giuliani, A. M., Studio dei processi elettrodici di alcuni complessi del piombo col metodo galvanostatico, *Ric. Sci.*, **3**, (1963), 819-836, in Italian. Cited on pages: 308, 398.
- [63GRI/HUG] Grimes, J. H., Huggard, A. J., Wilford, S. P., The stabilities of the alkaline earth chelates of some polyaminopolycarboxylic acids, *J. Inorg. Nucl. Chem.*, **25**, (1963), 1225-1238. Cited on pages: 399, 402, 446, 450, 451, 622.
- [63GRI/PET] Grinberg, A. A., Petrzhak, G. I., Supplementary data on the solubility of the oxalate of quadrivalent uranium, *Sov. Radiochem.*, **5**, (1963), 289-297, in Russian. Cited on pages: 207, 208, 209, 210, 568, 580, 584, 602, 623.
- [63JEZ] Jezowska-Trzebiatowska, B., Structure électronique de l'uranium dans ses composés tri- et tétra-valents, *J. Ch. Phys.*, **60**, (1963), 843-848, in French. Cited on page: 225.
- [63KYR/CAL] Kyrš, M., Caletka, R., The stability constant of the complex of  $Zr^{IV}$  with edta, *Talanta*, **10**, (1963), 1115-1116. Cited on pages: 472, 473, 623.
- [63MAT] Matsushima, Y., Determination of complex stability constants by ion exchange method. (Extension of Schubert's method to lower pH region), *Chem. Pharm. Bull.*, **11**, (1963), 566-570. Cited on pages: 308, 337, 339, 342, 623.
- [63PAL] Palaty, V., Sodium chelates of ethylenediaminetetraacetic acid, *Can. J. Chem.*, **41**, (1963), 18-20. Cited on pages: 398, 438.
- [63PAR/BAR] Paramonova, V. I., Bartenev, S. A., Formation of iron(III) complexes in oxalate solutions, *Russ. J. Inorg. Chem.*, **8**, (1963), 157-161. Cited on page: 114.
- [63STA] Starý, J., Systematic study of the solvent extraction of metal oxinates, *Anal. Chim. Acta*, **28**, (1963), 132-149. Cited on pages: 114, 167, 169, 178, 181, 195, 196, 461, 466, 624.
- [63TAN/TER] Tananaev, I. V., Terëshin, G. S., Complex formation by yttrium with ethylenediaminetetraacetic acid, *Russ. J. Inorg. Chem.*, **8**, (1963), 1182-1189. Cited on pages: 394, 399, 624.

- [63TOB/MIL] Tobia, S. K., Milad, N. E., Ion-exchange study of the stability and composition of magnesium citrate complex, *J. Chem. Soc.*, (1963), 734-736. Cited on pages: 335, 342, 625.
- [63WAT/TRO] Watanabe, S., Trosper, T., Lynn, M., Evenson, L., The magnesium binding constants of adenosinetriphosphate and some other compounds estimated by the use of fluorescence of magnesium-8-hydroxyquinoline, *J. Biochem.*, **54**, (1963), 17-24. Cited on pages: 178, 181, 335, 625.
- [63WHI/BEM] Whistler, R. L., BeMiller, J. N., "α"-D-isosaccharino-1,4-lactone. Action of lime water on lactose, in: *Methods in carbohydrate chemistry. Vol.II: Reactions of carbohydrates*, Whistler, R. L., Wolfrom, M. L., BeMiller, J. N., Eds, Academic Press, New York, (1963), pp. 477-479. Cited on page: 512.
- [63ZOL/ALI] Zolotov, Y. A., Alimarin, I. P., Investigation of the chemistry of pentavalent neptunium, *J. Inorg. Nucl. Chem.*, **25**, (1963), 691-696. Cited on pages: 254, 255, 256, 493, 626.
- [64AND] Anderegg, G., Komplexe XXXVI. Reaktionsenthalpie und -entropie bei der Bildung der Metallkomplexe der höheren EDTA-Homologen, *Helv. Chim. Acta*, **47**, (1964), 1801-1814, in German. Cited on pages: 428, 432.
- [64BAN/SHA] Bansal, B. M. L., Sharma, H. D., Oxalato complexes of neptunium(IV), *J. Inorg. Nucl. Chem.*, **26**, (1964), 799-805. Cited on pages: 246, 247, 248, 250, 251, 252, 626, 627, 628.
- [64BAS/KRI] Baskin, Y., Krishna Prasad, N. S., Crystalline ammonium uranyl peroxy-oxalate, *J. Inorg. Nucl. Chem.*, **26**, (1964), 1385-1390. Cited on page: 213.
- [64BHA/KRI] Bhat, T. R., Krishnamurthy, M., Studies on edta complexes-II Uranyl-edta system, *J. Inorg. Nucl. Chem.*, **26**, (1964), 587-594. Cited on pages: 477, 484, 485, 486, 629, 746, 800.
- [64BRE/CLA] Bressat, R., Claudel, B., Trambouze, Y., Relations structurales entre l'oxalate d'uranyle et ses hydrates, *J. Chem. Phys.*, **61**, (1964), 816-818, in French. Cited on page: 213.

- [64CAL] Caletka, R., *Chemie vodných roztoků zirkonia*, *Chem. Listy*, **58**, (1964), 349-376, in Czech. Cited on pages: 205, 629.
- [64CAL/KYR] Caletka, R., Kyrš, M., Rais, J., Sorption of zirconium by silica gel from nitrate medium in the presence of oxalic acid, EDTA and arsenazo I, *J. Inorg. Nucl. Chem.*, **26**, (1964), 1443-1453. Cited on pages: 205, 473, 474, 623, 629.
- [64CAM/OST] Campi, E., Ostacoli, G., Meirone, M., Saini, G., Stability of the complexes of tricarballic and citric acids with bivalent metal ions in aqueous solution, *J. Inorg. Nucl. Chem.*, **26**, (1964), 553-564. Cited on pages: 310, 335, 336, 337, 339, 340, 342, 343, 344, 354, 355, 359, 630, 667, 760.
- [64DAV] David, D. J., Determination of specific heat and heat of fusion by differential thermal analysis, *Anal. Chem.*, **36**, (1964), 2162-2166. Cited on page: 108.
- [64GEL/ZAI] Gel'man, A. D., Zaitseva, V. P., On the preparation of certain Pu(V) compounds, *Proc. Acad. Sci. USSR Chem. Sect. (Doklady Chemistry)*, **157**, (1964), 805-807. Cited on pages: 263, 273.
- [64HAA] Haas, D. J., The crystal structure of potassium tetraoxalate,  $K(HC_2O_4)(H_2C_2O_4) \cdot 2H_2O$ , *Acta Crystallogr.*, **17**, (1964), 1511-1516. Cited on pages: 153, 154.
- [64HOC/GER] Hocart, R., Gérard, N., Watelle-Marion, G., Sur la pyrolyse des oxalates de calcium hydratés, *C. R. Hebd. Séances Acad. Sci.*, **258**, (1964), 3709-3712, in French. Cited on pages: 165, 166.
- [64INT/MAR] Intorre, B. J., Martell, A. E., Zirconium complexes in aqueous solution. III. Estimation of formation constants, *Inorg. Chem.*, **3**, (1964), 81-87. Cited on pages: 472, 473, 474, 630, 631, 654, 722.
- [64KHA/BOC2] Kharitonov, Y. Y., Bochkarev, G. S., Zaitsev, L. M., Infrared absorption spectra of oxalato-complexes of zirconium(IV), *Russ. J. Inorg. Chem.*, **9**, (1964), 745-752. Cited on pages: 204, 631.
- [64KHA/ZAI2] Kharitonov, Y. Y., Zaitsev, L. M., Bochkarev, G. S., Evstaf'eva, O. N., Infrared absorption spectra of complexes of zirconium(IV) with some ligands containing oxygen, *Russ. J. Inorg. Chem.*, **9**, (1964), 876-879. Cited on pages: 204, 631.

- [64PAN/VLA] Pankratova, L. N., Vlasov, L. G., Lapitskii, A. V., The reaction of zirconium with certain complexones, *Russ. J. Inorg. Chem.*, **9**, (1964), 954-956. Cited on pages: 472, 631.
- [64POR] Porter, J. A., Production of neptunium dioxide, *Ind. Eng. Chem. Process Design Develop.*, **3**, (1964), 289-292. Cited on pages: 246, 247, 632.
- [64REC/ZAM] Rechnitz, G. A., Zamochnick, S. B., Application of cation-sensitive glass electrodes to the study of alkali metal complexes-II: Use of a potential comparison method, *Talanta*, **11**, (1964), 1061-1065. Cited on pages: 332, 334.
- [64RYA/MAR] Ryabchikov, D. I., Marov, I. N., Ermakov, A. N., Belyaeva, V. K., Stability of some inorganic and organic complex compounds of zirconium and hafnium, *J. Inorg. Nucl. Chem.*, **26**, (1964), 965-980. Cited on pages: 205, 362, 632.
- [64SEK] Sekine, T., Complex formation of La(III), Eu(III), Lu(III) and Am(III) with oxalate, sulphate, chloride and thiocyanate ions, *J. Inorg. Nucl. Chem.*, **26**, (1964), 1463-1465. Cited on pages: 114, 286, 287, 632.
- [64SIL/MAR] Sillén, L. G., Martell, A. E., *Stability constants of metal ion complexes, Special Publication*, No. 17, Chemical Society, London, (1964), 754 pp. Cited on pages: 15, 16, 449, 735.
- [64SIM/NEW] Simons, E. L., Newkirk, A. E., New studies on calcium oxalate monohydrate. A guide to the interpretation of thermogravimetric measurements, *Talanta*, **11**, (1964), 549-571. Cited on page: 165.
- [64TIM] Timberlake, C. F., Iron-malate and iron-citrate complexes, *J. Chem. Soc.*, (1964), 5078-5085. Cited on page: 310.
- [64TOB/MIL] Tobia, S. K., Milad, N. E., Ion-exchange study of the magnesium citrate complex. Effect of ionic strength, temperature, and pH, *J. Chem. Soc.*, (1964), 1915-1918. Cited on pages: 335, 342, 632.
- [64WAL/LAN] Walter-Lévy, L., Laniepce, J., Sur la thermolyse des hydrates de l'oxalate de calcium, *C. R. Hebd. Séances Acad. Sci.*, **259**, (1964), 4685-4688, in French. Cited on page: 165.



- [64WIL/SHI] Wilhoit, R. C., Shiao, D., Thermochemistry of biologically important compounds. Heats of combustion of solid organic acids, *J. Chem. Eng. Data*, **9**, (1964), 595-599. Cited on pages: 107, 110, 304.
- [64YEN/LIU] Yen, C. H., Liu, S. C., Mercury electrode in the study of complexes. I. Stability constants of EDTA chelates of bivalent metals, *Acta Chem. Sin.*, **30**, (1964), 546-556, in Chinese, abstract in English. Cited on pages: 445, 446, 450, 451, 452, 633.
- [64ZAI2] Zaitsev, L. M., Zirconyl oxalate and its derivatives, *Russ. J. Inorg. Chem.*, **9**, (1964), 1279-1286. Cited on pages: 203, 633.
- [64ZAI3] Zaitsev, L. M., The behaviour of the oxalato-group in complex compounds, *Russ. J. Inorg. Chem.*, **9**, (1964), 1286-1288. Cited on pages: 203, 633.
- [64ZAI/BOC2] Zaitsev, L. M., Bochkarev, G. S., Solubility product of zirconium oxide oxalate, *Russ. J. Inorg. Chem.*, **9**, (1964), 1147-1148. Cited on pages: 204, 633.
- [65BAU/SMI] Bauer, R. F., Smith, W. M., The mono-oxalato complexes of iron(III). Part I. Equilibria, *Can. J. Chem.*, **43**, (1965), 2755-2762. Cited on pages: 116, 129.
- [65BHA/RAD] Bhat, T. R., Radhamma, D., Shankar, J., Studies on edta complexes-VI. Mixed complexes of copper (II), nickel (II) and cobalt (II) versenates with pyridine, hydrazine, hydroxylamine, ethylenediamine and propylenediamine, *J. Inorg. Nucl. Chem.*, **27**, (1965), 2641-2651. Cited on pages: 463, 634.
- [65BOT/CHA] Botts, J., Chashin, A., Young, H. L., Alkali metal binding by ethylenediaminetetraacetate, adenosine 5'-triphosphate, and pyrophosphate, *Biochemistry*, **4**, (1965), 1788-1796. Cited on pages: 398, 438, 441.
- [65BOT/CIA] Bottari, E., Ciavatta, L., Potentiometric study of Fe(II) oxalate complexes, *Gazz. Chim. Ital.*, **95**, (1965), 908-920, in Italian. Cited on pages: 116, 129.

- [65FUG/CUN] Fuger, J., Cunningham, B. B., Microcalorimetric determination of the enthalpy of formation of the complex ions of trivalent plutonium, americium and lanthanum with edta, *J. Inorg. Nucl. Chem.*, **27**, (1965), 1079-1084. Cited on pages: 503, 508, 509, 635, 762.
- [65GER/WAT] Gérard, N., Watelle-Marion, G., Diagramme pression-température de  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  et des deux variétés polymorphiques de  $\text{CaC}_2\text{O}_4$ , *C. R. Hebd. Séances Acad. Sci.*, **261**, (1965), 2363-2366, in French. Cited on page: 165.
- [65HOC/WAT] Hocart, R., Watelle-Marion, G., Thrierr-Sorel, A., Gérard, N., Nature topotactique de la déshydratation de  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , *C. R. Hebd. Séances Acad. Sci.*, **260**, (1965), 2509-2511, in French. Cited on page: 165.
- [65JEN/MOO] Jenkins, I. L., Moore, F. H., Waterman, M. J., X-ray powder crystallographic data on plutonium and other oxalates - I. The oxalates of plutonium(III) and plutonium(VI) and their isomorphs, *J. Inorg. Nucl. Chem.*, **27**, (1965), 77-80. Cited on pages: 262, 263.
- [65JEN/MOO2] Jenkins, I. L., Moore, F. H., Waterman, M. J., X-ray powder crystallographic data on plutonium and other oxalates - II. Plutonium(IV) oxalate dihydrate, uranium(IV) oxalate hexahydrate, uranium(IV) oxalate dihydrate and thorium oxalate dihydrate, *J. Inorg. Nucl. Chem.*, **27**, (1965), 81-87. Cited on pages: 263, 268.
- [65JOK/MAJ] Jokl, V., Majer, J., Studium komplexních sloučenin v roztoku pomocí elektroforézy na papíře (IV). Komplexy kyseliny 1,3-diaminopropanol(2)-N, N, N', N'-tetraoctové, *Chem. Zvesti*, **19**, (1965), 249-258, in Slovak. Cited on pages: 445, 446, 449, 461, 466, 635.
- [65MOE/MAR] Moeller, T., Martin, D. F., Thompson, L. C., Ferrus, R., Feistel, G. R., Randall, W. J., The coordination chemistry of yttrium and the rare earth metal ions, *Chem. Rev.*, **65**, (1965), 1-50. Cited on page: 676.
- [65NAG/UMA] Nagata, K., Umayahara, A., Tsuchiya, R., Formation constants of chromium(III)-oxalato complexes, *Bull. Chem. Soc. Jpn.*, **38**, (1965), 1059-1061. Cited on pages: 116, 129.

- [65OGI] Ogino, H., The stability constant of ethylenediaminetetraacetato, trimethylenediaminetetraacetato and propylenediaminetetraacetato complexes of some divalent metal ions, *Bull. Chem. Soc. Jpn.*, **38**, (1965), 771-777. Cited on pages: 461, 466, 635, 636.
- [65PAT/PAN] Patnaik, R. K., Pani, S., Studies on the citrate complexes of magnesium and barium, *J. Indian Chem. Soc.*, **42**, (1965), 527-530. Cited on pages: 335, 342, 353, 636.
- [65PAT/PAN2] Patnaik, R. K., Pani, S., Studies on the citrate complex of nickel by solubility, pH-titration, and conductometric titration methods, *J. Indian Chem. Soc.*, **42**, (1965), 793-798. Cited on pages: 322, 353, 354, 355, 358, 636.
- [65PRI/SEB] Priestley, P. T., Sebborn, W. S., Selman, R. F. W., Continuous-flow enthalpimetry, *Analyst (Cambridge U.K.)*, **90**, (1965), 589-593. Cited on pages: 437, 439, 455, 456, 457, 468, 469, 636.
- [65RAJ/MAR] Rajan, K. S., Martell, A. E., Equilibrium studies of uranyl complexes. III. Interaction of uranyl ion with citric acid, *Inorg. Chem.*, **4**, (1965), 462-469. Cited on pages: 310, 364, 365, 366, 369, 594, 636, 637, 703, 805.
- [65SEK] Sekine, T., Solvent extraction study of trivalent actinide and lanthanide complexes in aqueous solutions. I. Chloride complexes of La(III), Eu(III), Lu(III), and Am(III) in 4 M Na(ClO<sub>4</sub>), *Acta Chem. Scand.*, **19**, (1965), 1435-1444. Cited on page: 632.
- [65SEK2] Sekine, T., Solvent extraction study of trivalent actinide and lanthanide complexes in aqueous solutions. II. Sulfate complexes of La(III), Eu(III), Lu(III), and Am(III) in 1 M Na(ClO<sub>4</sub>), *Acta Chem. Scand.*, **19**, (1965), 1469-1475. Cited on page: 632.
- [65SEK3] Sekine, T., Solvent extraction study of trivalent actinide and lanthanide complexes in aqueous solutions. IV. Thiocyanate complexes of La(III), Eu(III), Lu(III), and Am(III) in 5 M Na(ClO<sub>4</sub>) solutions at 25°C, *Acta Chem. Scand.*, **19**, (1965), 1519-1525. Cited on page: 632.

- [65SEK4] Sekine, T., Solvent extraction study of trivalent actinide and lanthanide complexes in aqueous solutions. III. Oxalate complexes of La(III), Eu(III), Lu(III), and Am(III) in 1 M Na(ClO<sub>4</sub>), *Acta Chem. Scand.*, **19**, (1965), 1476-1482. Cited on pages: 114, 285, 286, 287, 288, 632, 638, 691.
- [65SKO/SER] Skorik, N. A., Serebrennikov, V. V., Dependence of the solubility of the citrates of some rare-earth elements on pH, *Russ. J. Inorg. Chem.*, **10**, (1965), 219-220. Cited on page: 301.
- [65STE/MAK] Stepanov, A. V., Makarova, T. P., Use of the electromigration method to study complex oxalates of Am(III), *Sov. Radiochem.*, **7**, (1965), 669-671. Cited on pages: 286, 638.
- [65STE/MAK2] Stepanov, A. V., Makarova, T. P., Electromigration investigation of the complexation of trivalent plutonium with solutions of ethylenediaminetetraacetic acid, *Sov. Radiochem.*, **7**, (1965), 663-668. Cited on pages: 499, 639.
- [65TAT/GRZ] Tate, S. S., Grzybowski, A. K., Datta, S. P., The stability constants of magnesium citrate complexes, *J. Chem. Soc.*, (1965), 3905-3912. Cited on pages: 308, 335, 336, 342, 343, 639, 671.
- [65WRI/HOL] Wright, D. L., Holloway, J. H., Reilley, C. N., Heats and entropies of formation of metal chelates of polyamine and polyaminocarboxylate ligands, *Anal. Chem.*, **37**, (1965), 884-892. Cited on pages: 457, 468, 469, 639.
- [65ZAI/BOC] Zaitsev, L. M., Bochkarev, G. S., Kozhenkova, V. N., Polynuclear zirconium compounds, *Russ. J. Inorg. Chem.*, **10**, (1965), 590-594. Cited on pages: 203, 640.
- [66CHE] Chernyaev, I. I., *Complex compounds of uranium*, Govreen, M., Ed., Israel program for scientific translations, Jerusalem, (1966). Cited on pages: 207, 212, 225.
- [66CON/VER] Conway, B. E., Verrall, R. E., Desnoyers, J. E., Partial molal volumes of tetraalkylammonium halides and assignment of individual ionic contributions, *Trans. Faraday Soc.*, **62**, (1966), 2738-2749. Cited on page: 99.

- [66ERM/MAR] Ermakov, A. N., Marov, I. N., Evtikova, G. A., Zirconium and hafnium complexonates, *Russ. J. Inorg. Chem.*, **11**, (1966), 618-620. Cited on pages: 472, 473, 640.
- [66GUG] Guggenheim, E. A., *Applications of Statistical Mechanics*, Clarendon Press, Oxford, (1966). Cited on pages: 821, 822.
- [66KOR/SHE2] Korenman, I. M., Sheyanova, F. R., Gur'eva, Z. M., Instability constants of complexes of zirconium with some organic ligands, *Russ. J. Inorg. Chem.*, **11**, (1966), 1485-1488. Cited on pages: 205, 301, 362, 640, 641.
- [66KUL] Kula, R. J., Solution equilibria and structures of molybdenum(VI) chelates. (Ethylenedinitrilo)tetraacetic acid, *Anal. Chem.*, **38**, (1966), 1581-1584. Cited on page: 398.
- [66KUL/RAB] Kula, R. J., Rabenstein, D. L., Potentiometric determination of stabilities of molybdenum(VI) and tungsten(VI) chelates, *Anal. Chem.*, **38**, (1966), 1934-1936. Cited on page: 398.
- [66KUL/REE] Kula, R. J., Reed, G. H., Nuclear magnetic resonance investigation of ligand exchange kinetics in the calcium(II)-EDTA system, *Anal. Chem.*, **38**, (1966), 697-701. Cited on pages: 446, 447, 449, 641.
- [66LAP/PAN] Lapitskii, A. V., Pankratova, L. N., The reaction of zirconium with various complexons, *Moscow Univ. Chem. Bull.*, **21**, (1966), 204-207. Cited on pages: 472, 474, 641.
- [66LHE/MAR] L'Heureux, G. A., Martell, A. E., Mixed ligand chelates of copper(II), *J. Inorg. Nucl. Chem.*, **28**, (1966), 481-491. Cited on pages: 116, 132.
- [66LYL/NAQ] Lyle, S. J., Naqvi, S. J., A study of the distribution of series of positively charged europium complexes between a cation-exchanger and an external aqueous phase, *J. Inorg. Nucl. Chem.*, **28**, (1966), 2993-3004. Cited on page: 114.
- [66MAK/YUS] Maksimova, I. N., Yushkevich, V. F., Electric conductivity of aqueous solutions of formic, acetic, oxalic, sulfuric, and phosphoric acids at high temperatures, *Russ. J. Electrochem.*, **2**, (1966), 532-542. Cited on pages: 114, 651.

- [66MOE/CHU] Moeller, T., Chu, S.-K., The stabilities and thermodynamic functions for the formation of aluminium and mercury(II) chelates of certain polyaminepolyacetic acids, *J. Inorg. Nucl. Chem.*, **28**, (1966), 153-159. Cited on pages: 399, 402, 427, 428.
- [66MOO/SUT] Moorhead, E. G., Sutin, N., Rate and equilibrium constants for the formation of the monooxalate complex of iron(III), *Inorg. Chem.*, **5**, (1966), 1866-1871. Cited on pages: 116, 117, 129, 669, 716.
- [66NEB] Nebel, D., Spektralphotometrische Untersuchung des Gleichgewichtes Pu(IV)-Citrat in wäßriger Lösung, *Z. Phys. Chem. (Leipzig)*, **232**, (1966), 161-175, in German. Cited on pages: 301, 308, 379, 380, 641, 642.
- [66NEB2] Nebel, D., Potentiometrische Untersuchungen des Gleichgewichtes Pu(IV)-Citrat in wäßriger Lösung, *Z. Phys. Chem. (Leipzig)*, **232**, (1966), 368-376, in German. Cited on pages: 301, 379, 380, 643.
- [66NEB/URB] Nebel, D., Urban, G., Potentiometrische Untersuchungen zur Komplexbildung von Ce(III), Ce(IV), Th(IV), U(IV) und Citrat in wäßriger Lösung, *Z. Phys. Chem. (Leipzig)*, **233**, (1966), 73-84, in German. Cited on pages: 361, 362, 363, 643.
- [66PAE] Paetzold, R., Selenoxidacetat und Selenoxidoxalat, *Z. Chem.*, **6**, (1966), 72, in German. Cited on page: 189.
- [66SKO/SER] Skorik, N. A., Serebrennikov, V. V., Citrates of the rare-earth elements in aqueous solutions, *Russ. J. Inorg. Chem.*, **11**, (1966), 416-417. Cited on page: 301.
- [66SOL/IVA] Solovkin, A. S., Ivantsov, A. I., Hydrolysis constants of the  $Zr^{4+}$  ion in perchlorate media, *Russ. J. Inorg. Chem.*, **11**, (1966), 1013-1016. Cited on page: 678.
- [66STA] Sary, I., Study of complex formation of americium and promethium by the extraction method, *Sov. Radiochem.*, **8**, (1966), 467-470. Cited on pages: 285, 286, 287, 504, 505, 506, 643, 644.
- [66ZAI2] Zaitsev, L. M., Zirconium hydroxides, *Russ. J. Inorg. Chem.*, **11**, (1966), 900-904. Cited on pages: 203, 645, 655.

- [67ABR] Abrahamson, S. G., Precipitation of plutonium-238 (IV) oxalate from homogeneous solution, *J. Inorg. Nucl. Chem.*, **29**, (1967), 842-844. Cited on pages: 269, 646.
- [67ADA/CAR] Adams, G. P., Carson, A. S., Laye, P. G., The heats of formation of ethylenediaminetetra-acetic acid and diethylenetriaminepenta-acetic acid, *J. Chem. Soc. A*, (1967), 1832-1833. Cited on page: 394.
- [67AND] Anderegg, G., Komplexe XL. Die Protonierungskonstanten einiger Komplexe in verschiedenen wässrigen Salzmedien ( $\text{NaClO}_4$ ,  $(\text{CH}_3)_4\text{NCl}$ ,  $\text{KNO}_3$ ), *Helv. Chim. Acta*, **50**, (1967), 2333-2340, in German. Cited on pages: 394, 395, 399, 402, 438, 450, 673, 693, 695, 715.
- [67BHA/KRI] Bhat, T. R., Krishna Iyer, R., Studies on edta complexes-VIII. Thermal behaviour in air and nitrogen atmosphere of some metal-edta complexes, *J. Inorg. Nucl. Chem.*, **29**, (1967), 179-185. Cited on pages: 443, 460.
- [67BOT/AND] Bottari, E., Anderegg, G., Komplexe XLII. Die Untersuchung der 1:1-Komplexe von einigen drei- und vierwertigen Metall-Ionen mit Polyaminocarboxylaten mittels Redoxmessungen, *Helv. Chim. Acta*, **50**, (1967), 2349-2356, in German. Cited on pages: 472, 473, 474, 704.
- [67BUD/HAA] Budesinsky, B., Haas, K., Extraction of metal cations with chlorophosphonazo dal, *Solvent extraction chemistry*, pp. 173-181, Amsterdam, (1967). Cited on pages: 472, 473, 646.
- [67BUR/POR] Burney, G. A., Porter, J. A., Solubilities of Pu(III), Am(III) and Cm(III) oxalates, *Inorg. Nucl. Chem. Lett.*, **3**, (1967), 79-85. Cited on pages: 263, 264, 284, 646.
- [67CAR/MAR] Carey, G. H., Martell, A. E., Mixed ligand chelates of uranium(IV), *J. Am. Chem. Soc.*, **89**, (1967), 2859-2865. Cited on pages: 480, 482, 597, 647.
- [67CHR/IZA] Christensen, J. J., Izatt, R. M., Hansen, L. D., Thermodynamics of proton ionization in dilute aqueous solution. VII.  $\Delta H^\circ$  and  $\Delta S^\circ$  values for proton ionization from carboxylic acids at  $25^\circ$ , *J. Am. Chem. Soc.*, **89**, (1967), 213-222. Cited on pages: 143, 145, 647.

- [67ERM/KRO2] Ermolaev, N. P., Krot, N. N., Gel'man, A. D., Disproportionation of plutonium(V) in oxalate solutions, *Sov. Radiochem.*, **9**, (1967), 169-176. Cited on pages: 282, 283, 647.
- [67FIS2] Fischer, R., Détermination de la constante apparente de dissociation du 2,4-dinitrophénol et de la constante apparente de la deuxième acidité de l'acide citrique dans diverses solutions de sels de fond, *Bull. Soc. Chim. Fr.*, (1967), 2094-2100, in French. Cited on page: 310.
- [67GEL/MOS] Gel'man, A. D., Moskvina, A. I., Zaitsev, L. M., Mefod'eva, M. P., *Complex compounds of transuranides*, Israel Program for Scientific Translations Ltd., Jerusalem, (1967), 152 pp., the Russian original was printed in 1961. Cited on pages: 248, 261, 262, 264, 265, 276, 282, 283.
- [67HAS/MAK] Hasegawa, Y., Maki, K., Sekine, T., Studies of the alkaline earth complexes in various solutions. III. Calcium(II) and strontium(II) complexes with sulfate and oxalate ions in 1M perchlorate media, *Bull. Chem. Soc. Jpn.*, **40**, (1967), 1845-1848. Cited on pages: 179, 180, 182, 183, 187, 188, 648, 708, 779.
- [67IRV/MIL] Irving, H. M., Miles, M. G., Pettit, L. D., A study of some problems in determining the stoichiometric proton dissociation constants of complexes by potentiometric titrations using a glass electrode, *Anal. Chim. Acta*, **38**, (1967), 475-488. Cited on pages: 399, 402.
- [67JAC/MAR] Jackobs, N. E., Margerum, D. W., Stability constants of nickel aminocarboxylate, ammine, and polyamine mixed-ligand complexes, *Inorg. Chem.*, **31**, (1967), 2038-2043. Cited on pages: 463, 648.
- [67KRO/MEF2] Krot, N. N., Mefod'eva, M. P., Smirnova, T. V., Gel'man, A. D., Investigation of the kinetics of the disproportionation of neptunium(V) in oxalate solutions, *Sov. Radiochem.*, **9**, (1967), 436-444. Cited on pages: 254, 255, 256, 261, 566, 649.
- [67KUM/SER] Kumok, V. N., Serebrennikov, V. V., *Chemistry of the transuranium elements and fission products*, Nauka, Leningrad, (1967), 144 pp., in Russian. Cited on pages: 226, 649.



- [67LEB/MAK] Lebedev, I. A., Maksimova, A. M., Stepanov, A. V., Shalinets, A. B., Determination of the stability constants of complexes of Am and Cm with edta by the method of electromigration, *Sov. Radiochem.*, **9**, (1967), 664-666. Cited on pages: 504, 505, 506, 507, 649, 650, 678, 684, 688, 725.
- [67MAK2] Maksimova, I. N., Free energy, entropy, and enthalpy of ionic equilibria in aqueous solution at high temperatures, *Russ. J. Phys. Chem.*, **41**, (1967), 27-30. Cited on pages: 143, 651.
- [67MEF/GEL2] Mefod'eva, M. P., Gel'man, A. D., On oxalate compounds of neptunium(IV), in: *The chemistry of transuranium and fission elements (Conference proceedings)*, pp. 87-96, Izdatel'stvo Nauka, Leningrad, (1967), in Russian. Cited on pages: 248, 250, 251, 252, 651, 652.
- [67MES/VIN] Mészáros, P., Vinek, G., Konopik, N., Bestimmung der Dissoziationskonstanten der Formen  $H_5Y^+$ ,  $H_4Y$  and  $H_3Y^-$  der ÄDT, *Monatsh. Chem.*, **98**, (1967), 1810-1825, in German. Cited on pages: 394, 395, 400, 402, 719.
- [67MIY/NUR] Miyake, C., Nürnberg, H. W., Co-ordination compounds of actinides. I. The determination of the stability constants of uranyl complexes with anions of carboxylic acids, *J. Inorg. Nucl. Chem.*, **29**, (1967), 2411-2429. Cited on pages: 231, 232, 233, 234, 652.
- [67RAJ/MAR] Rajan, K. S., Martell, A. E., Equilibrium studies of uranyl complexes-IV. Reactions with carboxylic acids, *J. Inorg. Nucl. Chem.*, **29**, (1967), 523-529. Cited on pages: 117, 132, 232, 234, 652.
- [67RIC] Richard, P., Procédé continu de précipitation des sels de plutonium, CEA, Centre d'Etudes Nucléaires de Fontenay-aux-roses, Report CEA-R-3198, (1967), in French. Cited on pages: 269, 270, 653.
- [67SHC/BEL] Shchelokov, R. N., Belomestnykh, V. I., Dinuclear oxalato-compounds of uranyl, of the penta-acido-type, *Russ. J. Inorg. Chem.*, **12**, (1967), 45-50. Cited on pages: 214, 653.
- [67SHC/BEL2] Shchelokov, R. N., Belomestnykh, V. I., Oxalato(urea)-complexes of uranyl, of the tetra-acido-type, *Russ. J. Inorg. Chem.*, **12**, (1967), 843-849. Cited on pages: 213, 214, 653.

- [67SKO/KUM] Skorik, N. A., Kumok, V. N., Serebrennikov, V. V., Thorium citrate, *Sov. Radiochem.*, **9**, (1967), 499-500. Cited on pages: 301, 654.
- [67SOL/TSV] Solovkin, A. S., Tsvetkova, Z. N., Ivantsov, A. I., Thermodynamic constants for complex formation by  $U^{4+}$  with  $OH^-$  ions and by  $Zr^{4+}$  with  $OH^-$  and  $NO_3^-$  ions, *Russ. J. Inorg. Chem.*, **12**, (1967), 326-330. Cited on page: 678.
- [67STE/MAK2] Stepanov, A. V., Makarova, T. P., Determination of the formation functions of complexes in the  $UO_2^{2+}$ - $C_2O_4^{2-}$  system, *Russ. J. Inorg. Chem.*, **12**, (1967), 1262-1266. Cited on pages: 231, 232, 234, 654.
- [67TIK] Tikhonova, L. I., Dissociation constants of ethylenediamine-tetraacetic acid at 1.2 M KCl concentration, *Russ. J. Appl. Chem.*, **40**, (1967), 1826-1828. Cited on page: 398.
- [67TIK2] Tikhonova, L. I., Complex formation by zirconium with polyaminopolyacetic acids, *Russ. J. Inorg. Chem.*, **12**, (1967), 494-497. Cited on pages: 398, 472, 473, 654, 655.
- [67WEI/MEE] Weigel, F., ter Meer, N., The unit cells of some americium(III)-salts with organic anions, *Inorg. Nucl. Chem. Lett.*, **3**, (1967), 403-408. Cited on pages: 284, 655, 764.
- [67ZAI/SHU2] Zaitsev, L. M., Shubina, T. M., Investigation of the interconversion of dizirconyl oxalates, *Russ. J. Inorg. Chem.*, **12**, (1967), 635-639. Cited on pages: 204, 634, 655.
- [67ZAK/ORL2] Zakharova, F. A., Orlova, M. M., Sulphito-oxalato-compounds formed by the uranyl ion, *Russ. J. Inorg. Chem.*, **12**, (1967), 1384-1386. Cited on pages: 213, 214, 242, 243, 656, 657.
- [68AZI/LYL] Aziz, A., Lyle, S. J., Naqvi, S. J., Chemical equilibria in americium and curium sulphate and oxalate systems and an application of a liquid scintillation counting method, *J. Inorg. Nucl. Chem.*, **30**, (1968), 1013-1018. Cited on pages: 286, 657.
- [68CAR/MAR] Carey, G. H., Martell, A. E., Formation, hydrolysis, andolation of uranium(IV) chelates, *J. Am. Chem. Soc.*, **90**, (1968), 32-38. Cited on pages: 478, 479, 480, 482, 658.

- [68DEN/MEI] Deneux, M., Meilleur, R., Benoit, R. L., Chélates du fer(III) avec des anions dicarboxylates, *Can. J. Chem.*, **46**, (1968), 1383-1388, in French. Cited on pages: 117, 129.
- [68EBE/SCH] Eberle, S. H., Schaefer, J. B., Brandau, E., Spectrophotometric study of equilibria of plutonium(VI) complexes: plutonyl acetates, *Radiochim. Acta*, **10**, (1968), 91-97, in German. Cited on page: 725.
- [68FRI/VER] Fridman, Y. D., Veresova, R. A., Stability of mixed compounds of nickel with glycine, ethylenediamine, and oxalate in solutions, *Russ. J. Inorg. Chem.*, **13**, (1968), 399-403. Cited on pages: 195, 196, 659.
- [68GER/WAT] Gérard, N., Watelle-Marion, G., Thierri-Sorel, A., Étude sous pression de vapeur d'eau contrôlée de la déshydratation des oxalates de calcium hydratés, *Bull. Soc. Chim. Fr.*, **11**, (1968), 4367-4378, in French. Cited on pages: 165, 166.
- [68GOR/FIL] Gordievskii, A. V., Filippov, E. L., Shterman, V. S., Krivoshein, A. S., Ion-exchange membranes. III. Application of an ion-exchange membrane electrode in the study of complex-formation reactions, *Russ. J. Phys. Chem.*, **42**, (1968), 1050-1054. Cited on pages: 179, 187, 659.
- [68GUI] Guillaumont, R., Complexes citriques de protactinium pentavalent, *Bull. Soc. Chim. Fr.*, (1968), 1956-1961, in French. Cited on page: 311.
- [68HAR] Harries, R. J. N., Thermometric titration of some monoprotic and diprotic acids in aqueous and non-aqueous media, *Talanta*, **15**, (1968), 1345-1352. Cited on page: 114.
- [68KOZ] Koźlicka, M., Investigation of the stability of some complex compounds of zirconium by metal indicator method, *Chem. Anal. (Warsaw)*, **13**, (1968), 809-815, in Polish. Cited on pages: 205, 362, 472, 659.
- [68KUE/SCH] Kuempel, J. R., Schaap, W. B., Cyclic voltammetric study of the rate of ligand exchange between cadmium ion and calcium ethylenediaminetetraacetate, *Inorg. Chem.*, **7**, (1968), 2435-2442. Cited on pages: 398, 446, 449, 660.

- [68LEY/WHI] Leyden, D. E., Whidby, J. F., Nuclear magnetic resonance studies of edta in the presence of excess calcium or strontium, *Anal. Chim. Acta*, **42**, (1968), 271-278. Cited on page: 447.
- [68MAT/KRO] Matyukha, V. A., Krot, N. N., Gel'man, A. D., The form in which plutonium(IV) exists in oxalate solutions, *Russ. J. Inorg. Chem.*, **13**, (1968), 1099-1101. Cited on pages: 152, 153, 279, 660.
- [68MOS2] Moskvina, A. I., On the complex formation of U(VI) and Np(IV) with hydrogen peroxide and Np(IV) in oxalate solutions, *Sov. Radiochem.*, **10**, (1968), 10-16. Cited on pages: 247, 603, 632.
- [68NAA/POD] Naarová, M., Podlahová, J., Podlaha, J., Herstellung und Eigenschaften von Äthylendiamintetraessigsäure-Komplexen VIII. Verbindungen mit sechswertigem Molybdän, *Collect. Czech. Chem. Commun.*, **33**, (1968), 1991-2003, in German. Cited on page: 398.
- [68NOR/WER] Norrestam, R., Werner, P.-E., von Glehn, M., The crystal structure of calcium- $\alpha$ -D-glucosaccharate and some extended Hückel calculations on  $\alpha$ -D-glucosaccharinic acid, *Acta Chem. Scand.*, **22**, (1968), 1395-1403. Cited on page: 520.
- [68PED] Pedersen, B. F., The crystal structure of potassium hydrogen oxalate,  $\text{KHC}_2\text{O}_4$ , *Acta Chem. Scand.*, **22**, (1968), 2953-2964. Cited on pages: 153, 154.
- [68POS/ZAI2] Pospelova, L. A., Zaitsev, L. M., Carbonato-oxalato-compounds of zirconium, *Russ. J. Inorg. Chem.*, **13**, (1968), 1535-1538. Cited on pages: 205, 660.
- [68PRI/FAZ] Pribylov, E. P., Fazlullina, L. S., Chechetkin, R. M., Thermal decomposition of calcium oxalate studied by the gasvolumographic method at reduced pressures, *Russ. J. Inorg. Chem.*, **13**, (1968), 1640-1642. Cited on page: 165.
- [68REC/LIN] Rechnitz, G. A., Lin, Z. F., Potentiometric measurements with calcium-selective liquid-liquid membrane electrodes, *Anal. Chem.*, **40**, (1968), 696-699. Cited on pages: 446, 449.
- [68SHC/BEL] Shchelokov, R. N., Belomestnykh, V. I., Reaction of oxofluorouranates with oxalate ions, *Russ. J. Inorg. Chem.*, **13**, (1968), 733-736. Cited on pages: 213, 214, 242, 245, 661.

- [68SIL/SIM] da Silva, J. J. R. F., Simões, M. L. S., Studies on uranyl complexes - III. Uranyl complexes of EDTA, *Talanta*, **15**, (1968), 609-622. Cited on pages: 400, 402, 484, 485, 486, 603, 629, 661, 672, 744, 746, 747, 748, 800.
- [68SPI/MAR] Spitsyn, V. I., Martynenko, L. I., Rivina, Z. M., Rivin, K. N., Dobrynina, N. A., Nemukhin, A. V., Stability constants of citrate complexes of the rare-earth elements, *Dokl. Chem. (Trans. of Dokl. Akad. Nauk)*, **179**, (1968), 364-367. Cited on page: 308.
- [68WAT/SCH] Watters, J. I., Schupp, III, O. E., Acidimetric investigation of complex formation by potassium ions with ethylenediaminetetraacetate, *J. Inorg. Nucl. Chem.*, **30**, (1968), 3359-3362. Cited on pages: 398, 438.
- [68WIK/RIN] Wikberg, H., Ringbom, A., Stability constants of the silver complexes of some polyaminopolycarboxylic acids, *Suom. Kemistil. B*, **41**, (1968), 177-183. Cited on page: 398.
- [69BEV] Bevington, P. R., *Data reduction and error analysis for the physical sciences*, McGraw-Hill, New York, (1969), 336 pp. Cited on pages: 857, 863.
- [69BOS/MAR] Bosch-Reig, F., Marti, F. B., Sobre la determinación de pK del ácido cítrico y del complejo citrato-calcio. Nota III, *Inf. Quim. Anal.*, **23**, (1969), 5-10, in Spanish. Cited on pages: 337, 342, 662.
- [69BRU/NAN] Brunetti, A. P., Nancollas, G. H., Smith, P. N., Thermodynamics of ion association. XIX. Complexes of divalent metal ions with monoprotinated ethylenediaminetetraacetate, *J. Am. Chem. Soc.*, **91**, (1969), 4680-4683. Cited on pages: 462, 464, 465, 466, 467, 468, 470, 662.
- [69CHR/IZA] Christensen, J. J., Izatt, R. M., Wrathall, D. P., Hansen, L. D., Thermodynamics of proton ionization in dilute aqueous solution. Part XI. pK,  $\Delta H^\circ$ , and  $\Delta S^\circ$  values for proton ionization from protonated amines at 25°, *J. Chem. Soc. A*, (1969), 1212-1223. Cited on page: 428.

- [69COM] Comité International des Poids et des Mesures, The International Practical Temperature Scale of 1968, *Metrologia*, **5**, (1969), 35-47. Cited on page: 32.
- [69CON/MAR] Condike, G. F., Martell, A. E., Mixed ligand chelates of copper(II), *J. Inorg. Nucl. Chem.*, **31**, (1969), 2455-2466. Cited on pages: 117, 132, 751.
- [69COP/SAB] Coppens, P., Sabine, T. M., Neutron diffraction study of hydrogen bonding and thermal motion in deuterated  $\alpha$  and  $\beta$  oxalic acid dihydrate, *Acta Crystallogr.*, **B25**, (1969), 2442-2451. Cited on page: 111.
- [69COP/SAB2] Coppens, P., Sabine, T. M., Delaplane, R. G., Ibers, J. A., An experimental determination of the asphericity of the atomic charge distribution in oxalic acid dihydrate, *Acta Crystallogr.*, **B25**, (1969), 2451-2458. Cited on page: 111.
- [69DEL/BAY] Delle Site, A., Baybarz, R. D., A spectrophotometric study of the complexing of  $\text{Am}^{3+}$  with aminopolyacetic acids, *J. Inorg. Nucl. Chem.*, **31**, (1969), 2201-2233. Cited on pages: 504, 505, 507, 662.
- [69FRI/DYA] Fridman, A. Y., Dyatlova, N. M., Fridman, Y. D., Formation of compounds of nickel complexonates with amines in solution, *Russ. J. Inorg. Chem.*, **14**, (1969), 1741-1744. Cited on pages: 463, 663.
- [69GLU/MIN] Glusker, J. P., Minkin, J. A., Patterson, A. L., X-ray crystal analysis of the substrates of aconitase. IX. A refinement of the structure of anhydrous citric acid, *Acta Crystallogr.*, **B25**, (1969), 1066-1072. Cited on page: 303.
- [69GOR/KOC] Gorski, B., Koch, H., Zur Chemie des Technetium in wäßriger Lösung - I. Über den Zustand des vierwertigen Technetium in wäßriger Lösung, *J. Inorg. Nucl. Chem.*, **31**, (1969), 3565-3571, in German. Cited on page: 471.
- [69GRE/GAR] Grenthe, I., Gårdhammar, G., Rundcrantz, E., Thermodynamic properties of rare earth complexes. VI. Stability constants for the oxalate complexes of Ce(III), Eu(III), Tb(III), and Lu(III), *Acta Chem. Scand.*, **23**, (1969), 93-108. Cited on pages: 115, 117, 129.

- [69HAV] Havel, J., Spectrophotometric study of complex formation of uranyl with oxalic acid, *Collect. Czech. Chem. Commun.*, **34**, (1969), 3248-3265. Cited on pages: 114, 229, 231, 232, 233, 235, 236, 237, 239, 663.
- [69HOD/IBE] Hodgson, D. J., Ibers, J. A., Refinement of the crystal and molecular structure of potassium oxalate monohydrate, *Acta Crystallogr.*, **B25**, (1969), 469-477. Cited on pages: 153, 155.
- [69KUR/FAR] Kurz, J. L., Farrar, J. M., The entropies of dissociation of some moderately strong acids, *J. Am. Chem. Soc.*, **91**, (1969), 6057-6062. Cited on pages: 115, 117, 143, 145, 664, 670, 770.
- [69LIT/PUR] Litchinsky, D., Purdie, N., Tomson, M. B., White, W. D., A rigorous solution to the problem of interfering dissociation steps in the titration of polybasic acids, *Anal. Chem.*, **41**, (1969), 1726-1730. Cited on pages: 308, 323.
- [69MAN/BHA] Manku, G. S., Bhat, A. N., Jain, B. D., Solvent extraction studies of complexes of oximidobenzotetronic acid with iron(II), nickel(II) and copper(II), *J. Inorg. Nucl. Chem.*, **31**, (1969), 2533-2543. Cited on pages: 194, 195, 196, 665.
- [69MEF/KRO2] Mefod'eva, M. P., Krot, N. N., Smirnova, T. V., Gel'man, A. D., Oxalate compounds of hexavalent neptunium, *Sov. Radiochem.*, **11**, (1969), 187-192. Cited on pages: 249, 261, 665.
- [69MIK] Mikhailov, V. A., Solubility of plutonium arylarsonates, *Russ. J. Inorg. Chem.*, **14**, (1969), 1119-1122. Cited on pages: 278, 280, 501, 665.
- [69MOS] Moskvina, A. I., Complex formation of the actinides with anions of acids in aqueous solutions, *Sov. Radiochem.*, **11**, (1969), 447-449. Cited on pages: 477, 490, 491.
- [69PER/KRO] Peretrukhin, V. F., Krot, N. N., Gel'man, A. D., Electrolytic reduction of uranyl in oxalate solutions, *Sov. Radiochem.*, **11**, (1969), 417-421. Cited on pages: 228, 666.

- [69POS/VED] Postel, M., Vedel, J., Comportement des diacides organiques dans un solvant structuré, un mélange N-méthylacétamide-diméthyl formamide, *C. R. Séances Acad. Sci., Ser. C*, **269**, (1969), 372-374, in French. Cited on pages: 115, 117.
- [69REC/HSE] Rechnitz, G. A., Hseu, T. M., Analytical and biochemical measurements with a new, solid-membrane calcium-selective electrode, *Anal. Chem.*, **41**, (1969), 111-115. Cited on pages: 337, 343, 666.
- [69ROS] Rossotti, H., *Chemical applications of potentiometry*, D. Van Nostrand, Princeton N. J., (1969), 229 pp. Cited on pages: 22, 23.
- [69SHA/AMI] Shastri, N. K., Amis, E. S., Kinetics of reduction of neptunium(VI) with oxalic acid in aqueous perchloric acid, *Inorg. Chem.*, **8**, (1969), 2487-2489. Cited on page: 261.
- [69SHC/BEL] Shchelokov, R. N., Belomestnykh, V. I., Oxalatoaquouranyl compounds of the tetra-acido-type, *Russ. J. Inorg. Chem.*, **14**, (1969), 1491-1494. Cited on pages: 213, 214, 667.
- [69SIL/SIM] da Silva, J. J. R. F., Simões, M. L. S., Studies on uranyl complexes - V. Heats and entropies of formation of uranyl chelates of polyaminocarboxylic acids, *Rev. Port. Quim.*, **11**, (1969), 54-60. Cited on pages: 400, 427, 428.
- [69SIL/WAR2] Sillén, L. G., Warnquist, B., High-speed computers as a supplement to graphical methods. 10. Application of LETAGROP to spectrophotometric data, for testing models and adjusting equilibrium constants, *Ark. Kemi*, **31**, (1969), 377-390. Cited on pages: 566, 652, 686.
- [69SKO/KUM] Skorik, N. A., Kumok, V. N., Solubility products of some metal citrates, *Russ. J. Inorg. Chem.*, **14**, (1969), 52-53. Cited on pages: 301, 350, 667.
- [69SKO/MAM] Skorik, N. A., Mamynova, A. A., Serebrennikov, V. V., Reactions of citric acid with rare-earth ions, *Tr. Nauch. Konf. Tomsk. Otd. Vses. Khim. Obshchest.*, Usov, P.G., Ed., pp. 59-62, Izd. Tomsk. Univ.: Tomsk, USSR, (1969), in Russian. Cited on page: 301.



- [69SOC/VOL] Sochevanov, V. G., Volkova, G. A., Use of polarography in the determination of the instability constants of complexonates of readily hydrolysable elements, *Russ. J. Inorg. Chem.*, **14**, (1969), 61-64. Cited on pages: 473, 474, 667, 668.
- [69STE/MAK2] Stepanov, A. V., Makarova, T. P., Use of the electromigration method in investigating complex formation of U(VI) with edta, *Sov. Radiochem.*, **11**, (1969), 286-289. Cited on pages: 484, 486, 487, 488, 489, 668, 746, 800.
- [69SUB/COR] Subbaraman, P. R., Cordes, S. M., Freiser, H., Effect of auxiliary complexing agents on the rate of extraction of zinc(II) and nickel(II) with diphenylthiocarbazone, *Anal. Chem.*, **41**, (1969), 1878-1880. Cited on pages: 195, 196, 668.
- [69SUB/SIN] Subramanian, M. S., Singh, R. N., Sharma, H. D., Reaction kinetics of some actinide oxalates by differential thermal analysis, *J. Inorg. Nucl. Chem.*, **31**, (1969), 3789-3795. Cited on pages: 207, 263.
- [69VAN/PER] Le Van, M., Perinet, G., Les enthalpies normales de formation des carboxylates et des sels d'oxacides. I. Mesures calorimétriques des enthalpies de formation des carboxylates de cobalt, de nickel et de cuivre, *Bull. Soc. Chim. Fr.*, (8), (1969), 2681-2683, in French. Cited on page: 192.
- [69VOR/IVA] Voronova, E. M., Ivakin, A. A., Spectrophotometric study of oxalato-complexes of vanadium(V) in aqueous solution, *Russ. J. Inorg. Chem.*, **14**, (1969), 818-821. Cited on pages: 117, 129.
- [69WER/NOR] Werner, P.-E., Norrestam, R., Rönquist, O., The crystal structure of strontium 3-deoxy-2-C-hydroxymethyl-D-erythro-pentolate, *Acta Crystallogr.*, **B25**, (1969), 714-719. Cited on page: 520.
- [70ADI/KLO] Adin, A., Klotz, P., Newman, L., Mixed-metal complexes between indium(III) and uranium(VI) with malic, citric, and tartaric acids, *Inorg. Chem.*, **9**, (1970), 2499-2505. Cited on pages: 364, 368, 668, 683.
- [70AND/MAL] Anderegg, G., Malik, S., Komplexe XLIII. Die Komplexe des dreiwertigen Antimons mit Polyaminocarboxylaten, *Helv. Chim. Acta*, **53**, (1970), 564-569, in German. Cited on pages: 446, 449, 450, 451.

- [70AND/MAL2] Anderegg, G., Malik, S., Die Komplexbildungstendenz des dreiwertigen Antimons in wässriger Lösung, *Helv. Chim. Acta*, **53**, (1970), 577-600, in German. Cited on pages: 400, 402.
- [70ASC/BRI] Ascanio, J., Brito, F., Hydrazonium ion as a depolarizer, *An. Quim.*, **A66**, (1970), 617-621, in Spanish. Cited on pages: 117, 130.
- [70BAR2] Bartušek, M., Thorium chelates 1:1 with catechol and catechol-5-sulfonic acid, *Spisy Prirodoved. Fak. Univ. J. E. Purkyne Brne*, **517**, (1970), 397-405. Cited on page: 398.
- [70BAR/BRI] Barnes, J. C., Bristow, P. A., Lanthanum citrate complexes in acid solutions, *J. Less-Common Met.*, **22**, (1970), 463-465. Cited on page: 308.
- [70BES/CHA] Besse, G., Chabard, J. L., Voissière, G., Petit, J., Berger, J. A., Étude de la stabilité des complexes par électrophorèse sur couches minces. II.- Complexes citriques, *Bull. Soc. Chim. Fr.*, (1970), 4166-4169, in French. Cited on pages: 353, 354, 355, 358, 669.
- [70BRA/LEP] Braibanti, A., Leporati, E., Dallavalle, F., The protonation constant of oxamic acid in aqueous solution and in water-tetrahydrofuran mixture, at different temperatures and ionic strengths, *Inorg. Chim. Acta*, **4**, (1970), 529-532. Cited on page: 115.
- [70CIA/GRI] Ciavatta, L., Grimaldi, M., Paoletta, G., Formation of complexes between Co(II) and oxalate ions, *Gazz. Chim. Ital.*, **100**, (1970), 100-109, in Italian. Cited on pages: 117, 129.
- [70COO/MAR] Coombes, L. C., Margerum, D. W., Nigam, P. C., Mechanism of tetracyanonickelate formation from mono(aminocarboxylate)nickel(II) complexes, *Inorg. Chem.*, **9**, (1970), 2081-2087. Cited on pages: 463, 742.
- [70COU/FAU] Couturier, Y., Faucherre, J., Structure and stability of the oxalic chelates of beryllium, *Bull. Soc. Chim. Fr.*, série 5, (1970), 1323-1330, in French. Cited on page: 114.

- [70DAV/WAT] Davies, G., Watkins, K. O., Inner-sphere mechanisms of oxidation. Stoichiometry and kinetics of the cobalt(III) oxidation of oxalic acid in acid perchlorate solution, *Inorg. Chem.*, **9**, (1970), 2735-2739. Cited on pages: 115, 143, 669, 670.
- [70DEY/PEN] Deyrieux, R., Péneloux, A., Contribution à l'étude des oxalates de certains métaux bivalents. II.- Détermination des produits de solubilité des oxalates dihydratés de Mn, Fe, Co, Ni et Zn, *Bull. Soc. Chim. Fr.*, (6), (1970), 2160-2165, in French. Cited on pages: 190, 191, 192, 194, 195, 196, 200, 670, 697, 698, 699, 700.
- [70EBE/WED] Eberle, S. H., Wede, U., Chelatgleichgewichte fünfwertiger Transurane mit Aminopolykarbonsäuren, *J. Inorg. Nucl. Chem.*, **32**, (1970), 109-117, in German. Cited on pages: 492, 493, 494, 495, 496, 497, 502, 503, 670, 671, 799.
- [70FOL/KAN] Follner, H., Kanters, J. A., Kroon, J., Kristallstrukturbestimmung von  $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , *Z. Anorg. Allg. Chem.*, **379**, (1970), 225-233, in German. Cited on pages: 152, 153.
- [70GEL/BLO2] Gel'man, A. D., Blokhin, V. I., Bukhtiyarova, T. N., Krot, N. N., Isolation of oxalato- and ethylenediaminetetra-acetato- complexes of neptunium(V) in solid form, *Russ. J. Inorg. Chem.*, **15**, (1970), 975-978. Cited on page: 248.
- [70GOR/KOC] Gorski, B., Koch, H., Über die Komplexbildung von Technetium mit chelatbildenden Liganden-II, *J. Inorg. Nucl. Chem.*, **32**, (1970), 3831-3836, in German. Cited on page: 471.
- [70GRE/BRY2] Grebenshchikova, V. I., Bryzgalova, R. V., Rogozin, Y. M., Oxalate complexes of thorium, *Sov. Radiochem.*, **12**, (1970), 252-258. Cited on page: 114.
- [70GRZ/TAT] Grzybowski, A. K., Tate, S. S., Datta, S. P., Magnesium and manganese complexes of citric and isocitric acids, *J. Chem. Soc. A*, (1970), 241-245. Cited on pages: 308, 335, 336, 342, 343, 671.
- [70HIG/SAM] Higginson, W. C. E., Samuel, B., Structures of the ethylenediaminetetra-acetate complexes of some bivalent cations in aqueous solution, *J. Chem. Soc. A*, (1970), 1579-1586. Cited on pages: 464, 465, 470.

- [70KUG/CAR] Kugler, G. C., Carey, G. H., Thermometric titration studies of mixed ligand complexes of thorium, *Talanta*, **17**, (1970), 907-914. Cited on page: 428.
- [70LUK] Lukachina, V. V., State of oxalic acid in solutions of strong acids, *Sov. Progr. Chem.*, **36**, (1970), 62-68. Cited on page: 113.
- [70MER/KUM] Merkusheva, S. A., Kumok, V. N., Skorik, N. A., Serebrennikov, V. V., Stability of complexes of thorium and uranium(IV) with anions of dicarboxylic acids, *Sov. Radiochem.*, **12**, (1970), 155-157. Cited on page: 649.
- [70PER/KRO] Peretrukhin, V. F., Krot, N. N., Gel'man, A. D., Influence of anions on the kinetics of the spontaneous oxidation of trivalent uranium in aqueous solutions, *Sov. Radiochem.*, **12**, (1970), 85-88. Cited on page: 225.
- [70PET/STE2] Petrazhak, G. I., Stepanova, L. N., Karago, L. V., An investigation of complex formation in solution by determining the charge of anionic complexes by the ion-exchange method, *Sov. Radiochem.*, **12**, (1970), 240-245. Cited on pages: 207, 209, 210, 225, 671.
- [70PRA/HAV] Prášilová, J., Havlíček, J., Determination of stability constants of some complexes of zirconium using dinonyl naphthalene sulphonic acid as liquid ion exchanger, *J. Inorg. Nucl. Chem.*, **32**, (1970), 953-960. Cited on pages: 473, 474, 671.
- [70SCH/HOW] Schwartz, L. M., Howard, L. O., Aqueous dissociation of squaric acid, *J. Phys. Chem.*, **74**, (1970), 4374-4377. Cited on page: 115.
- [70SHI/KRO] Shilov, V. P., Krot, N. N., Gel'man, A. D., Supplementary data on the oxidative properties of neptunium(VII) in alkaline solutions, *Sov. Radiochem.*, **12**, (1970), 661-663. Cited on page: 261.
- [70SIL/SIM] da Silva, J. J. R. F., Simões, M. L. S., Studies on uranyl complexes-IV: Simple and polynuclear uranyl complexes of some polyaminocarboxylic acids, *J. Inorg. Nucl. Chem.*, **32**, (1970), 1313-1322. Cited on pages: 486, 672, 744, 748.
- [70SIL/SIM2] da Silva, J. J. R. F., Simões, M. L. S., Quelatos do iao uranilo com ácidos poliaminocarboxílicos, *Rev. Port. Quím.*, **12**, (1970), 95-103, in Portuguese. Cited on pages: 486, 744.

- [70STE/PAZ] Stepanov, A. V., Pazukhin, E. M., Determination of the dissociation constants of oxalic acid and of the stability constant of the oxalatocomplex of calcium by the electromigration method, *Russ. J. Inorg. Chem.*, **15**, (1970), 761-765. Cited on pages: 115, 179, 182, 187, 188, 672, 676.
- [70VOR/RVK] Vorob'ev, G. I., Rykova, G. A., Shternina, E. B., Solubilities of complexonate compounds of the alkaline earth elements, *Russ. J. Inorg. Chem.*, **15**, (1970), 1371-1375. Cited on pages: 443, 444.
- [71AND/WEN] Anderegg, G., Wenk, F., Komplexe VL. Reaktionsenthalpie und-entropie bei der Bildung der 1:1-Komplexe der Seltenen Erden mit 1,3-Diaminopropan-N,N',N'-tetraacetat, *Helv. Chim. Acta*, **54**, (1971), 216-229, in German. Cited on page: 470.
- [71CHA/LIA] Chang, C.-T., Liaw, C.-F., The behaviors of neptunium in aqueous solutions - I Stability of tetravalent neptunium ion, *J. Inorg. Nucl. Chem.*, **33**, (1971), 2623-2630. Cited on pages: 491, 590, 673.
- [71CHA/LIA2] Chang, C.-T., Liaw, C.-F., The behaviors of neptunium in aqueous solutions - II. Stability of pentavalent neptunium ion, *J. Inorg. Nucl. Chem.*, **33**, (1971), 2717-2720. Cited on pages: 492, 493, 673.
- [71CHE2] Cheneau, G., Etude de la précipitation et de la filtration de l'oxalate de plutonium trivalent, CEA, Centre de production de plutonium de Marcoule, Rapport CEA-R-4109, (1971), in French. Cited on page: 264.
- [71CHU/REE] Chulkaratana, S., van Reen, R., Valyasevi, A., Studies on bladder stone disease in Thailand. XV. Factors affecting the solubility of calcium oxalate, *Invest. Urol.*, **9**, (1971), 246-250. Cited on pages: 161, 166, 167.
- [71EBE/PAU] Eberle, S. H., Paul, M. T., Über Aminopolykarbonsäurekomplexe des Np(IV)-Ions, *J. Inorg. Nucl. Chem.*, **33**, (1971), 3067-3075, in German. Cited on pages: 491, 590, 670, 673.
- [71ELE/ZAI] Elesin, A. A., Zaitsev, A. A., Ion-exchange behavior of trivalent americium, curium, and promethium ions in the presence of edta, *Sov. Radiochem.*, **13**, (1971), 798-801. Cited on pages: 504, 505, 674.

- [71GEL] Gelb, R. I., Conductometric determination of  $pK_a$  values - oxalic and squaric acids, *Anal. Chem.*, **43**, (1971), 1110-1113. Cited on page: 114.
- [71GOR/MIK] Gordienko, V. I., Mikhailyuk, Y. I., Sidorenko, V. I., Amperometric investigation of oxalate and malonate complexes of trivalent iron, *J. Gen. Chem. USSR*, **41**, (1971), 501-503. Cited on page: 114.
- [71GUI/BOU] Guillaumont, R., Bourderie, L., Complexes critiques d'éléments 4f et 5f, *Bull. Soc. Chim. Fr.*, (1971), 2806-2809, in French. Cited on pages: 381, 382, 383, 384, 674, 692, 745.
- [71JEN] Jensen, K. A., *Nomenclature of inorganic chemistry, IUPAC Commission on Nomenclature of Inorganic Compounds*, Pergamon Press, Oxford, (1971), 110 pp. Cited on page: 13.
- [71LIE] Liem, D. H., High-speed computers as a supplement to graphical methods. 12. Application of LETAGROP to data for liquid-liquid distribution equilibria, *Acta Chem. Scand.*, **25**, (1971), 1521-1534. Cited on pages: 628, 716, 717.
- [71MEF/GEL2] Mefod'eva, M. P., Gel'man, A. D., Production of solid compounds of neptunium(III) from aqueous solutions, *Sov. Radiochem.*, **13**, (1971), 613-618. Cited on pages: 245, 249.
- [71MOO/POW] Moore, F. H., Power, L. F., The crystal structure of potassium hydrogen oxalate by neutron diffraction, *Inorg. Nucl. Chem. Lett.*, **7**, (1971), 873-875. Cited on pages: 153, 154.
- [71MOS6] Moskvina, A. I., Correlation of the stability constants of complexes of the actinides with the properties of the metal ions and ligand forming them, *Sov. Radiochem.*, **13**, (1971), 230-237. Cited on pages: 229, 674.
- [71OHY/OHY] Ohyoshi, E., Ohyoshi, A., A study of complexes with a polybasic acid: Am(III) citrate complexes, *J. Inorg. Nucl. Chem.*, **33**, (1971), 4265-4273. Cited on pages: 381, 382, 383, 384, 674.
- [71OLI/CHO] D'Olieslager, W., Choppin, G. R., The kinetics of exchange between lanthanide ions and lanthanum ethylenediaminetetraacetate, *J. Inorg. Nucl. Chem.*, **33**, (1971), 127-135. Cited on pages: 504, 505, 676.

- [71PAZ/STE] Pazukhin, E. M., Sterlyadkina, G. V., Solubility of calcium oxalate in nitric acid solutions and in mixed solutions of nitric and oxalic acids, *Russ. J. Inorg. Chem.*, **16**, (1971), 612-614. Cited on pages: 168, 169, 180, 187, 676.
- [71PYA/KRA2] Pyatnitskii, I. V., Kravchenko, T. I., A study of oxalic acid complexes of zirconium and hafnium, *Sov. Progr. Chem.*, **37**, (1971), 79-82. Cited on pages: 205, 206, 677.
- [71ROR/MAC] Rorabacher, D. B., MacKellar, W. J., Shu, F. R., Bonavita, M., Solvent effects on protonation constants: Ammonia, acetate, polyamine, and polyaminocarboxylate ligands in methanol-water mixtures, *Anal. Chem.*, **43**, (1971), 561-573. Cited on pages: 398, 438.
- [71RUM] Rumbaut, N. A., Stability of alkaline-earth citrate complexes, *Bull. Soc. Chim. Belg.*, **80**, (1971), 63-71. Cited on pages: 337, 339, 340, 342, 677.
- [71SHA] Shalinets, A. B., Investigation of the complex formation of trivalent actinide and lanthanide elements by the method of electromigration. XI. Relationship of the strength of complexes to the strength of the acid, *Sov. Radiochem.*, **13**, (1971), 583-586. Cited on pages: 505, 678.
- [71SIL/MAR] Sillén, L. G., Martell, A. E., *Stability constants of metal ion complexes, Suppl. No. 1, Special Publication*, No. 25, Chemical Society, London, (1971), 865 pp. Cited on pages: 15, 16, 449.
- [71SKO/KUM] Skorik, N. A., Kumok, V. N., Protonation of the anions of certain acids in aqueous alcoholic solutions, *Russ. J. Inorg. Chem.*, **16**, (1971), 1643-1645. Cited on page: 308.
- [71SOL/IVA2] Solovkin, A. S., Ivantsov, A. I., Thermodynamics of the extraction of zirconium from perchloric and nitric acid solutions in the presence of oxalic acid, *Russ. J. Inorg. Chem.*, **16**, (1971), 1199-1201. Cited on pages: 205, 206, 678, 685, 695.

- [71STE] Stepanov, A. V., Comparative stability of the complexes of yttrium and various rare earth and actinide elements with oxalate, citrate, ethylenediaminetetra-acetate, and 1,2-diaminecyclohexanetetra-acetate, *Russ. J. Inorg. Chem.*, **16**, (1971), 1583-1586. Cited on pages: 286, 381, 679.
- [71VAN] Le Van, M., Enthalpies normales de formation des oxalates malonates et succinates de cobalt, de nickel et de cuivre, *C. R. Séances Acad. Sci., Ser. C*, **272**, (1971), 2141-2143, in French. Cited on page: 192.
- [71VAS/KOC2] Vasil'ev, V. P., Kochergina, L. A., Eremenko, V. I., Heat of the first dissociation of oxalic acid at 25°C in the presence of various electrolytes, *Russ. J. Phys. Chem.*, **45**, (1971), 1196-1197. Cited on pages: 143, 145, 679, 680.
- [72ARM/DUN] Armitage, G. M., Dunsmore, H. S., Effect of ionic strength on the stability of the calcium oxalate complex, *J. Inorg. Nucl. Chem.*, **34**, (1972), 2811-2815. Cited on pages: 179, 187, 680.
- [72BAR/FRI] Barkhanova, N. N., Fridman, A. Y., Dyatlova, N. M., The formation of mixed transition metal complexes with ethylenediaminetetra-acetic acid, *Russ. J. Inorg. Chem.*, **17**, (1972), 1569-1573. Cited on page: 465.
- [72BEL/KAZ] Beloedova, T. V., Kazakova, L. V., Skorik, N. A., Stability of citrato-complexes of the rare earth elements and yttrium in water and aqueous alcohol, *Russ. J. Inorg. Chem.*, **17**, (1972), 816-818. Cited on page: 308.
- [72DOM] Domalski, E. S., Selected values of heats of combustion and heats of formation of organic compounds containing the elements C, H, N, O, P, and S, *J. Phys. Chem. Ref. Data*, **1**, (1972), 221-277. Cited on pages: 107, 108, 110, 111, 303, 304.
- [72EBE/MOA] Eberle, S. H., Moattar, F., Die Komplexe des Am(III) mit Zitronensäure, *Inorg. Nucl. Chem. Lett.*, **8**, (1972), 265-270, in German. Cited on pages: 301, 381, 382, 383, 384, 680.
- [72GRI/PET2] Grinberg, A. A., Petrzhak, G. I., Lozhkina, G. S., Karago, L. V., Compounds of tetravalent uranium, *Sov. Radiochem.*, **14**, (1972), 407-410. Cited on page: 226.



- [72HOS/UEN] Hoshi, M., Ueno, K., The precipitation of thorium, uranium(IV) and plutonium(IV) oxalate complex ions with hexaurea chromium(III) chloride, *J. Inorg. Nucl. Chem.*, **34**, (1972), 981-986. Cited on pages: 263, 272.
- [72JAY/CHA] Jayadevan, N. C., Chackraburty, D. M., The crystal and molecular structure of uranyl oxalate trihydrate, *Acta Crystallogr.*, **B28**, (1975), 3178-3182. Cited on page: 213.
- [72JON/STO] Jones, Jr., E. R., Stone, J. A., Metamagnetism in neptunium(V) oxalate, *J. Chem. Phys.*, **56**, (1972), 1343-1347. Cited on page: 248.
- [72KAN] Kankare, J. J., Determination of dissociation constants of acids and bases by potentiostatic titration, *Anal. Chem.*, **44**, (1972), 2376-2379. Cited on page: 311.
- [72KER/CHU] Kereichuk, A. S., Churikova, I. M., Complex formation by cobalt and nickel ions with citric acid in acidic solutions, *Russ. J. Inorg. Chem.*, **17**, (1972), 1300-1303. Cited on pages: 354, 355, 358, 681.
- [72KUK/KOB] Kukushkin, Y. N., Kobzev, V. V., Morozova, L. P., Solubility of oxalic acid in aqueous nitric and sulfuric acid solutions, *Russ. J. Appl. Chem.*, **45**, (1972), 2673-2675. Cited on page: 112.
- [72KUP] Küppers, H., Die Züchtung grosser Einkristalle von Kalium- und Ammoniumoxalaten, *J. Cryst. Growth*, **15**, (1972), 89-92, in German. Cited on pages: 153, 154, 681.
- [72LAG/LAG] Lagrange, J., Lagrange, P., Etude du complexe vanadium(V)-EDTA en milieu acide ( $1,5 \leq \text{pH} \leq 2$ ) et  $\text{NaClO}_4$  3 M. I. Constante apparente d'équilibre, *Bull. Soc. Chim. Fr.*, (1972), 13-18, in French. Cited on pages: 400, 402.
- [72MAG/BIS] Magon, L., Bismondo, A., Tomat, G., Cassol, A., Interaction of neptunium(V) with dicarboxylate ligands, *Radiochim. Acta*, **17**, (1972), 164-167. Cited on pages: 115, 117, 129, 254, 255, 257, 565, 682.

- [72MAN/VAR] Mánok, F., Várhelyi, C., Gălăţeanu-Titieni, M., Polarographische Untersuchung des  $\text{UO}_2^{2+}$ -Oxalsäure-Systems, *Rev. Roum. Chim.*, **17**, (1972), 675-682, in German. Cited on pages: 228, 229, 231, 232, 234, 682.
- [72MAR/KLO] Markovits, G., Klotz, P., Newman, L., Formation constants for the mixed-metal complexes between indium(III) and uranium(VI) with malic, citric, and tartaric acids, *Inorg. Chem.*, **11**, (1972), 2405-2408. Cited on pages: 364, 365, 366, 369, 594, 683, 703.
- [72MEN] Mentre, I., Tautomérie "zwitterionique" des acides amino-benzoïques et amino-naphtoïques. I. Constantes de dissociation apparentes, *Ann. Chim. (Paris)*, **7**, (1972), 333-341, in French. Cited on page: 114.
- [72MET/GUI3] Metivier, H., Guillaumont, R., Complexes citriques du plutonium tétravalent, *Radiochem. Radioanal. Lett.*, **10**, (1972), 239-250, in French. Cited on pages: 311, 379, 380, 683.
- [72MUN] Münze, R., Thermodynamische Funktionen der Komplexbildung und Ionenradien - I. Bestimmung der freien Enthalpie, Entropie und Enthalpie von Azetatokomplexen der Lanthaniden und Aktiniden aus zwischenatomaren Donor-Akzeptorabständen, *J. Inorg. Nucl. Chem.*, **34**, (1972), 661-668, in German. Cited on page: 749.
- [72NIK/ANT] Nikolaeva, N. M., Antipina, V. A., The dissociation constants of oxalic acid in water at temperatures from 25 to 90°C, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **6**, (1972), 13-17, in Russian. Cited on pages: 115, 684.
- [72ROE/KAN] Roelofsen, G., Kanters, J. A., Citric acid monohydrate,  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , *Cryst. Struct. Commun.*, **1**, (1972), 23-26. Cited on page: 297.
- [72SHA] Shalinets, A. B., Investigation of the complex formation of trivalent actinide and lanthanide elements by the method of electromigration. XVI. Ethylenediaminetetraacetic acid, *Sov. Radiochem.*, **14**, (1972), 285-289. Cited on pages: 505, 507, 684.
- [72SMY] Smyshlyaev, S. I., Solubility product of difficultly soluble acids, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **15**, (1972), 6-8, in Russian. Cited on pages: 394, 684.

- [72SOL/IVA] Solovkin, A. S., Ivantsov, A. I., Thermodynamics of the extraction of plutonium (IV) from perchloric and nitric acid solutions in the presence of oxalic acid, *Sov. At. Energy*, **32**, (1972), 182-183. Cited on pages: 279, 679, 685, 695.
- [72STO] Stöber, H., Mischkomplexe und höhere Uniligandenkomplexe des fünfwertigen Neptuniums - Zur Koordinationsfähigkeit des  $\text{NpO}_2^+$ -Ions, Institut für Radiochemie, Kernforschungszentrum Karlsruhe, Report KFK 1657, (1972), in German. Cited on pages: 254, 255, 256, 257, 374, 686, 687, 763.
- [73ALC] Alcock, N. W., Uranyl oxalate complexes. Part I. Preparation and crystal and molecular structure of ammonium uranyl trioxalate, *J. Chem. Soc. Dalton Trans.*, (1973), 1610-1613. Cited on page: 213.
- [73ALC2] Alcock, N. W., Uranyl oxalate complexes. Part II. Preparation and crystal and molecular structure of ammonium uranyl dioxalate, *J. Chem. Soc. Dalton Trans.*, (1973), 1614-1616. Cited on page: 213.
- [73ALC3] Alcock, N. W., Uranyl oxalate complexes. Part III. Preparation and crystal and molecular structure of ammonium diuranyl trioxalate, *J. Chem. Soc. Dalton Trans.*, (1973), 1616-1620. Cited on page: 213.
- [73ARM/DUN] Armitage, G. M., Dunsmore, H. S., Stability of the hydrogen-oxalate complexes of calcium and strontium, *J. Inorg. Nucl. Chem.*, **35**, (1973), 817-822. Cited on pages: 117, 129, 180, 187, 687.
- [73BAR/DYA] Barkhanova, N. N., Dyatlova, N. M., Fridman, A. Y., Reactions of coproportionation of dinuclear mixed compounds of the transition metals with the ethylenediaminetetra-acetate ion and with ethylenediamine, glycine, and oxalate in solution, *Russ. J. Inorg. Chem.*, **18**, (1973), 785-788. Cited on page: 465.
- [73BAR/FRI] Barkhanova, N. N., Fridman, A. Y., Dyatlova, N. M., Mono- and dinuclear compounds formed by ethylenediaminetetraacetato-compounds of nickel, cobalt, and copper with glycinate and oxalate in solution, *Russ. J. Inorg. Chem.*, **18**, (1973), 227-229. Cited on pages: 463, 464, 465, 467.

- [73BAR/RED] Barres, M., Redoute, J.-P., Romanetti, R., Tachoire, H., Zahra, C., Calorimétrie des complexes en solution, *C. R. Séances Acad. Sci., Ser. C*, **276**, (1973), 363-366, in French. Cited on pages: 143, 145, 687.
- [73BAT] Bates, R. G., *Determination of pH, theory and practice*, John Wiley & Sons, New York, (1973), 479 pp. Cited on page: 22.
- [73BOT/VIC] Bottari, E., Vicedomini, M., On the complex formation between lead(II) and citrate ions in acid solution, *J. Inorg. Nucl. Chem.*, **35**, (1973), 1269-1278. Cited on pages: 311, 322.
- [73BOT/VIC2] Bottari, E., Vicedomini, M., On the protonation of citrate ions in 2M Na(ClO<sub>4</sub>), *J. Inorg. Nucl. Chem.*, **35**, (1973), 1657-1663. Cited on pages: 311, 322.
- [73CAR/SWA] Carr, J. D., Swartzfager, D. G., Studies of the alkali metal ion complexes of 2,3-diaminobutane-N,N',N'-tetraacetic acid, *J. Am. Chem. Soc.*, **95**, (1973), 3569-3572. Cited on pages: 398, 438.
- [73CAU/GUI] Cauchetier, P., Guichard, C., Etude électrochimique et spectrophotométrique des complexes des ions du plutonium avec l'edta. Première partie: plutonium(III) et (IV), *Radiochim. Acta*, **19**, (1973), 137-146, in French. Cited on pages: 499, 501, 687, 688.
- [73CHA/RAO] Charan Das, P., Rao, G. S., The stability of beryllium complexes with organic ligands. II. Amino carboxylic acids, *J. Indian Chem. Soc.*, **50**, (1973), 172-176. Cited on page: 398.
- [73CHU/SKO2] Chubakova, E. I., Skorik, N. A., The stability of lanthanum, yttrium, scandium, and thorium glutarate and oxalate complexes in aqueous and aqueous alcoholic solutions, *Russ. J. Inorg. Chem.*, **18**, (1973), 1446-1448. Cited on page: 114.
- [73DEY/BER] Deyrieux, R., Berro, C., Péneloux, A., Contribution à l'étude des oxalates de certains métaux bivalents. III. Structure cristalline des oxalates dihydratés de managanèse, de cobalt, de nickel, et de zinc. Polymorphisme des oxalates dihydratés de cobal et de nickel, *Bull. Soc. Chim. Fr.*, (1973), 25-34, in French. Cited on pages: 190, 697.

- [73DUD/SHT] Dudakov, V. G., Shternina, E. B., Solubility of magnesium carbonate in aqueous solutions of disodium dihydrogen ethylenediaminetetraacetate, *Russ. J. Inorg. Chem.*, **18**, (1973), 1657-1658. Cited on pages: 443, 444.
- [73FIN/ROT] Finlayson, B., Roth, R., DuBois, L., Calcium oxalate solubility studies, in: *Urinari Calculi, Int. Symp. Renal Stone Res., Madrid, 1972*, pp. 1-7, Karger, Basel (1973). Cited on pages: 157, 159, 161, 166, 168, 169, 171.
- [73FIN/SMI] Finlayson, B., Smith, A., Spectrophotometry of stability constant of  $\text{CaC}_2\text{O}_4$  based on competition between murexide and oxalate for  $\text{Ca}^{2+}$ , *J. Chem. Eng. Data*, **18**, (1973), 368-370. Cited on pages: 179, 187, 688, 689.
- [73GOR/KHU] Gordienko, V. I., Khudyakova, L. P., Concentrational dissociation constants of tartaric and citric acids at high ionic strengths, *J. Gen. Chem. USSR*, **43**, (1973), 323-326. Cited on page: 308.
- [73HAN/RUZ] Hansen, E. H., Ruzicka J., Selectrode - The universal ion-selective electrode - V, *Talanta*, **20**, (1973), 1105-1115. Cited on pages: 446, 450, 451, 772.
- [73HUB/HUS] Hubert, S., Hussonnois, M., Guillaumont, R., Mise en évidence de l'effet néphélauxétique dans un complexe citrique des éléments de la série 4f, *J. Inorg. Nucl. Chem.*, **35**, (1973), 2923-2944, in French. Cited on page: 308.
- [73JAY/DIA] Jayadevan, N. C., Dias, R. M. A., Chackraburttty, D. M., Preparation, characterization and thermal decomposition of  $\text{Ti}_2\text{UO}_2(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$ , *J. Inorg. Nucl. Chem.*, **35**, (1973), 1037-1040. Cited on page: 213.
- [73KHA/MOS2] Kharitonov, Y. Y., Moskvina, A. I., IR absorption spectra of some neptunium compounds: IV. Oxalate compounds, *Sov. Radiochem.*, **15**, (1973), 608-611. Cited on page: 248.
- [73KHA/PET] Khalil, I., Petit-Ramel, M., Etude potentiométrique et polarimétrique du système cuivre-acide citrique-L-proline, *Bull. Soc. Chim. Fr.*, (1973), 1908-1912, in French. Cited on page: 308.

- [73KNA/MAT] Knappwost, A., Matouschek E., Experimentelle Untersuchungen zur Löslichkeitsbeeinflussung mineralischer Harnkonkremente, *Urol. Int.*, **28**, (1973), 9-20, in German. Cited on pages: 166, 167, 168, 169, 171.
- [73LAD/POV] Ladd, M. F. C., Povey, D. C., Crystallographic and spectroscopic studies on ethylenediaminetetraacetic acid (edta). I. Crystal and molecular structure of  $\beta$ -edta, *J. Cryst. Mol. Struct.*, **3**, (1973), 15-23. Cited on page: 394.
- [73MOS] Moskvina, A. I., Some thermodynamic characteristics of the processes of formation of actinide compounds in a solid form. I. Energy and entropy of the crystal lattice. Heats of formation and heats of solution, *Sov. Radiochem.*, **15**, (1973), 356-363. Cited on pages: 207, 215, 245, 246, 249, 262, 268, 274.
- [73PIT] Pitzer, K. S., Thermodynamics of electrolytes: I. Theoretical basis and general equations, *J. Phys. Chem.*, **77**, (1973), 268-277. Cited on pages: 819, 822.
- [73PIT/MAY] Pitzer, K. S., Mayorga, G., Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent, *J. Phys. Chem.*, **77**, (1973), 2300-2308. Cited on page: 822.
- [73POR/PAO] Portanova, R., De Paoli, G., Bismondo, A., Magon, L., Interaction of plutonyl(VI) with dicarboxylate ligands. A comparison of the strength of corresponding complexes of other actinide elements., *Gazz. Chim. Ital.*, **103**, (1973), 691-697. Cited on pages: 283, 284, 689.
- [73RAM/MAN2] Ramamoorthy, S., Manning, P. G., Equilibrium studies of metal-ion complexes of interest to natural waters-VI: Simple and mixed complexes of Fe(III) involving NTA as primary ligand and a series of oxygen-bonding organic anions as secondary ligands, *J. Inorg. Nucl. Chem.*, **35**, (1973), 1571-1575. Cited on page: 308.
- [73RYK/SHT] Rykova, G. A., Shternina, E. B., The solubility of calcium dihydrogen ethylenediaminetetra-acetate in aqueous salt solutions, *Russ. J. Inorg. Chem.*, **18**, (1973), 633-635. Cited on pages: 443, 444.

- [73SHI/RUM2] Shilin, I. V., Rumyantseva, T. A., Kinetics of reduction of neptunium(V) by oxalic acid, *Sov. Radiochem.*, **15**, (1973), 519-525. Cited on page: 254.
- [73VAS/KOC] Vasil'ev, V. P., Kochergina, L. A., Yastrebova, T. D., Heat of ionization of (ethylenedinitrilo)-tetraacetic acid in presence of various electrolytes, *J. Gen. Chem. USSR*, **43**, (1973), 971-975. Cited on pages: 427, 428, 689, 710, 727.
- [73VAS/SHE2] Vasil'ev, V. P., Shekhanova, L. D., Kochergina, L. A., Heat of ionization of oxalic acid in presence of various electrolytes, *J. Gen. Chem. USSR*, **43**, (1973), 967-970. Cited on pages: 143, 145, 680, 690, 710.
- [73ZAI/ALE] Zaitseva, V. P., Alekseeva, D. P., Gel'man, A. D., Soluble compounds of Pu<sup>V</sup>. I. Complex formation of Pu<sup>V</sup> with oxalate ion, *Sov. Radiochem.*, **15**, (1973), 386-390. Cited on pages: 263, 273, 282, 690.
- [73ZAK/ORL] Zakharova, F. A., Orlova, M. M., Krot, N. N., Kinetics of reduction of plutonium(VI) by oxalate ions, *Sov. Radiochem.*, **15**, (1973), 796-799. Cited on page: 283.
- [74BAU] Baumann, E. W., Investigation of copper(II) chelates of EDTA and DTPA with cupric-selective electrodes, *J. Inorg. Nucl. Chem.*, **36**, (1974), 1827-1832. Cited on pages: 400, 402.
- [74BUL] Bulatov, M. I., Determination of the solubility and solubility product of slightly soluble acids, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **17**, (1974), 507-510, in Russian. Cited on pages: 394, 691.
- [74BYK/PET2] Bykhovskii, D. N., Petrova, I. K., Reaction of americium(III) with oxalate ions during adsorption on barium oxalate, *Sov. Radiochem.*, **16**, (1974), 27-30. Cited on pages: 285, 691.
- [74DER/SMI] Derissen, J. L., Smit, P. H., Refinement of the crystal structures of anhydrous  $\alpha$ - and  $\beta$ -oxalic acids, *Acta Crystallogr.*, **B30**, (1974), 2240-2242. Cited on page: 106.

- [74DUD/SHT] Dudakov, V. G., Shternina, E. B., Reaction of dibasic magnesium phosphate and sodium ethylenediaminetetraacetate in an aqueous medium, VINITI, Report 468-74, (1974), in Russian. Cited on page: 443.
- [74DUD/SHT2] Dudakov, V. G., Shternina, E. B., Solubility of dibasic sodium and magnesium ethylenediaminetetraacetates in aqueous salt solutions, VINITI, Report 469-74, (1974), in Russian. Cited on pages: 443, 444.
- [74FIE/MCC] Field, T. B., McCourt, J. L., McBryde, W. A. E., Composition and stability of iron and copper citrate complexes in aqueous solution, *Can. J. Chem.*, **52**, (1974), 3119-3124. Cited on pages: 311, 805.
- [74HEL/KIR] Helgeson, H. C., Kirkham, D. H., Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: I. Summary of the thermodynamic/electrostatic properties of the solvent, *Am. J. Sci.*, **274**, (1974), 1089-1198. Cited on page: 827.
- [74HUB/HUS] Hubert, S., Hussonnois, M., Brillard, L., Goby, G., Guillaumont, R., Détermination simultanée de constantes de formation des complexes citrique de l'américium, du curium, du californium, de l'einsteinium et du fermium, *J. Inorg. Nucl. Chem.*, **36**, (1974), 2361-2366, in French. Cited on pages: 381, 382, 383, 692, 707, 745.
- [74KRO/MEF] Krot, N. N., Mefod'eva, M. P., Stability of neptunium(III) complexes with some complexons, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **9**, (1974), 2052-2054. Cited on pages: 490, 491.
- [74LAD/POV] Ladd, M. F. C., Povey, D. C., Stace, B. C., Crystallographic and spectroscopic studies on ethylenediaminetetraacetic acid (edta). III. Crystal and molecular structure of  $\alpha$ -edta and infrared studies on  $\alpha$ - and  $\beta$ -edta, *J. Cryst. Mol. Struct.*, **4**, (1974), 313-325. Cited on pages: 392, 394.
- [74MEY] Meyer, J. L., Formation constants for interaction of citrate with calcium and magnesium ions, *Anal. Biochem.*, **62**, (1974), 295-300. Cited on pages: 308, 335, 336, 337, 339, 342, 343, 344, 692.



- [74MOR/SEK] Moriya, H., Sekine, T., A solvent-extraction study of zinc(II) complexes with several divalent anions of carboxylic and inorganic acids, *Bull. Chem. Soc. Jpn.*, **47**, (1974), 747-748. Cited on page: 114.
- [74MYA/LOG] Myachina, L. I., Logvinenko, V. A., Knyazeva, N. N., Binuclear complexes of EDTA. 1. The synthesis of binuclear ethylenediaminetetraacetates of alkaline-earth and transition metals, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **6**, (1974), 77-82, in Russian. Cited on pages: 443, 459, 460.
- [74NAN/GAR] Nancollas, G. H., Gardner, G. L., Kinetics of crystal growth of calcium oxalate monohydrate, *J. Cryst. Growth*, **21**, (1974), 267-276. Cited on pages: 166, 168, 174, 175, 176, 179, 182, 187, 693.
- [74NAZ/FLY2] Nazarenko, V. A., Flyantikova, G. V., Ionization constants of triazirinsulfonategermanic acid, *Sov. Progr. Chem.*, **40**, (1974), 62-65. Cited on page: 114.
- [74NIK/SHI] Nikolaevskii, V. B., Shilov, V. P., Krot, N. N., Complex compounds of pentavalent americium in solutions of ethylenediaminetetraacetic and diethylenetriaminepentaacetic acids, *Sov. Radiochem.*, **16**, (1974), 57-61. Cited on pages: 508, 693, 725.
- [74PAR] Parsons, R., Manual of Symbols and Terminology for Physicochemical Quantities and Units. Appendix III. Electrochemical nomenclature, *Pure Appl. Chem.*, **37**, (1974), 503-516. Cited on page: 22.
- [74PET/KHA] Petit-Ramel, M., Khalil, I., Études des complexes mixtes bimétalliques. I. Détermination des constantes de stabilité de l'acide citrique et des citrates de cuivre, *Bull. Soc. Chim. Fr.*, (1974), 1255-1258, in French. Cited on page: 308.
- [74PIT/KIM] Pitzer, K. S., Kim, J. J., Thermodynamics of electrolytes. IV. Activity and osmotic coefficients for mixed electrolytes, *J. Am. Chem. Soc.*, **96**, (1974), 5701-5707. Cited on page: 822.
- [74PIT/MAY] Pitzer, K. S., Mayorga, G., Thermodynamics of electrolytes. III. Activity and osmotic coefficients for 2-2 electrolytes, *J. Solution Chem.*, **3**, (1974), 539-546. Cited on page: 822.

- [74POZ/POR] Pozhidaev, A. I., Porai-Koshits, M. A., Polynova, T. N., Crystal structure of zirconium ethylenediaminetetraacetate tetrahydrate, *J. Struct. Chem. USSR*, **15**, (1974), 548-553. Cited on page: 472.
- [74SHA/KII] Shalimov, V. V., Kiiko, N. I., Zaitsev, B. N., Tebelev, L. G., Mikolaev, V. M., Uranium(IV) citrate complexes, *Complexing and extraction of actinides and lanthanides*, Vdovenko, V. M., Ed., pp. 3-7, Akademiya Nauk SSSR, Moscow, USSR, (1974), in Russian. Cited on pages: 361, 362, 363, 694.
- [74SHI/NIK2] Shilov, V. P., Nikolaevskii, V. B., Krot, N. N., Complex formation by americium(V) with oxalate ions, *Russ. J. Inorg. Chem.*, **19**, (1974), 254-257. Cited on pages: 294, 694.
- [74SIN/GHO] Sinha, A. K., Ghosh, J. C., Prasad, B., Second dissociation constant of oxalic acid from 0° to 50°, *J. Indian Chem. Soc.*, **51**, (1974), 586-588. Cited on page: 114.
- [74SIN/TAN] Singh, S. P., Tandon, J. P., pH-metric studies on the interaction of oxovanadium(IV) with some dicarboxylic acids, *Acta Chim. Acad. Sci. Hung.*, **80**, (1974), 425-435. Cited on page: 114.
- [74SOL] Solovkin, A. S., Thermodynamics of extraction of tetravalent plutonium, uranium, thorium and zirconium, *J. Radioanal. Chem.*, **21**, (1974), 15-29. Cited on pages: 279, 678, 685, 695.
- [74TER/NIK] Terëshin, G. S., Nikiforova, E. V., Solubility products of certain complexones, *Russ. J. Inorg. Chem.*, **19**, (1974), 796-798. Cited on pages: 394, 695.
- [74TER/NIK2] Terëshin, G. S., Nikiforova, E. V., Determination of the stability constant of the nickel ethylenediaminetetraacetate complex by the solubility of EDTA method, *Russ. J. Inorg. Chem.*, **19**, (1974), 1020-1022. Cited on pages: 461, 462, 466, 695.
- [74VAN/GEN] Vanni, A., Gennaro, M. C., Equilibrium studies of beryllium complexes. Interaction of beryllium ion with citric and tricarballic acids, *Ann. Chim. (Rome)*, **64**, (1974), 397-408. Cited on page: 311.

- [74VAS/KOC] Vasil'ev, V. P., Kochergina, L. A., Yastrebova, T. D., Heats of neutralization and ionization of (ethylenedinitrolo)tetraacetic acid at stages III and IV, *J. Gen. Chem. USSR*, **44**, (1974), 1346-1349. Cited on pages: 427, 428, 695, 721, 751.
- [75AND/POD] Anderegg, G., Podder, N. G., Bläuenstein, P., Hangartner, M., Stünzi, H., Pyridine derivatives as complexing agents X. Thermodynamics of complex formation of N,N'-bis-(2-pyridylmethyl)-ethylenediamine and of two higher homologues, *J. Coord. Chem.*, **4**, (1975), 267-275. Cited on pages: 400, 402, 446, 447, 450, 451, 455, 461, 464, 465, 466, 467, 566, 772.
- [75BAR/DUB] Barres, M., Dubes, J. P., Romanetti, R., Tachoire, H., Zahra, C., Détermination des constantes thermodynamiques d'équilibres en solution par calorimétrie à conduction et flux de réactif. I. Description de la méthode, *Thermochim. Acta*, **11**, (1975), 235-246, in French. Cited on pages: 143, 144, 145, 687, 696.
- [75BIE] Biedermann, G., Ionic media, *Dahlem workshop on the nature of seawater*, pp. 339-362, Dahlem Konferenzen, Berlin, (1975). Cited on page: 821.
- [75BOT] Bottari, E., Complexes between cadmium(II) and oxalate ion, *Monatsh. Chem.*, **106**, (1975), 451-458, in German. Cited on page: 114.
- [75BRI/STU] Briggs, T. N., Stuehr, J. E., Simultaneous potentiometric determination of precise equivalence points and pK values of two- and three-pK systems, *Anal. Chem.*, **47**, (1975), 1916-1920. Cited on page: 308.
- [75BRU/KIR] Brücher, E., Király, R., Nagypál, I., Equilibrium relations of rare earth ethylene-diaminetetraacetate complexes in the presence of a ligand excess, *J. Inorg. Nucl. Chem.*, **37**, (1975), 1009-1012. Cited on page: 400.
- [75CAR/SWA] Carr, J. D., Swartzfager, D. G., Kinetics of the ligand exchange and dissociation reactions of calcium-aminocarboxylate complexes, *J. Am. Chem. Soc.*, **97**, (1975), 315-321. Cited on pages: 399, 400, 402, 446, 447, 449, 696.

- [75CAU/GUI] Cauchetier, P., Guichard, C., Etude électrochimique et spectrophotométrique des complexes des ions du plutonium avec l'edta. Plutonium(V) et (VI), *J. Inorg. Nucl. Chem.*, **37**, (1975), 1771-1778, in French. Cited on pages: 502, 503, 697.
- [75DAN/OST] Daniele, P. G., Ostacoli, G., Vanni, A., Mixed complexes formed by  $\text{Cu}^{2+}$  ion with 2,2'-dipyridyl and citric acid in aqueous solution, *Ann. Chim. (Rome)*, **65**, (1975), 465-472. Cited on page: 308.
- [75DEY/CAN] Deyrieux, R., Canals, E., Détermination des grandeurs thermodynamiques des constituants d'un système chimique complexe à l'équilibre, *J. Chim. Phys. Phys.-Chim. Biol.*, **71**, (1975), 793-798, in French. Cited on pages: 190, 191, 192, 193, 194, 195, 196, 199, 200, 670, 697, 698, 699, 700.
- [75FIE/COB] Field, T. B., Coburn, J., McCourt, J. L., McBryde, W. A. E., Composition and stability of some metal citrate and diglycolate complexes in aqueous solution, *Anal. Chim. Acta*, **74**, (1975), 101-106. Cited on pages: 335, 336, 337, 339, 342, 343, 344, 354, 355, 359, 701, 760.
- [75FRI/PIZ] Friedman, S., Pizer, R., Mechanism of the complexation of phenylboronic acid with oxalic acid. A reaction which requires ligand donor atom protonation, *J. Am. Chem. Soc.*, **97**, (1975), 6059-6062. Cited on page: 114.
- [75GAR] Gardner, G. L., Nucleation and crystal growth of calcium oxalate trihydrate, *J. Cryst. Growth*, **30**, (1975), 158-168. Cited on pages: 166, 168, 169.
- [75GAR/NAN] Gardner, G. L., Nancollas, G. H., Kinetics of dissolution of calcium oxalate monohydrate, *J. Phys. Chem.*, **79**, (1975), 2597-2600. Cited on page: 166.
- [75HOI] Høiland, H., Volumes of ionization of dicarboxylic acids in aqueous solution from density measurements at 25°C, *J. Chem. Soc. Faraday Trans. 1*, **71**, (1975), 797-802. Cited on page: 113.
- [75JAY/SIN] Jayadevan, N. C., Singh Mudher, K. D., Chackraburttty, D. M., The crystal and molecular structure of potassium diuranil trisoxalate tetrahydrate, *Acta Crystallogr.*, **B31**, (1975), 2277-2280. Cited on page: 213.

- [75KOR/PAT] Korpusov, G. V., Patrusheva, E. N., Dolidze, M. S., Trubnikova, A. I., Investigation of certain extraction systems based on nitrogen-containing extraction reagents and complexones, *Sov. Radiochem.*, **17**, (1975), 496-501. Cited on pages: 504, 505, 701.
- [75LAG/LAG] Lagrange, J., Lagrange, P., Solubilité et constantes d'acidité des acides nitrilotriacétique et éthylène diaminetétracétique en milieu NaClO<sub>4</sub>, *C. R. Hebd. Séances Acad. Sci., Ser. C*, **280**, (1975), 423-426, in French. Cited on pages: 394, 395, 400, 402.
- [75LIT/NIK] Litovchenko, K. I., Nikitenko, V. N., Kublanovskii, V. S., Complexing in the cadmium(II) - ethylenediaminetetraacetate - water system, *Sov. J. Coord. Chem.*, **1**, (1975), 1152-1153. Cited on page: 398.
- [75MAT/HIR] Matsushita, H., Hironaka, H., Determination of dissociation constants by potentiostatic titration, *Nippon Kagaku Kaishi (J. Chem. Soc. Japan)*, (1975), 1252-1254, in Japanese. Cited on page: 311.
- [75MER/GAT] Merciny, E., Gatez, J. M., Swennen, L., Duyckaerts, G., Réalisation et mise au point d'un appareil de titrage automatique de grande précision, *Anal. Chim. Acta*, **78**, (1975), 159-169, in French. Cited on page: 499.
- [75NEB/AND] Nebel, D., Anders, G., Zur Komplexbildung und Solvation einiger Actinide I. Untersuchungen zur Komplexbildung mit Acetat und Citrat, *Isotopenpraxis*, **11**, (1975), 152-155, in German. Cited on pages: 378, 701, 702.
- [75OHY] Ohyoshi, A., Synthesis of metal complexes and recovery of metal ions by controlled reaction conditions (Part I). Controlling the chemical species of uranyl citrate complexes, *Kenkyu Hokoku - Asahi Garasu Kogyo Gijutsu Shoreikai*, **26**, (1975), 49-56. Cited on pages: 364, 368, 702.
- [75OHY/ODA] Ohyoshi, E., Oda, J., Ohyoshi, A., Complex formation between the uranyl ion and citric acid, *Bull. Chem. Soc. Jpn.*, **48**, (1975), 227-229. Cited on pages: 364, 365, 368, 369, 702, 703.

- [75PAK/OHA] Pak, C. Y. C., Ohata M., Holt, K., Effect of diphosphonate on crystallization of calcium oxalate in vitro, *Kidney Int.*, **7**, (1975), 154-160. Cited on pages: 161, 168, 169.
- [75PEA/CRE] Pearce, K. N., Creamer, L. K., The complete ionization scheme for citric acid, *Aust. J. Chem.*, **28**, (1975), 2409-2415. Cited on pages: 308, 730.
- [75PIT] Pitzer, K. S., Thermodynamics of electrolytes. V. Effects of higher-order electrostatic terms, *J. Solution Chem.*, **4**, (1975), 249-265. Cited on page: 822.
- [75PRA/JON] Pratt, T. H., Jones, M. M., Stability constant studies on some new thioether carboxylic acid chelating agents II: derivatives of  $\beta$ -mercaptopropionic acid, *J. Inorg. Nucl. Chem.*, **37**, (1975), 2403-2307. Cited on pages: 178, 179, 181, 187, 704.
- [75RAM/MAN] Ramamoorthy, S., Manning, P. G., Equilibrium studies of solutions containing  $\text{Al}^{3+}$ ,  $\text{Ca}^{2+}$  or  $\text{Cd}^{2+}$  and cysteine, orthophosphate and a carboxylic acid, *J. Inorg. Nucl. Chem.*, **37**, (1975), 363-367. Cited on pages: 338, 342, 704.
- [75SIN/TAN] Singh, S. P., Tandon, J. P., pH-metric studies on the mixed-ligand chelates of oxovanadium(IV) with picolinic acid and some dicarboxylic acids, *Acta Chim. Acad. Sci. Hung.*, **84**, (1975), 419-430. Cited on page: 114.
- [75TER/SHE] Ternovaya, T. V., Shelest, V. P., Kostromina, N. A., Konunova, T. B., Spectrographic study of complex formation by zirconium and neodymium with EDTA, *Russ. J. Inorg. Chem.*, **20**, (1975), 1779-1784. Cited on pages: 472, 704, 713.
- [75VAS/BEL] Vasil'ev, V. P., Belonogova, A. K., Thermodynamic characteristics of the formation reaction of the magnesium ethylenediaminetetraacetato complex in aqueous solution, *Russ. J. Inorg. Chem.*, **20**, (1975), 16-18. Cited on page: 457.
- [75VOT/BAR] Votava, J., Bartušek, M., Complexes of beryllium with five- and six-membered chelate rings, *Collect. Czech. Chem. Commun.*, **40**, (1975), 2050-2058. Cited on pages: 114, 398.

- [75ZAI/NIK] Zaitsev, B. N., Nikolaev, V. M., Shalimov, V. V., Interaction of tetravalent plutonium and zirconium with citric acid in nitric acid solutions, *Sov. Radiochem.*, **17**, (1975), 287-290. Cited on pages: 301, 362, 379, 380, 704.
- [76AND] Anderegg, G., Komplexe XLVII. Die Thermodynamik der Komplexbildung von einigen ein- und zweiwertigen Metallionen mit Aethylenediaminetetraacetat- und Uramildiacetat- Ion, *Z. Naturforsch.*, **31B**, (1976), 786-789, in German. Cited on pages: 428, 432, 438, 439.
- [76AND/MAL] Anderegg, G., Malik, S. C., Komplexe XLVII. The stability of palladium(II) complexes with aminopolycarboxylate anions, *Helv. Chim. Acta*, **59**, (1976), 1498-1511. Cited on pages: 400, 402.
- [76BAE/MES] Baes, Jr., C. F., Mesmer, R. E., *The hydrolysis of cations*, Wiley & Sons, New York, (1976), 489 pp. Cited on pages: 26, 202, 473, 758, 822.
- [76BAG/RAM3] Bagawde, S. V., Ramakrishna, V. V., Patil, S. K., Oxalate complexing of tetravalent actinides, *J. Inorg. Nucl. Chem.*, **38**, (1976), 1669-1672. Cited on pages: 250, 251, 252, 278, 279, 280, 706, 716, 717, 724.
- [76BRI/ELD] Brits, A. G., van Eldik, R., van den Berg, J. A., Equilibrium studies of the uranyl oxalate system in acidic aqueous solution, *Z. Phys. Chem. (Munich)*, **99**, (1976), 107-116. Cited on pages: 114, 232, 233, 234, 235, 576, 706.
- [76BRI/ELD2] Brits, A. G., van Eldik, R., van den Berg, J. A., The photolysis of the uranyl oxalate system. I. Photochemical behaviour in strongly acidic aqueous solution, *Z. Phys. Chem. (Munich)*, **102**, (1976), 203-212. Cited on pages: 228, 230, 231.
- [76BRI/ELD3] Brits, A. G., van Eldik, R., van den Berg, J. A., The photolysis of the uranyl oxalate system. II. Kinetics and mechanism in strongly acidic aqueous solution, *Z. Phys. Chem. (Munich)*, **102**, (1976), 213-220. Cited on pages: 228, 230, 231.

- [76CHO/UNR] Choppin, G. R., Unrein, P. J., Thermodynamic study of actinide fluoride complexation, in: *Transplutonium 1975: Proc. Symp. Baden Baden, Sept. 13-17, 1975, 4th Int. Transplutonium Symp.*, pp. 97-107, Müller, W. and Lindner, R., Eds., North-Holland Publ., Amsterdam, Holland, (1976). Cited on page: 749.
- [76COR/WAL] Corrie, A. M., Walker, M. D., Williams, D. R., Thermodynamic considerations in co-ordination. Part XXII. Sequestering ligands for improving the treatment of plumbism and cadmiumism, *J. Chem. Soc. Dalton Trans.*, (1976), 1012-1015. Cited on pages: 400, 402.
- [76DAN/OST] Daniele, P. G., Ostacoli, G., Mixed complexes of Ni(II) and citric acid with L-histidine or histamine in aqueous solution, *Ann. Chim. (Rome)*, **66**, (1976), 537-549. Cited on pages: 353, 354, 355, 356, 359, 707.
- [76DUD] Dudakov, V. G., Properties of aqueous solutions of acidic magnesium ethylenediaminetetraacetate, VINITI, Report 260-76, (1976), in Russian. Cited on pages: 443, 444.
- [76GAT/MER] Gatez, J. M., Merciny, E., Duyckaerts, G., Etude thermodynamique de la complexation des lanthanides trivalents avec l'acide hydroxyéthyléthylènediaminotriacétique et d'autres acides aminoacétiques. I. Détermination, par potentiométrie, des constantes d'acidité de certains acides aminopolyacétiques, *Anal. Chim. Acta*, **84**, (1976), 383-395, in French. Cited on pages: 400, 402.
- [76HAR/MAR] Harris, W. R., Martell, A. E., Aqueous complexes of gallium(III), *Inorg. Chem.*, **15**, (1976), 713-720. Cited on page: 311.
- [76HUB/HUS] Hubert, S., Hussonnois, M., Brillard, L., Guillaumont, R., Thermodynamic functions for complexing of  $M^{3+}_{(aq)}$  ions ( $M = Pu^{3+}_{(aq)}$  to  $Fm^{3+}_{(aq)}$ ) in: *Transplutonium 1975: Proc. Symp. Baden Baden, Sept. 13-17, 1975, 4th Int. Transplutonium Symp.*, pp. 109-118, Müller, W. and Lindner, R., Eds., North-Holland Publ., Amsterdam, Holland, (1976). Cited on pages: 381, 707.
- [76KAL] Kallen, T. W., Reactions of the trans- and cis-diaquobis(oxalato)chromate(III) ions in solutions which contain oxalic acid, *Inorg. Chem.*, **15**, (1976), 440-445. Cited on pages: 115, 117, 143, 145, 670, 707, 708.



- [76LAG/AUB] Laguerie, C., Aubry, M., Couderc, J.-P., Some physicochemical data on monohydrate citric acid solutions in water: Solubility, density, viscosity, diffusivity, pH of standard solution, and refractive index, *J. Chem. Eng. Data*, **21**, (1976), 85-87. Cited on page: 305.
- [76LEG/JEA] Legros, J. P., Jeannin, Y., Structure de l'ion  $\mu$ -oxalato-bis[dioxalatodioxouranium(VI)],  $[(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5]^{6-}$ , *Acta Crystallogr.*, **B32**, (1976), 2497-2503. Cited on page: 214.
- [76MAK/STE] Makarova, T. P., Stepanov, A. V., Deuterium isotope effects in the dissociation of ethylenediaminetetraacetic and cyclohexylene-1,2-diaminetetraacetic acids, *Russ. J. Inorg. Chem.*, **21**, (1976), 146-147. Cited on pages: 400, 402.
- [76MAK/TOU] Makar, G. K. R., Touche, M. L. D., Williams, D. R., Thermodynamic considerations in co-ordination. Part XXIII. Formation constants for complexes of protons, zinc(II), and acid anions and their use in computer evaluation of a better zinc therapeutical, *J. Chem. Soc. Dalton Trans.*, (1976), 1016-1019. Cited on pages: 115, 117, 129.
- [76MCD/KEL] McDowell, W. J., Keller, Jr., O. L., Dittner, P. E., Tarrant, J. R., Case, G. N., Nobelium chemistry: aqueous complexing with carboxylate ions, *J. Inorg. Nucl. Chem.*, **38**, (1976), 1207-1210. Cited on pages: 179, 182, 183, 187, 188, 648, 708, 709, 779.
- [76MEF/BLO] Mefod'eva, M. P., Blokhin, V. I., Gel'man, A. D., Krot, N. N., On the synthesis of some new neptunium compounds, in: *Proceeding of the Moscow symposium on the chemistry of transuranium elements*, pp. 161-163, Pergamon, Oxford, UK, (1976), (Sept. 4-8, 1972), Spitsyn, V. I. and Katz, J. J. Eds.. Cited on pages: 248, 490.
- [76MUR/KUR] Murai, R., Kurakane, K., Sekine, T., The stability constants of nickel(II) complexes with chloride, thiocyanate, sulfate, thiosulfate and oxalate ions, as determined by a solvent extraction method, *Bull. Chem. Soc. Jpn.*, **49**, (1976), 335-336. Cited on pages: 194, 195, 197.
- [76MYA/LOG] Myachina, L. I., Logvinenko, V. A., Knyazeva, N. N., Binuclear complexes of EDTA. II. Study of isothermal solubility in systems  $\text{Mg}_2\text{L}-\text{Me}_2\text{L}-\text{H}_2\text{O}$ , *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **6**, (1976), 32-35, in Russian. Cited on page: 443.

- [76NOW/CAN] Nowogrocki, G., Canonne, J., Wozniak, M., Potentiométrie des mélanges de protolytes: élimination de l'étalonnage de la chaîne de mesure, *Bull. Soc. Chim. Fr.*, (1976), 1369-1374, in French. Cited on page: 308.
- [76PIT/SIL] Pitzer, K. S., Silvester, L. F., Thermodynamics of electrolytes. VI. Weak electrolytes including  $\text{H}_3\text{PO}_4$ , *J. Solution Chem.*, **5**, (1976), 269-278. Cited on page: 822.
- [76SCA] Scatchard, G., *Equilibrium in solutions: Surface and colloid chemistry*, Harvard University Press, Cambridge, Massachusetts, (1976), 306 pp. Cited on page: 821.
- [76TRI/SCH] Tribalat, S., Schriver, L., Etude de quelques complexes du zirconium(IV) et du hafnium(IV) au moyen de l'extraction des isopropyltropolonates par le chloroforme, *J. Inorg. Nucl. Chem.*, **38**, (1976), 145-148, in French. Cited on pages: 205, 206, 709.
- [76VAN/KUC] Vaňura, P., Kuča, L., Extraction of citric acid by the toluene solutions of trilaurylamine, *Collect. Czech. Chem. Commun.*, **41**, (1976), 2857-2877. Cited on pages: 308, 731.
- [76VAS/BEL] Vasil'ev, V. P., Belonogova, A. K., Thermodynamic characteristics of the formation of the ethylenediaminetetra-acetato-complex of sodium in aqueous solution, *Russ. J. Inorg. Chem.*, **21**, (1976), 350-353. Cited on page: 439.
- [76VAS/BEL2] Vasil'ev, V. P., Belonogova, A. K., Thermodynamic characteristics of the formation of the calcium ethylenediaminetetraacetate complex in aqueous solution, *Russ. J. Inorg. Chem.*, **21**, (1976), 31-33. Cited on pages: 455, 456, 457, 458, 459, 469, 598.
- [76VAS/BEL3] Vasil'ev, V. P., Belonogova, A. K., Thermodynamic characteristics of the formation of ethylenediaminetetra-acetato-complexes of nickel and cobalt in aqueous solution, *Russ. J. Inorg. Chem.*, **21**, (1976), 1646-1648. Cited on pages: 468, 469.
- [76VAS/KOC] Vasil'ev, V. P., Kochergina, L. A., Orlova, T. D., Heats of the second-stage ionization of (ethylenedinitrilo)tetrakisacetic acid at various temperatures, *J. Gen. Chem. USSR*, **46**, (1976), 2109-2112. Cited on pages: 427, 429, 433, 709.

- [76VAS/SHE] Vasil'ev, V. P., Shekhanova, L. D., Kochergina, L. A., Heats of ionization of oxalic acid in sodium nitrate solutions at various temperatures, *J. Gen. Chem. USSR*, **46**, (1976), 729-732. Cited on pages: 143, 146, 680, 710, 711.
- [76YAD/GHO] Yadava, P. C., Ghose, A. K., Yadava, K. L., Dey, A. K., Stability constants of oxalate complexes of copper(II) and nickel(II) by paper electrophoresis, *Chromatographia*, **9**, (1976), 410-412. Cited on pages: 114, 195, 196, 711, 777.
- [77AND] Anderegg, G., *Critical survey of stability constants of EDTA complexes*, IUPAC Chemical Data Series, No. 14, Pergamon Press, Oxford, (1977), 42 pp. Cited on page: 438.
- [77ANS/SUR] d'Ans, J., Surawski, H., Synowietz, C., Landolt-Börnstein (New Series). Group IV: Macroscopic and technical properties of matter, vol. 1: Densities of liquid systems and their heat capacities. Part b: Densities of binary aqueous systems and heat capacities of liquid systems, pp. 12-22, Springer-Verlag, Berlin, (1977). Cited on page: 99.
- [77BRI/ELD] Brits, A. G., van Eldik, R., van den Berg, J. A., The photolysis of the uranyl oxalate system. III. Photochemical behaviour, kinetics and mechanism in aqueous solution, *J. Inorg. Nucl. Chem.*, **39**, (1977), 1195-1199. Cited on pages: 228, 230, 231.
- [77BRO/PET] Brookes, G., Pettit, L. D., Complex formation and stereoselectivity in the ternary systems copper(II) - D/L-histidine - L-amino-acids, *J. Chem. Soc. Dalton Trans.*, (1977), 1918-1924. Cited on pages: 117, 132.
- [77CHO/GOE] Choppin, G. R., Goedken, M. P., Gritmon, T. F., The complexation of lanthanides by aminocarboxylate ligands - II. Thermodynamic parameters., *J. Inorg. Nucl. Chem.*, **39**, (1977), 2025-2030. Cited on pages: 427, 429, 711, 712.
- [77CHR/BOR] Christensen, H. H., Borggaard, O. K., The protolytic properties of iron(III)-EDTA complexes in weakly alkaline solution and the solubility product of iron(III) hydroxide, *Acta Chem. Scand.*, **A31**, (1977), 793-794. Cited on page: 398.

- [77DEL2] Dellien, I., Thermodynamic properties of iron oxalates and malonates in perchlorate medium, *Acta Chem. Scand.*, **A31**, (1977), 473-479. Cited on page: 114.
- [77DUC/BER] Duc, G., Bertin, F., Thomas-David, G., Contribution to the study of beryllium complexes. VII. Chelation of beryllium ions with oxalic acid. Potentiometric study., *Bull. Soc. Chim. Fr.*, (1977), 196-198, in French. Cited on page: 114.
- [77FED/KHO] Fedorov, V. A., Khokhlova, A. I., Interaction of magnesium ions with the anions of certain monocarboxylic acids, *Russ. J. Inorg. Chem.*, **22**, (1977), 662-665. Cited on pages: 159, 160, 162, 167, 178, 181, 712.
- [77FER] Fernelius, W. C., *How to name an inorganic substance*, IUPAC Commission on Nomenclature of Inorganic Compounds, Pergamon Press, Oxford, (1977), 36 pp. Cited on page: 13.
- [77GRA/CRO] Graustein, W. C., Cromack, Jr., K., Sollins, P., Calcium oxalate: Occurrence in soils and effect on nutrient and geochemical cycles, *Science*, **198**, (1977), 1251-1254. Cited on page: 164.
- [77GRI/GOE] Gritmon, T. F., Goedken, M. P., Choppin, G. R., The complexation of lanthanides by aminocarboxylate ligands - I. Stability constants, *J. Inorg. Nucl. Chem.*, **39**, (1977), 2021-2023. Cited on pages: 399, 711.
- [77HED/OLI] Hedström, H., Olin, Å., Svanström, P., Åslin, E., The complex formation between  $Pb^{2+}$  and the oxalate and hydrogen oxalate ions, *J. Inorg. Nucl. Chem.*, **39**, (1977), 1191-1194. Cited on pages: 117, 129.
- [77HOJ/SUG] Hojo, Y., Sugiura, Y., Tanaka, H., Chelate and non-chelate complexes of organomercury with polymethylenediamines, *J. Inorg. Nucl. Chem.*, **39**, (1977), 715-720. Cited on page: 398.
- [77HOS/UEN] Hoshi, M., Ueno, K., The precipitations of thorium, uranium(VI) and plutonium(IV) citrato complex ions with hexaminecobalt(III) ion, *Radiochem. Radioanal. Lett.*, **30**, (1977), 145-153. Cited on pages: 301, 713.

- [77HOS/UEN2] Hoshi, M., Ueno, K., The precipitation of thorium or plutonium(IV) oxalato complex with cobalt(III) or chromium(III) complex cation, *Radiochem. Radioanal. Lett.*, **29**, (1977), 331-340. Cited on pages: 263, 272.
- [77JAI/KUM] Jain, U., Kumari, V., Sharma, R. C., Chaturvedi, G. K., Potentiometric studies on the ternary systems beryllium-iminodiacetic acid-dicarboxylic or hydroxy acids, *J. Chim. Phys. Phys.-Chim. Biol.*, **74**, (1977), 1038-1041. Cited on page: 114.
- [77KOS/SHE] Kostromina, N. A., Shelest, V. P., Ternovaya, T. V., Konunova, T. B., Proton resonance investigation of zirconium and hafnium complexes with ethylenediaminetetra-acetate, *Russ. J. Inorg. Chem.*, **22**, (1977), 1659-1662. Cited on pages: 398, 472, 474, 713.
- [77KUB/NIK] Kublanovskii, V. S., Nikitenko, V. N., Litovchenko, K. I., Kostromina, N. A., Investigation of complex formation in the cadmium(II)-ethylenediaminetetraacetate-water system by the proton resonance method, *Sov. J. Coord. Chem.*, **3**, (1977), 518-522. Cited on page: 398.
- [77LYM/VAS] Lymar, V. P., Vasil'ev, V. P., Lytkin, A. I., Effect of temperature on thermodynamic characteristics of dissociation of protonated ethylenediaminetetraacetic acid, VINITI, Report 3433-77, (1977), in Russian. Cited on pages: 431, 436, 713, 714, 717.
- [77MAR/SMI] Martell, A. E., Smith, R. M., *Critical stability constants, Vol. 3: Other Organic Ligands*, Plenum Press, New York, (1977), 495 pp. Cited on pages: 519, 742.
- [77MOY/FRI] Moyers, E. M., Fritz, J. S., Preparation and analytical applications of a propylenediaminetetraacetic acid resin, *Anal. Chem.*, **49**, (1977), 418-423. Cited on pages: 446, 449, 714.
- [77MUN] Münze, R., Zur Bildung von Citratkomplexen des Technetiums, *Radiochem. Radioanal. Lett.*, **30**, (1977), 61-64, in German. Cited on page: 361.
- [77MUN2] Münze, R., Bildung einer Citratverbindung des Tc(III), *Radiochem. Radioanal. Lett.*, **30**, (1977), 117-122, in German. Cited on pages: 301, 361.

- [77MUN/GRO] Münze, R., Grossmann, B., Verbindungen des Technetiums(IV) mit Citronensäure, *Radiochem. Radioanal. Lett.*, **31**, (1977), 95-104, in German. Cited on pages: 361, 362, 363, 714.
- [77OHA] O'Hare, P. A. G., Thermochemistry of uranium compounds: X. Standard enthalpies of formation of uranyl oxalate, uranyl acetate, and their hydrates. Thermodynamics of the  $\text{UO}_2\text{C}_2\text{O}_4 + \text{H}_2\text{O}$  and  $\text{UO}_2(\text{CH}_3\text{COO})_2 + \text{H}_2\text{O}$  systems, *J. Chem. Thermodyn.*, **9**, (1977), 1077-1086. Cited on pages: 214, 215, 715, 775.
- [77OYA/MAT] Oyama, N., Matsuda, H., Ohtaki, H., A potentiometric study on complex formation of cadmium(II) and lead(II) ions with ethylenediaminetetraacetic acid, *Bull. Chem. Soc. Jpn.*, **50**, (1977), 406-409. Cited on pages: 399, 400, 405, 715.
- [77PAS/WHI] Passer, E., White, J. G., Cheng, K. L., The crystal structure of  $\text{Mg}_2\text{edta} \cdot 9\text{H}_2\text{O}$ , *Inorg. Chim. Acta*, **24**, (1977), 13-23. Cited on page: 444.
- [77RAM/RAM] Ramanujam, A., Ramakrishna, V. V., Patil, S. K., Thermodynamic studies on the oxalate complexing of tetravalent actinides by solvent extraction, *Radiochem. Radioanal. Lett.*, **31**, (1977), 119-128. Cited on pages: 250, 251, 252, 278, 715, 716, 724.
- [77RAM/RAM2] Ramanujam, A., Ramakrishna, V. V., Patil, S. K., The study of oxalate complexing of tetravalent actinides by DNNS extraction, *Radiochem. Radioanal. Lett.*, **31**, (1977), 337-346. Cited on pages: 250, 251, 252, 278, 279, 706, 715, 716, 717, 724.
- [77REB/BAR] Rebštocková, T., Bartušek, M., Reactions of boric acid with oxalic, glycolic and tartaric acids, *Collect. Czech. Chem. Commun.*, **42**, (1977), 627-636. Cited on page: 114.
- [77ROO/WIL] Roos, J. T. H., Williams, D. R., Formation constants for citrate-, folic acid-, gluconate- and succinate-proton, -manganese(II), and -zinc(II) systems: relevance to absorption of dietary manganese, zinc and iron, *J. Inorg. Nucl. Chem.*, **39**, (1977), 367-369. Cited on page: 308.

- [77SHI/TAN] Shimizu, S., Taniguchi, M., Equilibrium vapor pressures for the dehydration of crystallization water in salts by transpiration method, *Nippon Kagaku Kaishi (J. Chem. Soc. Japan)*, (1977), 953-958, in Japanese. Cited on page: 165.
- [77VAS/LYM] Vasil'ev, V. P., Lymar, V. P., Lytkin, A. I., Thermodynamic characteristics of the dissociation of protonated ethylenediaminetetra-acetic acid, *Russ. J. Inorg. Chem.*, **22**, (1977), 1357-1360. Cited on pages: 431, 436, 439, 714, 717, 718.
- [77VAS/LYM2] Vasil'ev, V. P., Lymar, V. P., Lytkin, A. I., Influence of temperature on the thermodynamic characteristics of the dissociation of protonated ethylenediaminetetra-acetic acid, *Russ. J. Inorg. Chem.*, **22**, (1977), 1440-1443. Cited on pages: 431, 432, 436, 714, 718.
- [77WIL] Williams, D. R., Analytical and computer simulation studies of a colloidal bismuth citrate system used as an ulcer treatment, *J. Inorg. Nucl. Chem.*, **39**, (1977), 711-714. Cited on page: 308.
- [77ZAK/KOR] Zakolupin, S. A., Korablin, E. V., Solubility of americium oxalate, *Sov. Radiochem.*, **19**, (1977), 581-584. Cited on pages: 284, 285, 718.
- [78ARE/MUS] Arena, G., Musumeci, S., Rizzarelli, E., Sammartano, S., Williams, D. R., Formation and stability of ternary complexes of copper(II) with EDTA and some amino acids, *Ann. Chim. (Rome)*, **68**, (1978), 535-541. Cited on pages: 399, 400, 402, 719.
- [78BER/MAY] Berthon, G., May, P. M., Williams, D. R., Computer simulation of metal-ion equilibria in biofluids. Part 2. Formation constants for zinc(II)-citrate-cysteinate binary and ternary complexes and improved models of low-molecular-weight zinc species in blood plasma, *J. Chem. Soc. Dalton Trans.*, (1978), 1433-1438. Cited on pages: 311, 755.
- [78CHA/BHA] Chakravorti, M. C., Bharadwaj, P. K., Pandit, S. C., Mathur, B. K., Fluoro complexes of hexavalent uranium-V. Fluorooxalato complexes of dioxouranium(VI), *J. Inorg. Nucl. Chem.*, **40**, (1978), 1365-1367. Cited on page: 213.

- [78COO/WOO] Cooper, J. N., Woods, M., Sjoblom, R., Sullivan, J. C., The oxidation of americium(V) and other reductants by aqueous acidic Np(VII), *J. Inorg. Nucl. Chem.*, **40**, (1978), 659-661. Cited on page: 261.
- [78DAV/LEC] Davis, J. A., Leckie, J. O., Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides, *Environ. Sci. Technol.*, **12**, (1978), 1309-1315. Cited on page: 725.
- [78DER/SMI] Derissen, J. L., Smit, P. H., Intermolecular interactions in crystals of carboxylic acids. IV. Empirical interatomic potential functions, *Acta Crystallogr.*, **A34**, (1978), 842-853. Cited on pages: 107, 108, 110.
- [78FLY/KOR] Flyantikova, G. V., Korolenko, L. I., A general method for the calculation of the thermodynamic ionisation constants of tribasic acids, *Russ. J. Phys. Chem.*, **52**, (1978), 1592-1595. Cited on pages: 308, 323.
- [78JAI/SHA] Jain, A. K., Sharma, R. C., Chaturvedi, G. K., Studies on mixed ligand chelates of oxovanadium(IV) - IMDA - dicarboxylic or hydroxy acids, *Pol. Journ. Chem.*, **52**, (1978), 259-264. Cited on page: 114.
- [78JAW] Jawaid, M., Potentiometric studies of complex formation between methylmercury(II) and EDTA, *Talanta*, **25**, (1978), 215-220. Cited on pages: 399, 719, 730.
- [78KER/CHU] Kereichuk, A. S., Churikova, I. M., Existence of protonated complexes of cobalt and nickel in citric acid solutions, *Russ. J. Inorg. Chem.*, **23**, (1978), 928-929. Cited on pages: 301, 311, 354, 355, 359, 719.
- [78KOR/VAL] Kornev, V. I., Valyaeva, V. A., Zobnin, S. I., Spectrophotometric measurements for nickel(II) ethylenediaminetetraacetate and nitrilotriacetate complexes, *Russ. J. Phys. Chem.*, **52**, (1978), 1057-1058. Cited on pages: 461, 466, 719.



- [78MER/GAT] Merciny, E., Gatez, J. M., Duyckaerts, G., Constantes de formation des complexes de stoechiométrie 1:1 et 1:2 ainsi que des complexes mixtes formés entre le plutonium(III) et divers acides aminopolyacétiques, *Anal. Chim. Acta*, **100**, (1978), 329-342, in French. Cited on pages: 399, 400, 402, 405, 499, 500, 501, 503, 504, 573, 581, 688, 719.
- [78MOS/POZ] Moskvina, A. I., Poznyakov, A. N., Investigation of the complex formation of neptunium(V) and plutonium(V) in aqueous solutions by the coprecipitation method, *Sov. J. Coord. Chem.*, **4**, (1978), 811-819. Cited on pages: 254, 256, 257, 258, 259, 282, 507, 508, 720, 724, 725.
- [78NAZ/ANT] Nazarenko, V. A., Antonovich, V. P., Nevskaja, E. M., Gidroliz ionov metallov v razbavlennykh rastvorakh (Hydrolysis of metal ions in dilute solutions), *Moscow Atomizdat*, (1978), in Russian. Cited on page: 473.
- [78NOV/LUC] Novák, V., Lučanský, J., Svičková, M., Majer, J., Neue Komplexe. XXXII. Synthese und Studium der Eigenschaften der 2-Methyl-1,2-diaminopropan-N,N,N',N'-tetraessigsäure, *Chem. Zvesti*, **32**, (1978), 19-26, in German. Cited on page: 449.
- [78PIT/PET] Pitzer, K. S., Peterson, J. R., Silvester, L. F., Thermodynamics of electrolytes: IX. Rare earth chlorides, nitrates, and perchlorates, *J. Solution Chem.*, **7**, (1978), 45-56. Cited on page: 822.
- [78RAJ/MAI] Rajan, K. S., Mainer, S., Davis, J. M., Formation and stabilities of the ternary metal chelates of L-3,4-dihydroxyphenyl alanine (L-dopa) with a number of secondary ligands, *J. Inorg. Nucl. Chem.*, **40**, (1978), 2089-2099. Cited on pages: 311, 322.
- [78SIN] Sinha, A. K., Ion-solvent interaction parameter by e.m.f. method, *J. Electrochem. Soc. India*, **27**, (1978), 259-260. Cited on page: 114.
- [78STA/FRE] Starý, J., Freiser, H., *Equilibrium constants of liquid-liquid distribution reactions. Part IV. Chelating extractants, IUPAC Chemical Data Series, No 18*, Pergamon Press, Oxford, (1978). Cited on pages: 678, 679.

- [78STR/KAR] Strizhakova, N. G., Karlysheva, K. F., Sheka, I. A., Citrate complexes of zirconium, *Sov. Prog. Chem.*, **44**, (1978), 1-4. Cited on pages: 298, 361, 362, 363, 720.
- [78USS/BOS] Usseglio-Tomasset, L., Bosia, P. D., Determinazione delle costanti di dissociazione dei principali acidi del vino in soluzioni idroalcoliche di interesse enologico, *Riv. Vitic. Enol.*, **31**, (1978), 380-403, in Italian. Cited on pages: 308, 323.
- [78VAS/KOC] Vasil'ev, V. P., Kochergina, L. A., Orlova, T. D., Heats of third- and fourth-stage dissociation and neutralization of (ethylenedinitrilo)tetrakisacetic acid at various temperatures, *J. Gen. Chem. USSR*, **48**, (1978), 2511-2516. Cited on pages: 429, 433, 721.
- [78VAS/LYM] Vasil'ev, V. P., Lyman, V. P., Lytkin, A. I., Thermodynamic characteristics of the reaction of zirconium(IV) with ethylenediamine-tetra-acetic acid, *Russ. J. Inorg. Chem.*, **23**, (1978), 29-32. Cited on pages: 475, 722.
- [78VAS/LYM2] Vasil'ev, V. P., Lyman, V. P., Lytkin, A. I., Influence of temperature on the thermodynamic characteristics of the reaction of zirconium(IV) with ethylenediamine-tetra-acetic acid, *Russ. J. Inorg. Chem.*, **23**, (1978), 525-527. Cited on page: 475.
- [79AMI/DAN] Amico, P., Daniele, P. G., Cucinotta, V., Rizzarelli, E., Sammartano, S., Equilibrium study of iron(II) and manganese(II) complexes with citrate ion in aqueous solution: relevance to coordination of citrate to the active site of aconitase and to gastrointestinal absorption of some essential metal ions, *Inorg. Chim. Acta*, **36**, (1979), 1-7. Cited on page: 311.
- [79BAR/UCH] Barnett, B. L., Uchtman, V. A., Structural investigations of calcium-binding molecules 4. Calcium binding to aminocarboxylates. Crystal structures of  $\text{Ca}(\text{CaEDTA}) \cdot 7\text{H}_2\text{O}$  and  $\text{Na}(\text{CaNTA})$ , *Inorg. Chem.*, **18**, (1979), 2674-2678. Cited on pages: 444, 803.
- [79BAU] Baucke, F. G. K., Lower temperature limit of NBS (DIN) pH standard buffer solution potassium tetroxalate, *Electrochim. Acta*, **24**, (1979), 95-97. Cited on pages: 153, 155, 156, 722.

- [79BRA/PIT] Bradley, D. J., Pitzer, K. S., Thermodynamics of electrolytes. 12. Dielectric properties of water and Debye-Hückel parameters to 350°C and 1 kbar, *J. Phys. Chem.*, **83**, (1979), 1599-1603. Cited on page: 827.
- [79BUL/SAC] Bulos, B. A., Sacktor, B., Determination of the concentration of free  $\text{Ca}^{2+}$  in the presence of magnesium (or manganese) and chelating effectors of the  $\text{NAD}^+$ -linked isocitrate dehydrogenase, *Anal. Biochem.*, **95**, (1979), 62-72. Cited on pages: 338, 342, 722.
- [79CLE] Cleveland, J. M., *The chemistry of plutonium*, American Nuclear Society, LaGrange Park, IL, (1979), 653 pp. Cited on pages: 261, 262, 277.
- [79CRA/MOO] Craggs, A., Moody, G. J., Thomas, J. D. R., Calcium ion-selective electrode measurements in the presence of complexing ligands, *Analyst (Cambridge U.K.)*, **104**, (1979), 961-972. Cited on pages: 179, 187, 338, 343, 446, 451, 722, 723.
- [79EKS/OLI] Ekström, L.-G., Olin, Å., On the complex formation between lead(II) and citrate ions in acid, neutral and weakly alkaline solution, *Chem. Scr.*, **13**, (1979), 10-15. Cited on page: 311.
- [79ELE/ELD] El Ezaby, M. S., El Dessouky, M. A., Shuaib, N. M., Mixed ligand complexes of nickel(II) and copper(II) involving 2-pyridinecarboxaldehyde, *J. Inorg. Nucl. Chem.*, **41**, (1979), 1765-1769. Cited on page: 114.
- [79FRI/SYC] Fridman, A. Y., Sycheva, G. M., Afanas'ev, Y. A., The chelate effect of polydentate reagents, *Russ. J. Coord. Chem.*, **5**, (1979), 888-895. Cited on page: 114.
- [79HEU/POP] Heubel, P.-H. C., Popov, A. I., Acid properties of some phosphonocarboxylic acids, *J. Solution Chem.*, **8**, (1979), 615-625. Cited on page: 311.
- [79JAN/PFE] Janjić, T. J., Pfenndt, L. B., Popov, V., Study of equilibria in solutions of some protonated metal(II)-EDTA complexes, *J. Inorg. Nucl. Chem.*, **41**, (1979), 63-65. Cited on pages: 462, 464, 466.

- [79JOH/PYT] Johnson, K. S., Pytkowicz, R. M., Ion association and activity coefficients in multicomponent solutions, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., II, pp. 1-62, CRC Press, Boca Raton, Florida, (1979). Cited on page: 820.
- [79KUM/CHA] Kumari, V., Chaturvedi, G. K., pH-metric studies on binary, ternary and quaternary complexes of dioxouranium(VI), *J. Indian Chem. Soc.*, **56**, (1979), 854-856. Cited on pages: 231, 232, 233, 234, 242, 243, 723.
- [79KUS/GAN] Kusumakumari, K. M., Gandhe, S. P., Gudi, N. M., Bagawde, S. V., Vasudeva Rao, P. R., Ramakrishna, V. V., Ramanujam, A., Patil, S. K., Complex formation of actinide ions in aqueous solutions, Bhabha Atomic Research Centre, Bombay, India, Report B.A.R.C.-1005, pp. 33-38, (1979). Cited on pages: 250, 251, 252, 716, 724.
- [79LET/MAR] Letkeman, P., Martell, A. E., Nuclear magnetic resonance and potentiometric protonation study of polyaminopolyacetic acids containing from two to six nitrogen atoms, *Inorg. Chem.*, **18**, (1979), 1284-1289. Cited on pages: 400, 402.
- [79LIE/EKE] Liem, D. H., Ekelund, R., New types of input in DISTR. Application of LETAGROP for analysis of liquid-liquid distribution equilibria data, *Acta Chem. Scand.*, **A33**, (1979), 481-482. Cited on pages: 628, 716, 717.
- [79MAY/CHA] Mayadeo, M. S., Chaubal, A. M., Formation constants of Pr(III), Y(III) and Dy(III) complexes of some schiff bases of 2-hydroxy-1-naphthaldehyde. A potentiometric study, *J. Indian Chem. Soc.*, **56**, (1979), 921-922. Cited on page: 115.
- [79MIL] Millero, F. J., Effects of pressure and temperature on activity coefficients, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., II, pp. 63-151, CRC Press, Boca Raton, Florida, (1979). Cited on pages: 820, 827.
- [79MOS/POZ] Moskvina, A. I., Poznyakov, A. N., Coprecipitation study of complex formation by neptunium(V), plutonium(V), and americium(V) with the anions of various inorganic acids, *Russ. J. Inorg. Chem.*, **24**, (1979), 1357-1362. Cited on pages: 282, 507, 508, 720, 724, 725, 726.

- [79MOS/POZ4] Moskvina, A. I., Poznyakov, A. N., Investigation of complex formation by quinquivalent forms of actinides with certain anions of organic acids by the coprecipitation method, *Russ. J. Inorg. Chem.*, **24**, (1979), 1709-1712. Cited on pages: 254, 256, 257, 258, 259, 282, 294, 507, 508, 724, 725, 726.
- [79NIK] Nikolaeva, N. M., The solubility of U(IV) oxalate at elevated temperatures, *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, **6**, (1979), 64-69, in Russian. Cited on pages: 207, 208, 209, 210, 211, 212, 225, 226, 227, 228, 726, 736.
- [79PIT] Pitzer, K. S., Theory: Ion Interaction Approach, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., vol. 1, pp. 157-208, CRC Press, Boca Raton, Florida, (1979). Cited on pages: 820, 822.
- [79PYT] Pytkowicz, R. M., Activity coefficients, ionic media, and equilibria in solutions, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., II, pp. 301-305, CRC Press, Boca Raton, Florida, (1979). Cited on page: 820.
- [79SHI/STE2] Shilov, V. P., Stepanova, E. S., Krot, N. N., Mechanism of the oxidation of EDTA, DTPA, and oxalate ions by atmospheric oxygen in the presence of neptunium(V), *Sov. Radiochem.*, **21**, (1979), 524-529. Cited on pages: 254, 490.
- [79TOM/NAN] Tomažič, B., Nancollas, G. H., The kinetics of dissolution of calcium oxalate hydrates, *J. Cryst. Growth*, **46**, (1979), 355-361. Cited on pages: 157, 159, 161, 162, 166, 168, 169, 171.
- [79TOM/NAN2] Tomažič, B., Nancollas, G. H., A study of the phase transformation of calcium oxalate trihydrate - monohydrate, *Invest. Urol.*, **16**, (1979), 329-335. Cited on pages: 166, 168, 169, 171, 174, 176.
- [79VAS/KOC] Vasil'ev, V. P., Kochergina, L. A., Orlova, T. D., Heats of protonation of (ethylenedinitrilo)tetraacetic acid, *J. Gen. Chem. USSR*, **49**, (1979), 1440-1443. Cited on pages: 395, 431, 436, 726.
- [79WHI] Whitfield, M., Activity coefficients in natural waters, *Activity coefficients in electrolyte solutions*, Pytkowicz, R. M., Ed., II, pp. 153-299, CRC Press, Boca Raton, Florida, (1979). Cited on pages: 11, 12.

- [79WHI2] Whiffen, D. H., *Manual of symbols and terminology for physicochemical quantities and units, IUPAC Commission on Physicochemical Symbols, Terminology and Units*, Pergamon Press, Oxford, (1979), 41 pp. Cited on page: 820.
- [79ZHI/KOL] Zhikharev, M. I., Kol'ba, V. I., Sukhanov, L. P., The  $\text{Na}_2\text{C}_2\text{O}_4$ - $\text{NaNO}_3$ - $\text{H}_2\text{O}$  system at 20°C, *Russ. J. Inorg. Chem.*, **24**, (1979), 469-470. Cited on pages: 152, 153, 728, 730.
- [80AGR/SYS] Agre, V. M., Sysoeva, T. F., Trunov, V. K., Efremov, V. A., Fridman, A. Y., Barkhanova, N. N., Crystal structure of (ethylenediaminetetraacetato)nickel(II)bis(ethylenediamine)cuprate dihydrate, *J. Struct. Chem. USSR*, **21**, (1980), 210-216. Cited on page: 460.
- [80ARE/CAL] Arena, G., Cali, R., Grasso, M., Musumeci, S., Sammartano, S., Rigano, C., The formation of proton and alkali-metal complexes with ligands of biological interest in aqueous solution. Part I. Potentiometric and calorimetric investigation of  $\text{H}^+$  and  $\text{Na}^+$  complexes with citrate, tartrate and malate, *Thermochim. Acta*, **36**, (1980), 329-342. Cited on pages: 308, 326, 327, 332, 333, 335, 728.
- [80CIA] Ciavatta, L., The specific interaction theory in evaluating ionic equilibria, *Ann. Chim. (Rome)*, **70**, (1980), 551-567. Cited on pages: 94, 102, 802, 821, 822, 832, 833, 835, 840, 842, 845, 846.
- [80DAN/RIG] Daniele, P. G., Rigano, C., Sammartano, S., The formation of proton and alkali-metal complexes with ligands of biological interest in aqueous solution. Potentiometric study of the  $\text{H}^+$ - $\text{K}^+$ -citrate system at 37°C and  $0.03 < I < 1.0$ , *Ann. Chim. (Rome)*, **70**, (1980), 119-130. Cited on pages: 308, 311, 326, 327, 332, 333, 729, 732.
- [80GRA/MUS] Grasso, M., Musumeci, S., Rizzarelli, E., Sammartano, S., Formation and stability of ternary complexes of copper(II) with histamine and some dicarboxylic acids, *Ann. Chim. (Rome)*, **70**, (1980), 193-200. Cited on pages: 117, 132, 751.
- [80HED/LID] Hedwig, G. R., Liddle, J. R., Reeves, R. D., Complex formation of nickel(II) ions with citric acid in aqueous solution: a potentiometric and spectroscopic study, *Aust. J. Chem.*, **33**, (1980), 1685-1693. Cited on pages: 311, 353, 354, 355, 359, 729, 760.

- [80HOD] Hodgkinson, A., Solubility of calcium oxalate in human urine, simulated urine, and water, *Invest. Urol.*, **18**, (1980), 123-126. Cited on pages: 161, 166, 168, 169.
- [80JAW] Jawaid, M., On the complex-formation between Cd(II) and EDTA, *Talanta*, **27**, (1980), 95-100. Cited on pages: 399, 719, 730.
- [80KOL/ZHI] Kol'ba, V. I., Zhikharev, M. I., Sukhanov, L. P., The  $\text{Na}_2\text{C}_2\text{O}_4$ - $\text{NaNO}_3$ - $\text{H}_2\text{O}$  system at 50° and 75°C, *Russ. J. Inorg. Chem.*, **25**, (1980), 1583-1585. Cited on pages: 152, 153, 730.
- [80MAC/CHI] Macarovici, C. G., Chiş, E., A new EDTA-type reagent. III. Synthesis and physico-chemical study of 4,4'-diamino-diphenylmethane-N,N'-tetraacetic acid, *Rev. Roum. Chim.*, **25**, (1980), 503-511. Cited on page: 398.
- [80MIK/HAV] Mikan, A., Havel, J., Bartušek, M., Molybdate chelates of EDTA, *Scr. Fac. Sci. Nat. Univ. Purk. Brun.*, **10**, (1980), 23-28. Cited on page: 398.
- [80MIS/MIT] Misra, A., Mital, S., Chaturvedi, G. K., pH-metric studies on quaternary mixed ligand complex formation Ni(II), *J. Indian Chem. Soc.*, **57**, (1980), 42-45. Cited on page: 114.
- [80NIS] Nissen, D. A., The thermal decomposition of plutonium(IV) oxalate tetrahydrate, *J. Therm. Anal.*, **18**, (1980), 99-109. Cited on page: 263.
- [80PEA] Pearce, K. N., Formation constants for magnesium and calcium citrate complexes, *Aust. J. Chem.*, **33**, (1980), 1511-1517. Cited on pages: 335, 336, 338, 339, 340, 342, 343, 344, 730.
- [80PER/POL] Perfil'ev, V. A., Poluéktov, N. S., Investigation of complex formation in the system tetravalent uranium ion-ethylenediaminetetraacetic acid- $\beta$ -diketone by a spectrophotometric method, *Sov. Radiochem.*, **22**, (1980), 358-360. Cited on page: 480.
- [80STI/WIK] Still, E. R., Wikberg, P., Solution studies of systems with polynuclear complex formation. 2. The nickel(II) citrate system, *Inorg. Chim. Acta*, **46**, (1980), 153-155. Cited on pages: 353, 354, 355, 356, 358, 731, 760.

- [80TAN/MOR] Taniguchi, M., Moriguchi, H., Shimizu, S., Dehydration of crystallization water in salts using a new designed controlled-water vapor micro DTA, in: *Thermal analysis. Proceeding of the International Conference on Thermal Analysis*, pp. 163-168, ICTA 80, Birkhäuser, Basel (1980). Cited on pages: 165, 166.
- [80TAN/NEG] Tanaka, H., Negita, H., The deuterium isotope effect in enthalpy change on the thermal dehydration of calcium oxalate monohydrate, *Thermochim. Acta*, **41**, (1980), 305-310. Cited on pages: 165, 166.
- [80TAQ/HUS] Taqui Khan, M. M., Hussain, A., Aminopolycarboxylic acid complexes of Al(III), Ga(III) and In(III), *Indian J. Chem.*, **19A**, (1980), 50-57. Cited on page: 400.
- [80TAZ/DOM] Tazzoli, V., Domeneghetti, C., The crystal structures of whewellite and weddellite: re-examination and comparison, *Am. Mineral.*, **65**, (1980), 327-334. Cited on page: 164.
- [80TOM/NAN] Tomažič, B., Nancollas, G. H., The kinetics of dissolution of calcium oxalate hydrates. II. The dihydrate, *Invest. Urol.*, **18**, (1980), 97-101. Cited on pages: 162, 166, 168, 169, 171, 174, 175, 176.
- [80VAN/KUC] Vaňura, P., Kuča, L., Citrate complexes of uranyl in solutions with high citrate concentrations, *Collect. Czech. Chem. Commun.*, **45**, (1980), 41-53. Cited on pages: 301, 364, 365, 368, 369, 731.
- [80WIL/JON] Wilson, M. J., Jones, D., Russel, J. D., Glushinskite, a naturally occurring magnesium oxalate, *Mineral. Mag.*, **43**, (1980), 837-840. Cited on page: 159.
- [81AMI/DAN] Amico, P., Daniele, P. G., Rigano, C., Sammartano, S., Formation and stability of ammonium-sulphate, phosphate, oxalate and citrate complexes in aqueous solution, *Ann. Chim. (Rome)*, **71**, (1981), 659-667. Cited on page: 309.
- [81BEL/DRI] Beltrain, D., Drillon, M., Chaînes homo ou hétérométalliques dans des complexes MM'EDTA.6H<sub>2</sub>O, *Bull. Soc. Chim. Fr.*, (1981), 407, in French. Cited on page: 460.



- [81BLO/KAN] Blom, N. S., Kanters, J. A., Heijnen, W. M. M., Calcium oxalate trihydrate,  $\text{CaC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ , *Cryst. Struct. Commun.*, **10**, (1981), 1283-1288. Cited on page: 164.
- [81BOU] Bouhlassa, S., Complexes citriques et citrates de néodyme et d'américium, IPNO-T-81-07, Ph. D. Thesis, Univ. Paris-Sud, (1981), Orsay, France, in French. Cited on page: 308.
- [81BUE/AND] Bürgi, H. B., Anderegg, G., Bläuenstein, P., Preparation, characterization, and crystal, molecular, and electronic structure of  $(\text{H}_2\text{EDTA})^{99}\text{Tc}^{\text{IV}}(\mu\text{-O})_2^{99}\text{Tc}^{\text{IV}}(\text{H}_2\text{EDTA}) \cdot 5\text{H}_2\text{O}$ . A 2.33-Å Tc-Tc distance which may represent a  $\sigma^2\pi^2\delta^{*2}$  bond, *Inorg. Chem.*, **20**, (1981), 3829-3834. Cited on pages: 393, 470, 471.
- [81BUR/FIN] Burns, J. R., Finlayson, B., Smith, A., Determination of the stability constant of the calcium dioxalate complex, in: *Urolithiasis. Clinical and basic research*, pp. 447-451, Smith, L. H., Robertson, W. G. and Finlayson, B., Eds., Plenum Press, New York, N. Y., (1981). Cited on pages: 157, 159.
- [81CER/CAS] Cerda, V., Casassas, E., García Montelongo, F., Thermometric titration of mono- and poly-protic acids in water-methanol medium, *Thermochim. Acta*, **47**, (1981), 343-353. Cited on pages: 143, 732.
- [81CUC/DAN] Cucinotta, V., Daniele, P. G., Rigano, C., Sammartano, S., The formation of proton and alkali-metal complexes with ligands of biological interest in aqueous solution. Potentiometric and PMR investigation of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and  $\text{NH}_4^+$  complexes with citrate, *Inorg. Chim. Acta*, **56**, (1981), L45-L47. Cited on pages: 308, 332, 333, 732.
- [81DAN/RIG] Daniele, P. G., Rigano, C., Sammartano, S., The formation of proton and alkali-metal complexes with ligands of biological interest in aqueous solution. Thermodynamics of  $\text{H}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  - oxalate complexes, *Thermochim. Acta*, **46**, (1981), 103-116. Cited on pages: 115, 117, 131, 132, 156, 157, 158, 732, 733.
- [81DEG/PIR] Deganello, S., Piro, O. E., The crystal structure of calcium oxalate monohydrate (whewellite), *Neues Jahrb. Mineral., Monatsh.*, (1981), 81-88. Cited on page: 164.

- [81EMS/JON] Emsley, J., Jones, D. J., Kuroda, R., The hydrogen bonds of potassium tetraoxalate: An X-ray redetermination of the crystal structure of  $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , *J. Inorg. Nucl. Chem.*, **43**, (1981), 2243-2246. Cited on pages: 153, 154.
- [81HEL/KIR] Helgeson, H. C., Kirkham, D. H., Flowers, G. C., Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb, *Am. J. Sci.*, **281**, (1981), 1249-1516. Cited on page: 827.
- [81MAL/SEN] Mali, B. D., Sen, D. N., Equilibrium studies of mixed ligand complexes of zinc ion with citric acid & some aliphatic dicarboxylic acids, *Indian J. Chem.*, **20A**, (1981), 695-698. Cited on page: 308.
- [81MEF/GRI] Mefod'eva, M. P., Grigor'ev, M. S., Afonas'eva, T. V., Kryukov, E. B., New data on oxalate compounds of neptunium(VI), *Sov. Radiochem.*, **23**, (1981), 565-570. Cited on page: 249.
- [81MUE] Muenze, R., Polynuclear  $^{99}\text{technetium/IV/-citrate}$  complex, *Radiochem. Radioanal. Lett.*, **48**, (1981), 281-288. Cited on pages: 361, 733.
- [81NAS/MUL] Nash, K., Mulac, W., Noon, M., Fried, M., Sullivan, J. C., Pulse radiolysis studies of U(VI) complexes in aqueous media, *J. Inorg. Nucl. Chem.*, **43**, (1981), 897-899. Cited on page: 228.
- [81RAJ/MAI] Rajan, K. S., Mainer, S., Rajan, N. L., Davis, J. M., Studies on the chelation of aluminum for neurobiological application, *J. Inorg. Biochem.*, **14**, (1981), 339-350. Cited on pages: 311, 322, 398.
- [81REE/OLM] Reed, D. A., Olmstead, M. M., Sodium oxalate structure refinement, *Acta Crystallogr.*, **B37**, (1981), 938-939. Cited on pages: 152, 153.
- [81SIN/GHO] Sinha, A. K., Ghosh, J. C., Prasad, B., First dissociation equilibrium of oxalic acid, *Indian J. Chem.*, **20A**, (1981), 33-35. Cited on pages: 115, 733.

- [81SIR/KAL] Sirotková, L., Kalina, M., Dvořáková, E., Novák, V., Potentiometrisches Studium der Bildung von Silber(I)-Chelaten der Alkylderivate und Isoalkylderivate der EDTA, *Chem. Zvesti*, **35**, (1981), 339-343, in German. Cited on page: 398.
- [81STU/MOR] Stumm, W., Morgan, J. J., *Aquatic Chemistry. An introduction emphasizing chemical equilibria in natural waters*, 2nd. Edition, John Wiley and Sons, New York, (1981), 780 pp. Cited on page: 22.
- [81SYS/AGR] Sysoeva, T. F., Agre, V. M., Trunov, V. K., Dyatlova, N. M., Fridman, A. Y., Barkhanova, N. N., Crystal structure of the dinuclear complex of nickel(II) with ethylenediamine and ethylenediaminetetraacetic acid  $\text{Ni}_2\text{EnA} \cdot 4\text{H}_2\text{O}$ , *J. Struct. Chem. USSR*, **22**, (1981), 878-883. Cited on page: 460.
- [81URB/BIE] Urbańska, J., Biernat, J., Evaluation of stability constants of complexes based on irreversible polarographic waves with variable electrode mechanism. Part 1. The  $\text{Co}^{2+}$  -  $\text{C}_2\text{O}_4^{2-}$  system, *J. Electroanal. Chem.*, **130**, (1981), 123-140. Cited on page: 733.
- [81URB/BIE2] Urbańska, J., Biernat, J., Evaluation of stability constants of complexes based on irreversible polarographic waves with variable electrode mechanism. Part 2. The  $\text{Ni}^{2+}$  -  $\text{C}_2\text{O}_4^{2-}$  system, *J. Electroanal. Chem.*, **130**, (1981), 141-151. Cited on pages: 194, 195, 196, 733, 759.
- [81VAS/VAS] Vasil'ev, V. P., Vasil'eva, V. N., Kozlovskii, E. V., Kalachev, E. N., Chistyakova, G. V., Barkhanova, N. N., Thermochemical study of the formation of a mixed complex of nickel(II) with ethylenediaminetetraacetate and ethylenediamine in aqueous solution, *Russ. J. Inorg. Chem.*, **26**, (1981), 526-528. Cited on pages: 463, 734.
- [81ZUB/KRO] Zubarev, V. G., Krot, N. N., Composition and properties of certain neptunium(V) oxalate compounds, *Sov. Radiochem.*, **23**, (1981), 690-694. Cited on pages: 248, 249.
- [82AMI/DAN] Amico, P., Daniele, P. G., Rigano, C., Sammartano, S., Stability of calcium- and magnesium-citrate complexes in aqueous solution, *Ann. Chim. (Rome)*, **72**, (1982), 1-24. Cited on pages: 335, 336, 338, 339, 342, 343, 344, 734.

- [82AVD/KEA] Avdeef, A., Kearney, D. L., Brown, J. A., Chemotti, Jr., A. R., Bjerrum plots for the determination of systematic concentration errors in titration data, *Anal. Chem.*, **54**, (1982), 2322-2326. Cited on pages: 311, 398.
- [82BEL/ESC] Beltrán, D., Escrivá, E., Drillon, M., Ferrimagnetic-like coupling in ordered one-dimensional systems, *J. Chem. Soc. Faraday Trans. 2*, **78**, (1982), 1773-1779. Cited on page: 460.
- [82DAN/MAR] Daniele, P. G., Marangella, M., Ionic equilibria in urine: a computer model system improved by accurate stability constant values, *Ann. Chim. (Rome)*, **72**, (1982), 25-38. Cited on pages: 178, 179, 182, 185, 187, 188, 680, 689, 734, 735, 779.
- [82DRE] Drever, J. I., *The geochemistry of natural waters*, Prentice-Hall, Englewood Cliffs, N. J., (1982), 388 pp. Cited on page: 22.
- [82GAR/RAM] Garcia, M. C., Ramis, G., Mongay, C., A comparative study of the application of the method of least-squares in the potentiometric determination of protonation constants, *Talanta*, **29**, (1982), 435-439. Cited on page: 308.
- [82HAM] Hamann, S. D., The influence of pressure on ionization equilibria in aqueous solutions, *J. Solution Chem.*, **11**, (1982), 63-68. Cited on page: 34.
- [82HEI] Heijnen, W. M. M., The growth morphology of calcium oxalate trihydrate. A contribution to urinary stone research, *J. Cryst. Growth*, **57**, (1982), 216-232. Cited on pages: 164, 166.
- [82HIR/KIS] Hirokawa, T., Kiso, Y., Complex-forming equilibria in isotachopheresis II. Evaluation of stability constants of tartrate and citrate complexes, *J. Chromatogr.*, **248**, (1982), 341-362. Cited on pages: 335, 336, 338, 339, 342, 735.
- [82HUA/ALF] Huang, Z.-X., Al-Falahi, H. S., Cole, A., Duffield, J. R., Furnival, C., Jones, D. C., May, P. M., Smith, G. L., Williams, D. R., Potentiometric investigation of sparingly soluble metal-ligand systems using metal-ion buffers, *Polyhedron*, **1**, (1982), 153-155. Cited on page: 398.

- [82INO/TOC] Inoue, Y., Tochiyama, O., Takahashi, T., Study of the carboxylate complexing of Np(V) by solvent extraction with TTA and capriquat, *Radiochim. Acta*, **31**, (1982), 197-199. Cited on pages: 114, 254, 256, 308, 374, 735.
- [82JAC] Jackson, G. E., Studies on the chelation of aluminium for biological application. Part 1. Citric acid, *S. Afr. J. Chem.*, **35**, (1982), 89-92. Cited on page: 311.
- [82JAC/COS] Jackson, G. E., Cosgrove, A., Studies on the chelation of aluminium for biological application. Part 2. Oxalic, malonic, and succinic acids, *S. Afr. J. Chem.*, **35**, (1982), 93-95. Cited on pages: 115, 118.
- [82KRU/MIL] de Kruif, C. G., van Miltenburg, J. C., Sprenkels, A. J. J., Stevens, G., de Graaf, W., de Wit, H. G. M., Thermodynamic properties of citric acid and the system citric acid-water, *Thermochim. Acta*, **58**, (1982), 341-354. Cited on pages: 303, 304, 305.
- [82LAF] Laffitte, M., A report of IUPAC commission I.2 on thermodynamics: Notation for states and processes, significance of the word "standard" in chemical thermodynamics, and remarks on commonly tabulated forms of thermodynamic functions, *J. Chem. Thermodyn.*, **14**, (1982), 805-815. Cited on pages: 14, 15, 28, 29, 32, 819.
- [82LEP/TAW] Lepage, L., Tawashi, R., Growth and characterization of calcium oxalate dihydrate crystals (Weddelite), *J. Pharm. Sci.*, **71**, (1982), 1059-1062. Cited on pages: 166, 167.
- [82LUF/REE] Luff, B. B., Reed, R. B., Low-temperature heat capacity and entropy of oxalic acid and of biuret, *J. Chem. Eng. Data*, **27**, (1982), 290-292. Cited on pages: 108, 109.
- [82MAR/SMI] Martell, A. E., Smith, R. M., *Critical stability constants, Vol. 5: First supplement*, Plenum Press, New York, (1982), 604 pp. Cited on page: 781.
- [82NIK] Nikolaeva, N. M., *Uranium chemistry*, Laskorin, B. N., Ed., pp. 36-42, Nauka, Moscow, (1981), in Russian. Cited on pages: 726, 736.

- [82NIK2] Nikolaeva, N. M., *Chemical equilibria in aqueous solutions at elevated temperatures*, Nauka, Sibirskoje otddelenije, Novosibirsk, (1982), in Russian. Cited on pages: 726, 736.
- [82NIK/SHA] Nikonenko, E. A., Sharov, V. A., Olikov, I. I., Zhdanovskikh, T. M., The structure of the anhydrous oxalates of  $Mn^{II}$ ,  $Fe^{II}$ ,  $Co^{II}$ ,  $Ni^{II}$  and  $Zn^{II}$ , *Russ. J. Inorg. Chem.*, **27**, (1982), 547-550. Cited on page: 190.
- [82OVE/LUN] Overvoll, P. A., Lund, W., Complex formation of uranyl ions with polyaminopolycarboxylic acids, *Anal. Chim. Acta*, **143**, (1982), 153-161. Cited on pages: 399, 400, 484, 485, 486, 487, 488, 489, 603, 736, 746.
- [82RAO/AGA] Rao, M. V. R., Agarwal, J. S., Chhotray, N., On the association constant of calcium oxalate, *Indian J. Chem.*, **21A**, (1982), 1144-1145. Cited on pages: 179, 187, 737.
- [82SAC/CHA] Sachan, N. P., Chandel, C. P. S., Gupta, C. M., Electrochemical studies on mixed ligand complexes of cadmium ion with some dicarboxylic acids and N-[βhydroxyethyl]ethylenediamine, *Chem. Scr.*, **20**, (1982), 111-116. Cited on page: 114.
- [82SIG/SCH] Sigel, H., Scheller, K. H., Prijs, B., Metal ion/buffer interactions. Stability of alkali and alkaline earth ion complexes with triethanolamine (tea), 2-amino-2(hydroxymethyl)-1,3-propanediol (tris) and 2-[bis(2-hydroxyethyl)-amino]2(hydroxymethyl)-1,3-propanediol (bistris) in aqueous and mixed solvents, *Inorg. Chim. Acta*, **66**, (1982), 147-155. Cited on pages: 334, 616, 625, 688.
- [82TAY] Taylor, J. R., *An introduction to error analysis: The study of uncertainties in physical measurements*, University Science Books, Mill Valley, CA, USA, (1982), 270 pp. Cited on page: 852.
- [82TER/IVA] Terëshin, G. S., Ivanova, E. V., Krasnobaeva, N. A., Thermodynamics of EDTA dissolution, *Koord. Khim.*, **8**, (1982), 1169-1175, in Russian. Cited on pages: 394, 395, 399, 403, 427, 737, 738.

- [82VAS/BEL] Vasil'ev, V. P., Belonogova, A. K., Thermodynamic characteristics of the formation of a coordination compound of nickel with ethylenediaminetetra-acetic acid and glycine in aqueous solution, *Russ. J. Inorg. Chem.*, **27**, (1982), 1135-1138. Cited on pages: 464, 738.
- [82VAS/VAS] Vasil'eva, V. N., Vasil'ev, V. P., Dmitrieva, N. G., Lebedeva, N. A., Nickel(II) coordination compounds with ethylenediaminetetra-acetate and oxalate or pyrophosphate ions, *Russ. J. Inorg. Chem.*, **27**, (1982), 1449-1452. Cited on pages: 463, 467, 738, 739.
- [82WAG/EVA] Wagman, D. D., Evans, W. H., Parker, V. B., Schumm, R. H., Halow, I., Bailey, S. M., Churney, K. L., Nuttall, R. L., The NBS tables of chemical thermodynamic properties: Selected values for inorganic and C<sub>1</sub> and C<sub>2</sub> organic substances in (SI) units, *J. Phys. Chem. Ref. Data*, **11**, Suppl. 2, (1982), 1-392. Cited on pages: 24, 29, 30, 551.
- [82WIL/SUL] Williard, J. W., Sullivan, J. M., Kim, Y. K., Solubility of oxalic acid dihydrate in nitric and sulfuric acid solutions at 0, 25, and 50°C, *J. Chem. Eng. Data*, **27**, (1982), 442-445. Cited on page: 112.
- [82ZUB/KRO] Zubarev, V. G., Krot, N. N., Separation of americium(V) oxalate compounds from solution, *Sov. Radiochem.*, **24**, (1982), 264-267. Cited on pages: 285, 294, 739.
- [83AND/GAS] Anderegg, G., Gasche, W., Zollinger, K., Technetium aminopolycarboxylate complexes in aqueous solution, in: *Technetium in chemistry and nuclear medicine*, vol. 1, pp. 15-17, Deutsch, E., Nicolini, M. and Wagner, Jr., H. N., Eds., Cortina International, Verona, (1983). Cited on page: 471.
- [83ARE/MUS] Arena, G., Musumeci, S., Purrello, R., Sammartano, S., Calcium- and magnesium-EDTA complexes. Stability constants and their dependence on temperature and ionic strength, *Thermochim. Acta*, **61**, (1983), 129-138. Cited on pages: 437, 445, 446, 447, 450, 451, 452, 453, 454, 455, 456, 457, 566, 739.
- [83BAK/BAK] Baker, E. N., Baker, H. M., Anderson, B. F., Reeves, R. D., Chelation of nickel(II) by citrate. The crystal structure of a nickel-citrate complex, K<sub>2</sub>[Ni(C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·4H<sub>2</sub>O, *Inorg. Chim. Acta*, **78**, (1983), 281-285. Cited on pages: 298, 299, 301.

- [83BAR/SUS] Bartušek, M., Šustáček, V., Chelates of vanadium(V) with organic hydroxy compounds in aqueous solutions, *Collect. Czech. Chem. Commun.*, **48**, (1983), 2785-2797. Cited on page: 114.
- [83CAC/CHO] Caceci, M. S., Choppin, G. R., The determination of the first hydrolysis constant of Eu(III) and Am(III), *Radiochim. Acta*, **33**, (1983), 101-104. Cited on pages: 286, 288, 740.
- [83CHH/GOP] Chhapru, G. C., Gopinath, N., Jadhav, A. V., Kulkarni, N. K., Sankaran, P. S., Sesha Sayi, Y., Sharna, H. S., Subba Rao, M., Venkataramana, P., Natarajan, P. R., Some studies of the solution chemistry plutonium, in: *Proceedings of the nuclear chemistry and radiochemistry symposium*, pp. 561-564, Kulkarni, S. G., Manohar, S. B. and Sood, D. D., Eds., Dept. At. Energy, Bombay, India, (1983). Cited on page: 269.
- [83CHO/BOK] Choppin, G. R., Bokelund, H., Valkiers, S., Oxalate complexation in dissolved carbide systems, *Radiochim. Acta*, **33**, (1983), 229-232. Cited on pages: 231, 234, 235, 236, 239, 240, 278, 279, 280, 740, 741, 780.
- [83COV/BAT] Covington, A. K., Bates, R. G., Durst R. A., Definition of pH scales, standard reference values, measurement of pH and related terminology, *Pure Appl. Chem.*, **55**, (1983), 1467-1476. Cited on page: 155.
- [83CRU/HEY] Cruywagen, J. J., Heyns, J. B. B., Determination of the dissociation constants of oxalic acid and the ultraviolet spectra of the oxalate species in 3M perchlorate medium, *Talanta*, **30**, (1983), 197-200. Cited on pages: 118, 129, 670.
- [83DAN/RIG] Daniele, P. G., Rigano, C., Sammartano, S., Ionic strength dependence of formation constants. I. Protonation constants of organic and inorganic acids, *Talanta*, **30**, (1983), 81-87. Cited on pages: 115, 118, 132, 308, 311, 399, 400, 739, 741.
- [83DAN/RIG2] Daniele, P. G., Rigano, C., Sammartano, S., The formation of proton and alkali metal complexes with ligands of biological interest in aqueous solution. Thermodynamics of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$ -dicarboxylate complex formation, *Thermochim. Acta*, **62**, (1983), 101-112. Cited on pages: 115, 118, 129, 131, 132, 157, 158.



- [83FER/GRE] Ferri, D., Grenthe, I., Salvatore, F., Studies on metal carbonate equilibria. 7. Reduction of the tris(carbonato)dioxouranate(VI) ion,  $\text{UO}_2(\text{CO}_3)_3^{4-}$ , in carbonate solutions, *Inorg. Chem.*, **22**, (1983), 3162-3165. Cited on page: 832.
- [83GUP/CHA] Gupta, N., Chandel, C. P. S., Gupta, P. C., Gupta, C. M., Polarographic studies on mixed ligand complexes of cadmium with DL-3-(3,4-dihydroxyphenyl)alanine and some dicarboxylic acids, *Bull. Chem. Soc. Jpn.*, **56**, (1983), 3138-3141. Cited on page: 114.
- [83INO/TOC] Inoue, Y., Tochiyama, O., Study of the complexes of Np(V) with organic ligands by solvent extraction with TTA and 1,10-phenanthroline, *Polyhedron*, **2**, (1983), 627-630. Cited on pages: 255, 256, 257, 492, 494, 742.
- [83KOR/PRO] Korsse, J., Pronk, L. A., van Embden, C., Leurs, G., Louwrier, P. W. F., Ternary complexes of the Cu(II) and Ni(II) chelates of edta and dcta with cyanide and ethylenediamine, *Talanta*, **30**, (1983), 1-7. Cited on pages: 463, 742.
- [83KRA/DEC] Kragten, J., Decnop-Weever, L. G., Solubility and protonation of edta, dcta and dpta in acidic perchlorate medium, *Talanta*, **30**, (1983), 623-626. Cited on pages: 394, 395, 400, 403, 715.
- [83LUE] Luerkens, D. W., Neptunium(IV) oxalate solubility, E.I. du Pont de Nemours & Co, Savannah River Laboratory, Aiken, SC, Report DP-1655, (1983). Cited on pages: 246, 247, 248, 250, 251, 252, 742, 743.
- [83LUR/GON] Lurdes, M., Gonçalves, S. S., Mota, A. M. A., Da Silva, J. J. R. F., Note on the uranyl complexes of edta, *Talanta*, **30**, (1983), 69-71. Cited on pages: 486, 661, 744.
- [83OHM/SJO] Öhman, L.-O., Sjöberg, S., Equilibrium and structural studies of silicon(IV) and aluminium(III) in aqueous solution. Part 9. A potentiometric study of mono- and poly-nuclear aluminium(III) citrates, *J. Chem. Soc. Dalton Trans.*, (1983), 2513-2517. Cited on page: 311.
- [83OHM/SJO2] Öhman, L.-O., Sjöberg, S., Complex formation in the  $\text{Al}^{3+}$ -citrate system, *Inorg. Chim. Acta*, **79**, (1983), 215-216. Cited on page: 311.

- [83OLI/WIK] Olin, Å., Wikmark, G., Automated instrumentation for determination of stability constants from solubility, *Anal. Chem.*, **55**, (1983), 1402-1405. Cited on page: 114.
- [83PER/MIS] Perfil'ev, V. A., Mishchenko, V. T., Poluéktov, N. S., Kucher, A. A., Derivative spectrophotometry in the study of complexation of ions of f-elements. Complexation of U(VI) with ethylenediaminetetraacetic and oxalic acids, *Dokl. Phys. Chem.*, **271**, (1983), 627-630. Cited on pages: 226, 478, 480, 482, 744.
- [83SHC/MIK] Shchelokov, R. N., Mikhailov, Y. N., Orlova, I. M., Sergeev, A. V., Mixed uranyl, uranium(IV), and thorium(IV) ethylenediaminetetraacetates, *Dokl. Phys. Chem.*, **272**, (1983), 297-299. Cited on pages: 476, 477.
- [83SPA] Spahiu, K., Carbonate complex formation in lanthanoid and actinoid systems, Ph. D. Thesis, The Royal Institute of Technology, (1983), Stockholm, Sweden. Cited on pages: 832, 839, 840.
- [83WIL/WIL] Willes, M. J., Williams, D. R., A potentiometric study of the lead(II) - EDTA and lead(II) - D-penicillamine systems, *Inorg. Chim. Acta*, **80**, (1983), L35-L36. Cited on page: 398.
- [83ZUB/KRO] Zubarev, V. G., Krot, N. N., Synthesis of complex oxalates of americium(III) with potassium ions in the outer sphere, *Sov. Radiochem.*, **25**, (1983), 594-601. Cited on pages: 284, 744.
- [83ZUB/KRO2] Zubarev, V. G., Krot, N. N., Complex oxalates of americium(III) with sodium, ammonium and cesium ions in the outer sphere, *Sov. Radiochem.*, **25**, (1983), 601-604. Cited on pages: 284, 745.
- [83ZUB/KRO3] Zubarev, V. G., Krot, N. N., Spitsyn, V. I., Complex oxalates of americium(III) on plutonium(III), *Dokl. Phys. Chem.*, **273**, (1983), 378-380. Cited on pages: 263, 276.
- [84ANA/ATK] Ananthaswamy, J., Atkinson, G., Thermodynamics of concentrated electrolyte mixtures. 4. Pitzer-Debye-Hückel limiting slopes for water from 0 to 100°C and from 1 atm to 1 kbar, *J. Chem. Eng. Data*, **29**, (1984), 81-87. Cited on page: 827.

- [84AND/KIR] Andryushin, V. G., Kirillova, M. I., Sokhina, L. P., Teterin, E. G., Shesterikov, N. N., Shmidt, V. S., A compound of plutonium(IV) oxalate with urea, *Sov. Radiochem.*, **26**, (1984), 108-112. Cited on page: 263.
- [84BER/KIM] Bernkopf, M. F., Kim, J. I., Hydrolysereaktionen und Karbonatkomplexierung von dreiwertigem Americium im natürlichen aquatischen System, Inst. für Radiochemie der Tech. Univ. München, Report RCM-02884, in German, (1984), 200 pp., in German. Cited on pages: 536.
- [84BOU/GUI] Bouhlassa, S., Guillaumont, R., Complexes citriques et citrates d'américium, *J. Less-Common Met.*, **99**, (1984), 157-171, in French. Cited on pages: 301, 308, 381, 382, 383, 384, 745.
- [84BOU/PET] Bouhlassa, S., Petit-Ramel, M., Guillaumont, R., Complexes citriques de néodyme, *Bull. Soc. Chim. Fr.*, (1984), 15-111, in French. Cited on page: 308.
- [84BRE/SKR] Brečević, L. J., Škrtić, D., The transformation of calcium oxalate dihydrate in high ionic strength solutions, in: *Industrial Crystallization 84*, pp. 409-412, (1984), Jančić, S. and De Jong, E. J., Eds., Elsevier Science Publishers B. V., Amsterdam, The Netherlands. Cited on page: 165.
- [84BRI/LAG] Brighli, M., Lagrange, J., Lagrange, P., Complex formation of peroxouranyl (and uranyl) with polyaminocarboxylate ligands, *Polyhedron*, **3**, (1984), 469-474. Cited on pages: 484, 485, 486, 745, 746, 800.
- [84DAN/OST] Daniele, P. G., Ostacoli, G., Rigano, C., Sammartano, S., Ionic strength dependence of formation constants. Part 4. Potentiometric study of the system  $\text{Cu}^{2+}$ - $\text{Ni}^{2+}$ -citrate, *Transition Met. Chem. (London)*, **9**, (1984), 385-390. Cited on pages: 308, 311, 326, 327, 332, 333, 334, 354, 355, 356, 746, 759.
- [84DUF/MAY] Duffield, J. R., May, P. M., Williams, D. R., Computer simulation of metal ion equilibria in biofluids. IV. Plutonium speciation in human blood plasma and chelation therapy using polyaminopolycarboxylic acids, *J. Inorg. Biochem.*, **20**, (1984), 199-214. Cited on pages: 400, 445, 446, 449, 747.

- [84ESC/FUE] Escrivá, E., Fuertes, A., Beltrán, D., Order and disorder in mixed metal linear chains: the homo and heterobimetallic edta ( $M(H_2O)_4O_4O_{II}[M'(EDTA)].6H_2O$  complexes ( $M = Mg, Mn, Co, Zn$  and  $Ni$ ;  $M' = Co, Ni, Cu$  and  $Zn$ ), *Transition Met. Chem. (London)*, **9**, (1984), 184-190. Cited on page: 460.
- [84FRE] Freeman, R. D., Conversion of standard (1 atm) thermodynamic data to the new standard state pressure, 1 bar ( $10^5$  Pa), *J. Chem. Eng. Data*, **29**, (1984), 105-111. Cited on page: 30.
- [84FRE/LAN] *Handbook on the physics and chemistry of the actinides*, Freeman, A. J. and Lander, G. H., Eds., vol. 1, North-Holland, Amsterdam, (1984), 515 pp. Cited on page: 4.
- [84GON/MOT] Gonçalves, M. L. S., Mota, A. M. A., da Silva, J. J. R. F., Uranyl complexes of n-alkanediaminotetra-acetic acids, *Talanta*, **31**, (1984), 531-536. Cited on pages: 400, 403, 484, 485, 486, 489, 662, 747, 748.
- [84GRE/WIK] Grenthe, I., Wikberg, P., Still, E. R., Solution studies of systems with polynuclear complex formation. 3. The cadmium(II) citrate system, *Inorg. Chim. Acta*, **91**, (1984), 25-31. Cited on page: 311.
- [84HOS] Hostettler, J. D., Electrode electrons, aqueous electrons, and redox potentials in natural waters, *Am. J. Sci.*, **284**, (1984), 734-759. Cited on page: 22.
- [84JOH/JON] Johansen, E. S., Jøns, O., Testing the adequacy of equilibrium models for complex formation. Complexation between molybdate and oxalate revisited, *Talanta*, **31**, (1984), 743-747. Cited on pages: 118, 132, 751.
- [84KHA/AND] Khalturin, G. V., Andryushkeeva, N. I., Preparation of finely divided plutonium dioxide and study of its solubility in various media, *Sov. Radiochem.*, **26**, (1984), 365-369. Cited on page: 263.
- [84MAR/MES] Marshall, W. L., Mesmer, R. E., Pressure-density relationships and ionization equilibria in aqueous solutions, *J. Solution Chem.*, **13**, (1984), 383-391. Cited on page: 35.

- [84MED/DOM] Mederos, A., Domínguez, S., Hernandez Padilla, M., Brito, F., Chinae, E., Equilibrios en disolución acuosa entre el Be(II) y los ácidos etilendiaminotetracético (EDTA) y metafenilendiaminotetracético (mFDTA), *Bol. Soc. Quím. Peru*, **50**, (1984), 277-293, in Spanish. Cited on pages: 400, 403.
- [84MOS/GAL] Mosset, A., Galy, J., Coronado, E., Drillon, M., Beltrán, D., Amorphous chain complexes  $MM'(EDTA)(H_2O)_4 \cdot 2H_2O$ . LAXS investigation of the local structure and magnetic behavior, *J. Am. Chem. Soc.*, **106**, (1984), 2864-2869. Cited on page: 460.
- [84MOT/MAR] Motekaitis, R. J., Martell, A. E., Complexes of aluminum(III) with hydroxy carboxylic acids, *Inorg. Chem.*, **23**, (1984), 18-23. Cited on page: 311.
- [84NES/POR2] Nesterova, Y. M., Porai-Koshits, M. A., Crystal structure of the tetrahydrates of the calcium salts of Ni(II) and Cu(II) ethylenediaminetetraacetate, *Sov. J. Coord. Chem.*, **10**, (1984), 69-78. Cited on pages: 392, 460.
- [84RAO/CHO] Rao, L. F., Choppin, G. R., Kinetics of the reduction of neptunium(VI) by dicarboxylic acids, *Inorg. Chem.*, **23**, (1984), 2351-2354. Cited on pages: 261, 748.
- [84REE/DAN] Rees, T. F., Daniel, S. R., Complexation of neptunium(V) by salicylate, phthalate and citrate ligands in a pH 7.5 phosphate buffered system, *Polyhedron*, **3**, (1984), 667-673. Cited on pages: 374, 749.
- [84REK/GAL] Rekharskii, M. V., Gal'chenko, G. L., Egorov, A. M., Microcalorimetric determination of the enthalpies of ionization of biologically important buffer solutions, *J. Gen. Chem. USSR*, **54**, (1984), 173-176. Cited on pages: 327, 749.
- [84SAL/DEV] Sal'nikov, Y. I., Devyatov, F. V., Zhuravleva, N. E., Golodnitskaya, D. V., Formation of complexes of nickel(II) and cobalt(II) with citric acid, *Russ. J. Inorg. Chem.*, **29**, (1984), 1299-1302. Cited on pages: 353, 354, 355, 356, 358, 749.

- [84SIR] Sircar, J. K., Electrophoretic studies of cobalt(II)-, zinc(II)-, beryllium(II)-, uranyl(II)-, chromium(III)-, and thorium(IV)-oxalate-nitrilotriacetate complexes in solution, *J. Chem. Eng. Data*, **29**, (1984), 141-143. Cited on pages: 232, 234, 235, 242, 243, 749.
- [84TOM/VOL] Tomilin, S. V., Volkov, Y. F., Visyashcheva, G. I., Kapshukov, I. I., Crystal structure of the compound  $\text{NaNpO}_2\text{C}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ , *Sov. Radiochem.*, **26**, (1984), 696-701. Cited on page: 248.
- [84VAS/GRE] Vasil'ev, V. P., Grechina, N. K., Bugrova, N. Y., Dissociation of (ethylenedinitrilo)tetrakisacetic acid in mixed solvents (water-DMSO), *J. Gen. Chem. USSR*, **54**, (1984), 650-653. Cited on page: 398.
- [84VEN/SWA] Venkatnarayana, G., Swamy, S. J., Lingaiah, P., Stability constants of ternary complexes of copper(II) with phthalic acid and  $\text{O}^-$ ,  $\text{O}^-$ ;  $\text{O}^-$ ,  $\text{N}^-$  and N,N donor ligands, *Indian J. Chem.*, **23A**, (1984), 501-503. Cited on page: 114.
- [84ZHO/XU] Zhou, X.-Y., Xu, X.-L., Zhang, H.-L., Studies on  $\alpha$ -hydroxybenzylamine and its complexes IV. Stability of mixed-ligand copper(II) complexes, *Huax. Xue. (Acta Chim. Sin.)*, **42**, (1984), 867-871, in Chinese. Cited on page: 114.
- [84ZUB/KRO] Zubarev, V. G., Krot, N. N., Complex oxalates of plutonium(III), *Sov. Radiochem.*, **26**, (1984), 161-165. Cited on page: 263.
- [85BAR/PAR] Bard, A. J., Parsons, R., Jordan, J., *Standard Potentials in Aqueous Solution*, Bard, A. J. and Parsons, R. and Jordan, J., Eds., International Union of Pure and Applied Chemistry. Marcel Dekker, Inc., New York, (1985), 834 pp. Cited on page: 22.
- [85DAL/GUS] Dalidovich, S. V., Gusev, E. A., Shandakov, V. A., Vechev, A. A., Heat capacities of anhydrous ammonium oxalate and oxalic acid and their crystallohydrates, *Thermochim. Acta*, **89**, (1985), 387-389. Cited on pages: 108, 111.

- [85DAN/RIG] Daniele, P. G., Rigano, C., Sammartano, S., Ionic strength dependence of formation constants. Alkali metal complexes of ethylenediaminetetraacetate, nitrilotriacetate, diphosphate, and tripolyphosphate in aqueous solution, *Anal. Chem.*, **57**, (1985), 2956-2960, and supplementary material. Cited on pages: 399, 400, 403, 427, 429, 432, 434, 437, 438, 439, 739, 750.
- [85DAN/ROB] Daniele, P. G., de Robertis, A., Rigano, C., Sammartano, S., Ionic strength dependence of formation constants. VI.  $\text{La}^{3+}$  -acetate, -malonate and -citrate complexes in aqueous solution, *Ann. Chim. (Rome)*, **75**, (1985), 115-120. Cited on pages: 308, 332, 333, 751.
- [85DAN/SON] Daniele, P. G., Sonego, S., Ronzani, M., Marangella, M., Ionic strength dependence of formation constants. Part 8. Solubility of calcium oxalate monohydrate and calcium hydrogenphosphate dihydrate in aqueous solution, at 37°C and different ionic strengths, *Ann. Chim. (Rome)*, **75**, (1985), 245-251. Cited on pages: 159, 166, 168, 169, 173.
- [85FER/GRE] Ferri, D., Grenthe, I., Hietanen, S., Néher-Neumann, E., Salvatore, F., Studies on metal carbonate equilibria: 12. Zinc(II) carbonate complexes in acid solution, *Acta Chem. Scand.*, **A39**, (1985), 347-353. Cited on page: 839.
- [85FRE/KEL] *Handbook on the physics and chemistry of the actinides*, Freeman, A. J. and Keller, C., Eds., vol. 3, North-Holland, Amsterdam, (1985), 520 pp. Cited on page: 4.
- [85FRE/LAN] *Handbook on the physics and chemistry of the actinides*, Freeman, A. J. and Lander, G. H., Eds., vol. 2, North-Holland, Amsterdam, (1985), 503 pp. Cited on page: 4.
- [85FRI] Friedman, H. A., Separation of uranium from technetium in recovery of spent nuclear fuel, *Chem. Abstr.*, **103**, (1985), 94779f, Patent US 4,528,165. Cited on page: 201.
- [85GRA/FAR] Grases, F., Far, G., March, J. G., Studies on technetium and some carboxylic and hydroxamic acids, *J. Radioanal. Nucl. Chem.*, **91**, (1985), 129-134. Cited on page: 201.

- [85HOV/TRE] Hovey, J. K., Tremaine, P. R., Thermodynamics of the complexes of aqueous iron(III), aluminum, and several divalent cations with EDTA: heat capacities, volumes, and variations in stability with temperature, *J. Phys. Chem.*, **89**, (1985), 5541-5549. Cited on page: 432.
- [85KIL] Killa, H. M., Determination of stability constants using linear-scan and cyclic voltammograms, *J. Chem. Soc. Faraday Trans. I*, **81**, (1985), 2659-2666. Cited on page: 187.
- [85LAN/KRA] Langfelderová, H., Krajčiková, D., Ambrovič, P., The relationship between the structure of Cu(II) complexes and their chemical transformations: VI. Thermal decomposition of some pentacoordinated aqua complexes of Cu(II) with heterogeneous spheres, *J. Therm. Anal.*, **30**, (1981), 207-214. Cited on page: 460.
- [85LEC/MOS] Lecante, P., Mosset, A., Galy, J., LASIP: a liquid and amorphous structure investigation package, *J. Appl. Crystallogr.*, **18**, (1985), 214-218. Cited on page: 460.
- [85MAR/EVA] Marini, M. A., Evans, W. J., Berger, R. L., Use of the twin-cell differential titration calorimeter for binding studies. I. EDTA and its calcium complex, *J. Biochem. Biophys. Meth.*, **10**, (1985), 273-285. Cited on pages: 399, 427, 430, 447, 449, 456, 457, 751, 754.
- [85MIK/LOB] Mikhailov, Y. N., Lobanova, G. M., Kanishcheva, A. S., Sergeev, A. V., Bolotova, G. T., Shchelokov, R. N., Crystal structures of  $(\text{CN}_3\text{H}_6)_3[\text{U}(\text{EDTA})\text{F}_3]$  and  $(\text{CN}_3\text{H}_6)_3[\text{Th}(\text{EDTA})\text{F}_3]$ , *Sov. J. Coord. Chem.*, **11**, (1985), 312-317. Cited on page: 393.
- [85MUL] Muller, A. B., (1985), Private communication, OECD Nuclear Energy Agency, Paris. Cited on page: 4.
- [85RED/RAO] Reddy, P. R., Rao, V. B. M., Role of secondary ligands in the structure and stability of metal-cytidine complexes in solution, *Polyhedron*, **4**, (1985), 1603-1609. Cited on pages: 115, 178, 179, 181, 187, 194, 196, 751, 752, 755.
- [85RIZ/ANT] Rizkalla, E. N., Antonious, M. S., Anis, S. S., X-ray photoelectron and potentiometric studies of some calcium complexes, *Inorg. Chim. Acta*, **96**, (1985), 171-178. Cited on pages: 308, 335, 336, 338, 339, 342, 752.



- [85ROB/STE] de Robertis, A., de Stefano, C., Sammartano, S., Scarcella, R., Formation and stability of some dicarboxylate-NH<sub>4</sub><sup>+</sup> complexes in aqueous solution at 25°C, *J. Chem. Res. (S)*, (1985), 322-323. Cited on pages: 118, 132, 752.
- [85SEV] Sevost'yanova, E. P., Complex formation by neptunium(V) with citric acid, *Sov. Radiochem.*, **27**, (1985), 20-23. Cited on pages: 374, 375, 614, 752, 790.
- [85SHC/ORL] Shchelokov, R. N., Orlova, I. M., Sergeev, A. V., Mikhailov, Y. N., Lobanova, G. M., Kanishcheva, A. S., Mixed uranyl compounds with a bridging ethylenediaminetetraacetato group, *Sov. J. Coord. Chem.*, **11**, (1985), 103-111. Cited on pages: 393, 476, 477.
- [85SHI] Shilov, V. P., Mechanism of the interaction of Am(VI) and H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> in aqueous acid solutions, *Sov. Radiochem.*, **27**, (1985), 540-543. Cited on pages: 295, 753.
- [85SIN/YAD] Singh, S., Yadava, P. C., Yadava, K. L., Electrophoretic evaluation of doubtful dissociation of some amino acids, *J. Electrochem. Soc. India*, **34**, (1985), 181-183. Cited on page: 398.
- [85SJO/OEH2] Sjöberg, S., Öhman, L.-O., Equilibrium and structural studies of silicon(IV) and aluminium(III) in aqueous solution. Part 13. A potentiometric and <sup>27</sup>Al nuclear magnetic resonance study of speciation and equilibria in the aluminium(III)-oxalic acid-hydroxide system, *J. Chem. Soc. Dalton Trans.*, (1985), 2665-2669. Cited on pages: 118, 130.
- [85SMI/MOT] Smith, R. M., Motekaitis, R. J., Martell, A. E., New multidentate ligands. 23. Chelating tendencies of octadentate diamido diamino tetraacetic acids, *Inorg. Chem.*, **24**, (1985), 1132-1142. Cited on page: 401.
- [85SOH/NOV] Söhnle, O., Novotný, P., *Densities of aqueous solutions of inorganic substances*, Elsevier, Amsterdam, (1985), 335 pp. Cited on pages: 26, 27, 99.

- [85VAS/KOZ] Vasil'ev, V. P., Kozlovskii, E. V., Kalachev, E. N., Chistyakova, G. V., A thermochemical study of the reactions of  $\text{Ni}^{\text{II}}$ ,  $\text{Cu}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Cd}^{\text{II}}$  ethylenediaminetetraactates with the hydroxide ion in aqueous solution, *Russ. J. Inorg. Chem.*, **30**, (1985), 831-833. Cited on pages: 463, 466, 468, 469, 753.
- [85VEN/SWA] Venkatnarayana, G., Swamy, S. J., Lingaiah, P., Stability constants of ternary complexes of dioxouranium(VI) with phthalic acid and  $\text{O}^-$ ,  $\text{O}^-;\text{O}^-$ ,  $\text{N}^-$  and N,N donor ligands, *Indian J. Chem.*, **24A**, (1985), 624-626. Cited on pages: 231, 232, 234, 235, 242, 243, 754.
- [86AHR] Ahrlund, S., Solution chemistry and kinetics of ion reactions, in: *The chemistry of the actinide elements*, Vol.2, Katz, J. J., Seaborg, G. T. and Morss, L. R., Eds., pp. 1480-1546, Chapman and Hall, London, (1986). Cited on page: 758.
- [86APE] Apelblat, A., Enthalpy of solution of oxalic, succinic, adipic, maleic, malic, tartaric, and citric acids, oxalic acid dihydrate, and citric acid monohydrate in water at 298.15 K, *J. Chem. Thermodyn.*, **18**, (1986), 351-357. Cited on pages: 109, 110, 111, 112, 304, 305.
- [86BAR/HAV] Bartušek, M., Havel, J., Matula, D., Chelates of molybdenum(VI) with citrate and malate, *Collect. Czech. Chem. Commun.*, **51**, (1986), 2702-2711. Cited on page: 308.
- [86BRU] Bruno, J., Stoichiometric and structural studies on the  $\text{Be}^{2+}$ - $\text{H}_2\text{O}$ - $\text{CO}_2(\text{g})$  system, Ph. D. Thesis, The Royal Institute of Technology, (1986), Stockholm, Sweden. Cited on page: 840.
- [86CAP/ROB] Capone, S., de Robertis, A., de Stefano, C., Sammartano, S., Formation and stability of zinc(II) and cadmium(II) citrate complexes in aqueous solution at various temperatures, *Talanta*, **33**, (1986), 763-767. Cited on pages: 308, 326, 327, 328.
- [86CHO/DAD] Choppin, G. R., Dadgar, A., Rizkalla, E. N., Thermodynamics of complexation of lanthanides by dicarboxylate ligands, *Inorg. Chem.*, **25**, (1986), 3581-3584. Cited on page: 114.

- [86COD] CODATA, The 1986 adjustment of the fundamental physical constants. A report of the CODATA Task Group on Fundamental Constants, prepared by Cohen, E. R. and Taylor, B. N., Pergamon Journals, Oxford, CODATA Bulletin, Report 63, (1986), 36 pp. Cited on pages: 32, 33.
- [86COR/DRI] Coronado, E., Drillon, M., Fuertes, A., Beltrán, D., Mosset, A., Galy, J., Structural and magnetic study of  $\text{Ni}_2(\text{EDTA})(\text{H}_2\text{O})_4 \cdot 2\text{H}_2\text{O}$ . Alternating Landé factors in a two-sublattice 1D system, *J. Am. Chem. Soc.*, **108**, (1986), 900-905. Cited on page: 460.
- [86CRU/HEY] Cruywagen, J. J., Heyns, J. B., van de Water, R. F., A potentiometric, spectrophotometric, and calorimetric investigation of molybdenum(VI)-oxalate complex formation, *J. Chem. Soc. Dalton Trans.*, (1986), 1857-1862. Cited on pages: 118, 130.
- [86CRU/WAT] Cruywagen, J. J., van de Water, R. F., Complexation between molybdenum(VI) and citrate: a potentiometric and calorimetric investigation, *Polyhedron*, **5**, (1986), 521-526. Cited on pages: 308, 311, 326, 327, 754.
- [86DRI/COR] Drillon, M., Coronado, E., Beltrán, D., Curely, J., Georges, R., Nugteren, P. R., De Jongh, L. J., Genicon, J. L., Magnetic properties of ferrimagnetic chains, *J. Magn. Magn. Mater.*, **54-57**, (1986), 1507-1509. Cited on page: 460.
- [86ESC/FUE] Escrivá, E., Fuertes, A., Folgado, J. V., Martínez-Tamayo, E., Beltrán-Porter, A., Beltrán-Porter, D., Study of the thermal behaviour of ordered bimetallic edta complexes, *Thermochim. Acta*, **104**, (1986), 223-245. Cited on page: 460.
- [86FRE/KEL] *Handbook on the physics and chemistry of the actinides*, Freeman, A. J. and Keller, C., Eds., vol. 4, North-Holland, Amsterdam, (1986), 567 pp. Cited on page: 4.
- [86GOM/JAM] Gomez-Romero, P., Jameson, G. B., Casan-Pastor, N., Coronado, E., Beltrán, D., Low-dimensional bimetallic ordered systems: synthesis and characterization of the isomorphous series  $\text{Co}_x\text{Ni}_{2-x}\text{EDTA} \cdot 2\text{H}_2\text{O}$ . Crystal structure of  $\text{Co}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$  and preferential site occupation in  $\text{CoNiEDTA} \cdot 2\text{H}_2\text{O}$ , *Inorg. Chem.*, **25**, (1986), 3171-3176. Cited on page: 460.

- [86GOV/PAT] Govindarajan, S., Patil, K. C., Poojary, M. D., Manohar, H., Synthesis, characterization and X-ray structure of hexahydrazinium diuranyl pentaoxalate dihydrate,  $(\text{N}_2\text{H}_5)_6(\text{UO}_2)_2(\text{C}_2\text{O}_4)_5 \cdot 2\text{H}_2\text{O}$ , *Inorg. Chim. Acta*, **120**, (1986), 103-107. Cited on page: 213.
- [86GRE/POW] Gregor, J. E., Powell, H. K. J., Aluminium(III)-citrate complexes: a potentiometric and  $^{13}\text{C}$  N.M.R. study, *Aust. J. Chem.*, **39**, (1986), 1851-1864. Cited on page: 311.
- [86HOV/HEP] Hovey, J. K., Hepler, L. G., Tremaine, P. R., Thermodynamics of aqueous EDTA systems: Apparent and partial molar heat capacities and volumes of aqueous strontium and barium EDTA, *J. Solution Chem.*, **15**, (1986), 977-987. Cited on page: 432.
- [86KAN/KIM] Kanellakopulos, B., Kim, J. I., Dornberger, E., The autoradiolytic decomposition of Pu(IV)-oxalate, *Z. Anal. Chem.*, **323**, (1986), 818-820. Cited on page: 262.
- [86KAT/SEA] *The chemistry of the actinide elements*, 2nd. Edition, Katz, J. J. and Seaborg, G. T. and Morss, L. R., Eds., Chapman and Hall, London, (1986), 1674 pp. Cited on page: 4.
- [86MAR/EVA] Marini, M. A., Evans, W. J., Berger, R. L., The determination of binding constants with a differential thermal and potentiometric titration apparatus. II. EDTA, EGTA and calcium, *J. Biochem. Biophys. Meth.*, **12**, (1986), 135-146. Cited on pages: 399, 427, 430, 447, 449, 456, 457, 751, 754.
- [86MAT/PAS] Matusevich, L. A., Pashina, N. M., State of zirconium(IV) in the presence of oxalate ions, *Vestsi Akad. Navuk BSSR, Ser. Khim. Navuk*, **4**, (1986), 3-6, in Russian. Cited on pages: 205, 755.
- [86NOR/MUN] Nordstrom, D. K., Munoz, J. L., *Geochemical Thermodynamics*, Blackwell Sci. Publ., Palo Alto, (1986). Cited on page: 22.
- [86POL/FIL] Polynova, T. N., Filippova, T. V., Porai-Koshits, M. A., Crystal structure of lithium salt dihydrate of acidic nickel(II) ethylene-diaminetetraacetate, *Koord. Khim.*, **12**, (1986), 273-279, in Russian. Cited on pages: 392, 460.

- [86RAO/PIU] Rao, V. K., Pius, I. C., Subbarao, M., Chinnusamy, A., Natarajan, P. R., Precipitation of plutonium oxalate from homogeneous solutions, *J. Radioanal. Nucl. Chem.*, **100**, (1986), 129-134. Cited on page: 269.
- [86RED/RAO] Reddy, P. R., Rao, V. B. M., Rare earth metal complexes of cytidine, *Inorg. Chim. Acta*, **125**, (1986), 191-195. Cited on pages: 115, 755.
- [86SAL/BOO] Sal'nikov, Y. I., Boos, G. A., Complex formation by copper(II) with ethylenediaminetetra-acetic acid in aqueous and aqueous-dimethylsulphoxide solutions, *Russ. J. Inorg. Chem.*, **31**, (1986), 1393-1395. Cited on page: 398.
- [86SAL/ZHU] Sal'nikov, Y. I., Zhuravleva, N. E., Complex formation by gadolinium(III) and ions of the ytterbium group with citric acid, *Russ. J. Inorg. Chem.*, **31**, (1986), 496-498. Cited on page: 308.
- [86SYS/AGR] Sysoeva, T. F., Agre, V. M., Trunov, V. K., Dyatlova, N. M., Fridman, A. Y., Crystal structure of complex compound of nickel (II) with ethylenediaminetetraacetic acid  $\text{NC}_2\text{En}_3\text{A} \cdot 4\text{H}_2\text{O}$ , *J. Struct. Chem. USSR*, **27**, (1986), 97-103. Cited on page: 460.
- [86VAS/KOZ] Vasil'ev, V. P., Kozlovskii, E. V., Chistyakova, G. V., The thermodynamics of the formation of mixed-ligands complexes of  $\text{Cu}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$ ,  $\text{Zn}^{\text{II}}$  and  $\text{Cd}^{\text{II}}$  ethylenediaminetetra-acetates with glycine in aqueous solution, *Russ. J. Inorg. Chem.*, **31**, (1986), 1327-1329. Cited on pages: 464, 755.
- [86VIO/ROD] Viossat, B., Rodier, N., Eberle, J., Structure cristalline du citrate trisodique hydrate (2/11)  $\text{Na}_3(\text{C}_6\text{H}_5\text{O}_7) \cdot 5,5\text{H}_2\text{O}$ , *Bull. Soc. Chim. Fr.*, (1986), 522-525, in French. Cited on page: 297.
- [86WEI/KAT] Weigel, F., Katz, J. J., Seaborg, G. T., Plutonium, in: *The chemistry of the actinide elements, 2nd edition*, Katz, J. J., Seaborg, G. T. and Morss, L. R., Eds., vol. 1, pp. 499-886, Chapman and Hall, London, (1986). Cited on pages: 261, 268, 283.
- [87APE/MAN] Apelblat, A., Manzurola, E., Solubility of oxalic, malonic, succinic, adipic, maleic, malic, citric, and tartaric acids in water from 278.15 to 338.15 K, *J. Chem. Thermodyn.*, **19**, (1987), 317-320. Cited on pages: 110, 112, 305.

- [87BER/VAS] Bera, A. M., Vast, P., Palavit, G., Gosset, S., Détermination de constantes de complexation par automatisation et informatisation d'un calorimètre à circulation, *Journ. Calorim. Anal. Therm.*, **18**, (1987), 311-315, in French. Cited on pages: 437, 439, 755.
- [87BLA/BER] Blaquière, C., Berthon, G., Speciation studies in relation to magnesium bioavailability. Formation of Mg(II) complexes with glutamate, aspartate, glycinate, lactate, pyroglutamate, pyridoxine and citrate, and appraisal of their potential significance towards magnesium gastrointestinal absorption, *Inorg. Chim. Acta*, **135**, (1987), 179-189. Cited on pages: 335, 336, 337, 338, 339, 340, 342, 343, 344, 755.
- [87CAC/NEC] Caceci, M. S., Nectoux, F., Pagès, M., Stout, B. E., Choppin, G. R., Spectrophotometric studies of complexes of  $\text{NpO}_2^+$  in solution. I. Complexes with the anions of oxalic, malonic, succinic and maleic acid, *Inorg. Chim. Acta*, **140**, (1987), 243-244. Cited on pages: 255, 256, 756, 763.
- [87CIA/IUL] Ciavatta, L., Iuliano, M., Porto, R., The hydrolysis of the La(III) ion in aqueous perchlorate solution at 60°C, *Polyhedron*, **6**, (1987), 1283-1290. Cited on page: 37.
- [87COL/WIL] Colmanet, S. F., Williams, G. A., Mackay, M. F., Preparation and crystal structures of bis(tetraphenylarsonium)tris(oxalato)technetate(IV), and tetraphenylarsonium tris(benzene-1,2-dithiolato)Technetate(V): Octahedral versus trigonal prismatic geometry for tris-bidentate complexes of technetium, *J. Chem. Soc. Dalton Trans.*, (1987), 2305-2310. Cited on page: 201.
- [87DOL] Dollimore, D., The thermal decomposition of oxalates. A review., *Thermochim. Acta*, **117**, (1987), 331-363. Cited on pages: 165, 207, 214, 225.
- [87FIN/DUF] Findlow, J. A., Duffield, J. R., Evans, D. A., Williams, D. R., Speciation of aluminium in human and bovine milk, *Recl. Trav. Chim. Pays-Bas*, **106**, (1987), 403. Cited on page: 308.
- [87FRE/LAN] *Handbook on the physics and chemistry of the actinides*, Freeman, A. J. and Lander, G. H., Eds., vol. 5, North-Holland, Amsterdam, (1987), 375 pp. Cited on page: 4.

- [87GAM] Gampp, H., Investigation of pH-dependent complex equilibria at low ligand to metal ratio by nonlinear least-squares fit to linear-sweep or cyclic voltammetric data, *Anal. Chem.*, **59**, (1987), 2456-2460. Cited on page: 114.
- [87GAR/PAR] Garvin, D., Parker, V. B., White, Jr., H. J., *CODATA thermodynamic tables: Selection of some compounds of calcium and related mixtures: A prototype set of tables*, Springer-Verlag, Berlin, (1987), 356 pp. Cited on page: 25.
- [87HYN/ODO] Hynes, M. J., O'Dowd, M., Interactions of the trimethyltin(IV) cation with carboxylic acids, amino acids, and related ligands, *J. Chem. Soc. Dalton Trans.*, (1987), 563-566. Cited on page: 308.
- [87JOA/BIG] João, A., Bigot, S., Fromage, F., Etude des carbonates complexes des éléments IVB II. Détermination des constantes d'équilibre de formation des tétracarbonatozirconates(IV) et -hafnate(IV), *Bull. Soc. Chim. Fr.*, (1987), 943-947, in French. Cited on pages: 472, 474, 756.
- [87KIT/ITO] Kitamura, Y., Itoh, T., Reaction volume of protonic ionization for buffering agents. Prediction of pressure dependence of pH and pOH, *J. Solution Chem.*, **16**, (1987), 715-725. Cited on page: 308.
- [87LEO/FRI] Leont'eva, M. V., Fridman, A. Y., Dyatlova, N. M., Agre, V. M., Sysoeva, T. F., Preparation, structure, and properties of tetra-aquozinc ethylenediaminetetra-acetatocuprate dihydrate and tetra-aquozinc ethylenediaminetetra-acetatonickelate dihydrate, *Russ. J. Inorg. Chem.*, **32**, (1987), 1453-1456. Cited on page: 460.
- [87LIN/GU] Lin, H.-K., Gu, Z.-X., Chen, Y.-T., Calorimetric measurement of the heat of formation of competitive mixed-ligand complexes: The Cu(II)-oxalate-ethylenediamine system, *Gazz. Chim. Ital.*, **117**, (1987), 23-26. Cited on pages: 143, 146, 756, 757.
- [87MEF/KRO] Mefod'eva, M. P., Krot, N. N., *The compounds of transuranium elements*, Nauka, Moscow, (1987), in Russian. Cited on pages: 207, 212, 248, 261, 490.

- [87PAZ/KRI] Pazukhin, E. M., Krivokhatskii, A. S., Kochergin, S. M., Complex formation of americium(III) in oxalate solutions, *Sov. Radiochem.*, **29**, (1987), 9-13. Cited on pages: 284, 285, 286, 287, 757.
- [87RAY/DUF] Raymond, D. P., Duffield, J. R., Williams, D. R., Complexation of plutonium and thorium in aqueous environments, *Inorg. Chim. Acta*, **140**, (1987), 309-313. Cited on pages: 308, 379, 758.
- [87RIG/VIT] Riglet, C., Vitorge, P., Grenthe, I., Standard potentials of the ( $\text{MO}_2^{2+}/\text{MO}_2^+$ ) systems for uranium and other actinides, *Inorg. Chim. Acta*, **133**, (1987), 323-329. Cited on page: 839.
- [87SUE/HU] Sue, Z., Hu, H., Xue, S., Qing, Z., The solubility of Pu(III) oxalate, *Yuanzineng Kexue Jishu*, **21**, (1987), 326-329, in Chinese. Cited on pages: 264, 758.
- [87THE/BUS] The, P. J., Bush, J. F., Solubility of sodium oxalate in bayer liquor and a method of control, in: *Light Metals, 1987; proceedings of the technical sessions presented by the TMS Aluminium Committee at the TMS annual meeting*, pp. 5-10, Minerals, Metals and Materials Society, 420 Commonwealth Dr., Warrendale, PA, USA 15086, (1987). Cited on page: 158.
- [87THU/KUP] Thuan, L. B., Kupriyanova, G. N., Smirnova, N. S., Martynenko, L. I., Evseev, A. M., Evaluation of the stability of polycyclic complexes of rare earth elements with EDTA on a background of stable monocomplexonates, *Moscow Univ. Chem. Bull.*, **42**, (1987), 51-54. Cited on page: 398.
- [87VAS/KOZ] Vasil'ev, V. P., Kozlovskii, E. V., Chistyakova, G. V., Thermochemistry of the reactions of nickel, copper, zinc, and cadmium ethylenediaminetetra-acetates with iminodiacetate and nitrilotriacetate in aqueous solution, *Russ. J. Inorg. Chem.*, **32**, (1987), 911-913. Cited on page: 464.
- [88ALL/BOL] Allakhverdov, G. R., Bolyanovskii, A. D., Katkov, A. P., Matkovskaya, T. A., Mikhlin, A. L., Falin, V. A., Automated system for scientific studies of equilibria in solutions by the pH potentiometric method, *High-purity substances*, **5**, (1988), 914-916. Cited on page: 398.



- [88BAL/COL] Baldas, J., Colmanet, S. F., Mackay, M. F., Preparation and crystal structures of  $[\text{AsPh}_4]_4[\text{Tc}_4\text{N}_4\text{O}_2(\text{ox})_6]$  and  $[\text{AsPh}_4]_2[\text{TcO}(\text{ox})_2(\text{Hox})]\cdot 3\text{H}_2\text{O}$ : Technetium complexes containing quadridentate or unidentate oxalato ligands, *J. Chem. Soc. Dalton Trans.*, (1988), 1725-1731. Cited on page: 201.
- [88BYK/KUZ2] Bykhovskii, D. N., Kuzmina, M. A., Maksimov, V. F., Novikov, G. S., Smirnov, A. N., Solntseva, L. V., Synthesis conditions and some properties of neptunium(IV) oxalates in which  $\text{C}_2\text{O}_4/\text{Np} = 2.5$ , *Sov. Radiochem.*, **30**, (1988), 35-39. Cited on pages: 246, 248.
- [88CAM/MUN] Caminiti, R., Munoz Roca, C., Beltrán-Porter, D., Rossi, A., Amorphous complexes  $\text{MM}(\text{EDTA})(\text{H}_2\text{O})_4\cdot 2\text{H}_2\text{O}$ . LAXS and XPS investigation of the local structure, *Z. Naturforsch., A: Phys. Sci.*, **43**, (1988), 591-596. Cited on page: 460.
- [88CAS/FAU] Castro, I., Faus, J., Julve, M., Study of the interaction of  $[\text{Cu}(\text{bipy})]^{2+}$  with oxalate and squarate in aqueous solution, *Transition Met. Chem. (London)*, **13**, (1988), 455-458. Cited on page: 114.
- [88CIA] Ciavatta, L., (1988), Università di Napoli, Naples, Italy, Private Communication, (from the citation in [92GRE/FUG]). Cited on pages: 835, 842, 846.
- [88CRO] Crow, D. R., Diffusion phenomena and metal complex formation equilibria. Part 2.  $\text{Cd}^{\text{II}}$ -benzimidazole and  $\text{Ni}^{\text{II}}$ -oxalate systems in aqueous solution and general treatment of ion-molecule interactions, *J. Chem. Soc. Faraday Trans. 1*, **84**, (1988), 4285-4297. Cited on pages: 194, 195, 196, 759.
- [88DAN/OST] Daniele, P. G., Ostacoli, G., Zerbinati, O., Sammartano, S., De Robertis, A., Mixed metal complexes in solution. Thermodynamic and spectrophotometric study of copper(II)-citrate heterobinuclear complexes with nickel(II), zinc(II) or cadmium(II) in aqueous solution, *Transition Met. Chem. (London)*, **13**, (1988), 87-91. Cited on pages: 354, 355, 356, 759.
- [88DAS/KAL] Dash, U. N., Kalia, S. P., Thermodynamics of the homologous dicarboxylic acids and the silver-silver salt electrodes in aqueous medium, *J. Electrochem. Soc. India*, **37**, (1988), 333-338. Cited on page: 114.

- [88EVS/SMI] Evseev, A. M., Smirnova, N. S., Kir'yanov, Y. A., Nikolaeva, E. M., Ozerova, G. P., A study of complex formation in ethylenediaminetetraacetate solutions from chemical copper plating, *Moscow Univ. Chem. Bull.*, **43**, (1988), 16-20. Cited on pages: 398, 462, 466, 759.
- [88GHA/MAN] Ghandour, M. A., Mansour, H., Abu El-Wafa, M. H. M., Khodary, M., pH-metric studies of mixed-ligand complexes of cadmium-, magnesium-, strontium- and calcium-(II) with pyruvate and oxalate or citrate, *J. Indian Chem. Soc.*, **65**, (1988), 716-718. Cited on pages: 114, 178, 181, 308, 335, 338, 342, 759, 760.
- [88HED] Hedlund, T., Studies of complexation and precipitation equilibria in some aqueous aluminium(III) systems, Ph. D. Thesis, University of Umeå, (1988), Sweden. Cited on page: 839.
- [88HOV/HEP2] Hovey, J. K., Hepler, L. G., Tremaine, P. R., Thermodynamics of aqueous EDTA systems: Apparent and partial molar heat capacities and volumes of aqueous  $\text{EDTA}^{4-}$ ,  $\text{HEDTA}^{3-}$ ,  $\text{H}_2\text{EDTA}^{2-}$ ,  $\text{NaEDTA}^{3-}$ , and  $\text{KEDTA}^{3-}$  at 25°C. Relaxation effects in mixed aqueous electrolyte solutions and calculations of temperature dependent equilibrium constants, *Can. J. Chem.*, **66**, (1988), 881-896. Cited on pages: 432, 440.
- [88KIT] Kita, E., Model quasi-enzyme compounds of chromium(III) with vitamins B<sub>6</sub> and histamine. Part V. Kinetics of anation of the  $[\text{Cr}(\text{C}_2\text{O}_4)(\text{histamine})(\text{OH}_2)_2]^+$  ion by oxalate species, *Pol. Journ. Chem.*, **62**, (1988), 359-367. Cited on pages: 115, 118.
- [88LIN/GU] Lin, H.-K., Gu, Z.-X., Chen, X.-M., Chen, Y.-T., Calorimetric determination of the heats of formation of competitive ternary mixed-ligand complex compounds. Copper(II)-N-acetylglycine- $\alpha$ -amino acid system, *Thermochim. Acta*, **123**, (1988), 201-212. Cited on page: 765.
- [88MEL/BAR] Meloun, M., Bartoš, M., Högföldt, E., Multiparametric curve fitting -XIII. Reliability of formation constants determined by analysis of potentiometric titration data, *Talanta*, **35**, (1988), 981-991. Cited on page: 308.

- [88NER/VIT] Nerád, I., Vitková, S., Proks, I., Instrumentation of thermal analysis and calorimetry. New method for determination of the equilibrium state in systems involving reactions of the type  $A(s) \rightleftharpoons B(s) + C(g)$ , *J. Therm. Anal.*, **33**, (1988), 291-295. Cited on pages: 165, 166.
- [88NIK/DZY] Nikitenko, S. I., Dzyubenko, V. I., Malkova, N. N., Matyukha, V. A., Kinetics of intramolecular oxidation of the oxalate ion in a monooxalate complex with plutonium(IV) in nitric acid solution, *Sov. Radiochem.*, **30**, (1988), 634-638. Cited on pages: 270, 277, 279, 760.
- [88PET/TSY] Petropavlov, N. N., Tsygankova, I. G., Teslenko, L. A., Microcalorimetric investigation of polymorphic transitions in organic crystals, *Sov. Phys. Crystallogr.*, **33**, (1988), 853-855. Cited on page: 108.
- [88SHO/HEL] Shock, E. L., Helgeson, H. C., Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Correlation algorithms for ionic species and equation of state predictions to 5 kb and 1000°C, *Geochim. Cosmochim. Acta*, **52**, (1988), 2009-2036. Cited on pages: 35, 827.
- [88TAN/HEL] Tanger, IV, J. C., Helgeson, H. C., Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Revised equations of state for the standard partial molal properties of ions and electrolytes, *Am. J. Sci.*, **288**, (1988), 19-98. Cited on pages: 35, 827.
- [88TAQ/HUS] Taqui Khan, M. M., Hussain, A., Venkatasubramanian, K., Ramachandraiah, G., Oomen, V., Complexes of Ru(III) with aminopolycarboxylic acids and their interaction with molecular oxygen to form Ru(IV)-μ-peroxo complexes, *J. Mol. Catal.*, **44**, (1988), 117-127. Cited on page: 401.
- [88TOG/KOJ] Togashi, H., Kojima, N., Ban, T., Tsujikawa, I., Optical absorption by  $Mn^{2+}$  ions in  $MnM(edta).6H_2O$  ( $M = Zn, Cu, Ni, \text{ and } Co$ ), *Bull. Chem. Soc. Jpn.*, **61**, (1988), 1903-1909. Cited on page: 460.
- [88VAS/BOR] Vasil'ev, V. P., Borodin, V. A., Kopnyshev, S. B., Standard enthalpies of combustion and formation of iminodiacetic and ethylenediaminetetra-acetic acids, *Russ. J. Phys. Chem.*, **62**, (1988), 1156-1157. Cited on page: 394.

- [88WAN] Wanner, H., The NEA Thermochemical Data Base Project, *Radiochim. Acta*, **44/45**, (1988), 325-329. Cited on page: 4.
- [89ABD/ALI] Abdel Razik, A., Ali, F. A., Abu Attia, F., Evaluation of the stability constants of uranyl association complexes with phosphate, oxalate, tartrate, and citrate anions in solutions of constant ionic strength, *Microchem. J.*, **39**, (1989), 265-269. Cited on pages: 231, 234, 235, 364, 368, 760.
- [89COR/DRI] Coronado, E., Drillon, M., Nugteren, P. R., De Jongh, L. J., Beltrán, D., Georges, R., Low-temperature investigation of the ferrimagnetic chains  $\text{MnM' (EDTA).6H}_2\text{O}$  ( $\text{M}' = \text{Co, Ni, and Cu(II)}$ ): thermal and magnetic properties, *J. Am. Chem. Soc.*, **111**, (1989), 3874-3880. Cited on page: 460.
- [89COX/WAG] Cox, J. D., Wagman, D. D., Medvedev, V. A., *CODATA Key Values for Thermodynamics*, Hemisphere Publ. Corp., New York, (1989), 271 pp. Cited on pages: 6, 29, 34, 36, 57, 58, 59, 107, 222.
- [89CRO/EWA] Cross, J. E., Ewart, F. T., Greenfield, B. F., Modelling the behaviour of organic degradation products, *Mater. Res. Soc. Symp. Proc.*, **127**, (1989), 715-722. Cited on pages: 511, 531.
- [89DAS/DAS] Dash, U. N., Das, B. B., Biswal, U. K., Panda, T., Mishra, M. K., Ion - solvent interaction studies on homologous dicarboxylic acids in various mixed solvent systems, *Egypt. J. Chem.*, **32**, (1989), 181-194. Cited on page: 114.
- [89FEL/TOP] Feltz, A., Töpfer, J., Redoxreaktionen in kondensierten Oxidsystemen. X. Bildung von Defektspinellen und Phasenbeziehungen im System  $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ , *Z. Anorg. Allg. Chem.*, **576**, (1989), 71-80, in German. Cited on page: 191.
- [89FUE/REB] Fuentes, J., Reboso, R., Rodriguez, A., 2,5-toluenediamine-N,N'-disuccinic acid. Preparation, dissociation constants and coordinating capacity with divalent cations, *Polyhedron*, **8**, (1989), 1365-1370. Cited on page: 115.

- [89FUE/REB2] Fuentes, J., Reboso, R., Rodriguez, A., Binary and ternary complexes of 1,3-phenylenediamine- $N,N'$ -disuccinic acid with divalent cations, *Polyhedron*, **8**, (1989), 2693-2699. Cited on pages: 118, 130, 194, 195, 197.
- [89ISH/ENO] Ishikawa, M., Enomoto, H., Complexation of Ni(II) with citrate in nickel-citrate plating baths, *Hyomen Gijutsu*, **40**, (1989), 1266-1271, in Japanese. Cited on pages: 353, 760.
- [89MAN/APE] Manzurola, E., Apelblat, A., Markovits, G., Levy, O., Mixed-metal hydroxycarboxylic acid complexes: Formation constants of complexes of U(VI) with Fe(III), Al(III), In(III) and Cu(II), *J. Chem. Soc. Faraday Trans. 1*, **85**, (1989), 373-379. Cited on pages: 306, 308, 365, 368, 761.
- [89MIR] Mironov, I. V., Complex formation by silver(I) with EDTA<sup>4-</sup>, NTA<sup>3-</sup>, IDA<sup>2-</sup> and glycinate ions in aqueous solution (T = 298.2 K), *Russ. J. Inorg. Chem.*, **34**, (1989), 1075-1077. Cited on page: 398.
- [89NAG/SHA] Nagar, R., Sharma, R. C., Studies of some lanthanide quaternary complexes, *Indian J. Chem.*, **28A**, (1989), 627-629. Cited on page: 398.
- [89NES/HOF] Neshvad, G., Hoffman, M. Z., Mulazzani, Q. G., Venturi, M., Ciano, M., d'Angelantonio, M., One-electron reduction of tris(2,2'-bipyrimidine)ruthenium(2+) ion in aqueous solution. A photochemical, radiation chemical, and electrochemical study, *J. Phys. Chem.*, **93**, (1989), 6080-6088. Cited on page: 398.
- [89NIK/ION2] Nikitenko, S. I., Ionnikova, N. I., Influence of oxalic acid on equilibrium and kinetics of isotopic exchange between penta- and hexavalent neptunium in nitric acid solutions, *Sov. Radiochem.*, **31**, (1989), 250-254. Cited on pages: 255, 256, 761.
- [89PAP/ZIO] Papanastasiou, G., Ziogas, I., Acid-base equilibria in ternary water/methanol/dioxane solvent systems: Determination of pK values of citric acid at 25°C, *Anal. Chim. Acta*, **222**, (1989), 189-200. Cited on pages: 308, 323.

- [89POC] Poczynajło, A., Potentiometric determination of Pu(III) complexes formed by citric acid, EDTA, DHTP and DTPP, *J. Radioanal. Nucl. Chem.*, **134**, (1989), 97-108. Cited on pages: 301, 378, 446, 449, 499, 761, 762, 770.
- [89PRA/RAO] Prabhakar, B. K., Rao, P. S., Simultaneous elucidation of percentage composition and ionisation constants of acids by conductometric titration, *Indian J. Chem.*, **28A**, (1989), 407-412. Cited on page: 114.
- [89RED/RAM] Reddy, M. S., Ram, K., Reddy, M. G. R., Formation constants of binary and ternary complexes of Cu(II) with substituted 1,2,4-triazoles and some O,O; O,N and N,N donors in aqueous medium, *Indian J. Chem.*, **28A**, (1989), 437-439. Cited on page: 114.
- [89RIB/SAL] Ribas, X., Salvadó, V., Valiente, M., The chemistry of iron in biosystems. II. A hydrolytic model of the complex formation between Fe(III) and citric acid in aqueous solutions, *J. Chem. Res. (M)*, (1989), 2533-2553. Cited on page: 312.
- [89RIB/SAL2] Ribas, X., Salvadó, V., Valiente, M., The chemistry of iron in biosystems. Part 2. A hydrolytic model of the complex formation between iron(III) and citric acid in aqueous solutions, *J. Chem. Res. (S)*, (1989), 332. Cited on page: 312.
- [89RIG/ROB] Riglet, C., Robouch, P., Vitorge, P., Standard potentials of the ( $\text{MO}_2^{2+}/\text{MO}_2^+$ ) and ( $\text{M}^{4+}/\text{M}^{3+}$ ) redox systems for neptunium and plutonium, *Radiachim. Acta*, **46**, (1989), 85-94. Cited on pages: 839, 840.
- [89RIZ/SUL] Rizkalla, E. N., Sullivan, J. C., Choppin, G. R., Calorimetric studies of americium(III) complexation by amino carboxylates, *Inorg. Chem.*, **28**, (1989), 909-911. Cited on pages: 508, 509, 762, 763.
- [89ROB] Robouch, P., Contribution à la prévision du comportement de l'américium, du plutonium et du neptunium dans la géosphère; données chimiques, Commissariat à l'Energie Atomique, Report CEA-R-5473, (1989), partly in French, 216 p. Also published as Ph.D. thesis, Université Louis Pasteur de Strasbourg, France, 1987. Cited on pages: 839, 840.

- [89ROS/DIT] Rösch, F., Dittrich, S., Buklanov, G. V., Milanov, M., Khalkin, V. A., Dreyer, R., Electromigration of carrier-free radionuclides. 11. Complex formation of  $^{239}\text{Np(V)}$  with oxalate, tartrate and sulphate in neutral inert electrolytes, *Radiochim. Acta*, **48**, (1989), 205-211. Cited on pages: 255, 256, 763.
- [89SAL/BOO] Sal'nikov, Y. I., Boos, G. A., Ovchinnikova, I. V., Complex formation by copper(II) with ethylenediaminetetra-acetic acid in aqueous ethanol and aqueous acetone, *Russ. J. Inorg. Chem.*, **34**, (1989), 128-130. Cited on pages: 394, 398.
- [89SHO/HEL] Shock, E. L., Helgeson, H. C., Corrections to Shock and Helgeson *Geochimica et Cosmochimica Acta*, **52**, (1988) 2009-2036, *Geochim. Cosmochim. Acta*, **53**, (1989), 215. Cited on pages: 35, 827.
- [89SHO/HEL2] Shock, E. L., Helgeson, H. C., Sverjensky, D. A., Calculation of the thermodynamic and transport properties of aqueous species at high pressures and temperatures: Standard partial molal properties of inorganic neutral species, *Geochim. Cosmochim. Acta*, **53**, (1989), 2157-2183. Cited on pages: 35, 827.
- [89SIJ/ROS] Sijpkens, A. H., van Rossum, P., Raad, J. S., Somsen, G., Heat capacities and volumes of some polybasic carboxylic acids in water at 298.15 K, *J. Chem. Thermodyn.*, **21**, (1989), 1061-1067. Cited on pages: 113, 306.
- [89SIN] Singh, R. P., On the existence of  $\text{NaC}_2\text{O}_4^-$  ion pair complex, *Bull. Chem. Soc. Jpn.*, **62**, (1989), 4089-4091. Cited on pages: 159, 161, 166, 168, 169, 171.
- [89STO/CAC] Stout, B. E., Caceci, M. S., Nectoux, F., Pagès, M., Choppin, G. R., Complexes of  $\text{NpO}_2^+$  with aliphatic dicarboxylic acids, *Radiochim. Acta*, **46**, (1989), 181-184. Cited on pages: 255, 256, 257, 749, 756, 763.
- [89SVE/DOB] Svetlova, I. E., Dobrynina, N. A., Smirnova, N. S., Martynenko, L. I., Evseev, A. M., Savitskii, A. P., Mixed-ligand complex formation by europium with complexones and  $\beta$ -diketones in micellar solutions, *Russ. J. Inorg. Chem.*, **34**, (1989), 30-34. Cited on page: 398.

- [89VAS/KAL] Vasil'ev, V. I., Kalevich, E. S., Radchenko, V. M., Egunov, V. P., Izmailkov, A. N., Shimbarev, E. V., Vasil'ev, V. Y., Thermal decomposition of oxalates of An(III) (An = Am, Cm, Bk, and Cf), *Sov. Radiochem.*, **31**, (1989), 651-653. Cited on pages: 284, 763.
- [89VEN/BER] Venturini, M., Berthon, G., Aluminum speciation studies in biological fluids. Part 2. Quantitative investigation of aluminum-citrate complexes and appraisal of their potential significance in vivo, *J. Inorg. Biochem.*, **37**, (1989), 69-90. Cited on page: 312.
- [89YAD/GHO] Yadav, J., Ghosh, A. K., Ghosh, J. C., First dissociation constant and the related thermodynamic quantities of citric acid from 283.15 to 323.15 K, *Proc. Natl. Acad. Sci. India*, **A59**, (1989), 389-394. Cited on pages: 308, 323, 326, 328.
- [90AHR/DAH] Ahrlund, S., Dahlgren, Å., Persson, I., Stabilities and hydrolysis of some iron(III) and manganese(III) complexes with chelating ligands, *Act. Agr. Scand.*, **40**, (1990), 101-111. Cited on page: 398.
- [90ALB/AND] Alberto, R., Anderegg, G., Albinati, A., Synthesis and X-ray structure of a new Tc(IV) oxalato complex :  $K_4[(C_2O_4)_2Tc(\mu-O)_2Tc(C_2O_4)_2] \cdot 3H_2O$ , *Inorg. Chim. Acta*, **178**, (1990), 125-130. Cited on page: 201.
- [90APE/MAN] Apelblat, A., Manzurola, E., Apparent molar volumes of organic acids and salts in water at 298.15 K, *Fluid Phase Equilib.*, **60**, (1990), 157-171. Cited on pages: 113, 306.
- [90ARC/WAN] Archer, D. G., Wang, P., The dielectric constant of water and Debye-Hückel limiting law slopes, *J. Phys. Chem. Ref. Data*, **19**, (1990), 371-411. Cited on page: 827.
- [90ARE/CON] Arena, G., Contino, A., Musumeci, S., Purrello, R., Formation and stability constants of dimethyltin(IV) complexes with citrate, tripolyphosphate, and nitrilotriacetate in aqueous solution, *J. Chem. Soc. Dalton Trans.*, (1990), 3383-3387. Cited on page: 312.
- [90BAL/COL] Baldas, J., Colmanet, S. F., Technetium(VII) nitridoperoxo complexes, *Inorg. Chim. Acta*, **176**, (1990), 1-3. Cited on page: 201.



- [90BEC/NAG] Beck, M. T., Nagypál, I., *Chemistry of complex equilibria*, 2nd. Edition, Horwood Limited Publishers, New York, (1990), 402 pp. Cited on page: 24.
- [90BIA/BUC] Biader Ceipidor, U., Bucci, R., Magrí, A. D., Using thermoanalytical data. Part 2. The dependence of kinetic data available from thermogravimetry on sample and instrument parameters: a method for calculating "true" kinetic parameters, *Thermochim. Acta*, **161**, (1990), 37-49. Cited on pages: 165, 166.
- [90CIA] Ciavatta, L., The specific interaction theory in equilibrium analysis: Some empirical rules for estimating interaction coefficients of metal ion complexes, *Ann. Chim. (Rome)*, **80**, (1990), 255-263. Cited on pages: 820, 832, 833.
- [90COR/KON2] Cordfunke, E. H. P., Konings, R. J. M., Ouweltjes, W., The standard enthalpies of formation of MO(s), MCl<sub>2</sub>(s), and M<sup>2+</sup>(aq, ∞), (M = Ba, Sr), *J. Chem. Thermodyn.*, **22**, (1990), 991-996. Cited on page: 4.
- [90DAN/ROB] Daniele, P. G., de Robertis, A., de Stefano, C., Gianguzza, A., Sammartano, S., Studies on polyfunctional O-ligands. Formation thermodynamics of simple and mixed alkali metal complexes with citrate at different ionic strengths in aqueous solution, *J. Chem. Res. (S)*, (1990), 300-301. Cited on pages: 308, 312, 326, 327, 328, 332, 333, 334, 764.
- [90DAN/ROB2] Daniele, P. G., de Robertis, A., de Stefano, C., Gianguzza, A., Sammartano, S., Studies on polyfunctional O-ligands. Formation thermodynamics of simple and mixed alkali metal complexes with citrate at different ionic strengths in aqueous solution, *J. Chem. Res. (M)*, (1990), 2316-2350. Cited on pages: 308, 309, 312, 314, 326, 327, 328, 331, 332, 333, 335, 764.
- [90DOB/HEP] Dobrogowska, C., Hepler, L. G., Apelblat, A., The enthalpies of dilution of aqueous organic acids: oxalic acid and citric acid at 298.15 K, *J. Chem. Thermodyn.*, **22**, (1990), 167-172. Cited on page: 306.
- [90DZO/MOR] Dzombak, D. A., Morel, F. M. M., *Surface complexation modeling. Hydrous ferric oxide*, Wiley Intersc. Publ., New York, (1990), 393 pp. Cited on page: 724.

- [90FIN/DUF] Findlow, J. A., Duffield, J. R., Williams, D. R., The chemical speciation of aluminium in milk, *Chem. Spec. Bioavail.*, **2**, (1990), 3-32. Cited on page: 308.
- [90KOZ/VAS] Kozlovskii, E. V., Vasil'ev, V. P., Chistyakova, G. V., The thermodynamics of complex formation in the  $M(\text{Edta})^{2-}\text{-Cu}(\text{en})_2^{2+}$ - $\text{en-H}_2\text{O}$  systems ( $M = \text{Zn, Ni}$ ), *Russ. J. Inorg. Chem.*, **35**, (1990), 62-64. Cited on page: 460.
- [90LEI] Leigh, G. J., *Nomenclature of inorganic chemistry, recommendations 1990, issued by the Commission on Nomenclature of Inorganic Chemistry*, IUPAC, Ed., Blackwell Sci. Publ., Oxford, (1990), 289 pp. Cited on page: 13.
- [90LIN/GU] Lin, H.-K., Gu, Z.-X., Chen, Y.-T., Calorimetric measurement of the heat of formation of competitive mixed-ligands complexes: the  $\text{Ni(II)-oxalate-ethylenediamine}$  system, *Gazz. Chim. Ital.*, **120**, (1990), 657-660. Cited on pages: 199, 200, 765.
- [90MON] Monnin, C., The influence of pressure on the activity coefficients of the solutes and on the solubility of minerals in the system  $\text{Na-Ca-Cl-SO}_4\text{-H}_2\text{O}$  to  $200^\circ\text{C}$  and 1 kbar, and to high NaCl concentration, *Geochim. Cosmochim. Acta*, **54**, (1990), 3265-3282. Cited on page: 35.
- [90OEL/HEL] Oelkers, E. H., Helgeson, H. C., Triple-ion anions and polynuclear complexing in supercritical electrolyte solutions, *Geochim. Cosmochim. Acta*, **54**, (1990), 727-738. Cited on page: 827.
- [90RED/SAT] Reddy, G., Satyanarayana, S., Reddy, K. V., Ternary complexes of copper(II), nickel(II), cobalt(II) and zinc(II) with thiodiacetic acid and various secondary ligands, *Indian J. Chem.*, **29A**, (1990), 500-503. Cited on pages: 115, 194, 196, 765.
- [90RIG] Riglet, C., Chimie du neptunium et autres actinides en milieu carbonate, Commissariat à l'Energie Atomique, Report CEA-R-5535, (1990), 267 pp., in French, also published as Ph.D. thesis, Université Paris 6, (1989). Cited on pages: 839, 840.

- [90RIZ/NEC] Rizkalla, E. N., Nectoux, F., Dabos-Seignon, S., Pagès, M., Complexation of neptunium(V) by halo- and hydroxycarboxylate ligands, *Radiochim. Acta*, **51**, (1990), 113-117. Cited on pages: 374, 375, 753, 766.
- [90ROB/STE] de Robertis, A., de Stefano, C., Rigano, C., Sammartano, S., Thermodynamic parameters for the protonation of carboxylic acids in aqueous tetraethylammonium iodide solutions, *J. Solution Chem.*, **19**, (1990), 569-587. Cited on pages: 115, 118, 119, 132, 143, 144, 146, 312, 314, 326, 328, 331, 334, 766, 767.
- [90ROS/REI] Rösch, F., Reimann, T., Buklanov, V., Milanov, M., Khalkin, V. A., Dreyer, R., Electromigration of carrier-free radionuclides. XIV. Complex formation of  $^{241}\text{Am}$ -Am(III) with oxalate and sulfate in aqueous solution, *J. Radioanal. Nucl. Chem.*, **140**, (1990), 159-169. Cited on pages: 286, 287, 767.
- [90ULL/BHA] Ullah, M. R., Bhattacharya, P. K., Study of ternary complexes of Cu(II) involving aliphatic carboxylic acids and amino acid, *Indian J. Chem.*, **29A**, (1990), 150-153. Cited on page: 114.
- [90VAS/KAL2] Vasil'ev, V. I., Kalevich, E. S., Radchenko, V. M., Egunov, V. P., Izmalkov, A. N., Vasil'ev, V. Y., Thermal decomposition of oxalates and nitrates of transplutonium elements by differential thermal analysis, *J. Radioanal. Nucl. Chem.*, **143**, (1990), 269-274. Cited on page: 284.
- [90WAN/YAN] Wang, S., Yang, J., Improvement for calculating stepwise ionization constants of polybasic acids by pH method, *Fenxi Huaxue*, **18**, (1990), 275-279, in Chinese. Cited on page: 308.
- [91AND/CAS] Anderson, G. M., Castet, S., Schott, J., Mesmer, R. E., The density model for estimation of thermodynamic parameters of reactions at high temperatures and pressures, *Geochim. Cosmochim. Acta*, **55**, (1991), 1769-1779. Cited on page: 35.
- [91APE/BAR] Apelblat, A., Barthel, J., Conductance studies on aqueous citric acid, *Z. Naturforsch.*, **46a**, (1991), 131-140. Cited on pages: 308, 323, 327, 328, 331.

- [91AUK] van Auken, T. V., Solubility and heat of solution of potassium dihydrogen citrate, *J. Chem. Eng. Data*, **36**, (1991), 255-257. Cited on page: 300.
- [91BAL/COL] Baldas, J., Colmanet, S. F., Williams, G. A., Crystal structure of  $[\text{AsPh}_4]_2[\{\text{TcN}(\text{O}_2)_2\}_2(\text{ox})]\cdot 2\text{Me}_2\text{CO}$ : An oxalate-bridged technetium(VII) nitridoperoxo dimer, *J. Chem. Soc. Dalton Trans.*, (1991), 1631-1633. Cited on page: 201.
- [91BAP] Bapna, R. K., Binary and ternary complexes of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  with EDTA and citric acid, *Trans. SAEST*, **26**, (1991), 275-278. Cited on pages: 308, 327, 328, 463, 464, 467, 768.
- [91BEI/GRA] Beiriger, J. M., Grant, P. M., Enthalpy of reaction of thorium(IV) with oxalate, *J. Radioanal. Nucl. Chem.*, **154**, (1991), 89-94. Cited on pages: 143, 146, 768, 769, 791.
- [91BIC/EDW] Bickley, R. I., Edwards, H. G. M., Rose, S. J., A Raman spectroscopic study of nickel(II) oxalate dihydrate,  $\text{NiC}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ , and dipotassium bisoxalatonickel(II) hexahydrate,  $\text{K}_2\text{Ni}(\text{C}_2\text{O}_4)_2\cdot 6\text{H}_2\text{O}$ , *J. Mol. Struct.*, **243**, (1991), 341-350. Cited on page: 190.
- [91BOU/PHI] Bouzat, G., Philipponneau, G., Physical chemistry models of oxalate and gibbsite solubilities in Bayer solutions, in: *Light Metals, 1991; proceedings of the technical sessions presented by the TMS Aluminium Committee at the TMS annual meeting*, pp. 97-102, Elwin L. Rooy, Ed., Minerals, Metals and Materials Society, 420 Commonwealth Dr., Warrendale, PA, USA, 15086, (1991). Cited on pages: 152, 157, 158, 159, 769.
- [91CHR/CUM] Christie, G. L., Cummins, D., Duffield, J. R., Hurford, S. R., Morris, C. R., Riley, P. I., Vesey, J. A., Williams, D. R., Thermodynamic formation constants and solid state properties for the interaction of Zn(II) ions with citrate, phenolsulphonate, monofluorophosphate, and saccharinate, *J. Inorg. Biochem.*, **42**, (1991), 273-287. Cited on page: 308.
- [91DIN] Dinsdale, A. T., SGTE data for pure elements, *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.*, **15**, (1991), 317-425. Cited on page: 29.

- [91DUF/MAR] Duffield, J. R., Marsicano, F., Williams, D. R., Chemical speciation modelling and thermodynamic database compilation-I. Data uncertainties, *Polyhedron*, **10**, (1991), 1105-1111. Cited on page: 398.
- [91FRE/KEL] *Handbook on the physics and chemistry of the actinides*, Freeman, A. J. and Keller, C., Eds., vol. 6, North-Holland, Amsterdam, (1991), 742 pp. Cited on page: 4.
- [91GRI/BAT] Grigor'ev, M. S., Baturin, N. A., Regel', L. L., Krot, N. N., Synthesis, crystallization and molecular structure of crystal hydrates of the complex neptunium(V) oxalate  $[\text{Co}(\text{NH}_3)_6][\text{NpO}_2(\text{C}_2\text{O}_4)_2] \cdot n\text{H}_2\text{O}$  ( $n=3, 4$ ), *Sov. Radiochem.*, **33**, (1991), 121-126. Cited on page: 248.
- [91GRI/BES] Grigor'ev, M. S., Bessonov, A. A., Yanovskii, A. I., Struchkov, Y. T., Krot, N. N., Crystal structure of the complex neptunium(V) oxalate  $(\text{NH}_4)\text{NpO}_2\text{C}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ , *Sov. Radiochem.*, **33**, (1991), 499-503. Cited on page: 248.
- [91HAR/SMI] Hartley, D. W., Smith, G., Sagatys, D. S., Kennard, C. H. L., Antimony(III) complexes with carboxylic acids. 2. Preparation and crystal structures of  $[\text{Sb}_2\text{Ag}_2(\text{C}_6\text{H}_5\text{O}_7)_4]$  and  $[\text{SbNa}(\text{C}_6\text{H}_5\text{O}_7)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  [ $\text{C}_6\text{H}_5\text{O}_7 = \text{citrate}^{2-}$ ], *J. Chem. Soc. Dalton Trans.*, (1991), 2735-2739. Cited on page: 300.
- [91JAC/TOI] Jackson, G. E., du Toit, J., Gadolinium(III) *in vivo* speciation. Part 1. A potentiometric and spectroscopic study of gadolinium(III) citrate complexes, *J. Chem. Soc. Dalton Trans.*, (1991), 1463-1466. Cited on page: 312.
- [91KET/PAL] Kettler, R. M., Palmer, D. A., Wesolowski, D. J., Dissociation quotients of oxalic acid in aqueous sodium chloride media to 175°C, *J. Solution Chem.*, **20**, (1991), 905-927. Cited on pages: 769, 792.
- [91LI/ZHA] Li, J., Zhang, Y., The characteristics of EDTA's transition metal complexes (III) The d-d transition spectrum and structure characteristic of  $[\text{Pb.Ni}(\text{HEDTA})\text{H}_2\text{O}]\text{Cl}$  crystal, *Cryst. Res. Technol.*, **26**, (1991), 193-199. Cited on page: 460.

- [91LOO/KOP] Van Loon, L. R., Kopajtic, Z., Complexation of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{UO}_2^{2+}$  by radiolytic degradation products of bitumen, *Radiochim. Acta*, **54**, (1991), 193-199. Cited on pages: 194, 197, 231, 236, 239, 770.
- [91MAT/KAR] Matyukha, V. A., Karelin, A. I., *Oxalate compounds of lanthanides, actinides and some transition metals*, Energoatomizdat, Moscow, Russia, (1991), in Russian. Cited on pages: 207, 212, 225, 261, 263.
- [91NER/PRO] Nerád, I., Proks, I., Šaušová, S., Determination of equilibrium quantities of the systems formed by thermal decomposition according to the reaction  $\text{A}(\text{cond}) \rightleftharpoons \text{B}(\text{cond}) + \text{C}(\text{g})$ . II. Divariant equilibrium states at thermal dehydration of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ , *Chem. Pap.*, **45**, (1991), 721-730. Cited on pages: 165, 166.
- [91PIT] Pitzer, K. S., Ion interaction approach: theory and data correlation, in: *Activity coefficients in electrolyte solutions*, Pitzer, K. S., Ed., pp. 75-153, CRC Press, Boca Raton, Florida, (1991). Cited on page: 824.
- [91POC] Poczynajło, A., Extraction study of Pu(III)-edta chelates, *J. Radioanal. Nucl. Chem.*, **148**, (1991), 295-307. Cited on pages: 499, 770, 771.
- [91RED/DEV] Reddy, C. V. R., Devi, C. S., Reddy, M. G. R., Formation constants of binary and ternary complexes of Cu(II) with ninhydrin and some O, O; N, O and N, N donor ligands in aqueous medium, *Indian J. Chem.*, **30A**, (1991), 385-386. Cited on page: 781.
- [91SAL/BOO] Sal'nikov, Y. I., Boos, G. A., Gibadullina, K. V., Basyrova, R. R., Shakirova, N. L., Ethylenediaminetetraacetate complexes of potassium and sodium and dissociation of EDTA in aqueous-acetonitrile and aqueous-dioxane media, *Russ. J. Inorg. Chem.*, **36**, (1991), 745-749. Cited on pages: 398, 438.
- [91SIN/YEB] Singh, R. P., Yeboah, Y. D., Pambid, E. R., Debayle, P., Stability constant of the calcium-citrate(3-) ion pair complex, *J. Chem. Eng. Data*, **36**, (1991), 52-54. Cited on pages: 338, 344, 349, 771.
- [91WAN] Wanner, H., On the problem of consistency of chemical thermodynamic data bases, *Scientific basis for nuclear waste management XIV*, vol. 212, pp. 815-822, Materials Research Society, (1991). Cited on page: 4.

- [92AND] Anderegg, G., Complex formation of silver(I) ion with some aminopolycarboxylate ligands, *Inorg. Chim. Acta*, **194**, (1992), 31-35. Cited on page: 401.
- [92AZA/ELN] Azab, H. A., El-Nady, A.-B. M., Hassan, A., Azkal, R. S. A., Potentiometric studies on the formation equilibria of binary and ternary complexes of cobalt(II) with adenosine-5'-mono-, di- and triphosphate and some biologically important polybasic oxygen acids, *Bull. Pol. Aca. Scien. Chem.*, **40**, (1992), 267-276. Cited on pages: 119, 132.
- [92BAN/BLI] Bányai, I., Blixt, J., Glaser, J., Tóth, I., On the dissociation of hydrogen cyanide in aqueous solutions containing different ionic media. A combined potentiometric and carbon-13 NMR study, *Acta Chem. Scand.*, **46**, (1992), 138-141. Cited on page: 845.
- [92BIA/BUC] Biader Ceipidor, U., Bucci, R., Magrí, A. D., Using thermoanalytical data. Part 4. Processing DTA/DSC curves to calculate reaction enthalpy and kinetic parameters. An application to calcium oxalate, *Thermochim. Acta*, **199**, (1992), 85-103. Cited on pages: 165, 166.
- [92CAP] Capdevila, H., Données thermodynamiques sur l'oxydoréduction du plutonium en milieux acide et carbonate. Stabilité de Pu(V), Ph. D. Thesis, Université de Paris-Sud, Orsay, France, (1992), in French. Also published as CEA-R-5643 Commissariat à l'Energie Atomique, France, (1993). Cited on pages: 839, 840.
- [92DAN/ROB] Daniele, P. G., de Robertis, A., Sammartano, S., The effect of urea on the protonation of acetate, oxalate, malonate, citrate and sulfate in aqueous sodium, potassium, calcium chloride and tetraethylammonium iodide, *Ann. Chim. (Rome)*, **82**, (1992), 503-516. Cited on pages: 114, 308.
- [92FUG/KHO] Fuger, J., Khodakovsky, I. L., Sergeyeva, E. I., Medvedev, V. A., Navratil, J. D., *The chemical thermodynamics of actinide elements and compounds, Part 12. The actinide aqueous inorganic complexes*, International Atomic Energy Agency, Vienna, (1992), 224 pp. Cited on page: 4.

- [92GLA/HUL] Głąb, S., Hulanicki, A., Nowicka, U., Coulometric titration in the study of metal ion-ligand equilibria, *Talanta*, **39**, (1992), 1555-1559. Cited on pages: 312, 338, 343, 399, 401, 446, 449, 772..
- [92GRE/FUG] Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Muller, A. B., Nguyen-Trung, C., Wanner, H., *Chemical Thermodynamics of Uranium*, Wanner, H. and Forest, I., Nuclear Energy Agency, Organisation for Economic Co-operation and Development, Eds., vol. 1, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1992), 715 pp. Cited on pages: 4, 6, 24, 27, 36, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 102, 103, 369, 477, 481, 482, 487, 489, 597, 658, 797, 802, 820, 831, 832, 833, 839, 840, 844, 849, 860, 861.
- [92GRE/MOR] Greenfield, B. F., Moreton, A. D., Spindler, M. W., Williams, S. J., Woodwark, D. R., The effects of the degradation of organic materials in the near field of a radioactive waste repository, *Mater. Res. Soc. Symp. Proc.*, **257**, (1992), 299-306. Cited on pages: 511, 531.
- [92MIL/DOB] Miloserdova, N. A., Dobrynina, N. A., Nikolaeva, L. S., Mezhonova, E. A., Evseev, A. M., Mozhaev, A. P., A study by mathematical modelling and pH-potentiometry of complex formation by copper(II) with citric acid, *Russ. J. Inorg. Chem.*, **37**, (1992), 1418-1420. Cited on page: 308.
- [92MIL/GRA] Millan, A., Grases, F., Söhnel, O., Křivánková, I., Semi-batch precipitation of calcium oxalate monohydrate, *Cryst. Res. Technol.*, **27**, (1992), 31-39. Cited on page: 166.
- [92NGU/BEG] Nguyen-Trung, C., Begun, G. M., Palmer, D. A., Aqueous uranium complexes. 2. Raman spectroscopic study of the complex formation of the dioxouranium(VI) ion with a variety of inorganic and organic ligands, *Inorg. Chem.*, **31**, (1992), 5280-5287. Cited on pages: 230, 773.



- [92POG/KAP] Pogrebnaya, V. L., Kapustyanskaya, Z. V., Butina, E. A., Shakhrai, T. A., Kitaigorodskii, I. A., Volkov, O. N., Soklovskaya, T. M., Comparative estimation of protonation constants of citric, succinic, and hydroxyethylidenediphosphonic acids, *Izv. Vyss. Uchebn. Zaved. Pish. Tekhnol.*, (1992), 51-52, in Russian. Cited on page: 308.
- [92ROB/STE] de Robertis, A., de Stefano, C., Rigano, C., Sammartano, S., Salt effects on the protonation of oxalate in aqueous NaCl, KCl and tetraethylammonium iodide solution at  $5 \leq T \leq 50^\circ\text{C}$  and  $0 \leq I \leq 1 \text{ mol.dm}^{-3}$ , *Thermochim. Acta*, **202**, (1992), 133-149. Cited on pages: 115, 119, 120, 130, 132, 143, 144, 146, 157, 158, 670, 773, 774, 775, 783.
- [92SAP/COR] Sapiña, F., Coronado, E., Beltrán, D., Kuentzler, R., Thermal properties of the tetrahydrate series  $\text{M}^{\text{II}}\text{M}(\text{M}'\text{EDTA})_2 \cdot 4\text{H}_2\text{O}$   $\{\text{M}^{\text{II}}, \text{M}, \text{M}' = \text{Co(II)}, \text{Ni(II)}, \text{Zn(II)}\}$ , *J. Magn. Magn. Mater.*, **104-107**, (1992), 837-838. Cited on page: 460.
- [92SEI/MUE] Seifert, S., Muenze, R., Leibnitz, P., Reck, G., Stach, J., Preparation, characterization and crystal structure of a mixed ligand complex of technetium with DPPE and oxalic acid: oxalato-bis(1,2-bis(diphenylphosphino)ethane) technetium(II), *Inorg. Chim. Acta*, **193**, (1992), 167-172. Cited on page: 201.
- [92SHO/OEL] Shock, E. L., Oelkers, E. H., Johnson, J. W., Sverjensky, D. A., Helgeson, H. C., Calculation of the thermodynamic properties of aqueous species at high pressures and temperatures. Effective electrostatic radii, dissociation constants and standard partial molal properties to  $1000^\circ\text{C}$  and 5 kbar, *J. Chem. Soc. Faraday Trans.*, **88**, (1992), 803-826. Cited on page: 827.
- [92SIL] Silva, R. J., Mechanisms for the retardation of uranium(VI) migration, *Sci. Basis Nucl. Waste Management XV*, vol. 257, pp. 323-330, Sombret, C. G., Ed., (1992). Cited on page: 805.
- [92TAN/NOM] Tanaka, M., Nomura, H., Kawaizumi, F., A simple method for the evaluation of enthalpy of proton dissociation in water, *Bull. Chem. Soc. Jpn.*, **65**, (1992), 410-414. Cited on page: 328.

- [92THA/KUM] Thakur, S., Kumar, A., Standard heats of formation of some uranyl(II) and thorium(IV) carboxylates, *Proc. Natl. Acad. Sci. India*, **A62**, (1992), 15-18. Cited on pages: 214, 215, 715, 775.
- [92TOC/INO] Tochiyama, O., Inoue, Y., Narita, S., Complex formation of Np(V) with various carboxylates, *Radiochim. Acta*, **58/59**, (1992), 129-136. Cited on pages: 255, 256, 257, 742, 749, 776, 777, 791.
- [92TOC/INO3] Tochiyama, O., Inoue, Y., Narita, S., Study of the complexes of Np(V) with some organic ligands by solvent extraction, *Proceeding of the International Solvent Extraction Conference, Kyoto, 1990, Part A-B*, pp. 669-674, Elsevier Science Publisher B.V., (1992). Cited on page: 375, 777.
- [92TRI/TRI] Tripathi, S., Tripathi, S. R., Yadava, K. L., New electrophoretic study of mixed ligand complexes: oxalato and oxalato-NTA complexes of Cu(II), Ni(II) and Co(II), *J. Electrochem. Soc. India*, **41**, (1992), 231-234. Cited on pages: 114, 195, 196, 777.
- [92TUR/SAN] Turner, D. R., dos Santos, M. M. C., Coutinho, P., Gonçalves, M. L., Knox, S., Rapid pK measurements for multibasic weak acids by gradient flow injection titration, *Anal. Chim. Acta*, **258**, (1992), 259-267. Cited on page: 398.
- [92VEL/SOH] Velich, V., Söhnle, O., Costa-Bauzá, A., Kroupa, M., An isoperibolic reaction twin calorimeter for investigating precipitation, *Chem. Res. Technol.*, **27**, (1992), 1133-1139. Cited on pages: 174, 175.
- [93APE] Apelblat, A., Solubilities of organic salts of magnesium, calcium, and iron in water, *J. Chem. Thermodyn.*, **25**, (1993), 1443-1445. Cited on pages: 301, 350, 778.
- [93ATZ/FIL] Atzei, D., De Filippo, D., Rossi, A., Caminiti, R., X-ray photoelectron spectra of dinitrogen chelating ligands with some transition metals, *Spectrochim. Acta*, **49A**, (1993), 1779-1785. Cited on page: 460.

- [93AZA/HAS] Azab, H. A., Hassan, A., El-Nady, A. M., Azkal, R. S. A., Ternary complexes of nickel(II) with AMP, ADP and ATP as primary ligands and some biologically important polybasic oxygen acids as secondary ligands, *Monatsh. Chem.*, **124**, (1993), 267-276. Cited on pages: 194, 197, 355, 358, 778.
- [93BAL/BAR] Bald, A., Barczyńska, J., Enthalpies of solution of citric acid in water at 298.15 K. The effect of association processes on thermochemical properties of electrolyte solutions, *Thermochim. Acta*, **222**, (1993), 33-43. Cited on pages: 304, 306.
- [93BEC/GRO] Beckham, K. R., Grocott, S. C., A thermodynamically based model for oxalate solubility in Bayer liquor, in: *Light Metals, 1993; proceedings of the technical sessions presented by the TMS Aluminium Committee at the TMS annual meeting*, pp. 167-172, Minerals, Metals and Materials Society, 420 Commonwealth Dr., Warrendale, PA, USA 15086, (1993). Cited on pages: 158, 159.
- [93CHE/REI] Chen, M., Reid, R. S., Solution speciation in the aqueous Na(I)-EDTA and K(I)-EDTA systems, *Can. J. Chem.*, **71**, (1993), 763-768. Cited on pages: 401, 403, 438, 441.
- [93FON/SOL] Font-Bardia, M., Solans, X., Font-Altaba, M., Sodium ion complexes with ethylenediaminetetraacetic acid, *Acta Crystallogr.*, **C49**, (1993), 1452-1456. Cited on page: 437.
- [93GIF/VIT2] Giffaut, E., Vitorge, P., Capdevila, H., Corrections de température sur les coefficients d'activité calculés selon la TIS, Commissariat à l'Energie Atomique, Report CEA-N-2737, (1993), 29 pp., in French. Cited on page: 827.
- [93GLA/MAJ] Głąb, S., Maj-Zurawska, M., Łukomski, P., Hulanicki, A., Ion-selective electrode control based on coulometrically determined stability constants of biologically important calcium and magnesium complexes, *Anal. Chim. Acta*, **273**, (1993), 493-497. Cited on pages: 120, 130, 178, 179, 181, 187, 312, 314, 336, 338, 342, 344, 778, 779.
- [93GRE/HAR] Greenfield, B. F., Harrison, W. N., Robertson, G. P., Somers, P. J., Spindler, M. W., Mechanistic studies of the alkaline degradation of cellulose in cement, AEA Technology, Harwell, UK, Report NSS/R272, AEA-D&R-0219, (1993). Cited on pages: 511, 531.

- [93JAN] Janoš, P., Determination of stability constants of metal complexes from ion chromatographic measurements, *J. Chromatogr.*, **641**, (1993), 229-234. Cited on pages: 194, 196, 779.
- [93MAZ/DAN] Mazzocchin, G. A., Daniele, S., Corbetta, M., De Lorenzi, A., Titration of lanthanoids by pH-metric measurements. The use of unbuffered solutions, *Ann. Chim. (Rome)*, **83**, (1993), 1-17. Cited on page: 398.
- [93MIL/CVI] Mills, I., Cvitaš, T., Homann, K., Kallay, N., Kuchitsu, K., *Quantities, units and symbols in physical chemistry. (The green book)*, IUPAC, Blackwell Scientific Publications, Oxford, (1993), 176 pp. Cited on pages: 11, 20, 23.
- [93MIS/MIK] Mistryukov, V. E., Mikhailov, Y. N., Kanishcheva, A. S., Serezhkina, L. B., Serezhkin, V. N., The crystal structure of  $\text{Rb}_2\text{UO}_2(\text{SO}_4)\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ , *Russ. J. Inorg. Chem.*, **38**, (1993), 1413-1415. Cited on page: 214.
- [93MOR] Moreton, A. D., Thermodynamic modelling of the effect of hydroxycarboxylic acids on the solubility of plutonium at high pH, *Mater. Res. Soc. Symp. Proc.*, **294**, (1993), 753-758. Cited on pages: 511, 531, 532.
- [93ROM/GUZ] Román, P., Guzmán-Miralles, C., Luque, A., Structure of dipotassium trans-diaquabis(oxalato-O,O')nickelate(II)-water (1/4), *Acta Crystallogr.*, **C49**, (1993), 1336-1339. Cited on page: 190.
- [93SOH/COS] Söhnel, O., Costa-Bauzá, A., Velich, V., Calcium oxalate monohydrate precipitation investigation by thermometric method, *J. Cryst. Growth*, **126**, (1993), 493-498. Cited on pages: 174, 175, 176.
- [93SPI/RIB] Spirandeli Crespi, M., Ribeiro, C. A., Ionashiro, M., Preparation and thermal decomposition of solid state cobalt, nickel, copper and zinc chelates of ethylenediaminetetraacetic acid, *Thermochim. Acta*, **221**, (1993), 63-72. Cited on page: 460.
- [94CAP/VIT] Capdevila, H., Vitorge, P., Potentiels redox des couples  $\text{PuO}_2^{2+}/\text{PuO}_2^+$  et  $\text{Pu}^{4+}/\text{Pu}^{3+}$  à force ionique et température variables. Entropie et capacité calorifique, Commissariat à l'Energie Atomique, Report CEA-N-2762, (1994), 73 pp., in French. Cited on pages: 839, 840.

- [94ERT/MOH] Erten, H. N., Mohammed, A. K., Choppin, G. R., Variation of stability constants of thorium and uranium oxalate complexes with ionic strength, *Radiochim. Acta*, **66/67**, (1994), 123-128. Cited on pages: 115, 231, 232, 233, 234, 235, 236, 237, 239, 670, 779, 780, 807, 808.
- [94GIF] Giffaut, E., Influence des ions chlorure sur la chimie des actinides, Ph. D. Thesis, Université de Paris-Sud, Orsay, France, (1994), 259 pp., in French. Cited on page: 839.
- [94GRE/HUR] Greenfield, B. F., Hurdus, M. H., Pilkington, N. J., Spindler, M. W., Williams, S. J., The degradation of cellulose in the near field of a radioactive waste repository, *Mater. Res. Soc. Symp. Proc.*, **333**, (1994), 705-710. Cited on pages: 511, 531.
- [94GRE/LIN] Greenfield, B. F., Linklater, C. M., Moreton, A. D., Spindler, M. W., Williams, S. J., The effects of organic degradation products on actinide disposal, in: *Actinide Processing: Methods and Materials*, pp. 289-303, Mishra, B., Ed., Minerals, Metals and Materials Society, Warrendale, Pa., (1994). Cited on pages: 511, 531, 532.
- [94HAS/KHE] Hasilkar, S. P., Khedekar, N. B., Chander, K., Jadhav, A. V., Jain, H. C., Studies on the solubility of Pu(III) oxalate, *J. Radioanal. Nucl. Chem.*, **185**, (1994), 119-125, errata in [95HAS/KHE]. Cited on page: 264.
- [94KIS/SOV] Kiss, T., Sóvágó, I., Martin, R. B., Pursiainen, J., Ternary complex formation between Al(III)-adenosine-5'-phosphates and carboxylic acid derivatives, *J. Inorg. Biochem.*, **55**, (1994), 53-65. Cited on pages: 120, 132.
- [94KUM/CHA] Kumar, K., Chang, C. A., Francesconi, L. C., Dischino, D. D., Malley, M. F., Gougoutas, J. Z., Tweedle, M. F., Synthesis, stability, and structure of gadolinium(III) and yttrium(III) macrocyclic poly(amino carboxylates), *Inorg. Chem.*, **33**, (1994), 3567-3575. Cited on pages: 399, 401, 403, 780, 781.
- [94LEH/LUG] Lehmann, A., Luger, P., Lehmann, C. W., Ibberson, R. M., Oxalic acid dihydrate - an accurate low-temperature structural study using high-resolution neutron powder diffraction, *Acta Crystallogr.*, **B50**, (1994), 344-348. Cited on page: 111.

- [94MUL/HAE] Müller, M., Haeberli, A., pH-dependent formation of ethylenediaminetetraacetic acid supramolecular aggregates, *FEBS Lett.*, **340**, (1994), 17-21. Cited on page: 397.
- [94NAG] Nagar, R., Relative stabilisation and relative astatisticality of stability parameters of some lanthanide mixed ligand complexes, *J. Electrochem. Soc. India*, **43**, (1994), 41-46. Cited on page: 398.
- [94RED/SHI] Reddy, C. V. R., Shivaraj, Reddy, M. G. R., Equilibrium studies on binary and ternary complexes of transition metal ions with 3-methyl-1,2-cyclopentanedione and other ligands in solution, *J. Indian Chem. Soc.*, **71**, (1994), 59-63. Cited on pages: 115, 194, 196, 781.
- [94SAR/SIV] Saravanan, N., Sivasankar, B. N., Govindarajan, S., Reaction of dihydrazinium ethylenediaminetetraacetate with nitrates of Co(II), Ni(II), Cu(II) and Zn(II), *Synth. React. Inorg. Met.-Org. Chem.*, **24**, (1994), 703-713. Cited on page: 460.
- [94TOC/SIR] Tochiyama, O., Siregar, C., Inoue, Y., Complex formation of Np(V) with nitrogen-containing ligands, *Radiochim. Acta*, **66/67**, (1994), 103-108. Cited on pages: 492, 494, 781.
- [94ZHI/MAT2] Zhiganov, A. N., Matyukha, V. A., Saltan, N. P., Size and shape of  $\text{Np}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  crystals as a function of preparation conditions, *Radiochemistry (Moscow)*, **36**, (1994), 252-256. Cited on page: 246.
- [94ZHI/MAT3] Zhiganov, A. N., Matyukha, V. A., Saltan, N. P., Size and shape of  $\text{Pu}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$  crystals as a function of preparation conditions, *Radiochemistry (Moscow)*, **36**, (1994), 240-245. Cited on page: 263.
- [94ZHI/MAT4] Zhiganov, A. N., Matyukha, V. A., Saltan, N. P., Size and shape of  $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  crystals as a function of preparation conditions, *Radiochemistry (Moscow)*, **36**, (1994), 246-251. Cited on page: 263.
- [95APE/DOV] Apelblat, A., Dov, M., Wisniak, J., Zabicky, J., The vapour pressure of water over saturated aqueous solutions of malic, tartaric, and citric acids, at temperatures from 288 to 323 K, *J. Chem. Thermodyn.*, **27**, (1995), 35-41. Cited on page: 305.

- [95APE/DOV2] Apelblat, A., Dov, M., Wisniak, J., Zabicky, J., Osmotic and activity coefficients of  $\text{HO}_2\text{CCH}_2\text{C}(\text{OH})(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$  (citric acid) in concentrated aqueous solutions at temperatures from 298.15 K to 318.15 K, *J. Chem. Thermodyn.*, **27**, (1995), 347-353. Cited on pages: 305, 815.
- [95BOR/COR] Borrás-Almenar, J. J., Coronado, E., Curely, J., Georges, R., Exchange alternation and single-ion anisotropy in the antiferromagnetic Heisenberg Chain  $S = 1$ . Magnetic and thermal properties of the compound  $\text{Ni}_2(\text{EDTA}) \cdot 6\text{H}_2\text{O}$ , *Inorg. Chem.*, **34**, (1995), 2699-2704. Cited on page: 460.
- [95CAP/VIT] Capdevila, H., Vitorge, P., Redox potentials of  $\text{PuO}_2^{2+} / \text{PuO}_2^+$  and  $\text{Pu}^{4+} / \text{Pu}^{3+}$  at different ionic strengths and temperatures. Entropy and heat capacity, *Radiochim. Acta*, **68**, (1995), 51-62. Cited on pages: 839, 840.
- [95CHI/DOM] China, E., Domínguez, S., Mederos, A., Brito, F., Arrieta, J. M., Sánchez, A., Germain, G., Nitrilotripropionic acid (NTP) and other polyamino carboxylic acids as sequestering agents for beryllium(II). X-ray crystal structure of sodium (nitrilotripropionato)beryllate(II) trihydrate,  $\text{Na}[\text{Be}(\text{NTP})] \cdot 3\text{H}_2\text{O}$ , *Inorg. Chem.*, **34**, (1995), 1579-1587. Cited on pages: 401, 403.
- [95GRE/HOL] Greenfield, B. F., Holtom, G. J., Hurdus, M. H., O'Kelly, N., Pilkington, N. J., Rosevear, A., Spindler, M. W., Williams, S. J., The identification and degradation of isosaccharinic acid, a cellulose degradation product, *Mater. Res. Soc. Symp. Proc.*, **353**, (1995), 1151-1158. Cited on pages: 511, 531.
- [95GRE/PUI] Grenthe, I., Puigdomènech, I., Rand, M. H., Sandino, M. C. A., *Corrections to the Uranium NEA-TDB review, Appendix D, in: Chemical Thermodynamics of Americium (authored by Silva, R. J., Bidoglio, G., Rand, M. H. and Robouch, P. B., Wanner, H., Puigdomènech, I.)*, Nuclear Energy Agency, Organisation for Economic Co-operation and Development, Ed., pp. 347-374, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1995). Cited on pages: 805, 845.
- [95HAS/KHE] Haskar, S. P., Khedekar N. B., Chander, K., Jadhav, A. V., Jain, H. C., Errata to the paper: Studies on the solubility of  $\text{Pu}(\text{III})$  oxalate, *J. Radioanal. Nucl. Chem.*, **191**, (1995), 427. Cited on page: 264.

- [95ISU/TAR] Isupov, V. P., Tarasov, K. A., Chupakhina, L. E., Mitrofanova, R. P., Skvortsova, L. I., Boldyrev, V. V., Synthesis and thermal decomposition of the aluminum hydroxide intercalation compounds  $\text{Li}_2\text{M}(\text{EDTA}) \cdot 4\text{Al}(\text{OH})_3 \cdot 4\text{H}_2\text{O}$  ( $\text{M} = \text{Co}, \text{Ni}, \text{and Cu}$ ), *Russ. J. Inorg. Chem.*, **40**, (1995), 20-24. Cited on page: 460.
- [95KIS/BUG] Kiss, T., Buglyó, P., Sanna, D., Micera, G., Decock, P., Dewaele, D., Oxovanadium(IV) complexes of citric and tartaric acids in aqueous solution, *Inorg. Chim. Acta*, **239**, (1995), 145-153. Cited on page: 312.
- [95LIS/CHO] Lis, S., Choppin, G. R., Complexation study of uranyl ion with several organic ligands in aqueous solutions of high ionic strength, in: *Current trends in coordination chemistry*, pp. 185-190, Ondrejovič, G. and Sirota, A., Eds., Slovak Technical University Press, Bratislava, (1995). Cited on pages: 308, 399, 781, 784.
- [95LU/MOT] Lu, Q., Motekaitis, R. J., Reibenspies, J. J., Martell, A. E., Molecular recognition by the protonated hexaaza macrocyclic ligand 3,6,9,16,19,22-hexaaza-27,28-dioxatricyclo[22.2.1.1]octacosal(26),11,13,24-tetraene, *Inorg. Chem.*, **34**, (1995), 4958-4964. Cited on pages: 120, 132, 783.
- [95MIR/SAD] Mironov, I. V., Sadofeev, I. G., Constants of equilibria involving dicarboxylic acids: the effect of the ionic composition of the medium, *Russ. J. Phys. Chem.*, **69**, (1995), 1102-1108. Cited on pages: 120, 121, 129, 130, 670, 781.
- [95MIS/SER] Mistryukov, V. E., Sergeev, A. V., Mikhailov, Y. N., Shchelokov, R. N., Chuklanova, E. B., Crystal structure of guanidinium carbonato(ethylenediaminetetraacetato)zirconate  $(\text{CN}_3\text{H}_6)[\text{Zr}(\text{edta})\text{CO}_3] \cdot 3\text{H}_2\text{O}$ , *Russ. J. Inorg. Chem.*, **40**, (1995), 1570-1571. Cited on pages: 393, 472.
- [95PAL/NGU2] Palmer, D. A., Nguyen-Trung, C., A potentiometric study of the hydrolysis of ethylenediaminetetraacetic acid to 150°C, in: *Physical chemistry of aqueous systems: meeting the needs of industry*, pp. 809-815, White, Jr., H. J., Sengers, J. V., Neumann, D. B. and Bellows, J. C., Eds., Begell House, New York, N. Y., USA, (1995). Cited on pages: 401, 430, 432, 434.



- [95PAP/ZIO] Papanastasiou, G., Ziogas, I., Simultaneous determination of equivalence volumes and acid dissociation constants from potentiometric titration data, *Talanta*, **42**, (1995), 827-836. Cited on page: 308.
- [95PII/LAJ] Piispanen, J., Lajunen, L. H. J., Complex formation equilibria of some aliphatic  $\alpha$ -hydroxycarboxylic acids. 1. The determination of protonation constants and the study of calcium(II) and magnesium(II) complexes, *Acta Chem. Scand.*, **49**, (1995), 235-240. Cited on pages: 312, 336, 338, 339, 342, 343, 344, 782.
- [95RAK/SKU] Rak, J., Skurski, P., Gutowski, M., Błażejowski, J., Thermodynamics of the thermal decomposition of calcium oxalate monohydrate examined theoretically, *J. Therm. Anal.*, **43**, (1995), 239-246. Cited on page: 165.
- [95ROB/GIA] de Robertis, A., di Giacomo, P., Foti, C., Ion-selective electrode measurements for the determination of formation constants of alkali and alkaline earth metals with low-molecular-weight ligands, *Anal. Chim. Acta*, **300**, (1995), 45-51. Cited on pages: 332, 334.
- [95ROB/GIA2] de Robertis, A., Gianguzza, A., Sammartano, S., Solubility of some calcium-carboxylic ligand complexes in aqueous solution, *Talanta*, **42**, (1995), 1651-1662. Cited on pages: 301, 350, 351, 782.
- [95SIL/BID] Silva, R. J., Bidoglio, G., Rand, M. H., Robouch, P., Wanner, H., Puigdomènech, I., *Chemical Thermodynamics of Americium*, Nuclear Energy Agency, Organisation for Economic Co-operation and Development, Ed., vol. 2, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1995), 374 pp. Cited on pages: 4, 58, 59, 69, 101, 383, 504, 801, 839, 840, 844, 849.
- [95STR/GRI] Strom, C. S., Grimbergen, R. F. P., Hiralal, I. D. K., Koenders, B. G., Bennema, P., Growth layers. II. Comparison of theoretical and experimental morphology of sodium oxalate, *J. Cryst. Growth*, **149**, (1995), 107-112. Cited on pages: 152, 153.

- [95SUN/MOT] Sun, Y., Motekaitis, R. J., Martell, A. E., Welch, M. J., Stabilities of some trivalent and divalent metal ion complexes of N,N'-bis(2-mercaptoethyl)ethylenediamine-N,N'-diacetic acid, an effective ligand for indium(III), *J. Coord. Chem.*, **36**, (1995), 235-246. Cited on page: 398.
- [96AIZ/NAT] Aizawa, S.-I., Natsume, T., Hatano, K., Funahashi, S., Complexation equilibria and structures of dimethyltin(IV) complexes with N-methyliminodiacetate, pyridine-2,6-dicarboxylate, ethylenediamine-N,N'-diacetate and ethylenediamine-N,N,N',N'-tetraacetate, *Inorg. Chim. Acta*, **248**, (1996), 215-224. Cited on pages: 401, 403.
- [96ARA/ARC] Aragoni, M. C., Arca, M., Crisponi, G., Cristiani, F., Isaia, F., Nurchi, V. M., Characterization of the ionization and spectral properties of mercapto-carboxylic acids. Correlation with substituents and structural features, *Talanta*, **43**, (1996), 1357-1366. Cited on pages: 115, 783.
- [96BES/KRO] Bessonov, A. A., Krot, N. N., Budantseva, N. A., Afonas'eva, T. V., Electronic absorption spectra of some plutonium(VI) oxalates, *Radiochemistry (Moscow)*, **38**, (1996), 210-212. Cited on pages: 263, 283.
- [96BOR/LIS] Borkowski, M., Lis, S., Choppin, G. R., Complexation study of  $\text{NpO}_2^+$  and  $\text{UO}_2^{2+}$  ions with several organic ligands in aqueous solutions of high ionic strength, *Radiochim. Acta*, **74**, (1996), 117-121. Cited on pages: 115, 231, 232, 236, 237, 239, 255, 256, 308, 364, 374, 399, 485, 486, 487, 492, 493, 494, 781, 783, 784, 785, 786, 800, 807, 808.
- [96CHO/CHE] Choppin, G. R., Chen, J.-F., Complexation of Am(III) by oxalate in  $\text{NaClO}_4$  media, *Radiochim. Acta*, **74**, (1996), 105-110. Cited on pages: 121, 129, 286, 287, 288, 670, 770, 779, 780, 786, 790, 807, 808.
- [96CHO/ERT] Choppin, G. R., Erten, H. N., Xia, Y.-X., Variation of stability constants of thorium citrate complexes with ionic strength, *Radiochim. Acta*, **74**, (1996), 123-127. Cited on pages: 312, 313, 314, 379, 380, 642, 783, 784, 787, 790, 807, 808.

- [96DAS/MOH] Dash, U. N., Mohanty, B. K., Ion association of homologous dicarboxylic acids in aqueous acetone solutions at different temperatures, *Indian J. Chem.*, **35A**, (1996), 983-988. Cited on page: 114.
- [96DEB/BAR] Deb, N., Baruah, S. D., Dass, N. N., Synthesis, characterization and the thermal decomposition of calcium(II)bis(oxalato)-calcium(II)dihydrate, *Thermochim. Acta*, **285**, (1996), 301-308. Cited on page: 177.
- [96DOM/HEA] Domalski, E. S., Hearing, E. D., Heat capacities and entropies of organic compounds in the condensed phase. Volume III., *J. Phys. Chem. Ref. Data*, **25**, (1996), 1-525. Cited on page: 108.
- [96GRI/CHA2] Grigor'ev, M. S., Charushnikova, I. A., Krot, N. N., Yanovskii, A. I., Struchkov, Y. T., Crystal structure of neptunyl oxalate hexahydrate  $(\text{NpO}_2)_2\text{C}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$ , *Russ. J. Inorg. Chem.*, **41**, (1996), 517-520. Cited on page: 248.
- [96KIR/MAU] Kirsch, T., Maurer, G., Distribution of oxalic acid between water and organic solutions of tri-n-octylamine, *Ind. Eng. Chem. Res.*, **35**, (1996), 1722-2735. Cited on page: 112.
- [96KIS/JEZ] Kiss, E. E., Jezowska-Bojczuk, M., Kiss, T., Complexes of aminophosphonates. Part 9. Copper(II) complexes of citric acid derivatives, *J. Coord. Chem.*, **40**, (1996), 157-166. Cited on page: 312.
- [96KOC/GAL] Kociba, K. J., Gallagher, P. K., A study of calcium oxalate monohydrate using dynamic differential scanning calorimetry and other thermoanalytical techniques, *Thermochim. Acta*, **282/283**, (1996), 277-296. Cited on page: 164.
- [96MIK/GOR2] Mikhailov, Y. N., Gorbunova, Y. E., Serezhkina, L. B., Losev, V. Y., Serezhkin, V. N., Crystal structure of  $(\text{NH}_4)_2\text{UO}_2(\text{SeO}_4)\text{C}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ , *Russ. J. Inorg. Chem.*, **41**, (1996), 1953-1957. Cited on pages: 189, 214.
- [96MIR/PAS] Mironov, V. E., Pashkov, G. L., Kiselev, V. P., Stupko, T. V., Thermochemical study of formation of citratocalcium(II) complexes in aqueous solutions, *Russ. J. Inorg. Chem.*, **41**, (1996), 268-269. Cited on pages: 338, 342, 349, 787.

- [96REY/TER] Rey, A., Terán, M., Kremer, C., Molina, S., Gambino, D., Kremer, E., León, A., Preparation of  $^{99m}\text{Tc}$ -thiourea complex as a precursor for Tc(III) labeled compounds, *J. Radioanal. Nucl. Chem.*, **214**, (1996), 499-508. Cited on page: 471.
- [96SAE/KHA] Saeeduddin, Khanzada, A. W. K., Mufti, A. T., Dissociation constant studies of citric acid at different temperatures and in different organic-water solvent systems, *J. Chem. Soc. Pak.*, **18**, (1996), 81-87. Cited on pages: 308, 323, 327.
- [96SCH/CON] Schwarz, J. A., Contescu, C., Popa, V. T., Contescu, A., Lin, Y., Determination of dissociation constants of weak acids by deconvolution of proton binding isotherms derived from potentiometric data, *J. Solution Chem.*, **25**, (1996), 877-894. Cited on page: 308.
- [96STU/MOR] Stumm, W., Morgan, J. J., *Aquatic Chemistry*, 3rd. Edition, John Wiley & Sons, New York, (1996). Cited on page: 515.
- [96SUN/AND] Sun, Y., Anderson, C. J., Pajean, T. S., Reichert, D. E., Hancock, R. D., Motekaitis, R. J., Martell, A. E., Welch, M. J., Indium(III) and gallium(III) complexes of bis(aminoethanethiol) ligands with different denticities: stabilities, molecular modeling, and in vivo behavior, *J. Med. Chem.*, **39**, (1996), 458-470. Cited on page: 398.
- [96XUE/TRA] Xue, Y., Traina, S. J., Hille, R., Stability of metal-organic complexes in acetone- and methanol-water mixtures, *Environ. Sci. Technol.*, **30**, (1996), 3177-3183. Cited on pages: 121, 132, 308, 313, 399, 788.
- [96YUC/HOK] Yuchi, A., Hokari, N., Terao, H., Wada, H., Complexes of hard metal ions with amine-N-polycarboxylates as fluoride receptors, *Bull. Chem. Soc. Jpn.*, **69**, (1996), 3173-3177. Cited on pages: 472, 474.

- [97ALL/BAN] Allard, B., Banwart, S. A., Bruno, J., Ephraim, J. H., Grauer, R., Grenthe, I., Hadermann, J., Hummel, W., Jakob, A., Karapiperis, T., Plyasunov, A. V., Puigdomènech, I., Rard, J. A., Saxena, S., Spahiu, K., *Modelling in Aquatic Chemistry*, Grenthe, I. and Puigdomènech, I., Eds., Nuclear Energy Agency, Organisation for Economic Co-operation and Development, Paris, France, (1997), 724 pp. Cited on pages: 24,245.
- [97BAG/GAR] Baggio, R., Garland, M. T., Perec, M., Preparation and X-ray crystal structure of the polymeric zirconium(IV) oxalate complex  $[K_2\{Zr(C_2O_4)_3\} \cdot H_2C_2O_4 \cdot H_2O]_n$ , *Inorg. Chem.*, **36**, (1997), 737-739. Cited on pages: 204, 788.
- [97BAG/GAR2] Baggio, R., Garland, M. T., Perec, M., A binuclear zirconium(IV) oxalate complex with a  $\mu$ -oxalate coordination mode. Crystal structure of  $K_6[\{Zr(C_2O_4)_3\}_2(\mu-C_2O_4)] \cdot 4H_2O$ , *Inorg. Chem.*, **36**, (1997), 3198-3200. Cited on pages: 204, 788.
- [97BAR/CEC] Barbaro, P., Cecconi, F., Ghilardi, C. A., Midollini, S., Orlandini, A., Alderighi, L., Peters, D., Vacca, A., Chinea, E., Mederos, A., Preparative, potentiometric and NMR studies of the interaction of beryllium(II) with oxalate and malonate. X-ray structure of  $K_3[Be_3(OH)_3(O_2C-CH_2-CO_2)_3] \cdot 6H_2O$ , *Inorg. Chim. Acta*, **262**, (1997), 187-194. Cited on pages: 121, 129.
- [97BEN/PAL] Bénézech, P., Palmer, D. A., Wesolowski, D. J., Dissociation quotients for citric acid in aqueous sodium chloride media to 150°C, *J. Solution Chem.*, **26**, (1997), 63-84. Cited on pages: 313, 314, 327, 328, 331, 754, 788, 789, 790.
- [97DAH/CHA2] Dahale, N. D., Chawla, K. L., Jayadevan, N. C., Venugopal, V., X-ray, thermal and infrared spectroscopic studies on lithium and sodium oxalate hydrates, *Thermochim. Acta*, **293**, (1997), 163-166. Cited on page: 213.
- [97DEL/FIG] Delgado, R., do Carmo Figueira, M., Quintino, S., Redox method for the determination of stability constants of some trivalent metal complexes, *Talanta*, **45**, (1997), 451-462. Cited on page: 398.

- [97DEL/QUI] Delgado, R., Quintino, S., Teixeira, M., Zhang, A., Metal complexes of a 12-membered tetraaza macrocycle containing pyridine and N-carboxymethyl groups, *J. Chem. Soc. Dalton Trans.*, (1997), 55-63. Cited on pages: 401, 403.
- [97FOT/GIA] Foti, C., Gianguzza, A., Sammartano, S., A comparison of equations for fitting protonation constants of carboxylic acids in aqueous tetramethylammonium chloride at various ionic strengths, *J. Solution Chem.*, **26**, (1997), 631-648. Cited on pages: 313, 314, 334.
- [97GRE/HUR] Greenfield, B. F., Hurdus, M. H., Spindler, M. W., Thomason, H. P., The effects of the products from the anaerobic degradation of cellulose on the solubility and sorption of radioelements in the near field, AEA Technology, Harwell, UK, Report NSS/R376, (1997). Cited on pages: 511, 527, 531.
- [97GRE/PLY] Grenthe, I., Plyasunov, A. V., On the use of semiempirical electrolyte theories for the modeling of solution chemical data, *Pure Appl. Chem.*, **69**, (1997), 951-958. Cited on page: 827.
- [97GRE/PLY2] Grenthe, I., Plyasunov, A. V., Spahiu, K., Estimations of medium effects on thermodynamic data, in: *Modelling in Aquatic Chemistry*, Grenthe, I. and Puigdomènech, I., Eds., pp. 325-426, Nuclear Energy Agency, Organisation for Economic Co-operation and Development, Paris, France, (1997). Cited on page: 99.
- [97GRI/CHA] Grigor'ev, M. S., Charushnikova, I. A., Krot, N. N., Yanovskii, A. I., Struchkov, Y. T., Crystal structure of neptunium(IV) oxalate hexahydrate  $\text{Np}(\text{C}_2\text{O}_4) \cdot 6\text{H}_2\text{O}$ , *Radiochemistry (Moscow)*, **39**, (1997), 420-423. Cited on page: 246.
- [97HAG] Hagberg, J., Metal complexing abilities of products obtained from alkaline degradation of cellulose: Complexation of isosaccharinic acid with copper, Linköping University, Sweden, Thesis, diploma work Number 970606, (1997). Cited on pages: 511, 515, 516, 517, 525, 526.
- [97KON/FAN] Könnecke, T., Fanghänel, T., Kim, J. I., Thermodynamics of trivalent actinides in concentrated electrolyte solutions. Modelling the chloride complexation of Cm(III), *Radiochim. Acta*, **76**, (1997), 131-135. Cited on pages: 102, 802, 840.

- [97KON/TRA] Königsberger, E., Tran-Ho, L.-C., Solubility of substances related to urolithiasis - experiments and computer modelling, *Curr. Top. Solution Chem.*, **2**, (1997), 183-202. Cited on pages: 164, 166.
- [97POK/CHO] Pokrovsky, O. S., Choppin, G. R., Neptunium(V) complexation by acetate, oxalate and citrate in NaClO<sub>4</sub> media at 25°C, *Radiochim. Acta*, **79**, (1997), 167-171. Cited on pages: 254, 255, 256, 257, 258, 259, 374, 375, 790, 791.
- [97PUI/RAR] Puigdomènech, I., Rard, J. A., Plyasunov, A. V., Grenthe, I., Temperature corrections to thermodynamic data and enthalpy calculations, in: *Modelling in Aquatic Chemistry*, Grenthe, I. and Puigdomènech, I., Eds., pp. 427-493, Nuclear Energy Agency, Organisation for Economic Co-operation and Development, Paris, France, (1997). Cited on pages: 36, 37, 99, 549, 551, 608.
- [97RIC] Richens, D. T., *The chemistry of aqua ions*, John Wiley and Sons, Chichester, (1997). Cited on page: 202.
- [97SOH/KRO] Söhnel, O., Kroupa, M., Franková, G., Velich, V., Calcium oxalate crystallization kinetics from calorimetric measurements, *Thermochim. Acta*, **306**, (1997), 7-12. Cited on pages: 174, 175, 176.
- [97VAZ/ATB] Vaz, J. L. L., Atbir, T., Albourine, A., Petit-Ramel, M., Binary and ternary interactions of mercury(II) with seven pyrimidines and ethylenediaminetetraacetic acid, *J. Chem. Res. (S)*, (1997), 281-281. Cited on page: 398.
- [97VAZ/ATB2] Vaz, J. L. L., Atbir, T., Albourine, A., Petit-Ramel, M., Interactions binaires et ternaires des ions mercuriques avec sept dérivés pyrimidiques et l'EDTA, *J. Chem. Res. (M)*, (1997), 1917-1928. Cited on page: 398.
- [98ALD/BIA] Alderighi, L., Bianchi, A., Mederos, A., Midollini, S., Rodriguez, A., Vacca, A., Thermodynamic and multinuclear NMR study of beryllium(II) hydrolysis and beryllium(II) complex formation with oxalate, malonate, and succinate anions in aqueous solution, *Eur. J. Inorg. Chem.*, (1998), 1209-1215. Cited on pages: 114, 143, 146, 670, 791.

- [98ALM/NOV] Al Mahamid, I., Novak, C. F., Becraft, K. A., Carpenter, S. A., Hakem, N., Solubility of Np(V) in K-Cl-CO<sub>3</sub> and Na-K-Cl-CO<sub>3</sub> solutions to high concentrations: measurements and thermodynamic model predictions, *Radiochim. Acta*, **81**, (1998), 93-101. Cited on page: 845.
- [98BUR/FAH] Burnett, M. G., Faharty, C., Hardacre, C., Mallon, J. M., Ormerod, R. M., Saunders, G. C., Adsorption of metal cations by hydrous aluminium(III) or iron(III) hydroxide precipitates: enhancement by EDTA and related chelate molecules, *Chem. Commun.*, (1998), 2525-2526. Cited on page: 725.
- [98CHA/KRO] Charushnikova, I. A., Krot, N. N., Katser, S. B., Electronic absorption spectra and structure of some neptunium(IV) oxalates, *Radiochemistry (Moscow)*, **40**, (1998), 558-564. Cited on page: 246.
- [98EVA/DZO] Evanko, C. R., Dzombak, D. A., Influence of structural features on sorption of NOM-analogue organic acids to goethite, *Environ. Sci. Technol.*, **32**, (1998), 2846-2855. Cited on page: 724.
- [98FER/MAN] Ferri, D., Manfredi, C., Salvatore, F., Trifuoggi, M., Vasca, E., Fina, E., On a reversible electrode for potentiometric determinations of oxalate, *Ann. Chim. (Rome)*, **88**, (1998), 111-120. Cited on pages: 121, 129.
- [98GON/KRE] González, R., Kremer, C., Chiozzzone, R., Torres, J., Rivero, M., León, A., Kremer, E., Preparation and chemical studies on Tc(III) complexes containing polyaminocarboxylic acids, *Radiochim. Acta*, **81**, (1998), 207-213. Cited on page: 471.
- [98KET/WES] Kettler, R. M., Wesolowski, D. J., Palmer, D. A., Dissociation constants of oxalic acid in aqueous sodium chloride and sodium trifluoromethanesulfonate media to 175°C, *J. Chem. Eng. Data*, **43**, (1998), 337-350. Cited on pages: 115, 121, 122, 123, 124, 125, 126, 127, 128, 130, 131, 132, 133, 136, 143, 146, 147, 149, 554, 558, 670, 770, 792, 793, 794.
- [98KHA/RAD] Khalil, M. M., Radalla, A. M., Binary and ternary complexes of inosine, *Talanta*, **46**, (1998), 53-61. Cited on pages: 115, 194, 195, 196, 795.



- [98KOC/VAS] Kochergina, L. A., Vasil'ev, V. P., Peculiarities of thermochemical investigations of acid-base equilibria in complexon solutions, *J. Therm. Anal.*, **54**, (1998), 317-322. Cited on pages: 427, 795.
- [98MAR/SHL] Martynenko, L. I., Shlyakhtin, O. A., Milovanov, S. V., Gorel'skii, S. I., Charkin, D. O., Synthesis of fine-particle barium zirconate using zirconium ethylenediaminetetraacetate, *Inorg. Mater.*, **34**, (1998), 487-490. Cited on page: 472.
- [98MAT/RAP] Matzapetakis, M., Raptopoulou, C. P., Tsohos, A., Papaefthymiou, V., Moo, N., Salifoglou, A., Synthesis, spectroscopic and structural characterization of the first mononuclear, water soluble iron-citrate complex,  $(\text{NH}_4)_5\text{Fe}(\text{C}_6\text{H}_4\text{O}_7)_2 \cdot 2\text{H}_2\text{O}$ , *J. Am. Chem. Soc.*, **120**, (1998), 13266-13267. Cited on pages: 298, 299.
- [98MOR/ALM] Morris, S., Almond, M. J., Cardin, C. J., Drew, M. G. B., Rice, D. A., Zubavichus, Y., The anions  $[(\text{ZrOH}(\text{CO}_3)_3)_2]^{6-}$  and  $[(\text{ZrOH}(\text{C}_2\text{O}_4)_3)_2]^{6-}$ : single crystal X-ray diffraction studies of the complexes guanidinium zirconium carbonate  $[(\text{C}(\text{NH}_2)_3)_3\text{ZrOH}(\text{CO}_3)_3 \cdot \text{H}_2\text{O}]_2$  and sodium zirconium oxalate  $\text{Na}_6(\text{ZrOH}(\text{C}_2\text{O}_4)_3)_2 \cdot 7\text{H}_2\text{O}$ , *Polyhedron*, **17**, (1998), 2301-2307. Cited on pages: 204, 795.
- [98MOT/CHA] Motellier, S., Charles, Y., Characterization of acid-base and complexation properties of cellulose degradation products using capillary electrophoresis, *Anal. Chim. Acta*, **375**, (1998), 243-254. Cited on pages: 515, 516, 517, 525, 526, 534, 535.
- [98MOT/RIC] Motellier, S., Richet, C., Merel, P., Analysis of cellulose degradation products by capillary electrophoresis, *J. Chromatogr., A*, **804**, (1998), 363-370. Cited on pages: 515, 516, 517.
- [98OBR/MIT] Obradović, M. V., Mitić, S. S., Sunarić, S. M., Conductometric and pH metric investigation of oxalic acid and  $\text{SeO}_3^{2-}$  ion complex, in: *Physical chemistry '98*, pp. 582-584, 4<sup>th</sup> International Conference on Fundamental and Applied Aspects of Physical Chemistry, September 23-25, 1998, Belgrade, Yugoslavia, (1998). Cited on pages: 190, 795, 796, 797.

- [98PLY/ZHA] Plyasunova, N. V., Zhang, Y., Muhammed, M., Critical evaluation of thermodynamics of complex formation of metal ions in solutions. IV. Hydrolysis and hydroxo-complexes of  $\text{Ni}^{2+}$  at 298.15 K, *Hydrometallurgy*, **48**, (1998), 43-63. Cited on pages: 356, 357.
- [98POK/BRO] Pokrovsky, O. S., Bronikowski, M. G., Moore, R. C., Choppin, G. R., Interaction of neptunyl(V) and uranyl(VI) with EDTA in NaCl media: experimental study and pitzer modeling, *Radiochim. Acta*, **80**, (1998), 23-29. Cited on pages: 484, 485, 486, 487, 488, 489, 492, 493, 494, 495, 496, 497, 670, 671, 746, 785, 797, 798, 799, 800.
- [98RAI/FEL] Rai, D., Felmy, A. R., Hess, N. J., Moore, D. A., Yui, M., A thermodynamic model for the solubility of  $\text{UO}_2(\text{am})$  in the aqueous  $\text{K}^+ - \text{Na}^+ - \text{HCO}_3^- - \text{CO}_3^{2-} - \text{OH}^- - \text{H}_2\text{O}$  system, *Radiochim. Acta*, **82**, (1998), 17-25. Cited on page: 845.
- [98RAI/RAO] Rai, D., Rao, L., Moore, D. A., The influence of isosaccharinic acid on the solubility of  $\text{Np}(\text{IV})$  hydrous oxide, *Radiochim. Acta*, **83**, (1998), 9-13. Cited on pages: 530, 531.
- [98RAI/RAO2] Rai, D., Rao, L., Xia, Y., Solubility of crystalline calcium isosaccharinate, *J. Solution Chem.*, **27**, (1998), 1109-1122. Cited on pages: 515, 517, 520, 521, 522, 523.
- [98REE/WYG] Reed, D. T., Wygmans, D. G., Aase, S. B., Banaszak, J. E., Reduction of  $\text{Np}(\text{VI})$  and  $\text{Pu}(\text{VI})$  by organic chelating agents, *Radiochim. Acta*, **82**, (1998), 109-114. Cited on pages: 261, 283, 498, 502, 572, 573, 589.
- [98SAL/BOO] Sal'nikov, Y. I., Boos, G. A., Bagmanova, A. G., Dissociation of ethylenediaminetetraacetic acid and stability of copper(II) ethylenediaminetetraacetates in aqueous solutions of ammonium nitrate, *Russ. J. Coord. Chem.*, **24**, (1998), 423-428. Cited on page: 399.
- [98SAL/BOO2] Sal'nikov, Y. I., Boos, G. A., Effect of background electrolyte on dissociation constants of EDTA and ethylenediamine conjugated acids, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, **41**, (1998), 6-9, in Russian. Cited on page: 399.

- [98STR/TRA] Streit, J., Tran-Ho, L.-C., Königsberger, E., Solubility of the three calcium oxalate hydrates in sodium chloride solutions and urine-like liquors, *Monatsh. Chem.*, **129**, (1998), 1225-1236. Cited on pages: 166, 168, 169, 171, 174, 175, 176, 689.
- [98SUN/MAR] Sun, Y., Martell, A. E., Motekaitis, R. J., Welch, M. J., Synthesis and stabilities of the Ga(III) and In(III) chelates of a new diaminodithiol bifunctional ligand, *Tetrahedron*, **54**, (1998), 4203-4210. Cited on pages: 401, 403.
- [99ARC] Archer, D. G., Thermodynamic properties of import to environmental processes and remediation. II. Previous thermodynamic property values for nickel and some of its compounds, *J. Phys. Chem. Ref. Data*, **28**, (1999), 1485-1507. Cited on page: 698.
- [99BRO/POK] Bronikowski, M. G., Pokrovsky, O. S., Borkowski, M., Choppin, G. R.,  $\text{UO}_2^{2+}$  and  $\text{NpO}_2^+$  complexation with citrate in brine solutions, in: *Actinide speciation in high ionic strength media*, Reed, D. T. and Clark, S. B. and Rao, L., Eds., pp. 177-185, Kluwer Academic/Plenum Publ., New York, USA, (1999). Cited on pages: 364, 368, 369, 374, 375, 785, 801, 809.
- [99CHE/CHO] Chen, J.-F., Choppin, G. R., Moore, R. C., Complexation and ion interactions in Am(III)/EDTA/NaCl ternary system, in: *Actinide speciation in high ionic strength media*, pp. 187-197, Reed, D. T., Clark, S. B. and Rao, L., Eds., Kluwer Academic/Plenum Publ., New York, USA, (1999). Cited on pages: 504, 505, 506, 676, 763, 801, 802, 803.
- [99CIA/IUL] Ciavatta, L., Iuliano, M., Porto, R., A potentiometric study of aluminium(III) hydroxo oxalates, *Ann. Chim. (Rome)*, **89**, (1999), 51-61. Cited on page: 114.
- [99GRI] Griko, Y. V., Energetics of  $\text{Ca}^{2+}$ -EDTA interactions: calorimetric study, *Biophys. Chem.*, **79**, (1999), 117-127. Cited on pages: 446, 449, 456, 457, 803.
- [99KAR/HAR] Karhu, J., Harju, L., Ivaska, A., Determination of the solubility products of nitrilotriacetic acid, ethylenediaminetetraacetic acid and diethylenetriaminepentaacetic acid, *Anal. Chim. Acta*, **380**, (1999), 105-111. Cited on page: 394.

- [99LOO/GLA] Van Loon, L. R., Glaus, M. A., Vercammen, K., Solubility products of calcium isosaccharinate and calcium gluconate, *Acta Chem. Scand.*, **53**, (1999), 235-240. Cited on pages: 520, 521, 522, 523, 524.
- [99MAJ/SAR] Majumdar, R., Sarkar, P., Ray, U., Mukhopadhyay, M. R., Secondary catalytic reactions during thermal decomposition of oxalates of zinc, nickel and iron(II), *Thermochim. Acta*, **335**, (1999), 43-53. Cited on page: 190.
- [99MIZ/BON] Mizera, J., Bond, A. H., Choppin, G. R., Moore, R. C., Dissociation constants of carboxylic acids at high ionic strengths, in: *Actinide speciation in high ionic strength media*, Reed, D. T., Clark, S. B. and Rao, L., Eds., pp. 113-124, Kluwer Academic/ Plenum Publ., New York, USA, (1999). Cited on pages: 128, 131, 314, 401, 403, 784, 803, 807, 808.
- [99PAV] Pavasars, I., Characterisation of organic substances in waste materials under alkaline conditions, Ph. D. Thesis, Linköping University, Sweden, (1999), Linköping Studies in Arts and Science 196. Cited on page: 511.
- [99RAR/RAN] Rard, J. A., Rand, M. H., Anderegg, G., Wanner, H., *Chemical Thermodynamics of Technetium*, Sandino, M. C. A. and Östhols, E., Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Eds., vol. 3, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (1999). Cited on pages: 4, 6, 36, 57, 58, 67, 201, 849.
- [99ROB/STE] de Robertis, A., de Stefano, C., Foti, C., Medium effects on the protonation of carboxylic acids at different temperatures, *J. Chem. Eng. Data*, **44**, (1999), 262-270. Cited on pages: 308, 314, 804.
- [99STE/GIA] De Stefano, C., Gianguzza, A., Piazzese, D., Sammartano, S., Speciation of low molecular weight carboxylic ligands in natural fluids: protonation constants and association with major components of seawater of oxydiacetic and citric acids, *Anal. Chim. Acta*, **398**, (1999), 103-110. Cited on page: 309.

- [99VER/GLA] Vercammen, K., Glaus, M. A., Van Loon, L. R., Complexation of calcium by  $\alpha$ -isosaccharinic acid under alkaline conditions, *Acta Chem. Scand.*, **53**, (1999), 241-246. Cited on pages: 520, 521, 522, 523, 524.
- [99VER/GLA2] Vercammen, K., Glaus, M. A., Van Loon, L. R., Evidence for the existence of complexes between Th(IV) and  $\alpha$ -isosaccharinic acid under alkaline condition, *Radiochim. Acta*, **84**, (1999), 221-224. Cited on page: 538.
- [99WAN] Wanner, H., TDB-6: Guidelines for the independent peer review of TDB reports, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Report, (1999), 8 pp. Cited on pages: 7, 8.
- [99WAN/OST] Wanner, H., Östhols, E., TDB-3: Guidelines for the assignment of uncertainties, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Report, (1999), 17 pp. Cited on pages: 7, 849.
- [2000ASK/CHA] Askarieh, M. M., Chambers, A. V., Daniel, F. B. D., FitzGerald, P. L., Holtom, G. J., Pilkington, N. J., Rees, J. H., The chemical and microbial degradation of cellulose in the near field of a repository for radioactive wastes, *Waste Manage. (Oxford)*, **20**, (2000), 93-106. Cited on page: 511.
- [2000BOR/CHO] Borkowski, M., Choppin, G. R., Moore, R. C., Free, S. J., Thermodynamic modeling of metal-ligand interactions in high ionic strength NaCl solutions: the  $\text{Co}^{2+}$ -citrate and  $\text{Ni}^{2+}$ -citrate systems, *Inorg. Chim. Acta*, **298**, (2000), 141-145. Cited on pages: 355, 359, 804.
- [2000BUG/KIS] Buglyó, P., Kiss, E., Fábián, I., Kiss, T., Sanna, D., Garribba, E., Micera, G., Speciation and NMR relaxation studies of VO(IV) complexes with several O-donor containing ligands: oxalate, malonate, maltolate and kojate, *Inorg. Chim. Acta*, **306**, (2000), 174-183. Cited on pages: 128, 132.
- [2000CIA/IUL] Ciavatta, L., Iuliano, M., Vitiello, A., Stability constants of chromium(III) oxalate complexes in 1m  $\text{NaClO}_4$  at 60°C, *Ann. Chim. (Rome)*, **90**, (2000), 169-179. Cited on pages: 115, 128.

- [2000FER/IUL] Ferri, D., Iuliano, M., Manfredi, C., Vasca, E., Caruso, T., Clemente, M., Fontanella, C., Dioxouranium(VI) oxalate complexes, *J. Chem. Soc. Dalton Trans.*, (2000), 3460-3466. Cited on pages: 128, 129, 130, 229, 231, 232, 233, 236, 237, 239, 240, 804.
- [2000GAM/WOO] Gammons, C. H., Wood, S. A., The aqueous geochemistry of REE. Part 8: Solubility of ytterbium oxalate and the stability of Yb(III)-oxalate complexes in water at 25°C to 80°C, *Chem. Geol.*, **166**, (2000), 103-124. Cited on page: 266.
- [2000GRE/WAN] Grenthe, I., Wanner, H., Östholts, E., TDB-2: Guidelines for the extrapolation to zero ionic strength, OECD Nuclear Energy Agency, Data Bank, Report , (2000), 34 pp. Cited on pages: 7, 819, 820, 826.
- [2000HER] Herstein, F. H., How precise are measurements of unit-cell dimensions from single crystals?, *Acta Crystallogr.*, **B56**, (2000), 547-557. Cited on page: 111.
- [2000LEN/CAB] Lenhart, J. J., Cabaniss, S. E., MacCarthy, P., Honeyman, B. D., Uranium(VI) complexation with citric, humic and fulvic acids, *Radiochim. Acta*, **88**, (2000), 345-353. Cited on pages: 364, 368, 805.
- [2000LVO] L'vov, B. V., Kinetics and mechanism of thermal decomposition of nickel, manganese, silver, mercury and lead oxalates, *Thermochim. Acta*, **364**, (2000), 99-109. Cited on page: 190.
- [2000MIK/GOR2] Mikhailov, Y. N., Gorbunova, Y. E., Shishkina, O. V., Serezhkina, L. B., Serezhkin, V. N., Crystal structure of  $\text{Cs}_2[\text{UO}_2(\text{C}_2\text{O}_4)(\text{SeO}_4)]$ , *Russ. J. Inorg. Chem.*, **45**, (2000), 1848-1851. Cited on pages: 189, 214.
- [2000OST/WAN] Östholts, E., Wanner, H., TDB-0: The NEA Thermochemical Data Base Project, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, (2000), 21 pp. Cited on page: 7.
- [2000PAL] Palladino, G., Migrazione di radionuclidi nell'ambiente: studio degli equilibri di formazione di complessi nel sistema  $\text{UO}_2^{2+}$ - $\text{H}_2\text{O}$ - $\text{C}_2\text{O}_4^{2-}$ , Ph. D. Thesis, Università degli studi di Salerno, (2000), Salerno, Italy, in Italian. Cited on pages: 242, 243, 805.

- [2000ROB/STE] de Robertis, A., de Stefano, C., Foti, C., Gianguzza, A., Piazzese, D., Sammartano, S., Protonation constants and association of polycarboxylic ligands with the major components of seawater, *J. Chem. Eng. Data*, **45**, (2000), 996-1000. Cited on page: 309.
- [2000VAS/CAR] Vasca, E., Caruso, T., Iuliano, M., Manfredi, C., Fontanella, C., Trifuoggi, M., Studies on metal oxalate complexes. I. Validation of the reversibility of the Hg, Hg<sub>2</sub>C<sub>2</sub>O<sub>4</sub>(s) electrochemical couple, *Ann. Chim. (Rome)*, **90**, (2000), 181-192. Cited on pages: 128, 130, 232, 233, 236, 237, 239, 240, 804, 806.
- [2000VER] Vercammen, K., Complexation of calcium, thorium and europium by  $\alpha$ -isosaccharinic acid under alkaline conditions, Ph. D. Thesis, Swiss Federal Institute of Technology Zürich, Switzerland, (2000), Diss. ETH No.13466. Cited on pages: 511, 520, 521, 522, 523, 524, 534, 535, 536, 538, 539, 540.
- [2000WAN/OST] Wanner, H., Östhols, E., TDB-1: Guidelines for the review procedure and data selection, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, (2000), 5 pp. Cited on page: 7.
- [2000YOS/OKA] Yoshimura, N., Okazaki, M., Nakagawa, N., Simultaneous estimation of the dissociation constant and concentration by a linear least-squares method with non-negative constraint, *Anal. Sci.*, **16**, (2000), 1331-1335. Cited on page: 308.
- [2001BER/BAU] Bernard, J. G., Bauer, E., Richards, M. P., Aterburn, J. B., Chamberlin, R. M., Catalytic reduction of pertechnetate (<sup>99</sup>TcO<sub>4</sub><sup>-</sup>) in simulated alkaline nuclear wastes, *Radiochim. Acta*, **89**, (2001), 59-61. Cited on page: 201.
- [2001BOR/MOO] Borkowski, M., Moore, R. C., Bronikowski, M. G., Chen, J.-F., Pokrovsky, O. S., Xia, Y.-X., Choppin, G. R., Thermodynamic modeling of actinide complexation with oxalate at high ionic strength, *J. Radioanal. Nucl. Chem.*, **248**, (2001), 467-471. Cited on pages: 232, 233, 236, 237, 239, 255, 256, 257, 258, 259, 286, 287, 288, 785, 786, 806, 807, 808.

- [2001CHO/BON] Choppin, G. R., Bond, A. H., Borkowski, M., Bronikowski, M. G., Chen, J.-F., Lis, S., Mizera, J., Pokrovsky, O. S., Wall, N. A., Xia, Y.-X., Moore, R. C., Waste isolation pilot plant actinide source term test program: solubility studies and development of modeling parameters, Sandia National Lab., Albuquerque, New Mexico and Livermore, California, Report SAND99-0943, (2001), 344 pp. Cited on pages: 178, 179, 182, 183, 184, 186, 255, 256, 257, 258, 259, 312, 313, 336, 342, 343, 381, 382, 383, 384, 401, 403, 445, 450, 452, 454, 712, 779, 783, 784, 803, 806, 807, 808, 809, 810.
- [2001CIA/TOM] Ciavatta, L., de Tommaso, G., Iuliano, M., The solubility of calcium citrate hydrate in sodium perchlorate solutions, *Anal. Lett.*, **34**, (2001), 1053-1062. Cited on pages: 301, 350, 351, 352, 810.
- [2001CIA/TOM2] Ciavatta, L., De Tommaso, G., Iuliano, M., A potentiometric study on oxalate and citrate complexes of tin(II), *Ann. Chim. (Rome)*, **91**, (2001), 285-293. Cited on pages: 128, 130, 314.
- [2001GUO/LIA] Guo, Y.-F., Liang, J.-F., Liu, B.-R., Song, C.-L., Liu, X.-Q., Jiao, R.-Z., Solubility of plutonium(IV) oxalate, *Journal of Nuclear and Radiochemistry (Beijing)*, **23**, (2001), 184-188, in Chinese. Cited on pages: 269, 811.
- [2001HAL/NAV] Hala, J., Navratil, J. D., IUPAC-NIST solubility data series. 74 actinide carbon compounds, *J. Phys. Chem. Ref. Data*, **30**, (2001), 531-698. From a citation in this Bibliography.
- [2001JAN/HAR] Jano, I., Hardcastle, J., Jano, L. A., Bates, K. R., McCreary, H. E., General equation for determining the dissociation constants of polyprotic acids and bases from additive properties. Part IV. Application to potentiometric titration, *Anal. Chim. Acta*, **428**, (2001), 309-321. Cited on page: 308.
- [2001LAK/BAN] Lakatos, A., Bányai, I., Decock, P., Kiss, T., Time-dependent solution speciation of the Al<sup>(III)</sup>-citrate system: Potentiometric and NMR studies, *Eur. J. Inorg. Chem.*, (2001), 461-469. Cited on page: 314.



- [2001LEM/FUG] Lemire, R. J., Fuger, J., Nitsche, H., Potter, P. E., Rand, M. H., Rydberg, J., Spahiu, K., Sullivan, J. C., Ullman, W. J., Vitorge, P., Wanner, H., *Chemical Thermodynamics of Neptunium and Plutonium*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 4, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2001). Cited on pages: 4, 36, 57, 58, 59, 64, 69, 71, 72, 258, 259, 261, 369, 376, 481, 492, 494, 561, 586, 587, 589, 651, 685, 686, 741, 743, 744, 799, 839, 840, 845, 849.
- [2001MAF/MEI] Maffia, M. C., Meirelles, A. J. A., Water activity and pH in aqueous polycarboxylic acid systems, *J. Chem. Eng. Data*, **46**, (2001), 582-587. Cited on pages: 112, 114.
- [2001MIA] Mianowski, A., Analysis of the thermokinetics under dynamic conditions by relative rate of thermal decomposition, *J. Therm. Anal. Calorim.*, **63**, (2001), 765-776. Cited on page: 165.
- [2001NEC/KIM] Neck, V., Kim, J. I., Solubility and hydrolysis of tetravalent actinides, *Radiochim. Acta*, **89**, (2001), 1-16. Cited on pages: 561, 587, 628, 744.
- [2001PAT/WOO] Patterson, B. A., Wooley, E. M., Thermodynamics of proton dissociations from aqueous citric acid: apparent molar volumes and apparent molar heat capacities of citric acid and its sodium salts at the pressure 0.35 MPa and at temperatures from 278.15 K to 393.15 K, *J. Chem. Thermodyn.*, **33**, (2001), 1735-1764. Cited on page: 331.
- [2001SAR] Sari, H., Determination of stability constants of citrate complexes with divalent metal ions ( $M^{2+} = \text{Mg, Ca, Ni, Cu and Zn}$ ) in aqueous solutions, *Energy Educ. Sci. Technol.*, **6**, (2001), 85-103. Cited on pages: 308, 336, 337, 338, 339, 340, 342, 353, 354, 355, 356, 358, 811, 812.
- [2001STE/FOT] De Stefano, C., Foti, C., Giuffrè, O., Sammartano, S., Dependence on ionic strength of protonation enthalpies of polycarboxylate anions in NaCl aqueous solution, *J. Chem. Eng. Data*, **46**, (2001), 1417-1424. Cited on page: 327.

- [2001TAN/FUR] Taniguchi, M., Furusawa, M., Kiba, Y., Enthalpies of dehydrations of oxalate, sulfate and chloride hydrates by transpiration method and DSC, *J. Therm. Anal. Calorim.*, **64**, (2001), 177-183. Cited on pages: 159, 166.
- [2001VER/GLA] Vercammen, K., Glaus, M. A., Van Loon, L. R., Complexation of Th(IV) and Eu(III) by  $\alpha$ -isosaccharinic acid under alkaline conditions, *Radiochim. Acta*, **89**, (2001), 393-401. Cited on pages: 534, 535, 536, 538, 539, 540.
- [2002CUR/TEN] Curini, R., Tentolini, U., Materazzi, S., Vasca, E., Caruso, T., Fontanella, C., Palladino, G., Modeling of radionuclides in natural fluids: synthesis and characterization of the  $\text{Na}_4(\text{UO}_2)_2(\text{OH})_4(\text{C}_2\text{O}_4)_2$  complex, *Thermochim. Acta*, **387**, (2002), 17-21. Cited on pages: 805, 806.
- [2002HAG/DUK] Hagberg, J., Düker, A., Karlsson, S., Determination of dissociation constants of low molecular weight organic acids by capillary zone electrophoresis and indirect UV detection, *Chromatographia*, **56**, (2002), 641-644. Cited on pages: 515, 517.
- [2002HAV/SOT] Havel, J., Soto-Guerrero, J., Lubal, P., Spectrophotometric study of uranyl-oxalate complexation in solution, *Polyhedron*, **21**, (2002), 1411-1420. Cited on pages: 128, 130, 229, 232, 233, 237, 239, 240, 241, 242, 569, 598, 663, 812, 814.
- [2002HUM/BER] Hummel, W., Berner, U., Curti, E., Pearson, F. J., Thoenen, T., Nagra/PSI chemical thermodynamic data base 01/01, Nagra Report NTB 02-16 and Universal Publishers/uPublish.com, Parkland, Florida, USA, (2002). Cited on pages: 536.
- [2002LOW/OGD] Lowe, J., Ogden, M., McKinnon, A., Parkinson G., Crystal growth of sodium oxalate from aqueous solution, *J. Cryst. Growth*, **237-239**, (2002), 408-413. Cited on pages: 152, 153.
- [2002MAK/MER] El Makhfouk, M., El Meray, M., Castetbon, A., Astruc, M., Effect of citrate, oxalate and pyrophosphate ligands on the electrochemical reduction of the uranyl ion in perchloric acid medium, *Bull. Electrochem.*, **18**, (2002), 63-70. Cited on pages: 228, 229, 813.

- [2002NOW] Nowack, B., Environmental chemistry of aminopolycarboxylate chelating agents, *Environ. Sci. Technol.*, **36**, (2002), 4009-4016. Cited on page: 725.
- [2002PET/POW] Pettit, L. D., Powell, K. J., *IUPAC stability constants database*, Academic Software, Timble, Otley, Yorkshire, U. K., (2002). Cited on page: 114.
- [2002RAO/JIA] Rao, L., Jiang, J., Zanonato, P., di Bernardo, P., Bismondo, A., Garnov, A. Y., Complexation of uranium(VI) with malonate at variable temperatures, *Radiochim. Acta*, **90**, (2002), 581-588. Cited on pages: 236, 609.
- [2002SHA] Sharma, K. R., Recycle of uranium in fission products, *AIChE Symp. Ser.*, (2002), 710-716, Spring National Meeting, New Orleans, LA. Cited on page: 201.
- [2002SOT] Soto-Guerrero, J. A., Uranyl complexation with some dicarboxylic acids and uranium determination with MALDI-TOF mass spectrometry, Ph. D. Thesis, Masaryk University, Brno, (2002). Cited on page: 814.
- [2002SZA/FIS] Szabó, Z., Fischer, A., Redetermination of dipotassium diuranyl tris(oxalate) tetrahydrate, *Acta Crystallogr.*, **E58**, (2002), i56-i58. Cited on page: 213.
- [2002TIT/WIE] Tits, J., Wieland, E., Bradbury, M. H., Eckert, P., Schaible, A., The uptake of Eu(III) and Th(IV) by calcite under hyperalkaline conditions, Paul Scherrer Institut, PSI Report No. 02-03, (2002). Cited on pages: 511, 534, 535, 536, 538, 539, 540.
- [2003BAE/BRA] Baeyens, B., Bradbury, M. H., Hummel, W., Determination of aqueous nickel-carbonate and nickel-oxalate complexation constants, *J. Solution Chem.*, **32**, (2003), 319-339. Cited on pages: 194, 197.
- [2003BOR/CHO] Borkowski, M., Choppin, G. R., Moore, R. C., Thermodynamic modeling of metal-ligand interactions in high ionic strength NaCl solutions: the  $\text{Ni}^{2+}$ -oxalate system, *Radiochim. Acta*, **91**, (2003), 169-172. Cited on pages: 194, 195, 196, 197.

- [2003CHO/RAI] Cho, H., Rai, D., Hess, N. J., Xia, Y., Rao, L., Acidity and structure of isosaccharinate in aqueous solution: a nuclear magnetic resonance study, *J. Solution Chem.*, **32**, (2003), 691-702. Cited on pages: 514, 515, 517, 519, 522, 524, 531.
- [2003EKB/EKB] Ekberg, S., Ekberg, C., Albinsson, Y., Characterization of  $\alpha$ -isosaccharinic acid:  $pK_a$ -determination, *Mater. Res. Soc. Symp. Proc.*, **757**, (2003), 503-508. Cited on pages: 514, 515, 517, 518, 519.
- [2003FRO/WEI] Frost, R. L., Weier, M. L., Thermal treatment of weddellite - a Raman and infrared emission spectroscopic study, *Thermochim. Acta*, **406**, (2003), 221-232. Cited on page: 165.
- [2003GUI/FAN] Guillaumont, R., Fanghänel, T., Fuger, J., Grenthe, I., Neck, V., Palmer, D. A., Rand, M. H., *Update on the chemical thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 5, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2003). Cited on pages: 4, 6, 57, 58, 59, 62, 68, 69, 70, 71, 101, 102, 218, 222, 224, 235, 240, 244, 266, 383, 532, 536, 596, 628, 656, 675, 706, 741, 777, 785, 786, 801, 802, 839, 845, 849.
- [2003RAI/HES] Rai, D., Hess, N. J., Xia, Y., Rao, L., Cho, H. M., Moore, R. C., Van Loon, L. R., Comprehensive thermodynamic model applicable to highly acidic to basic conditions for isosaccharinate reactions with Ca(II) and Np(IV), *J. Solution Chem.*, **32**, (2003), 665-689. Cited on pages: 514, 517, 520, 521, 522, 523, 524, 530, 531.
- [2003SMI/MAR] Smith, R. M., Martell, A. E., Motekaitis, R. J., *NIST Standard Reference Database 46: NIST Critically selected stability constants of metals complexes database, Version 7.0*, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA, (2003). Cited on page: 114.
- [2003VAL/MOL] Vallet, V., Moll, H., Wahlgren, U., Szabó, Z., Grenthe, I., Structure and bonding in solution of dioxouranium(VI) oxalate complexes: isomers and intramolecular ligand exchange, *Inorg. Chem.*, **42**, (2003), 1982-1993. Cited on page: 229.

- [2003WAR/EVA] Warwick, P., Evans, N., Hall, T., Vines, S., Complexation of Ni(II) by  $\alpha$ -isosaccharinic acid and gluconic acid from pH 7 to pH 13, *Radiochim. Acta*, **91**, (2003), 233-240. Cited on pages: 525, 526.
- [2003ZHE/MAU] Zhernosekov, K. P., Mauerhofer, E., Getahun, G., Warwick, P., Rösch, F., Complex formation of Tb<sup>3+</sup> with glycolate, D-gluconate and  $\alpha$ -isosaccharinate in neutral aqueous perchlorate solutions, *Radiochim. Acta*, **91**, (2003), 599-602. Cited on pages: 534, 537.
- [2004BON/MOO] Bontchev, R. P., Moore, R. C., Crystal structure of sodium isosaccharate, NaC<sub>6</sub>H<sub>11</sub>O<sub>6</sub>·H<sub>2</sub>O, *Carbohydr. Res.*, **339**, (2004), 801-805. Cited on page: 519.
- [2004BOU/REI] Boukhalfa, H., Reilly, S. D., Smith, W. H., Neu, M. P., EDTA and mixed-ligand complexes of tetravalent and trivalent plutonium, *Inorg. Chem.*, **43**, (2004), 5816-5823. Cited on page: 501.
- [2004CRE/ROB] Crea, F., de Robertis, A., Sammartano, S., Medium and alkyl chain effects on the protonation of dicarboxylates in NaCl<sub>aq</sub> and Et<sub>4</sub>Nl<sub>aq</sub> at 25°C, *J. Solution Chem.*, **33**, (2004), 499-528. Cited on pages: 128, 131, 132, 157, 158.
- [2004EKB/EKB] Ekberg, S., Ekberg, C., Albinsson, Y., Characterization of  $\alpha$ -isosaccharinic acid: lactone and carboxylic conformations, *J. Solution Chem.*, **33**, (2004), 465-477. Cited on pages: 514, 518.
- [2004FRO/ADE] Frost, R. L., Adebajo, M., Weier, M. L., A Raman spectroscopic study of thermally treated glushinskite - the natural magnesium oxalate dihydrate, *Spectrochim. Acta*, **A60**, (2004), 643-651. Cited on pages: 159, 160, 562.
- [2004FRO/WEI] Frost, R. L., Weier, M. L., Thermal treatment of whewellite - a thermal analysis and Raman spectroscopic study, *Thermochim. Acta*, **409**, (2004), 79-85. Cited on page: 165.
- [2004LOO/GLA] Van Loon, L. R., Glaus, M. A., Vercammen, K., Stability of the ion-pair between Ca<sup>2+</sup> and 2-(hydroxymethyl)-3-deoxy-D-erythropentionate ( $\alpha$ -isosaccharinate), *J. Solution Chem.*, **33**, (2004), 1573-1583. Cited on pages: 520, 521, 522, 523.

- [2004MEN/APE] Menczel, B., Apelblat, A., Korin, E., The molar enthalpies of solution and solubilities of ammonium, sodium and potassium oxalates in water, *J. Chem. Thermodyn.*, **36**, (2004), 41-44. Cited on pages: 152, 153, 155, 156.
- [2004RAO/GAR] Rao, L., Garnov, A. Y., Rai, D., Xia, Y., Moore, R. C., Protonation and complexation of isosaccharinic acid with U(VI) and Fe(III) in acidic solutions: potentiometric and calorimetric studies, *Radiochim. Acta*, **92**, (2004), 575-581. Cited on pages: 515, 517, 518, 519, 528, 529, 537, 538.
- [2004SCH/MAU] Schunk, A., Maurer, G., Activity of water in aqueous solutions of sodium citrate and in aqueous solutions of (an inorganic salt and citric acid) at 298.15 K, *J. Chem. Eng. Data*, **49**, (2004), 944-949. Cited on pages: 325, 814, 815, 816, 817.
- [2004TIT/WIE] Tits, J., Wieland, E., Bradbury, M. H., The effect of isosaccharinic acid and gluconic acid on the retention of Eu(III), Am(III) and Th(IV) by calcite, *Appl. Geochem.*, (2004), submitted. Cited on pages: 532, 533, 534, 535, 536, 538, 539, 540.
- [2004WAR/EVA] Warwick, P., Evans, N., Hall, T., Vines, S., Stability constants of uranium(IV)- $\alpha$ -isosaccharinic acid and gluconic acid complexes, *Radiochim. Acta*, **92**, (2004), 897-902. Cited on pages: 526, 527.
- [2005BRO/CUR] Brown, P. L., Curti, E., Grambow, B., *Chemical thermodynamics of Zirconium*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 8, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2005). Cited on page: 4.
- [2005GAM/BUG] Gamsjäger, H., Bugajski, J., Gajda, T., Lemire, R. J., Preis, W., *Chemical thermodynamics of Nickel*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 6, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2005). Cited on pages: 4, 6, 29, 36, 57, 58, 59, 64, 68, 71, 361, 840, 841, 845, 847.

- [2005KAN/GIL] Kantar, C., Gillow, J. B., Harper-Arabie, R., Honeyman, B. D., Francis, A. J., Determination of stability constants of U(VI)-Fe(III)-citrate complexes, *Environ. Sci. Technol.*, **39**, (2005), 2161-2168. Cited on page: 373.
- [2005OLI/NOL] Olin, Å., Noläng, B., Öhman, L.-O., Osadchii, E. G., Rosén, E., *Chemical thermodynamics of Selenium*, Nuclear Energy Agency Data Bank, Organisation for Economic Co-operation and Development, Ed., vol. 7, *Chemical Thermodynamics*, North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands, (2005). Cited on pages: 4, 6, 29, 36, 57, 58, 59, 65, 73, 76.





# 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 correspond 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. No attempt has been made to correct for such inconsistencies in this volume.

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Blokhin, V. I.	[70GEL/BLO2], [76MEF/BLO]
Blom, N. S.	[81BLO/KAN]
Blumenthal, W. B.	[58BLU]
Bobtelsky, M.	[27BOB/MAL], [45BOB/JOR], [54HEI/BOB], [57BOB/RAF], [58BOB/BEN]
Bochkarev, G. S.	[57ZAI/SHU2], [62ZAI/BOC3], [64KHA/BOC2], [64KHA/ZAI2], [64ZAI/BOC2], [65ZAI/BOC]
Bohigian, Jr., T. A.	[60BOH/MAR]

Author	Reference
Bokelund, H.	[83CHO/BOK]
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Bolshakov, K. A.	[58BOL/KOR]
Bol'shakov, K. A.	[57BOL/KOR3], [57BOL/KOR4]
Bolyanovskii, A. D.	[88ALL/BOL]
Bonavita, M.	[71ROR/MAC]
Bond, A. H.	[99MIZ/BON], [2001CHO/BON]
Bontchev, R. P.	[2004BON/MOO]
Boos, G. A.	[86SAL/BOO], [89SAL/BOO], [91SAL/BOO], [98SAL/BOO], [98SAL/BOO2]
Borggaard, O. K.	[77CHR/BOR]
Borkowski, M.	[96BOR/LIS], [99BRO/POK], [2000BOR/CHO], [2001BOR/MOO], [2001CHO/BON], [2003BOR/CHO]
Borodin, V. A.	[88VAS/BOR]
Borrás-Almenar, J. J.	[95BOR/COR]
Bosch, W.	[28KOL/BOS]
Bosch-Reig, F.	[69BOS/MAR]
Bosia, P. D.	[78USS/BOS]
Bottari, E.	[65BOT/CIA], [67BOT/AND], [73BOT/VIC], [73BOT/VIC2], [75BOT]
Botts, J.	[65BOT/CHA]
Bouhdillon, R.	[13HAR/DRU]
Bouhlassa, S.	[81BOU], [84BOU/GUI], [84BOU/PET]
Boukhalfa, H.	[2004BOU/REI]
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Boulet, M.	[60BOU/MAR]
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Bradley, D. J.	[79BRA/PIT]
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Braibanti, A.	[70BRA/LEP]
Brandau, E.	[68EBE/SCH]
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Bressat, R.	[63BRE/CLA2], [64BRE/CLA]
Bricker, C. E.	[57BRI/PAR]
Briggs, T. N.	[75BRI/STU]
Brighli, M.	[84BRI/LAG]
Brillard, L.	[74HUB/HUS], [76HUB/HUS]
Brintzinger, H.	[42BRI/HES], [43BRI/THI]
Bristow, P. A.	[70BAR/BRI]
Brito, F.	[70ASC/BRI], [84MED/DOM], [95CHI/DOM]
Brits, A. G.	[76BRI/ELD], [76BRI/ELD2], [76BRI/ELD3], [77BRI/ELD]
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Brown, P. L.	[2005BRO/CUR]
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Bruno, J.	[86BRU], [97ALL/BAN]
Bryzgalova, R. V.	[70GRE/BRY2]
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Budantseva, N. A.	[96BES/KRO]
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Bugajski, J.	[2005GAM/BUG]
Buglyó, P.	[95KIS/BUG], [2000BUG/KIS]
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Buklanov, G. V.	[89ROS/DIT]
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Burney, G. A.	[67BUR/POR]
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Bykhovskii, D. N.	[74BYK/PET2], [88BYK/KUZ2]
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Cahn, M.	[08KOP/CAH]
Caletka, R.	[63KYR/CAL], [64CAL], [64CAL/KYR]
Cali, R.	[80ARE/CAL]
Caminiti, R.	[88CAM/MUN], [93ATZ/FIL]
Campi, E.	[64CAM/OST]
Canals, E.	[75DEY/CAN]
Cannan, R. K.	[38CAN/KIB]
Canonne, J.	[76NOW/CAN]
Capdevila, H.	[92CAP], [93GIF/VIT2], [94CAP/VIT], [95CAP/VIT]
Capone, S.	[86CAP/ROB]
Cardin, C. J.	[98MOR/ALM]
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Carey, G. H.	[67CAR/MAR], [68CAR/MAR], [70KUG/CAR]
Carini, F. F.	[52CAR/MAR], [53CAR/MAR], [54CAR/MAR]
Carpenter, S. A.	[98ALM/NOV]

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Chang, C.-T.	[71CHA/LIA], [71CHA/LIA2]
Chapin, E. M.	[31CHA/BEL]
Chappel, F. P.	[58CHA/HOA]
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Charushnikova, I. A.	[96GRI/CHA2], [97GRI/CHA], [98CHA/KRO]
Chashin, A.	[65BOT/CHA]
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Chaturvedi, G. K.	[77JAI/KUM], [78JAI/SHA], [79KUM/CHA], [80MIS/MIT]
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Chechetkin, R. M.	[68PRI/FAZ]
Chemotti, Jr., A. R.	[82AVD/KEA]
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Chinnusamy, A.	[86RAO/PIU]
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Chmutova, M. K.	[59ERM/BEL2]
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Christensen, H. H.	[77CHR/BOR]
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Churikova, I. M.	[72KER/CHU], [78KER/CHU]
Churney, K. L.	[82WAG/EVA]
Ciano, M.	[89NES/HOF]
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Claudel, B.	[63BRE/CLA2], [64BRE/CLA]
Clayton, W. J.	[37CLA/VOS]
Clemente, M.	[2000FER/IUL]
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Cole, A.	[82HUA/ALF]
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Connick, R. E.	[49CON/MCV], [51CON/REA], [54CON], [56ZIE/CON]
Contescu, A.	[96SCH/CON]
Contescu, C.	[96SCH/CON]
Contino, A.	[90ARE/CON]
Conway, B. E.	[66CON/VER]
Cook, G. P.	[58COO/FOR]
Cook, Jr., C. M.	[51COO/LON], [58COO/LON]
Coombes, L. C.	[70COO/MAR]
Cooper, J. N.	[78COO/WOO]
Coops, J.	[26VER/HAR]
Coppens, P.	[69COP/SAB], [69COP/SAB2]
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Cordes, S. M.	[69SUB/COR]
Cordfunke, E. H. P.	[90COR/KON2]
Coronado, E.	[84MOS/GAL], [86COR/DRI], [86DRI/COR], [86GOM/JAM], [89COR/DRI], [92SAP/COR], [95BOR/COR]
Corrie, A. M.	[76COR/WAL]
Cosgrove, A.	[82JAC/COS]
Costa-Bauzá, A.	[92VEL/SOH], [93SOH/COS]
Cotson, S.	[53BRA/COT]
Couderc, J.-P.	[76LAG/AUB]
Coutinho, P.	[92TUR/SAN]
Couturier, Y.	[70COU/FAU]
Covington, A. K.	[83COV/BAT]
Cox, E. G.	[52COX/DOU]
Cox, J. D.	[89COX/WAG]
Craggs, A.	[79CRA/MOO]
Crea, F.	[2004CRE/ROB]
Creamer, L. K.	[75PEA/CRE]
Crisponi, G.	[96ARA/ARC]
Cristiani, F.	[96ARA/ARC]
Cromack, Jr., K.	[77GRA/CRO]
Cromer, D. T.	[56STA/CRO3]
Cross, J. E.	[89CRO/EWA]
Crow, D. R.	[88CRO]
Cruickshank, D. W. J.	[53AHM/CRU]
Cruywagen, J. J.	[83CRU/HEY], [86CRU/HEY], [86CRU/WAT]
Cucinotta, V.	[79AMI/DAN], [81CUC/DAN]
Cummins, D.	[91CHR/CUM]
Cunningham, B. B.	[54CUN], [65FUG/CUN]
Curely, J.	[86DRI/COR], [95BOR/COR]
Curini, R.	[2002CUR/TEN]
Curti, E.	[2002HUM/BER], [2005BRO/CUR]
Cvitaš, T.	[93MIL/CVI]

Author	Reference
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Da Silva, J. J. R. F.	[68SIL/SIM], [69SIL/SIM], [70SIL/SIM], [70SIL/SIM2], [83LUR/GON], [84GON/MOT]
Dabos-Seignon, S.	[90RIZ/NEC]
Dadgar, A.	[86CHO/DAD]
Dahale, N. D.	[97DAH/CHA2]
Dahlgren, Å.	[90AHR/DAH]
Dalidovich, S. V.	[85DAL/GUS]
Dallavalle, F.	[70BRA/LEP]
Dalman, L. H.	[37DAL]
D'Angelantonio, M.	[89NES/HOF]
Daniel, F. B. D.	[2000ASK/CHA]
Daniel, S. R.	[84REE/DAN]
Daniele, P. G.	[75DAN/OST], [76DAN/OST], [79AMI/DAN], [80DAN/RIG], [81AMI/DAN], [81CUC/DAN], [81DAN/RIG], [82AMI/DAN], [82DAN/MAR], [83DAN/RIG], [83DAN/RIG2], [84DAN/OST], [85DAN/RIG], [85DAN/ROB], [85DAN/SON], [88DAN/OST], [90DAN/ROB], [90DAN/ROB2], [92DAN/ROB]
Daniele, S.	[93MAZ/DAN]
D'Ans, J.	[77ANS/SUR]
Darken, L. S.	[41DAR]
Das, B. B.	[89DAS/DAS]
Dash, U. N.	[88DAS/KAL], [89DAS/DAS], [96DAS/MOH]
Dass, N. N.	[96DEB/BAR]
Datta, S. P.	[65TAT/GRZ], [70GRZ/TAT]
David, D. J.	[64DAV]
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Davidson, N.	[60YAM/DAV]
Davies, C. W.	[27DAV], [31BAN/RIG], [32MON/DAV], [53DAV/HOY], [55DAV/HOY], [62DAV]
Davies, G.	[70DAV/WAT]
Davis, J. A.	[78DAV/LEC]
Davis, J. M.	[78RAJ/MAI], [81RAJ/MAI]
De Bruin, H. J.	[62BRU/KAI]
De Filippo, D.	[93ATZ/FIL]
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De Jongh, L. J.	[86DRI/COR], [89COR/DRI]
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Debayle, P.	[91SIN/YEB]
Decnop-Weever, L. G.	[83KRA/DEC]
Decock, P.	[95KIS/BUG], [2001LAK/BAN]
Deganello, S.	[81DEG/PIR]
Delaplane, R. G.	[69COP/SAB2]
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Delle Site, A.	[69DEL/BAY]
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Desnoyers, J. E.	[66CON/VER]
Devi, C. S.	[91RED/DEV]
Devyatov, F. V.	[84SAL/DEV]
Dewaele, D.	[95KIS/BUG]
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Dey, A. K.	[76YAD/GHO]
Deyrieux, R.	[70DEY/PEN], [73DEY/BER], [75DEY/CAN]
Dhar, N. R.	[24CHA/DHA]
Di Bernardo, P.	[2002RAO/JIA]
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Dischino, D. D.	[94KUM/CHA]
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Dittrich, S.	[89ROS/DIT]
Dmitrieva, N. G.	[82VAS/VAS]
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Domeneghetti, C.	[80TAZ/DOM]
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Dreyer, R.	[89ROS/DIT], [90ROS/REI]
Drillon, M.	[81BEL/DRI], [82BEL/ESC], [84MOS/GAL], [86COR/DRI], [86DRI/COR], [89COR/DRI]
Drugman, J.	[13HAR/DRU]
Du Toit, J.	[91JAC/TOI]
Dubes, J. P.	[75BAR/DUB]
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Ekberg, C.	[2003EKB/EKB], [2004EKB/EKB]
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Evans, W. H.	[82WAG/EVA]
Evans, W. J.	[85MAR/EVA], [86MAR/EVA]
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Evseev, A. M.	[87THU/KUP], [88EVS/SMI], [89SVE/DOB], [92MIL/DOB]
Evstaf'eva, O. N.	[64KHA/ZAI2]
Evteev, L. I.	[58GRI/PET2], [59GRI/PET], [60GRI/PET]
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Fanghänel, T.	[97KON/FAN], [2003GUI/FAN]
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Faucherre, J.	[70COU/FAU]
Faus, J.	[88CAS/FAU]
Fazlullina, L. S.	[68PRI/FAZ]
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Flyantikova, G. V.	[74NAZ/FLY2], [78FLY/KOR]
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Friedman, D.	[58HEI/FRI]
Friedman, H. A.	[85FRI]
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Fritz, J. S.	[77MOY/FRI]
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Grinberg, A. A.	[56GRI/PET2], [56GRI/PTI], [58GRI/PET2], [59GRI/PET], [60GRI/PET], [61GRI/AST], [63GRI/PET], [72GRI/PET2]
Gritmon, T. F.	[77CHO/GOE], [77GRI/GOE]

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Grzybowski, A. K.	[65TAT/GRZ], [70GRZ/TAT]
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Gudi, N. M.	[79KUS/GAN]
Guggenheim, E. A.	[35GUG], [66GUG]
Guichard, C.	[73CAU/GUI], [75CAU/GUI]
Guillaumont, R.	[68GUI], [71GUI/BOU], [72MET/GUI3], [73HUB/HUS], [74HUB/HUS], [76HUB/HUS], [84BOU/GUI], [84BOU/PET], [2003GUI/FAN]
Guo, Y.-F.	[2001GUO/LIA]
Gupta, C. M.	[82SAC/CHA], [83GUP/CHA]
Gupta, N.	[83GUP/CHA]
Gupta, P. C.	[83GUP/CHA]
Gur'eva, Z. M.	[66KOR/SHE2]
Gusev, E. A.	[85DAL/GUS]
Gut, R.	[54SCH/GUT]
Gutowski, M.	[95RAK/SKU]
Guzmán-Miralles, C.	[93ROM/GUZ]
Haas, D. J.	[64HAA]
Haas, K.	[67BUD/HAA]
Hadermann, J.	[97ALL/BAN]
Haerberli, A.	[94MUL/HAE]
Hagberg, J.	[97HAG], [2002HAG/DUK]
Hakem, N.	[98ALM/NOV]
Hala, J.	[2001HAL/NAV]
Hall, J. L.	[34HAS/MCL]
Hall, T.	[2003WAR/EVA], [2004WAR/EVA]
Halow, I.	[82WAG/EVA]
Hamann, S. D.	[82HAM]
Hammarsten, G.	[29HAM]
Hancock, R. D.	[96SUN/AND]
Hangartner, M.	[75AND/POD]
Hansen, E. H.	[73HAN/RUZ]
Hansen, H.-J.	[62AXT/HAN]
Hansen, L. D.	[67CHR/IZA], [69CHR/IZA]
Hardacre, C.	[98BUR/FAH]
Hardcastle, J.	[2001JAN/HAR]
Harju, L.	[99KAR/HAR]
Harned, H. S.	[39HAR/FAL]
Harper-Arabie, R.	[2005KAN/GIL]
Harries, R. J. N.	[68HAR]
Harris, W. E.	[46KOL/HAR]
Harris, W. R.	[76HAR/MAR]
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Hasilkar, S. P.	[94HAS/KHE], [95HAS/KHE]
Hassan, A.	[92AZA/ELN], [93AZA/HAS]
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Hatano, K.	[96AIZ/NAT]
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Havel, J.	[69HAV], [80MIK/HAV], [86BAR/HAV], [2002HAV/SOT]
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Hearing, E. D.	[96DOM/HEA]
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Heijnen, W. M. M.	[81BLO/KAN], [82HEI]
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Hill, L. M.	[46HIL/GOU]
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Hojo, Y.	[77HOJ/SUG]
Hokari, N.	[96YUC/HOK]
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Holt, K.	[75PAK/OHA]
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Kanellakopulos, B.	[86KAN/KIM]
Kanishcheva, A. S.	[85MIK/LOB], [85SHC/ORL], [93MIS/MIK]
Kankare, J. J.	[72KAN]
Kantar, C.	[2005KAN/GIL]
Kanters, J. A.	[70FOL/KAN], [72ROE/KAN], [81BLO/KAN]
Kapshukov, I. I.	[84TOM/VOL]
Kapustyanskaya, Z. V.	[92POG/KAP]
Karacheva, G. A.	[58YAT/KAR], [59YAT/KAR]
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Karapiperis, T.	[97ALL/BAN]
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Kartushova, R. E.	[56FOM/KAR]
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Leyden, D. E.	[68LEY/WHI]
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Liang, J.-F.	[2001GUO/LIA]
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Lindenbaum, A.	[52SCH/LIN], [57LI/WES], [59LI/LIN]
Lingaiah, P.	[84VEN/SWA], [85VEN/SWA]
Linklater, C. M.	[94GRE/LIN]
Lis, S.	[95LIS/CHO], [96BOR/LIS], [2001CHO/BON]
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Litovchenko, K. I.	[75LIT/NIK], [77KUB/NIK]
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Liu, S. C.	[64YEN/LIU]
Liu, X.-Q.	[2001GUO/LIA]
Lobanova, G. M.	[85MIK/LOB], [85SHC/ORL]
Logvinenko, V. A.	[74MYA/LOG], [76MYA/LOG]
Long, F. A.	[51COO/LON], [58COO/LON], [62MCD/LON]
Losev, V. Y.	[96MIK/GOR2]
Louguinine, W.	[1886LOU]
Louwrier, P. W. F.	[83KOR/PRO]
Lowe, J.	[2002LOW/OGD]
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Lubal, P.	[2002HAV/SOT]
Łukomski, P.	[93GLA/MAJ]
Luerkens, D. W.	[83LUE]
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Rigano, C.	[80ARE/CAL], [80DAN/RIG], [81AMI/DAN], [81CUC/DAN], [81DAN/RIG], [82AMI/DAN], [83DAN/RIG], [83DAN/RIG2], [84DAN/OST], [85DAN/RIG], [85DAN/ROB], [90ROB/STE], [92ROB/STE]
Righellato, E. C.	[31BAN/RIG]
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Smith, A.	[73FIN/SMI], [81BUR/FIN]
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Sysoeva, T. F.	[80AGR/SYS], [81SYS/AGR], [86SYS/AGR], [87LEO/FRI]
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Wall, N. A.	[2001CHO/BON]
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Wooley, E. M.	[2001PAT/WOO]
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